Lecture 23:

Non-Equilibrium Pt 3

Other kinds of Brownian Motion

The general theory we are learning is useful for other kinds of random processes besides a particle in solution

To illustrate this, lets look @ chemical reactions

Simplest reaction is

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

expect $\frac{dA}{dt} = Bk_B - Ak_f$

$$\frac{dB}{dt} = Ak_f - Bk_B$$

In this case, we know

$$A + B = N$$ ← const # molecules

@ Eq still true, $A_{eq} + B_{eq} = N$

In the spirit of our prev work, think about

$A = A_{eq} + C$, A at a particular time is a deviation from eq

This means $B = B_{eq} - C$

C measures reaction condition from all in A ($C = B_{eq}$) to all in B ($C = -A_{eq}$)

Lastly, we have our detailed balance condition

$$A_{eq} k_f = k_B B_{eq}$$

Combining this info, we have

$$\frac{d(A_{eq}+C)}{dt} = -k_f(A_{eq}+C) + k_B(B_{eq}-C)$$

$$\frac{d(B_{eq}-C)}{dt} = k_f(A_{eq}+C) - k_B(B_{eq}-C)$$

$$\frac{dA_{eq}}{dt} = \frac{dB_{eq}}{dt} = 0$$

Subtract: $2\frac{dC}{dt} = 2k_B(B_{eq}-C) - 2k_f(A_{eq}+C)$

$$\Rightarrow \frac{dC}{dt} = -(k_f + k_B)C$$

$$\Rightarrow C(t) = e^{-(k_f+k_B)t} \Leftarrow \tau_{rxn} = \frac{1}{k_f+k_B}$$

Macroscopic diff from eq decays to eq. exponentially

Onsager Regression Hypothesis (1931)

Small fluctuations decay on the average @ eq the same way as macroscopic non eq deviations

[not really a hypothesis, more like so far always true theory/law]

Makes sense, how would you know whether prepared in this state, or result of true dynamics

$$\Rightarrow \langle C(t)\, C(t') \rangle = \langle C^2 \rangle_{eq}\, e^{-(k_1+k_2)|t-t'|}$$

However, it can't be true that the non eq condition goes to $C=0$...

... and then the number of A & B are fixed, they have to fluctuate randomly

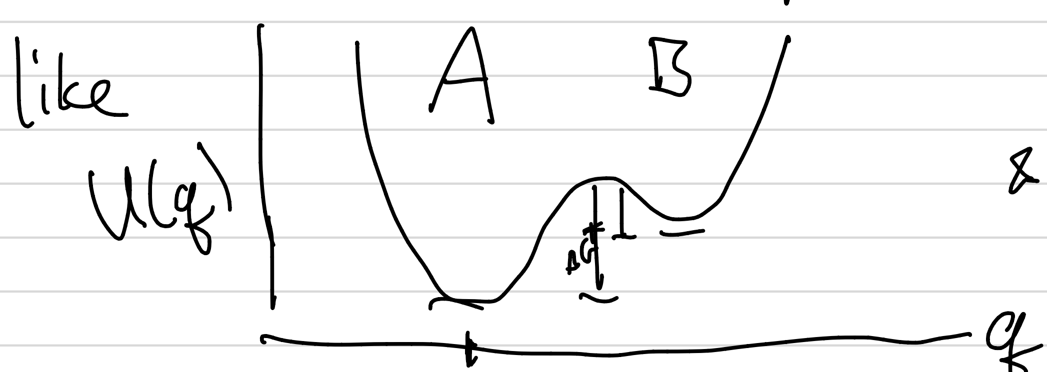
Have to maintain a $\langle c^2\rangle_{eq}$ that is non-zero

this is just like Brownian motion

so, postulate $\frac{dC}{dt} = -(k_1+k_2)C + \delta F$

HW → & now $\langle \delta F(t)\,\delta F(t')\rangle = 2(k_1+k_2)\langle C^2\rangle_{eq}\,\delta(t-t')$

This is a macroscopic view of chemical eq, but where do these rate constants come from. For this simple prob, we expect something like



