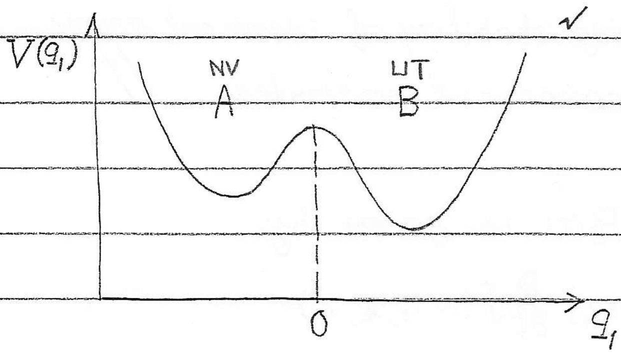
Transition State Theory

[R. Zwanzig, "Nonequilibrium Statistical Mechanics", P.67]

– Reaction cooridinate ~ mile sign on I15 (lowest-saddle path)

Consider a system of 3N degrees of freedom (N is the number of atoms), in which the "reaction coordinate" q_1 separates the phase space into two regions — A ($q_1 < 0$) and B ($q_1 > 0$). All the other coordinates and momenta are collectively denoted as $\mathbb{X} = (\mathbb{q}, \mathbb{P}) = (q_2, \ldots, q_{3N}, P_2, \ldots, P_{3N})$.



– Flux through the 3N-1 dimensional dividing surface

The probability of the system being in region B is

$$P_B(t) = \iiint \frac{dq_1\, dP_1\, d\mathbb{X}}{h^{3N}} \underbrace{\Theta(q_1)}_{\text{only in UT}} f(q_1, P_1, \mathbb{X}, t) \qquad (1)$$

where $f(q_1, P_1, \mathbb{X}, t)$ is the phase-space distribution and $\Theta(q)$ is the step function.

☺ Factor h (Planck constant) in Eq.(1)

Consider a one-dimensional quantum system in a box of length L with periodic boundary condition. An orthonormal basis set is $\{\frac{1}{\sqrt{L}} e^{ik_n x} \mid k_n = 2\pi n/L, n \in \mathbb{Z}\}$, and the partition function is

$$Q = \sum_n e^{-\beta H(q,P)} \quad \left(\frac{\hbar}{i}\frac{d}{dq} = \hbar k_n\right)$$

$$\rightarrow \frac{L}{2\pi}\int_{-\infty}^{\infty} \underbrace{dk}_{\frac{dP}{\hbar}}\, e^{-\beta H(q,P)} \quad (P = \hbar k) \quad (L \to \infty) \quad \left(∵ \text{In } dk, \text{ there are } \frac{L\,dk}{2\pi} \text{ wave numbers}\right)$$

$$= L\int_{-\infty}^{\infty} \frac{dP}{\underbrace{2\pi\hbar}_{h}} e^{-\beta H(q,P)}$$

$$= \iint \frac{dq\,dP}{h} e^{-\beta H(q,P)}$$

Note that Eq. (1) omits the factors, $1/N_a!$ (N_a is the number of a-th species), arising from the indistinguishability of identical atoms, since we work in a non-grandcanonical ensemble. //

The time change of $P_B(t)$ is given by

$$\frac{dP_B(t)}{dt} = \iiint \frac{dq_1 dP_1 d\mathbb{X}}{h^{3N}} \Theta(q_1) \underbrace{\frac{\partial}{\partial t} f(q_1, P_1, \mathbb{X}, t)}_{= -Lf(q_1,P_1,\mathbb{X},t)} \qquad (2)$$

$$= +\iiint \frac{dq_1 dP_1 d\mathbb{X}}{h^{3N}} [L\Theta(q_1)]\, f(q_1,P_1,\mathbb{X},t) \qquad (2b)$$

where L is the Liouville operator.

∵ Eq. (2b) ✓ integration by parts

For an arbitrary function $A(\mathbb{X} \in \mathbb{R}^{3N})$,

$$\frac{d}{dt}\langle A(t)\rangle = \frac{d}{dt}\int \frac{d\mathbb{X}}{h^{3N}} A(\mathbb{X}) f(\mathbb{X},t)$$

$$= \int \frac{d\mathbb{X}}{h^{3N}} A(\mathbb{X}) \underbrace{\frac{\partial f}{\partial t}}_{-Lf}$$

$$= -\int \frac{d\mathbb{X}}{h^{3N}} A(\mathbb{X}) \dot{\mathbb{X}} \cdot \frac{\partial}{\partial \mathbb{X}} f$$

