NOTES ON

Chapter 1

BARRIER CROSSINGS: CLASSICAL THEORY OF RARE BUT IMPORTANT EVENTS

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in "Classical and Quantum Dynamics in Condensed Phase Simulations: proceedings of the International School of Physics, Lerici, Villa Marigola, 7 July-18 July 1997", B. J. Berne, G. Ciccotti, and D. F. Coker, eds., pp 583-616, World Scientific, Singapore, 1998.

1. - INTRODUCTION (Excellent read!)

a. Rare events:

Bottleneck (a high barrier or pass) separates stable states

b. Importance sampling:

Chain folding: $\tau \approx 10^{-6} s$

Movie of this event runs at 1 minute/ps of trajectory.

Thus a display of this event requires 2 years of film for $10^{6} ps$**.**

Therefore want to explore only the relevant region of phase space, the bottleneck or barrier region, and to avoid watching the system when it is in the region of a stable state (where it is most of the time).

2. - CYCLOHEXANE ISOMERIZATION

... <--> chair <--> boat <--> chair <--> ... (1 = 2.1)

a. Time scales:

Slow reaction:

$$\tau(isomerization) \approx 0.1 s$$

Fast microscopic processes -

Brownian, coarse-grained in time:

$$\tau(diffusion) \approx 10^{-11} s$$

$$\tau(velocity \quad autocorrelation) \approx 10^{-12} s$$

Very fast collisional events:

$$\tau(collision) \approx 10^{-14} s$$

b. Properties of isomerization process:

i. Pressure dependence - Fig. 1

Analyze and seek to understand through MD simulations; note that the rate increases with increasing pressure.

ii. Potential energy function - Fig. 2

$V(\theta,\phi)$

iii. Free energy function - Fig. 3

$$-\beta F(\theta) = \ln \int_0^{2\pi} d\phi \; e^{-\beta V(\theta,\phi)} \qquad (2 = 2.2)$$

where $F(\theta)$ **is the free energy (the work function; the potential of mean force) along the reaction coordinate** θ**.**

3. - HIGH BARRIERS, RARE EVENTS

a. Free energy function - Fig. 4:

$q = q^*$, **the transition state,**
must be passed for A <--> B.

$F^* >> kT$**: passages rare.**

System committed to stable state at small displacement l **from** q^***.**

NOTE: The picture and symbols of Fig. 4 are used throughout the discussion of this Chapter.

b. Dynamics vs equilibrium:

Configurations near q^* **rare and not important for equilibrium properties.**

q^* **region governs dynamics.**

c. Kinetic energy (T_k):

T_k small when system near q^*.

T_k large after system passes q^*:
large $-\partial V/\partial q$ => large acceleration.

Deactivation and trapping by energy flow from q to other degrees of freedom.

d. Frequency of passage, ν:

passage through q^* fast, ca. 10^{-13}:

$$\tau_{mol} = \nu^{-1} \approx l/\langle|\dot{q}|\rangle \qquad (3\text{-}4 = 3.1\text{-}2)$$

e. Reaction rate:

$$k \approx \nu \ e^{-\beta F^*} \qquad (5 = 3.3)$$

$$k^{-1} = \tau_{rxn} \approx \tau_{mol} \ e^{\beta F^*} \qquad (6 = 3.4)$$

Arrhenius behavior - hallmark of a barrier crossing: characteristic time τ_{rxn} grows exponentially with F^*/kT.

4. - REACTION COORDINATE, $q(t)$

a. Trajectory - Fig. 5:

"instanton" - passage between stable states.

Note dithering at q^*.

b. Probability distribution:

Histogram:

$$P(q) = <\delta(q(t) - q)> \qquad (7 = 4.1)$$

$$= \frac{1}{T}\int_0^T dt\ \delta(q(t) - q)$$

$$= \int_\Gamma d\Gamma\ \delta(q(\Gamma) - q)\, e^{-\beta H(\Gamma)}\ /\ Q$$

c. Importance sampling:

For statistical significance, $T >> \tau_{rxn}$, which generally is not possible in a simulation.

Need to control q in order to examine rare states, near $q*$.

Use umbrella sampling.

For cyclohexane in liquid CS_2 solvent, find barrier to isomerization increases slightly with increased pressure; thus isomerization rate should decrease with pressure, counter to experiment (Fig. 1). The explanation must reside in the non-Arrhenius prefactor, ν.

5. - RATE CONSTANTS AND TIME CORRELATION FUNCTIONS

a. Time evolution of population operator:

Fig. 6.

The trajectory is for a time of 15 τ_{rxn}.

The population operator is:

$$h(q) = 1, \quad q > q^* \qquad (10 = 5.1)$$
$$= 0, \quad q < q^*$$

or equivalently,

$$h(q) = \theta(q - q^*)$$

The population operator is 1 for state B.