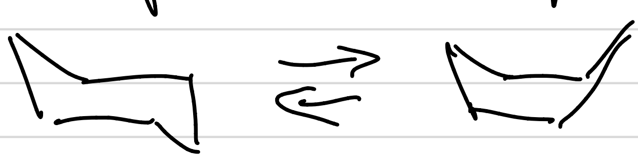
& $P_A/P_B \sim \Delta G$

& $k_{A\to B} \propto e^{-\beta\Delta G_A^{\ddagger}}$

$k_{B\to A} \propto e^{-\beta\Delta G_B^{\ddagger}}$

Now we have to connect this to the microscopic stat mech theory we've learned all semester. Molecularly, we still have $Q(x,p) = c\int d\vec{x}\int d\vec{p}\, e^{-\beta \mathcal{H}(\vec{x},\vec{p})}$

Real problem example could be



99.99%

Define q by a collective coordinate

transition state @ $q^\ddagger$

Can define a function $H_A(q) = \begin{cases} 1, & q < q^\ddagger \\ 0, & q \geq q^\ddagger \end{cases}$ (am I in A)

$$\langle H_A \rangle = X_A = \frac{A_{eq}}{A_{eq} + B_{eq}}$$

Since $H[A]$ is 1 in A & 0 otherwise

$$[H_A^2] = \frac{H_A(A)^2 P(A) + H_A(B)^2 P(B)}{P(A) + P(B)} = \frac{P(A)}{P(A)+P(B)} = X_A$$

$$\Rightarrow \langle \delta H_A^2 \rangle = \langle H_A^2 \rangle - \langle H_A \rangle^2 = x_A - x_A^2$$
$$= x_A(1-x_A) = x_A x_B$$

Now, already said

$$\langle C(t) C(0) \rangle = e^{-t/\tau_{rxn}} \cdot \langle c^2 \rangle$$

similarly at a microscopic level

$$\langle \delta H_A(q(t)) \delta H_A(q(0)) \rangle = e^{-t/\tau_{rxn}} \langle \delta H_A^2 \rangle$$

$$\Rightarrow e^{-t/\tau_{rxn}} = \frac{\langle \delta H_A(q(t)) \delta H_A(q(0)) \rangle}{x_A x_B}$$

call $H_A(q(t)) = H_A(t)$ for simplicity

since we care how the number in A is changing in time

take time deriv

$$-\frac{1}{\tau_{rxn}} e^{-t/\tau_{rxn}} = \frac{\langle \delta \dot{H}_A(t) \delta H_A(0) \rangle}{x_A x_B}$$

Last time sort of discussed @ eq 50

HW?
$$\langle A(t) A(t') \rangle = \langle A(0) A(t'-t) \rangle = \langle A(t-t') A(0) \rangle$$
$$\Rightarrow \langle A(0) \dot{A}(t) \rangle = \langle \dot{A}(0) A(t) \rangle$$

For our case $-\langle \delta H_A(0)\delta \dot{H}_A(t)\rangle = \langle \delta \dot{H}_A(0)\delta H_A(t)\rangle$

Important to note $\frac{dH[q]}{dt} = \dot{q}\frac{d}{dq}H_A = -\dot{q}\,\delta(q-q^*)$

Bc changes from $0 \to -\infty \to 0$ instantaneously

So $-\langle \delta H_A(0)\delta \dot{H}_A(t)\rangle = \langle -\dot{q}(0)\delta(q(0)-q^*)\ \delta H_A(q(t))\rangle$

$= \langle \dot{q}(0)\,\delta(q(0)-q^*)\,\delta H_B(q(t))\rangle$

Since $H_B = 1 - H_A$

and $\langle \dot{q}(0)\,\delta(q(0)-q^*)\rangle = 0$

b/c velocity & configs are uncorrelated

Finally

$$\frac{1}{\tau_{rxn}} e^{-t/\tau_{rxn}} = \frac{1}{x_A x_B}\langle \underset{\dot{q}}{\overset{\text{on surface}}{v^*}}(0)\,\delta[q(0)-q^*]\,H_B(q(t))\rangle$$

Right side is flux crossing surface if ends up in B

Left side is simple exponential & cant account for really short time flucs, hence evidence regression hypothesis is true only after coarse-graining over short time scales, so expect this to be true for $\tau_{mol} << t << \tau_{rxn}$ (fast barrier crossing)

If so $\frac{1}{\tau_{rxn}} = k_f + k_B = \frac{1}{x_A x_B} \langle \dot{v}(0) \delta(q(0) - q^*) H_B(q(t)) \rangle$

mult by x_B & detailed balance

$$x_B(k_f + k_B) = \frac{B}{A+B}(k_f + k_B) = \frac{B/A}{1 + B/A}(k_f + k_B) = \frac{\frac{k_f}{k_B}}{1 + \frac{k_f}{k_B}}(k_f + k_B)$$
$$= k_f$$