$$= -\int \frac{d\mathbb{X}}{h^{3N}} \frac{\partial}{\partial \mathbb{X}} \cdot (A(\mathbb{X})\dot{\mathbb{X}} f) + \int \frac{d\mathbb{X}}{h^{3N}} \frac{\partial}{\partial \mathbb{X}} \cdot (\dot{\mathbb{X}} A(\mathbb{X}))\, f(\mathbb{X},t)$$

$$\therefore \frac{d}{dt}\langle A(t)\rangle = \underbrace{-\int_{\text{surface}} \frac{dS}{h^{3N}} \cdot A(\mathbb{X})\,\dot{\mathbb{X}}\, f(\mathbb{X},t)}_{=0} + \int \frac{d\mathbb{X}}{h^{3N}} \underbrace{\left[\frac{\partial}{\partial \mathbb{q}} \cdot (\overbrace{\dot{\mathbb{q}}}^{\frac{\partial H}{\partial \mathbb{P}}} A) + \frac{\partial}{\partial \mathbb{P}} \cdot (\overbrace{\dot{\mathbb{P}}}^{-\frac{\partial H}{\partial \mathbb{q}}} A) \right]}_{\frac{\partial H}{\partial \mathbb{P}} \cdot \frac{\partial A}{\partial \mathbb{q}} + \cancel{\frac{\partial^2 H}{\partial \mathbb{q} \cdot \partial \mathbb{P}} A} - \frac{\partial H}{\partial \mathbb{q}} \cdot \frac{\partial A}{\partial \mathbb{P}} - \cancel{\frac{\partial^2 H}{\partial \mathbb{P} \cdot \partial \mathbb{q}} A}} f$$

$$= \int \frac{d\mathbb{X}}{h^{3N}} \left[\Big(\underbrace{\frac{\partial H}{\partial \mathbb{P}} \cdot \frac{\partial}{\partial \mathbb{q}} - \frac{\partial H}{\partial \mathbb{q}} \cdot \frac{\partial}{\partial \mathbb{P}}}_{L} \Big) A(\mathbb{X}) \right] f(\mathbb{X},t)$$

$$= \int \frac{d\mathbb{X}}{h^{3N}} \left[L\, A(\mathbb{X}) \right] f(\mathbb{X},t) \qquad //$$

We assume a Hamiltonian,

$$H(q_1, P_1, \mathbb{X}) = \sum_{j=1}^{3N} \frac{P_j^2}{2m_j} + V(q_1, q_2, \ldots, q_{3N}) \qquad (3)$$

Then,

$$L\,\Theta(q_1) = \frac{P_1}{m_1} \frac{d}{dq_1} \Theta(q_1) = \frac{P_1}{m_1} \delta(q_1) \qquad (4)$$

↳ flux @ saddle

where $\delta(q)$ is the delta function.

Substituting Eq. (4) in (2b)

$$\frac{dP_B(t)}{dt} = \iiint \frac{dq_1\, dP_1\, d\mathbb{X}}{h^{3N}} \frac{P_1}{m_1} \delta(q_1)\, f(q_1, P_1, \mathbb{X}, t) \qquad (5a)$$

$$= \iint \frac{dP_1\, d\mathbb{X}}{h^{3N}} \frac{P_1}{m_1} f(0, P_1, \mathbb{X}, t) \qquad (5b)$$

✓ $1 = \Theta(P_1) + \Theta(-P_1)$

Splitting the integral into the gain ($A \to B$) and loss ($B \to A$) terms,

$$\frac{dP_B(t)}{dt} = \left(\frac{dP_B}{dt}\right)_{A\to B} + \left(\frac{dP_B}{dt}\right)_{B\to A} \qquad (6a)$$

$$= \underbrace{\int_0^{\infty} \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f(0, P_1, \mathbb{X}, t)}_{(>0)\ \text{gain}} + \underbrace{\int_{-\infty}^{0} \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f(0, P_1, \mathbb{X}, t)}_{(<0)\ \text{loss}} \qquad (6b)$$

