

## 2.2: Onsager Regression Theory

At first glance, the relaxation of macroscopic non-equilibrium disturbances in a system might seem completely unrelated to the regression of microscopic fluctuations in the corresponding equilibrium system. However, they are intimately related by so-called **fluctuation-dissipation theorems**. The existence of this link between microscopic fluctuations and macroscopic relaxation was conjectured by Lars Onsager in 1931, some twenty years before it was finally proven to be true; hence it is often referred to as the **Onsager regression hypothesis**.

To formulate the hypothesis, we consider an observable  $A$  with  $\langle A \rangle_{eq} = 0$  that takes on a nonequilibrium average value  $\Delta A$  due to an applied external force  $f$  which acts during the time interval  $t \leq 0$  but becomes identically zero for  $t > 0$ .

For  $t \leq 0$ , the ensemble average of  $\Delta A$  can be expressed as

$$\Delta A = \frac{\langle A e^{-\beta(H-fA)} \rangle}{\langle e^{-\beta(H-fA)} \rangle} \approx \beta f [\langle A(0)A(0) \rangle - \langle A(0) \rangle^2] = \beta f C(0) \quad (2.2.1)$$

where the approximation being made is truncation of the Taylor series for each exponential to first order.

For  $t > 0$ , the system evolves according to  $H$  instead of  $H - fA$ , so  $\Delta A$  is no longer stationary, but acquires a time-dependence:

$$\Delta A = \frac{\langle A(t) e^{-\beta(H-fA)} \rangle}{\langle e^{-\beta(H-fA)} \rangle} \approx \beta f [\langle A(t)A(0) \rangle - \langle A(0) \rangle^2] = \beta f C(t) \quad (2.2.2)$$

Onsager's hypothesis states that the relaxation of the non-equilibrium value of  $\Delta A$  is related to its value at  $t = 0$  in the same way that the time correlation function for a spontaneous fluctuation is related to its value at  $t = 0$  :

$$\frac{\Delta A(t)}{\Delta A(0)} = \frac{C(t)}{C(0)} \quad (2.2.3)$$

### ✓ Example 2.2.1

The transition state theory of chemical kinetics can be formulated through the Onsager relation we've just presented. Consider a chemical equilibrium established between two species A and B,



with forward rate constant  $k_f$  and backward rate constant  $k_b$ .

### Equilibrium populations

We can describe the population dynamics of A and B deterministically in the macroscopic limit through a pair of coupled differential equations,

$$\begin{cases} \dot{P}_A = -k_f P_A + k_b P_B \\ \dot{P}_B = k_f P_A - k_b P_B \end{cases} \quad (2.2.5)$$

The equilibrium state of this system satisfies the detailed balance condition

$$k_f \langle P_A \rangle = k_b \langle P_B \rangle \quad (2.2.6)$$

where the angle brackets denote the equilibrium values of the populations. Taking the populations to be normalized to unity,  $\langle P_A \rangle + \langle P_B \rangle = 1$ , we can express  $\langle P_A \rangle$  in terms of the rate constants:

$$\langle P_A \rangle = \frac{\langle P_A \rangle}{\langle P_A \rangle + \langle P_B \rangle} = \frac{k_b}{k_f + k_b} \quad (2.2.7)$$

For notational simplicity, we introduce  $k = k_f + k_b$  and refer to the equilibrium populations  $\langle P_A \rangle$  and  $\langle P_B \rangle$  by  $q_A$  and  $q_B$ , respectively. With this new notation, we can express the equilibrium populations of A and B as

$$\begin{cases} q_A = \frac{k_b}{k} \\ q_B = \frac{k_f}{k} \end{cases} \quad (2.2.8)$$

If the initial state is all species A, the solution to the coupled differential equations indicates a decay to equilibrium with rate constant  $k$ , which we can write in terms of  $\Delta P_A(t) = P_A(t) - q_A$  as

$$\Delta P_A(t) = \Delta P_A(0)e^{-kt} \quad (2.2.9)$$

Setting this result aside for a moment, note that if we consider the energies of species A and B to be potential wells connected along a reaction coordinate  $x$ , then we can write down an expression for the fluctuation in occupation number  $n$  for each species as a function of  $x$ . The barrier between the A and B potential wells is a maximum at  $x = x_b$ ; see Figure 2.2.

