Master Equation

Partitioned configuration space

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

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

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

Let's define the probability to find the system in Rx at time t as

$$P_{\alpha}(t) = \iint \frac{dP dP}{h^{3N}} f(P, P, t)$$
 (2)

where $\mathfrak{A}=(\mathfrak{A}_1,...,\mathfrak{A}_{\mathfrak{DN}})$, $P=(P_1,...,P_{\mathfrak{N}})$, and $f(\mathfrak{A},P,t)$ is the phase space distribution.

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Time derivative

$$\frac{dR}{dt} = \iint \frac{d\mathbf{q} d\mathbf{P}}{h^{3N}} \frac{\partial}{\partial t} f(\mathbf{q}, \mathbf{P}, t)$$
(3)

$$= \iint \frac{dqdP}{h^{3N}} \left[-L \int (q,P,t) \right]$$
 (4)

$$= \iint_{\mathbb{R}} \frac{h^{3N}}{h^{3N}} \left[\frac{\partial H}{\partial P} \frac{\partial}{\partial P} \frac{\partial H}{\partial P} \frac{\partial}{\partial P} \right] \left(\frac{\partial H}{\partial P} \frac{\partial}{\partial P} \frac{\partial}{\partial P} \frac{\partial}{\partial P} \right) \left\{ \frac{\partial H}{\partial P} \frac{\partial}{\partial P} \frac{\partial}{\partial P} \frac{\partial}{\partial P} \frac{\partial}{\partial P} \right\}$$
(5)

where L is the Liouville operator and H(9,1P) is the Hamiltonian.

Consider a Hamiltonian

$$H(\mathfrak{A},P) = \sum_{i=1}^{\mathfrak{D}N} \frac{P_i^2}{2m_i} + V(\mathfrak{A})$$
 (6)

where m; is the mass associated with the i-th degree of freedom.

Substituting Eq.(6) in (5),

$$\frac{dP_{\mathcal{A}}}{dt} = \iint_{\mathbb{R}^{3N}} \frac{d\theta dP}{\hat{k}^{3N}} \frac{\partial \hat{P}_{i}}{\partial \hat{I}_{i}} \frac{\partial}{\partial \hat{I}_{i}} \int (\mathbf{q}_{i} P_{i} t) + \iint_{\mathbb{R}^{3N}} \frac{\partial V}{\partial \hat{I}_{i}} \frac{\partial V}{\partial \hat{I}_{i}} \frac{\partial}{\partial \hat{I}_{i}} \frac{\partial}{\partial \hat{I}_{i}} \frac{\partial}{\partial \hat{I}_{i}} \int (\mathbf{q}_{i} P_{i} t)$$

$$= \mathbb{R}_{\mathcal{A}}$$

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The second term in Eq. (7) is

$$C = \sum_{i=1}^{3N} \int_{h^{3N}} \frac{dq}{\partial q_i} \int_{h^{2N}} dp_i \dots dp_{i-1} dp_{i+1} \dots dp_{3N} \int_{-\infty}^{\infty} dp_i \frac{\partial}{\partial p_i} \int_{h^{2N}} (q_i p_i t)$$

 $\left[f(\mathfrak{A}, \mathbb{R}, t) \right]_{\mathbb{R} = -\infty}^{\mathbb{R}_i = +\infty} = 0$

(@ zero probability for infinite momentum)

= 0

$$\frac{dP_{a}}{dt} = \iint_{R_{a}} \frac{dP_{dP}}{dP_{i}} \frac{3N}{i=1} \frac{\partial Q_{i}}{\partial Q_{i}} \left(\frac{P_{i}}{m_{i}} f(Q_{i}P_{i}t) \right) \left(\bigodot \frac{\partial}{\partial Q_{i}} \notin P_{i} \text{ commute} \right) \\
= -\iint_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP_{i}}{m_{i}} f(Q_{i}P_{i}t) \int_{R_{a}} Gauge \text{ theorem}^{V}$$

$$= -\iint_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP_{i}}{m_{i}} f(Q_{i}P_{i}t) \int_{R_{a}} Gauge \text{ theorem}^{V}$$

$$= -\iint_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP_{i}}{m_{i}} f(Q_{i}P_{i},t) \int_{R_{a}} Gauge \text{ theorem}^{V}$$

$$= -\iint_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP_{i}}{m_{i}} f(Q_{i}P_{i},t) \int_{R_{a}} Gauge \text{ theorem}^{V}$$

$$= -\iint_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP_{i}}{m_{i}} f(Q_{i}P_{i},t) \int_{R_{a}} Gauge \text{ theorem}^{V}$$

Here, ds is the surface element pointing outward normal to the surface ∂R_{α} , and thus Eq.(8) is the negative of the outward flux through the surface ∂R_{α} .

Let's partition alk into

(9)

where S_{pa} is the surface splitting R_{d} and R_{p} , with normal pointing from d to g. We also distinguish the outgoing $\left(\sum_{i}dS_{i}\frac{R_{i}}{m_{i}}>0\right)$ and incoming $\left(\sum_{i}dS_{i}\frac{R_{i}}{m_{i}}<0\right)$ fluxes.