Transition state theory (TST) approximation

The TST approximation assumes that both A and B regions locally (i.e., within the region) maintain the equilibrium distributions all the time:

$$f_{\alpha,\,local} \cong \frac{P_\alpha(t)}{P_\alpha(eq)}\, f_{eq} \qquad (\alpha = A, B) \tag{7}$$

where the total equilibrium distribution is

$$f_{eq} = \frac{1}{Q}\, e^{-\beta H} \tag{8}$$

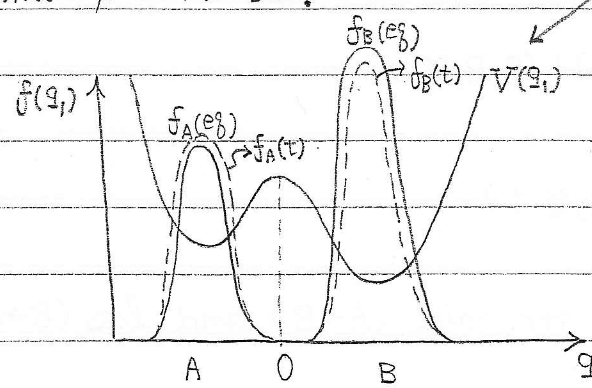
$$Q = \iiint \frac{dq_1\, dP_1\, dX}{h^{3N}}\, e^{-\beta H} = Q_A + Q_B \tag{9}$$

$$Q_A = \iiint_{q_1<0} \frac{dq_1\, dP_1\, dX}{h^{3N}}\, e^{-\beta H}, \quad Q_B = \iiint_{q_1>0} \frac{dq_1\, dP_1\, dX}{h^{3N}}\, e^{-\beta H} \tag{10}$$

$$P_\alpha(eq) = Q_\alpha / Q \qquad (\alpha = A, B) \tag{11}$$

and $\beta = 1/k_B T$.

weight to be consistent with current state population; its time change to be determined by master eq.



In the TST approximation, the distribution function in each region is the equilibrium distribution f_{eq}, multiplied by the normalization factor, $P_\alpha(t)/P_\alpha(eq)$, to make the region population the current value $P_\alpha(t)$ rather than its equilibrium value $P_\alpha(eq)$. This is valid if the equilibration in each region occurs at a much shorter time than the time scale of dP_α/dt.

Substituting the TST approximation (7) into Eq. (6), and noting that only $f(q_1, P_1, \mathbb{X}, t)$ just below ($q_1 \lesssim 0$) and above ($q_1 \gtrsim 0$) the dividing surface contributes to the gain ($A \to B$) and loss ($B \to A$) terms, respectively,

$$\left(\frac{dP_B}{dt}\right)_{A\to B} = \underbrace{\int_0^\infty \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f_{eq}(0, P_1, \mathbb{X}) \frac{1}{P_A(eq)}}_{k_{BA}} P_A(t) \qquad (12a)$$

$$\left(\frac{dP_B}{dt}\right)_{B\to A} = \int_{-\infty}^0 \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f_{eq}(0, P_1, \mathbb{X}) \frac{P_B(t)}{P_B(eq)}$$

$P_1 \to -P_1$

$$= -\underbrace{\int_0^\infty \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f_{eq}(0, P_1, \mathbb{X}) \frac{1}{P_B(eq)}}_{k_{AB}} P_B(t) \qquad (12b)$$

$$\therefore \frac{dP_B(t)}{dt} = k_{BA} P_A(t) - k_{AB} P_B(t) \qquad (13a)$$

and similarly,

$$\frac{dP_A(t)}{dt} = -k_{BA} P_A(t) + k_{AB} P_B(t) \qquad (13b)$$

where the rate constants are

$$\begin{cases} k_{BA} = \int_0^\infty \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f_{eq}(0, P_1, \mathbb{X}) \frac{1}{P_A(eq)} & (14a) \\ k_{AB} = \int_0^\infty \frac{dP_1}{h} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{P_1}{m_1} f_{eq}(0, P_1, \mathbb{X}) \frac{1}{P_B(eq)} & (14b) \end{cases}$$

(re-defined toward negative direction)

- We can perform the p_1 integration in Eq. (14) analytically,

$$k_{BA} = \underbrace{\int_0^\infty \frac{dp_1}{h}\frac{p_1}{m_1} e^{-p_1^2/2m_1 k_B T}}_{\substack{x = \frac{p_1^2}{2m_1 k_B T} \\ k_B T\,dx = \frac{p_1\,dp_1}{m_1}}} \int \frac{d\mathbb{X}}{h^{3N-1}} \frac{(e^{-\beta H})_{q_1=p_1=0}}{\cancel{Q}} \cdot \frac{\cancel{Q}}{Q_A}$$

$$= \frac{k_B T}{h} \underbrace{\int_0^\infty dx\, e^{-x}}_{[-e^{-x}]_0^\infty = 1} \frac{1}{Q_A} \underbrace{\int \frac{d\mathbb{X}}{h^{3N-1}} (e^{-\beta H})_{q_1=p_1=0}}_{\equiv Q^\ddagger}$$

$$\therefore\ k_{BA} = \frac{k_B T}{h}\frac{Q^\ddagger}{Q_A} \tag{15a}$$

and similarly

$$k_{AB} = \frac{k_B T}{h}\frac{Q^\ddagger}{Q_B} \tag{15b}$$

where

$$Q^\ddagger = \int \frac{d\mathbb{X}}{h^{3N-1}} (e^{-\beta H})_{q_1=p_1=0} \tag{16}$$