So $$k_f = \frac{1}{x_A} \langle \dot{v}(0) \delta(q - q^*) H_B[q(t)] \rangle$$

This connect microscopic behavior at the transition state to the macroscopic reaction rate let

$$n_A(t) = H_A[q(t)],$$

where

$$H_A[z] = 1, \quad z < q^*$$
$$= 0, \quad z > q^*.$$

Note

$$\langle H_A \rangle = x_A = \langle c_A \rangle / (\langle c_A \rangle + \langle c_B \rangle)$$

and

$$\langle H_A^2 \rangle = \langle H_A \rangle = x_A.$$

Hence

$$\langle (\delta H_A)^2 \rangle = x_A(1 - x_A)$$
$$\equiv x_A x_B.$$

Exercise 8.5 Verify these results.

According to the fluctuation-dissipation theorem, we now have

$$\exp(-t/\tau_{rxn}) = (x_A x_B)^{-1}[\langle H_A(0) H_A(t) \rangle - x_A^2].$$

To analyze the consequences of this relationship, we take a time derivative to obtain

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = -(x_A x_B)^{-1} \langle H_A(0) \dot{H}_A(t) \rangle,$$

where the dot denotes a time derivative. Since $\langle A(t)A(t')\rangle = \langle A(0)A(t'-t)\rangle = \langle A(t-t')A(0)\rangle$, we have

$$-\langle H_A(0) \dot{H}_A(t) \rangle = \langle \dot{H}_A(0) H_A(t) \rangle.$$

Exercise 8.6 Derive this result.

Furthermore,

$$\dot{H}_A[q] = \dot{q} \frac{d}{dq} H_A[q] = -\dot{q}\delta(q - q^*).$$

Hence

$$-\langle H_A(0) \dot{H}_A(t) \rangle = -\langle \dot{q}(0)\, \delta[q(0) - q^*] H_A[q(t)] \rangle$$
$$= \langle \dot{q}(0)\, \delta[q(0) - q^*] H_B[q(t)] \rangle,$$

where the second equality is obtained from

$$H_B[z] = 1 - H_A[z] = 1, \quad z > q^*,$$
$$= 0, \quad z < q^*,$$

and the fact that

$$\langle \dot{q}(0) \delta[q(0) - q^*] \rangle = 0.$$

This last result is true because the velocity is an odd vector function and the equilibrium ensemble distribution of velocities is even and uncorrelated with configurations. Combining these equations gives

$$\tau_{rxn}^{-1} \exp(-t/\tau_{rxn}) = (x_A x_B)^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(t)] \rangle,$$

where $v(0) = \dot{q}(0)$.

But this equality cannot be correct for all times. The left-hand side is a simple exponential. The right-hand side is an average flux crossing the "surface" at $q = q^*$ given that the trajectory ends up in state B. For short times, we expect transient behavior that should not correspond to the exponential macroscopic decay. This does not mean that the regression hypothesis is wrong. Rather, the phenomenological rate laws we have adopted can only be right after coarse graining in time. In other words, the phenomenology can only be right on a time scale that does not resolve the short time transient relaxation. On that time scale, let Δt be a small time. That is,

$$\Delta t \ll \tau_{rxn},$$

but at the same time

$$\Delta t \gg \tau_{mol},$$

where τ_{mol} is the time for transient behavior to relax. For such times, $\exp(-\Delta t/\tau_{rxn}) \approx 1$, and we obtain

$$\tau_{rxn}^{-1} = (x_A x_B)^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(\Delta t)] \rangle$$

or

$$k_{BA} = x_A^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(\Delta t)] \rangle.$$

To illustrate the transient behavior we have just described, let

$$k_{BA}(t) = x_A^{-1} \langle v(0) \delta[q(0) - q^*] H_B[q(t)] \rangle.$$

Exercise 8.7 Show that

$$k_{BA}(0) = (1/2x_A) \langle |v| \rangle \langle \delta(q - q^*) \rangle$$

and verify that this initial rate is precisely that of the transition state theory approximation,

$$k_{BA}^{(TST)} = (1/x_A) \langle v(0) \delta[q(0) - q^*] H_B^{(TST)}[q(t)] \rangle,$$

where

$$H_B^{(TST)}[q(t)] = 1, \quad v(0) > 0,$$
$$= 0, \quad v(0) < 0.$$