Lecture 23:
Non-Equilibrium Pt3
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, let's look at chemical reactions.

Simplest reaction is

\[ A \overset{k_f}{\underset{k_b}{\longrightarrow}} B \]

expect

\[ \frac{dA}{dt} = Bk_b - Ak_f \]

\[ \frac{dB}{dt} = Ak_f - Bk_b \]

In this case, we know

\[ A + B = N \text{ const \# molecules} \]
@ Eq still true, \( \text{Aeq} + \text{Beg} = N \)

In the spirit of our prev work, think about
\[
A = \text{Aeq} + C, \quad A \text{ at a particular time is a deviation from eq }
\]
This means \( B = \text{Beg} - C \)
\[
\text{C measures reaction condition from all in A (C = \text{Beg}) to all in B (C = -\text{Aeq})}
\]
Lastly, we have our detailed balance condition
\[
\text{Aeq} \text{t} = k_B \text{Beg}
\]
Combining this info, we have
\[
\frac{d(A_{eq} + C)}{dt} = -k_f(A_{eq} + C) + k_f(B_{eq} - C)
\]
\[
\frac{d(B_{eq} - C)}{dt} = k_f(A_{eq} + C) - k_B(B_{eq} - C)
\]
\[
\frac{dA_{eq}}{dt} = \frac{dB_{eq}}{dt} = 0
\]
Subtract:
\[
2 \frac{dC}{dt} = 2k_B(B_{eq} - C) - 2k_f(A_{eq} + C)
\]
\[ \frac{dc}{dt} = -(k_f + k_b)C \]

\[ \Rightarrow C(t) = e^{-(k_f + k_b)t} \]

Macroscopic shift from eg decays to eg, exponentially.

Onsager Regression Hypothesis [1931]
Small fluctuations decay on the average @ eg the same way as macroscopic deviations [not really a hypothesis, more like so for always true theory/law]
Makes sense, how would ya know whether prepared in this state, or result of true dynamics

\[ \Rightarrow \langle C(t)C(t') \rangle = \langle C^2 \rangle_{eq} e^{-(k_f + k_b)(t-t')} \]

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 nonzero, this is just like Brownian motion.

So, postulate \( \frac{dC}{dt} = (-kz + k2)C + SF \)

& now \( \langle SF(t) SF(t') \rangle = 2(k + k2) \langle c^2 \rangle_{eq} \delta(t - t') \)

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

\[
\text{H} \quad \frac{\text{H}}{2}
\]

\[
A \quad B
\]

\[
\text{h} \quad \text{h}
\]

\[
\frac{P_A}{P_B} \sim AG
\]

& \( k \sim \text{A} \Leftrightarrow \text{B} \quad \text{Ae} \Leftrightarrow \text{B} \)

& \( k \sim \text{A} \Leftrightarrow \text{B} \quad \text{Ae} \Leftrightarrow \text{B} \)
Now we have to connect this to the microscopic stat mech theory we've learned all semester. Molecularly, we still have \( Q(x,p) = e^{-\mathcal{H}(x,p)} \).

A real problem example could be

\[
\begin{array}{c}
\downarrow \quad \Leftrightarrow \quad \uparrow \\
99.99\%
\end{array}
\]

Define \( q \) by a collective coordinate transition state at \( q^* \) (can I in A).

Can define a function \( H_A(q) = \begin{cases} 1, & q < q^* \\ 0, & q \geq q^* \end{cases} \)

\[ <HA> = X_A = \frac{\text{Aeq}}{\text{Aeq} + \text{Beq}} \]

Since \( H[A,A] \) is 1 in A & 0 otherwise

\[
\left[ H_A^2 \right] = \frac{H_A(A)^2P(A) + H_A(B)^2P(B)}{P(A) + P(B)} = \frac{P(A)}{P(A) + P(B)} = X_A
\]
\[
\Rightarrow \langle 0 | \hat{H}_A^2 \rangle = \langle H_A^2 \rangle - \langle H_A \rangle^2 = X_A - X_A^2 = X_A(1 - X_A) = X_A \Lambda_B
\]

Now, already said

\[
\langle C(t) C(0) \rangle = e^{-t/\tau_{\text{ren}}} \cdot |x_4 \rangle
\]

Similarly at a microscopic level

\[
\langle \delta H_A(q_{\text{eff}}) \delta H_A(q_{\text{eff}}) \rangle = e^{-t/\tau_{\text{ren}}} \langle \delta H_A^2 \rangle
\]

\[
\Rightarrow e^{-t/\tau_{\text{ren}}} = \langle \delta H_A(q_{\text{eff}}) \delta H_A(q_{\text{eff}}) \rangle
\]

call \( H_A(q_{\text{eff}}) = H_A(q) \) for simplicity

since we are how the number in \( A \) is changing in time

take time data

\[
-\frac{1}{\tau_{\text{ren}}} e^{-t/\tau_{\text{ren}}} = \langle \delta H_A(t) \delta H_A(0) \rangle
\]

