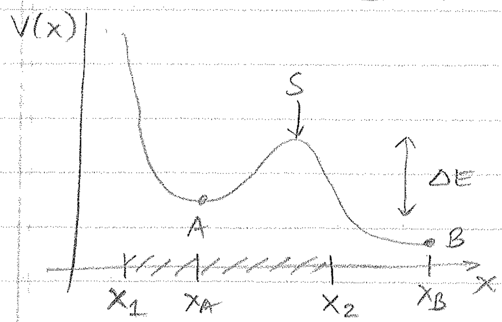
Transition Rates at Finite temperature



To find rate (transition probability per unit time) to go from $A \to B$:

- Assume damped motion (use Smoluchowski eqn)

$$\frac{\partial}{\partial t} P(x,t) + \frac{-1}{m\zeta} \frac{\partial}{\partial x}\left[P(x,t) \frac{\partial V}{\partial x} + k_B T \frac{\partial}{\partial x} P(x,t) \right] = 0$$

$$\equiv \frac{\partial}{\partial t} P(x,t) = -\frac{\partial}{\partial x} J(x,t)$$

Integrate from x_1 to x_2:

$$\frac{\partial}{\partial t} \int_{x_1}^{x_2} P(x,t)\, dx = -\int_{x_2}^{x_1} \frac{\partial}{\partial x} J(x,t)\, dx$$

$$= -J(x_1,t) + J(x_2,t)$$

This current represents rate at which transitions occur (through pt. 2)

- Assume high barrier (low rate)

$\hookrightarrow$ particles in vicinity of A assume Boltzmann (thermal) distribution

$$P(x,t) = \mathcal{N} e^{-V(x)/k_B T} \equiv \frac{1}{\int_A dx\, e^{-V(x)/k_B T}} e^{-V(x)/k_B T} \quad \left[\begin{matrix}\text{in vicinity} \\ \text{of } x_A\end{matrix}\right]$$

- Assume no particles in region B.

$$P(x,t) = 0 \quad \left[\begin{matrix}\text{in vicinity} \\ \text{of } x_B\end{matrix}\right]$$

- Assume this distribution for all times $\longrightarrow$ as particles make transition to B, they are filtered out and replaced in A.

Requirement of stationarity means: (see Sm. equation)

$$\frac{\partial}{\partial t} P(x,t) = 0 \quad \Rightarrow \quad \frac{\partial}{\partial x} J(x,t) = 0$$

$$\Rightarrow \frac{-1}{m\zeta} \frac{\partial}{\partial x}\left[P(x,t) \frac{\partial V}{\partial x} + k_B T \frac{\partial}{\partial x} P(x,t) \right] = 0$$

Integrate once:

integration constant

$$-\frac{1}{m\zeta}\left[P(x,t)\frac{\partial V}{\partial x} + k_B T \frac{\partial}{\partial x} P(x,t)\right] = C_{int} = J(x,t)$$

transition rate (indep of x)

then use ansatz: $P(x,t) = e^{-V(x)/k_B T} p(x,t)$

$$\underbrace{e^{-V(x)/k_BT} p(x,t)}\frac{\partial V}{\partial x} + k_B T\left[\frac{-1}{k_B T}\frac{\partial V}{\partial x} \underbrace{e^{-V(x)/k_BT} p(x,t)} + e^{-V(x)/k_BT}\frac{\partial p}{\partial x}\right] = -m\zeta C_{int}$$

cancel

$$\Rightarrow \frac{\partial p}{\partial x} = \frac{-m\zeta}{k_B T} C_{int}\, e^{V(x)/k_B T}$$

Integrate 2nd time:

Integration constant

$$p(x,t) = D_{int} - \frac{m\zeta}{k_B T} C_{int} \int_{x_A}^{x} dx'\, e^{V(x')/k_B T}$$

To determine integration constants, require that

① $P(x_A,t) = \mathcal{N} e^{-V(x_A)/k_BT} \quad \Rightarrow \quad p(x_A,t) = \mathcal{N} = \dfrac{1}{\int dx\, e^{-V(x)/k_BT}}$