Harmonic transition state theory

In the harmonic approximation, the potential in region A is approximated as

$$V(q_1, \ldots, q_{3N}) = V_A + \frac{1}{2} \sum_j m_j \omega_j^{A^2} (q_j - b_j)^2 \tag{17}$$

so that

$$Q_A = \iiint_{q_1<0} \frac{dq_1\, dP_1\, d\mathbb{X}}{h^{3N}} \exp\left[-\beta\left(\sum_j \frac{P_j^2}{2m_j} + V_A + \frac{1}{2}\sum_j m_j \omega_j^{A^2} (q_j - b_j)^2\right)\right]$$

$$= e^{-\beta V_A} \prod_{j=1}^{3N} \frac{1}{h} \underbrace{\int_{-\infty}^{\infty} dP_j\, e^{-\frac{P_j^2}{2m_j k_B T}}}_{\sqrt{2\pi \cancel{m_j} k_B T}} \underbrace{\int_{-\infty}^{\infty} d\underset{\overset{\parallel}{q_j - b_j}}{q_j'}\, e^{-\frac{m_j \omega_j^{A^2}}{2k_B T} q_j'^2}}_{\sqrt{\frac{2\pi k_B T}{\cancel{m_j} \omega_j^{A^2}}}} \quad \checkmark \text{ just Gaussian integration}$$

$$= e^{-\beta V_A} \prod_{j=1}^{3N} \frac{2\pi k_B T}{h \omega_j^A}$$

$$= \left(\frac{2\pi k_B T}{h}\right)^{3N} \frac{e^{-\beta V_A}}{\prod_{j=1}^{3N} \omega_j^A} \tag{18}$$

At the dividing surface, we assume

$$V(q_1, \ldots, q_{3N}) = V_S - \frac{1}{2} a_{11} q_1^2 + \frac{1}{2} \sum_{j=2}^{3N} m_j \omega_j^{\ddagger^2} q_j^2 \tag{19}$$

so that

$$Q^\ddagger = \int \frac{d\mathbb{X}}{h^{3N-1}} \exp\left[-\beta\left(\sum_{j=2}^{3N} \frac{P_j^2}{2m_j} + V_S + \frac{1}{2}\sum_{j=2}^{3N} m_j \omega_j^{\ddagger^2} q_j^2\right)\right]$$

$$= \left(\frac{2\pi k_B T}{h}\right)^{3N-1} \frac{e^{-\beta V_S}}{\prod_{j=2}^{3N} \omega_j^\ddagger} \tag{20}$$

Substituting Eqs. (18) and (20) in (15),

$$k_{BA} = \frac{\cancel{k_B T}}{\cancel{h}} \cdot \frac{\cancel{h}}{2\pi \cancel{k_B T}} e^{-\beta(V_S - V_A)} \frac{\prod_{j=1}^{3N} \omega_j^A}{\prod_{j=2}^{3N} \omega_j^{\ddagger}}$$

$$\therefore k_{BA} = \frac{1}{2\pi} e^{-\beta(V_S - V_A)} \frac{\prod_{j=1}^{3N} \omega_j^A}{\prod_{j=2}^{3N} \omega_j^{\ddagger}} \simeq \frac{\omega_1^A}{2\pi} e^{-\beta(V_S - V_A)} \qquad (21a)$$

and similarly

$$k_{AB} = \frac{1}{2\pi} e^{-\beta(V_S - V_B)} \frac{\prod_{j=1}^{3N} \omega_j^B}{\prod_{j=2}^{3N} \omega_j^{\ddagger}} \simeq \frac{\omega_1^B}{2\pi} e^{-\beta(V_S - V_B)} \qquad (21b)$$

In the last equalities in Eq. (21), we assume that the phonon frequencies parallel to the dividing surface are unchanged from $A \rightarrow \ddagger \rightarrow B$.