Last time sort of discussed

\[
\langle \hat{A}(t) \hat{A}(t') \rangle = \langle \hat{A}(0) \hat{A}(t - t') \rangle = \langle \hat{A}(t - t') \hat{A}(0) \rangle
\]

\[
\Rightarrow \langle \hat{A}(0) \hat{A}(t) \rangle = \langle \hat{A}(0) \hat{A}(t) \rangle
\]
For our case $- \langle \hat{H}_A(t) \hat{H}_A(t+1) \rangle = \langle \hat{H}_A(t) \hat{H}_A(t+1) \rangle$

Important to note $\frac{dH[f]}{dt} = -\frac{d}{df} H_A = -\frac{d}{df} S(\frac{f}{g})$

Be changes from $0 \rightarrow 0 \rightarrow 0$ instantaneously

So $- \langle \hat{H}_A(0) \hat{H}_A(t) \rangle = \langle -\delta_{g_0} \left( q_0, q \right) \ S \hat{H}_A(q(t)) \rangle$

$= \langle \delta_{q(0)} q_0(q_0(q) - q_0(q)) S \hat{H}_B(q(t)) \rangle$

Since $\hat{H}_B = -\hat{H}_A$

and $\langle \delta_{q(0)} S(q_0(q) - q_0(q)) \rangle = 0$

hence velocity & configs are uncorrelated

Finally $\frac{1}{2 \pi x_n} \ e^{-t/2 \pi x_n} \ L \langle \hat{U}(0) S \left[ q_0(q) q^+ \right] \hat{H}_B(q(t)) \rangle$

Right side is flux crossing surface it ends up in B

Left side is simple exponential & cant account for really short time fluxes, hence
Evidence regression hypothesis is true only after coarse-graining over short time scales, so expect this to be true for $t_{in} \ll t \ll t_{out}$ (fast barrier crossing).

If so, $\frac{1}{\tau_{\text{in}}} = k_f + k_0 = \frac{1}{\chi_A \chi_B} \langle U(0)S(g_1g_2)H_b(g,C_1) \rangle$

Multiply by $\chi_B$ & detailed balance

$\chi_B(k_f + k_0) = \frac{B}{A+B} (k_f + k_0) = \frac{\chi_B}{1 + \chi_B} (k_f + k_0) = \frac{k_f}{1 + \frac{k_f}{k_0}}$

$k_f = k_f$

So $k_f = \frac{1}{\chi_A} \langle U(0)S(g_1g_2)H_b[g,C_1] \rangle$

This connect microscopic behavior at the transition state to the macroscopic reaction rate
\[ 0 > (0)_n \quad 0 = \]
\[ 0 < (0)_n \quad I = [(i)b]_{LLS}^H H \]

Where the second equality is obtained from
\[ \langle (i)b \rangle_{LLS}^H H h_{\bar{b} - (0)b} \phi (0)_a \rangle \langle \psi x / 1 \rangle = \langle \psi \rangle \]

and verify that this initial state is precisely that of the
\[ \langle (\psi x - 1) \psi \rangle \psi x / 1 = \langle \psi \rangle \]

**Exercise 8.7:** Show that
\[ \langle (i)b \rangle_{HLS}^H H h_{\bar{b} - (0)b} \phi (0)_a \rangle \psi x = \langle \psi \rangle \]

To illustrate the transaction equation, we note that this state is defined as
\[ \langle (\psi x - 1) \psi \rangle \psi x / 1 = \langle \psi \rangle \]

For such times, where \( \tau \) is the time for transaction behavior to relax. For such times,

According to the equilibrium distribution theorem, we have

Where the second equality is obtained from
\[ \langle (i)b \rangle_{HLS}^H H h_{\bar{b} - (0)b} \phi (0)_a \rangle \psi x = \langle \psi \rangle \]

**Exercise 8.6:** Derive this result.

\[ \langle (0)^{\psi} H (0)^{\psi} \rangle = \langle (0)^{\psi} H (0)^{\psi} \rangle \]

where the last equality is obtained from
\[ \langle (0)^{\psi} H (0)^{\psi} \rangle \]

When the transaction equations, we have
\[ \langle (0)^{\psi} H (0)^{\psi} \rangle \]

According to the equilibrium distribution theorem, we have

This last result is true because the vectors are odd and even function.

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\[ 0 = ([b] - (0)b) \phi (0)_a \]

Furthermore,
\[ ([b] - (0)b) \phi (0)_a \]

**Exercise 8.5:** Verify these results.

\[ \langle (\psi x - 1) \psi \rangle \psi x / 1 = \langle \psi \rangle \]

Hence
\[ \langle (\psi x - 1) \psi \rangle \psi x / 1 = \langle \psi \rangle \]

and
\[ \langle (\psi x) \rangle \psi x / 1 = \langle \psi \rangle \]

Note
\[ \langle (\psi x) \rangle \psi x / 1 = \langle \psi \rangle \]

Therefore
\[ \langle (\psi x) \rangle \psi x / 1 = \langle \psi \rangle \]

where
\[ \langle (\psi x) \rangle \psi x / 1 = \langle \psi \rangle \]

Let
\[ \langle (\psi x) \rangle \psi x / 1 = \langle \psi \rangle \]