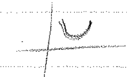
② $P(x_B,t) = 0 \quad \Rightarrow \quad p(x_B,t) = 0$

① $\Rightarrow$ $D_{int} = \mathcal{N}$

② $\Rightarrow$ $0 = \mathcal{N} - \dfrac{m\zeta}{k_BT} C_{int} \displaystyle\int_{x_A}^{x_B} dx'\, e^{V(x')/k_BT}$

$$\boxed{C_{int} = \frac{k_B T}{m\zeta} \frac{\mathcal{N}}{\int_{x_A}^{x_B} dx\, e^{V(x)/k_BT}} = J(x,t) \quad \text{: Transition Rate}}$$

- Make Gaussian approximation on $V(x)$ at x_A



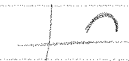
$$V(x) \simeq V(x_A) + \underbrace{(x-x_A)V'(x_A)}_{\text{vanishes at min.}} + \frac{1}{2}(x-x_A)^2 \underbrace{V''(x_A)}_{\equiv \omega_0^2} + \mathcal{O}(x^3) \qquad \left[\frac{\text{Energy}}{\text{length}^2}\right] = \left[\frac{kg}{s^2}\right]$$

$$= V(x_A) + \frac{1}{2}(x-x_A)^2\omega_0^2$$

$$\mathcal{N} = \left[\int_A dx\, e^{-[V(x_A)+\frac{1}{2}\omega_0^2(x-x_A)^2]/k_BT}\right]^{-1} \simeq \left[e^{-\frac{V(x_A)}{k_BT}}\int_{-\infty}^{+\infty} dx\, e^{-\frac{1}{2}\omega_0^2 x^2/k_BT}\right]^{-1}$$

$$= \left[\frac{\sqrt{2\pi k_BT}}{\omega_0} e^{-\frac{V(x_A)}{k_BT}}\right]^{-1} = \frac{\omega_0}{\sqrt{2\pi k_BT}} e^{V(x_A)/k_BT}$$

- Make Gaussian approximation on $V(x)$ at x_B



$$V(x) \simeq V(x_B) + \cancel{(x-x_B)V'(x_B)} + \frac{1}{2}(x-x_B)^2 \underbrace{V''(x_B)}_{\equiv \omega_-^2 < 0} + \mathcal{O}(x^3)$$

Then, $$\int_{x_A}^{x_B} dx\, e^{V(x)/k_BT} \simeq \int_{x_A}^{x_B} dx\, e^{[V(x_B)+\frac{1}{2}\omega_-^2(x-x_B)^2]/k_BT}$$

$$\simeq e^{V(x_B)/k_BT}\int_{-\infty}^{+\infty} dx\, e^{\frac{1}{2}\omega_-^2/k_BT}$$ integral converges since ω_-^2 is negative

$$= \frac{\sqrt{2\pi k_BT}}{|\omega_-|} e^{V(x_B)/k_BT}$$

So, the transition rate is:

$$J(x,t) = \frac{k_BT}{m\zeta}\frac{\omega_0}{\sqrt{2\pi k_BT}} e^{V(x_A)/k_BT}\frac{|\omega_-|}{\sqrt{2\pi k_BT}} e^{-V(x_B)/k_BT}$$

$$= \frac{1}{m\zeta}\frac{|\omega_-|}{2\pi}\omega_0\, e^{-[V(x_B)-V(x_A)]/k_BT}$$

$$\boxed{= \frac{1}{m\zeta}\frac{|\omega_-|}{2\pi}\omega_0\, e^{-\Delta E/k_BT}}$$

$$\frac{\partial[v]}{\partial t} = -k\frac{\partial[v]}{\partial x}$$

ω_0 = <u>Attempt frequency</u>: at which particle reaches barrier after which it has probability $e^{-\Delta E/k_BT}$ of making the transition.