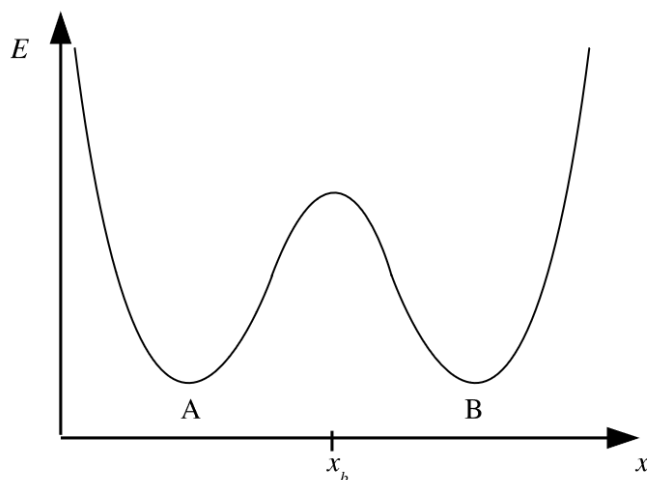


Figure 2.2: Projection of the potential energy surface connecting species A and B along reaction coordinate  $x$

### Application of Onsager Regression hypothesis

To reflect the fact that a particle to the left of the barrier is species A and a particle to the right is species B, we write the occupation numbers in terms of the Heaviside step function,

$$\begin{cases} n_A = \theta(x_b - x) \\ n_B = \theta(x - x_b) \end{cases} \quad (2.2.10)$$

where  $\langle n_A \rangle = q_A$  and  $\langle n_B \rangle = q_B$ . Applying Onsager's regression hypothesis to this example, we can relate the dissipation of  $P_A$  to the fluctuations in occupation number as follows:

$$\frac{C(t)}{C(0)} = \frac{\langle \delta n_A(t) \delta n_A(0) \rangle}{\langle \delta n_A^2(0) \rangle} = \frac{\Delta P_A(t)}{\Delta P_A(0)} = e^{-kt} \quad (2.2.11)$$

The second equality arises from our integrated rate equation for the dissipation of  $P_A$ . Also note that

$$\langle \delta n_A^2 \rangle = \langle n_A^2 \rangle - \langle n_A \rangle^2 = q_A - q_A^2 = q_A - q_A(1 - q_B) = q_A q_B \quad (2.2.12)$$

Differentiating the fluctuation-dissipation relation above with respect to  $t$  and invoking the identity just shown, we find

$$ke^{-kt} = -\frac{\langle \delta \dot{n}_A(t) \delta n_A(0) \rangle}{\langle \delta n_A^2(0) \rangle} = \frac{\langle n_A(t) \dot{n}_A(0) \rangle}{q_A q_B} \quad (2.2.13)$$

Recasting this equation in terms of the reaction coordinate  $x$ , we arrive at an expression for the time dependence of the forward rate constant  $k_f(t)$ ,

$$k_f(t) = k_f e^{-kt} = \frac{\langle \theta(x(t) - x_b) \delta(x_b - x(0)) v \rangle}{\langle \theta(x_b - x(t)) \rangle} \quad (2.2.14)$$

where  $v = \dot{n}_A(0)$  is the initial rate of reaction.

## Expression for the TST rate constant

Finally, to determine the transition state theory (TST) rate constant, we consider our time-dependent expression for  $k_f$  in the short-time limit, since transition states typically only survive a few molecular vibrations. In this limit,

$$\lim_{t \rightarrow 0^+} k_f(t) = \frac{\langle \theta(x(0^+) - x_b) \delta(x_b - x(0)) v \rangle}{\langle n_A \rangle} = \frac{\langle \theta(v) \delta(x_b - x(0)) v \rangle}{\langle n_A \rangle} \quad (2.2.15)$$

From the kinetic theory of gases, we recognize that

$$\langle \theta(v) v \rangle = \sqrt{\frac{k_B T}{2\pi m}} = (2\pi m \beta)^{-1/2} \quad (2.2.16)$$

If we stipulate now that the height of the barrier is  $E_b$ , some rearrangement of the preceding formulas reveals that

$$\frac{\langle \delta(x_b - x) \rangle}{\langle \theta(x_b - x) \rangle} = \sqrt{\frac{m \omega^2 \beta}{2\pi}} e^{-\beta E_b} \quad (2.2.17)$$

where  $\omega$  is the fundamental frequency of the left potential well. It follows that the TST rate constant takes on the simple form

$$k_{TST} = \frac{\omega}{2\pi} e^{-\beta E_b} \quad (2.2.18)$$

To conclude our excursion into TST kinetics, note that the ratio

$$\frac{k(t)}{k_{TST}} = \frac{\langle \theta(x(t) - x_b) \delta(x(0) - x_b) v \rangle}{\langle \theta(x(0^+) - x_b) \delta(x(0) - x_b) v \rangle} \quad (2.2.19)$$

is always less than or equal to one. This result indicates that the TST flux is partially trapped in the product well while part of the TST flux recrosses back to the reactant state. This result is in keeping with our intuition of chemical dynamics in that every macroscopic reaction is, to some degree, a process of establishing equilibrium rather than a perfect flow from all reactants to all products.

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