APPLICATIONS OF CORRELATION FUNCTIONS

Two important applications of correlation functions and Onsager's regression hypothesis as we use them in the Miller group:

CHEMICAL KINETICS

From phenomenological considerations, we have (for the reaction $A \rightleftarrows B$)

$$[\dot{A}] = -k_{BA}[A] + k_{AB}[B] \qquad (i)$$

$$[\dot{B}] = k_{BA}[A] - k_{AB}[B] \qquad (ii)$$

At equilibrium, detailed balance gives

$$K_{eq} \equiv \frac{[B]}{[A]} = \frac{k_{BA}}{k_{AB}}$$

Solving the differential equation (i):

$$\Delta[A] = \Delta[A]_0 e^{-(k_{AB}+k_{BA})t}$$

Now suppose we have $\bar{n}_A(t) \propto [A]$. From the fluctuation-dissipation theorem

$$\frac{\Delta[A]}{\Delta[A]_0} = \frac{\langle \delta n_A(0)\,\delta n_A(t)\rangle}{\langle (\delta n_A(0))^2\rangle} = e^{-(k_{AB}+k_{BA})t} \qquad (*)$$

Challenges: ① identify the dynamical variable $n_A(t)$
② do some integration of that correlation function

- ① We'll identify n_A as the Heaviside function on the surface separating A from B. That is, we define q^* along the reaction coordinate such that $q < q^*$ implies that we are in the A configuration, and $q > q^*$ implies that we are in B.

② That's what we really work on in the Miller group, now isn't it!

More details: w/ $n_A(t) = h_A(q(t))$

With $\langle h_A \rangle = \frac{\langle [A]\rangle}{\langle [A]\rangle + \langle [B]\rangle} \equiv x_A$ ($\langle h_A \rangle$ is the average of the time that the system is found in state A, which will be that)

We also have $\langle h_A^2 \rangle = \langle h_A \rangle = x_A$, since $h_A(q) = 1$ or 0 for any q.
From these, we obtain

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

Plugging this into (*):

$$e^{-(k_{AB}+k_{BA})t} = \frac{1}{x_A x_B}\left(\langle h_A(0)\, \dot{h}_A(t)\rangle - x_A^2\right)$$

Now an aside on the time derivative:

$$\langle A(t)A(t')\rangle = \langle A(0)A(t'-t)\rangle = \langle A(t'-t)A(0)\rangle \quad \text{(classically)}$$

so $\quad -\langle h_A(0)\,\dot{h}_A(t)\rangle = \langle \dot{h}_A(0)\, h_A(t)\rangle$

Also $\quad \dot{h}_A(q) = \dot{q}\frac{d}{dq}h_A(q) = -\dot{q}\,\delta(q-q^*)$

giving $\quad -\langle h_A(0)\,\dot{h}_A(t)\rangle = -\langle \dot{q}(0)\,\delta(q(0)-q^*)\, h_A(q(t))\rangle$

$$= \langle \dot{q}(0)\,\delta(q(0)-q^*)\, h_B(q(t))\rangle \qquad \text{from } \langle \dot{q}(0)\delta(q(0)-q^*)\rangle = 0$$

This gives us:

$$(k_{AB}+k_{BA})e^{-(k_{AB}+k_{BA})t} = (x_A x_B)^{-1}\langle \underbrace{v(0)\,\delta(q(0)-q^*)}_{\text{flux}}\ \underbrace{h_B(q(t))}_{\text{side}}\rangle$$

But this will only be true after transient (non-phenomenological) behavior has passed, so to get the rate, we have to take the long-time limit.