SUMMARY OF CHANDLER’S REACTIVE FLUX METHOD

I. ONSAGER’S HYPOTHESIS RELATES MACROSCOPIC AND MICROSCOPIC DYNAMICS:

By Onsager’s hypothesis (or by linear response theory) we may identify the rate constant for reaction of the macroscopic system with the rate constant for relaxation of the microscopic fluctuation of a relevant variable.

II. MACROSCOPIC PROPERTIES;
PHENOMENOLOGICAL DESCRIPTION OF A REACTING SYSTEM:

A. Prepare the system for study:

Prepare the system slightly perturbed from its equilibrium, such that $[B]_{t=0} > [B]_{eq}$ (and $[A]_{t=0} < [A]_{eq}$ by an exactly equal amount).

B. Measure the rate of reaction (rate of relaxation) as the system returns to equilibrium:

C. Analyze the data, to obtain the rate law:

$$\frac{\delta B(t)}{\delta B(0)} = e^{-kt} \qquad \text{(II.1)}$$

III. MICROSCOPIC DESCRIPTION; DECAY OF FLUCTUATIONS IN AN EQUILIBRIUM SYSTEM:

A. Background:

B. Construct a function describing the *isomerization* state of the system, and a function describing a *fluctuation* of the isomerization state about the equilibrium state:

$$h(q(t)) = \theta(q(t) - q^*) \qquad \text{(III.2)}$$

$$\delta h(t) = h(q(t)) - \langle h \rangle \qquad \text{(III.3)}$$

C. Analyze the relaxation of the fluctuations:

$$C_{\delta h} = \frac{\langle \delta h \delta h(t) \rangle}{\langle (\delta h)^2 \rangle} = \frac{\langle h \delta h(t) \rangle}{\langle h \delta h \rangle} = e^{-kt} \qquad \text{(III.4-6)}$$

D. Identify $k_{macroscopic} = k_{microscopic}$:

E. Definition of the reactive flux:

$$k(t) = -\frac{d}{dt} C_{\delta h} = k\ e^{-kt} \qquad \text{(III.7)}$$

$$k(t) = \frac{1}{x\ (1 - x)} P(q^*) \langle \dot{q}\ h(q(t)) \rangle_{q^*} \qquad \text{(III.9)}$$

$P(q^*)$ and the conditional average can be evaluated by MD methods. Eqn (III.9) is the central result of Chandler's reactive flux method.

F. Analysis of the reactive flux for the limit $t \rightarrow 0^+$:

$$k^{TST} = k(0^+) = \frac{1}{x\,(1 - x)} P(q^*) < \dot{q}\; \theta(\dot{q}) >_{q^*} \qquad \text{(III.9)}$$

Eqn. (III.9) is the transition state theory approximation (free flight of the activated complex over the barrier top, no recrossing, equilibrium on the reactant side).

$$k^{TST}_{A \rightarrow B} = \frac{1}{2} < |\dot{q}| >_{q^*} \frac{e^{-\Delta W^*/kT}}{Q} \qquad \text{(III.10)}$$

$$k^{TST}_{A \rightarrow B} = \frac{\omega_A}{2\pi} e^{-\Delta W^*/kT} \qquad \text{(III.11)}$$

G. Analysis of the reactive flux for times t^* in the range $\tau_{mol} < t^* << \tau_{rxn} = 1/k$:

Transient dynamics over a time $\approx O(\tau_{mol})$ reflect coupling of the reaction coordinate with other degrees of freedom, ...

$$k(t^*) = k\; e^{-kt^*} \qquad \text{(III.12)}$$

... there is a plateau value of the reactive flux that is the desired estimate of the macroscopic reaction rate:

$$k(t^*) \approx k \qquad \text{(III.13)}$$

$$k = \kappa\; k^{TST} \qquad \text{(III.14)}$$

$$\kappa = \frac{k}{k^{TST}} = \frac{k(t^*)}{k(0^+)}$$