Then

 $1 = \Theta(x) + \Theta(-x)^{1}$ Obama Hilary.

$$\frac{dP_{\alpha}}{dt} = \sum_{\beta} \int_{i=1}^{3N} dS_{i} \int_{k^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{M_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) f(P_{i}, P_{i}, t)$$

$$\sum_{\beta} \int_{\Sigma_{i}}^{3N} dS_{i} \int_{h^{3N}}^{2N} \frac{P_{i}}{m_{i}} O\left(-\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) f(P_{i}, P_{i}, t)$$

Redefining the surface $\mathfrak{S}_{pq} \to \mathfrak{S}_{ap}$ (or flipping the surface normal

 $dS \rightarrow -dS$) in the second term,

$$\frac{dP_{d}}{dt} = -\sum_{\beta} \int_{i=1}^{3N} dS_{i} \int_{K^{3N}}^{3N} \frac{dP}{m_{i}} O\left(\sum_{\xi} dS_{\xi} \frac{P_{\xi}}{m_{i}}\right) f(\mathbf{P}, P, t)$$

$$+\sum_{\beta} \int_{i=1}^{3N} dS_{\xi} \int_{K^{3N}}^{3N} \frac{dP}{m_{i}} O\left(\sum_{\xi} dS_{\xi} \frac{P_{\xi}}{m_{i}}\right) f(\mathbf{P}, P, t)$$

$$+\sum_{\beta} \int_{i=1}^{3N} dS_{\xi} \int_{K^{3N}}^{3N} \frac{dP}{m_{i}} O\left(\sum_{\xi} dS_{\xi} \frac{P_{\xi}}{m_{i}}\right) f(\mathbf{P}, P, t)$$

$$(11)$$

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

_	Transition state theory (TST) approximation
	In the TST approximation, we assume that within each Pa
	the phase-space distribution is locally in thermal equilibrium
The second secon	weighted to reproduce the current probability, i.e.,
100 m av 100	$\int (\P, P, t) = \frac{P_{\alpha}(t)}{P_{\alpha}(e_{\beta})} \int_{e_{\beta}} (\P, P) \qquad (\P \in \mathbb{R}_{\lambda})^{1/2} $ (12)
	where \
1	$\int_{e_{\overline{Q}}} (\mathfrak{A}, \mathbb{P}) = \frac{1}{Q} e^{-\beta H(\mathbf{Q}, \mathbb{P})} $ $\tag{13}$
The state of the s	$Q = \iint \frac{dq dP}{h^{3N}} e^{-\beta H(q, P)} \tag{14.4}$
	$= \sum_{\alpha} \iint \frac{d\theta dP}{h^{3N}} e^{-\beta H(\theta,P)} = \sum_{\alpha} Q_{\alpha}$ which region to pick. (146)
A province of the control of the con	$P_{\alpha}(e_{\delta}) = \frac{Q_{\alpha}}{Q} = \frac{1}{Q} \iint \frac{d\mathfrak{A}dP}{h^{3N}} e^{-\beta H(\mathfrak{P},P)} $ (15)
The control of the co	and $\beta = 1/k_BT$ is the inverse temperature.
And the control of th	Substituting the TST approximation (12) in Eq. (11),
The state of the s	$\frac{dP_{d}}{dt} = -\sum_{\beta} \sum_{i=1}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{i=1}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{i=1}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{i=1}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{i=1}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{eg}^{2N} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} O\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) \int_{eg}^{Q} (q_{i}P) \frac{P_{d}(t)}{P_{d}(eg)} $ $= \int_{g}^{2N} \int_{eg}^{2N} dS_{i} \int_{eg}^{2N} dS_{i} \int_{eg}^{2N} \frac{P_{d}(eg)}{P_{d}(eg)} \int_{eg}^{2N} P_{d$
Total programme and the state of the state o	$+\sum_{\beta}\sum_{i=1}^{3N}dS_{i}\int_{R^{3N}}\frac{dP}{m_{i}}\frac{P_{i}}{\Theta\left(\frac{\Sigma}{\epsilon}dS_{i}\frac{P_{i}}{m}\right)}\frac{P_{e}\left(q_{i}P\right)}{P_{e}\left(e_{S}^{N}\right)}\frac{P_{B}\left(t\right)}{\left(\frac{\odot}{\epsilon}\sigma nl_{y}}\frac{P_{B}\left(\sigma nl_{y}\right)}{P_{B}\left(e_{S}^{N}\right)}$
Character Strange and	(16)
of the state of th	
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$$\frac{dP_{\alpha}}{dt} = -\sum_{\beta} W_{\beta\alpha} P_{\alpha}(t) + \sum_{\beta} W_{\alpha\beta} P_{\beta}(t)$$
 (17)

where
$$W_{\alpha\beta} = \int_{i=1}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}}^{3N} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{dP}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}}^{3N} (9,P) / P_{p}(e_{g})$$

$$= \int_{a_{g}}^{3N} dS_{i} \int_{a_{g}}^{3N} dS_{i} \int_{h^{3N}} \frac{P_{i}}{m_{i}} \frac{P_{i}}{P_{i}} \left(\frac{Z}{i} dS_{i} \frac{P_{i}}{m_{i}} \right) \int_{e_{g}}^{3N} (9,P) / P_{p}(e_{g})$$

$$= \int_{\frac{2N}{c-1}}^{\frac{2N}{c}} dS_{i} \int_{h^{3N}}^{dP} \frac{P_{i}}{m_{i}} \Theta\left(\sum_{i} dS_{i} \frac{P_{i}}{m_{i}}\right) e^{-\beta H(\mathbf{q},P)} / \int_{h^{3N}}^{d\mathbf{q}dP} \frac{d\mathbf{q}dP}{h^{3N}} e^{-\beta H(\mathbf{q},P)}$$
(18b)