The fraction time spent in state B

$$x = < h >$$

b. Various relationships:

$$h(t) = h(q(t))$$

$$h = h(0) = h(q(0))$$

$$h^2 = h$$

$$\delta h = h - \langle h \rangle$$

$$\begin{aligned} \langle h\ \delta h \rangle &= \langle h^2 \rangle - \langle h \rangle^2 = \langle h \rangle - \langle h \rangle^2 \\ &= x\ (1-x) \\ &= x\ \overline{\delta h}(0)\ e^{-kt} \end{aligned}$$

$$\dot{h} = \frac{dh}{dt} = \frac{dh}{dq}\frac{dq}{dt} = \delta(q-q^*)\ \dot{q}$$

$$-\langle h\ \dot{h}(t) \rangle = \langle \dot{h}\ h(t) \rangle$$

$$P(q^*) = (1 - x_B)\ \frac{e^{-\Delta W^*/kT}}{Q_A}$$

$$k_f^{TST} = \frac{\omega_A}{2\pi} e^{-\Delta W^*/kT} \qquad \text{(Hynes-4)}$$

c. Time correlation of h with its fluctuation:

$$\delta h(t) \; = \; h(q(t)) - \langle h \rangle \qquad (11 = 5.2)$$

$$\langle h \; \delta h(t) \rangle \; = \; \frac{1}{T}\int_0^T dt' \; h(t')\,\delta h(t'+t) \qquad (12 = 5.3)$$

$$= \; x\frac{1}{T}\int_0^T dt' \; 1\cdot\delta h(t'+t)\Big]_{h(t')=1} \; +$$

$$(1 \; - \; x)\frac{1}{T}\int_0^T dt' \; 0\cdot\delta h(t'+t)\Big]_{h(t')=0}$$

$$= \; x \; \frac{1}{T}\int_0^T dt' \; \delta h(t'+t)\Big]_{h(t')=1}$$

$$= \; x \; \overline{\delta h}(t)$$

$\overline{\delta h}(t)$ **is a** *nonequilibrium* **average, over trajectories started in state B, with** $h \; = \; 1$**.**

d. Relaxation of $<h\ \delta h(t)>$:

Relaxation of the time correlation function is determined by the relaxation of $\overline{\delta h}(t)$. Correlation (memory of the initial state B) is lost as the system undergoes sequential transitions A<-->B. The transitions are rare events and are statistically independent. They constitute a Poisson stochastic process. The relaxation, like radioactive decay, is exponential in the time, i.e., a first order process:

$$\overline{\delta h}(t) \approx \overline{\delta h}(0)\ e^{-kt} \qquad (13 = 5.4)$$

The constant k is the average transition frequency, or equivalently, k^{-1} is the average lifetime of state B.

Both $<h\ \delta h(t)>$ and $\overline{\delta h}(t)$ go to zero in the limit of large time, $t >> 1/k$.

e. Phenomenology:

Consider now a macroscopic isomerization process, A<-->B, between species that we can understand correspond to the microscopic states A and B.

We can assert a rate law and test it by experiment.

A two-state isomerization is characterized by a first-order rate constant that is the sum of the forward and reverse reactions:

$$k = k_{A \rightarrow B} + k_{B \rightarrow A} \qquad (14a = 5.5a)$$

Also, by detailed balance,

$$x/(1 - x) = k_{A \rightarrow B}/k_{B \rightarrow A} \qquad (14b = 5.5b)$$

where $x = X_B$**, the mole fraction of the species B in the isomerization process.**

f. Onsager's Hypothesis:

Onsager asserted that for a system near equilibrium, on average the microscopic dynamics of the decay of large fluctuations in a variable (decay of the time correlation function), are the same as the dynamics of relaxation of the variable to its equilibrium value in a macroscopic system.

By Onsager's Hypothesis, we can identify the macroscopic rate constant k of Eqn. (14 = 5.5) with the microscopic relaxation constant k of Eqn. (13 = 5.4)

For the following discussion, the constant k is identified with both the microscopic and macroscopic processes.

6. - REACTIVE FLUX CORRELATION FUNCTION:

a. Definition:

Combining Eqns. (12 = 5.3) and (13 = 5.4):

$$\begin{aligned} < h \ \delta h(t) > \ &= \ x \ \overline{\delta h}(0) \ e^{-kt} \\ &= \ < h \ \delta h > e^{-kt} \end{aligned}$$

to give

$$\frac{< h \ \delta h(t) >}{< h \ \delta h >} \ = \ e^{-kt}$$

We define the reactive flux correlation function, $k(t)$, as the time derivative of the preceding expression:

$$k(t) \ = \ -\frac{d}{dt} \frac{< h \ \delta h(t) >}{< h \ \delta h >} \qquad \text{(15a = 5.6a)}$$

$$\approx \ k e^{-kt} \qquad \text{(15b = 5.6b)}$$

Carrying out the differentiation of Eqn. (15a = 5.6a),

$$k(t) = -\frac{d}{dt}\left[\frac{<h\ h(t)> - <h<h>>}{<h\ \delta h>}\right]$$

$$= -\frac{<h\ \dot{h}(t)>}{<h\ \delta h>}$$

$$= \frac{<\dot{h}\ h(t)>}{<h\ \delta h>}$$

to give

$$k(t) = \frac{1}{x\ (1 - x)} <\dot{q}\ \delta(q - q^*)\ h(q(t))> \qquad (16 = 6.1)$$

where we have used the chain rule and several identities and definitions,

$$\dot{h} = \frac{dh}{dt} = \frac{dh}{dq}\frac{dq}{dt} = \delta(q - q^*)\ \dot{q}$$

$$-<h\ \dot{h}(t)> = <\dot{h}\ h(t)>$$

$$<h\ \delta h> = x\ (1 - x)$$

$$h(t) = h(q(t))$$

b. Computable form of reactive flux correlation function:

Eqn. (16 = 6.1) can be rewritten for computation with importance sampling of the barrier top configurations:

$$k(t) = \frac{1}{x\,(1 - x)} P(q^*) < \dot{q}\; h(q(t)) >_{q^*} \tag{17 = 6.2}$$

where $P(q^*) = < \delta(q - q^*) >$ **and** $<\ldots>_{q^*}$ **means averaging with** q **initially (for** $t = 0$**) constrained to** q^***.**

$P(q^*)$ **can be evaluated with umbrella sampling, and the conditional average, with trajectories starting at the barrier top.**

Eqn. (17 = 6.2) is the central result of this Chapter.

c. How does this function behave? Limit of very small $t \to 0+$:

Since $q(0) = q^*$, a very short time later,

$$h(q(t)) = 1, \qquad \dot{q} > 0$$
$$h(q(t)) = 0, \qquad \dot{q} < 0$$

Thus

$$k(0^+) = \frac{1}{x(1-x)} P(q^*) < \dot{q}\,\theta(\dot{q}) >_{q^*} \qquad (18 = 6.3)$$
$$= \frac{1}{x(1-x)} P(q^*) \frac{1}{2} < |\dot{q}| >_{q^*}$$

Eqn. (18 = 6.3) is the Transition State Theory (TST) approximation: all trajectories at the barrier top are in the product direction and do not recross ("dither" at) the barrier top.

Evaluating $P(q^*)$ gives a more traditional TST equation.

For isomerization and a symmetrical two-well potential:

$$P(q^*) = x \frac{e^{-\Delta W^*/kT}}{Q}$$

$$k_{B \to A}^{TST} = (1 - x)\ k(0^+)$$

$$= \frac{1}{2} <|\dot{q}|>_{q^*} \frac{e^{-\Delta W^*/kT}}{Q}$$

Compare above with Ghosh and McCammon (1987).

Evaluating Q and $<|\dot{q}|>_{q^*}$,

$$k_{B \to A}^{TST} = \frac{\omega_A}{2\pi} e^{-\Delta W^*/kT}$$

Compare above with Hynes (1988).

c. How does this function behave?
For $\tau_{mol} \ < \ t \ << \ \tau_{rxn} = 1/k$**:**

[Read page 15.]

Any barrier recrossing reduces $k(t)$**:**
Examine Eqn. (17 = 6.2).

After a time $\geq\tau_{mol}$**, trajectories initiated at the barrier top will be committed to one of the stable states.**

At times $\tau_{mol} \ < \ t \ << \ \tau_{rxn} = 1/k$**,**
$exp(-kt) \ \approx \ 1$ **and** $k(t)$ **will have relaxed to the stable (constant) value** k**:**
Examine Fig. 7.

The factor κ **is evaluated as:**

$$\kappa \ = \ k(\tau_{mol})/k(0^+) \ = \ k/k(0^+) \ = \ k/k^{TST}$$

7. - CHOOSING THE TRANSITION STATE

Choose transition state q^* that minimizes $k(0^+)$.

8. - LINDEMANN-HINSHELWOOD AND KRAMERS REGIMES - Fig. 8

a. Weak coupling (Lindemann-Hinshelwood) regime: Coupling (inter- or intramolecular) of reaction coordinate to bath is necessary for deactivation after barrier crossing. Without coupling, barrier recrossed repeatedly. Reaction rate increases with increased coupling.

b. Strong coupling (Kramers) regime: Strong coupling of reaction coordinate to bath results in diffusive motion at barrier top. Expected for reaction in a condensed phase. Increased coupling (e.g., greater viscosity) reduces reaction rate.

Kramers equation for strong friction (high viscosity γ):

$$k_{A \to B}^{overdamped} = \frac{\omega_A \omega_{q^*}}{2\pi\gamma} e^{-\beta \Delta W^*}$$

$$= \frac{\omega_{q^*}}{\gamma} k_{A \to B}^{TST}$$

9. - CYCLOHEXANE REACTIVE FLUX

[Read pages 18-21.]

Central point: A short but not negligible time is required to commit a molecule to a stable state. Within this time, transient trajectories can recross the transition state. Since coupling to a solvent can accelerate the equililbration, the coupling will lower the number of recrossing trajectories and thus increase the net rate. For this to be the case, the isomerization of cyclohexane in CS_2 must be between the low and high coupling regimes.