



$$j(A) = j(B) = j_0$$

$$c(x_0) = 0$$

$$jV = \frac{F}{\gamma}$$

$$= -\frac{du}{dx}$$

$$j(x) = v(x) \cdot c(x) - D \frac{dc}{dx} = j_0$$

$$D = \frac{k_B T}{\gamma}$$

$$j_0 = -\frac{c(x)}{\gamma} \cdot \frac{du}{dx} - D \frac{dc}{dx} \quad | \cdot \gamma$$

$$-\gamma j_0 = c(x) \frac{du}{dx} + \gamma D \frac{dc}{dx}$$

$$\phi(x) = c(x) \cdot \exp\left(\frac{u(x)}{k_B T}\right)$$

Derivative  $\frac{d\phi}{dx} = c(x) \cdot \frac{1}{k_B T} \cdot \frac{du}{dx} \exp\left(\frac{u(x)}{k_B T}\right) + \exp\left(\frac{u(x)}{k_B T}\right) \cdot \frac{dc}{dx}$

$$\Rightarrow \frac{d\phi}{dx} = \frac{1}{k_B T} \cdot \exp\left(\frac{u(x)}{k_B T}\right) \left( c(x) \cdot \frac{du}{dx} + D \gamma \frac{dc}{dx} \right)$$

$$k_B T \exp\left(-\frac{u(x)}{k_B T}\right) \cdot \frac{d\phi}{dx} = c(x) \frac{du}{dx} + D \gamma \frac{dc}{dx}$$

$$\Rightarrow \frac{j_0}{D} \cdot \exp\left(\frac{u(x)}{k_B T}\right) = \frac{d}{dx} \left( c(x) \cdot \exp\left(\frac{u(x)}{k_B T}\right) \right)$$

Eq.  $j_0 = 0 \Rightarrow 0 = \frac{d}{dx} \left( c(x) \cdot \exp\left(\frac{u(x)}{k_B T}\right) \right) \Rightarrow c(x) = c_0 \cdot \exp\left(-\frac{u(x)}{k_B T}\right)$   
 $\hookrightarrow$  Boltzmann

Perfect absorber  $\Rightarrow c(x_0) = 0$

$$\int_x^{x_0} -\frac{j_0}{D} \exp\left(\frac{u(x')}{k_B T}\right) dx' = c(x_0) \cdot \exp\left(\frac{u(x_0)}{k_B T}\right) - c(x) \cdot \exp\left(\frac{u(x)}{k_B T}\right)$$

$$\Rightarrow c(x) = \frac{j_0}{D} \exp\left(-\frac{u(x)}{k_B T}\right) \cdot \int_x^{x_0} \exp\left(\frac{u(x')}{k_B T}\right) dx'$$

$$c_T = \int_0^{x_0} c(x) dx \Leftrightarrow j_0 = k_{on} c_T$$

$$c_T = \int_0^{x_0} \frac{j_0}{D} \exp\left(-\frac{u(x)}{k_B T}\right) \cdot \int_x^{x_0} \exp\left(\frac{u(x')}{k_B T}\right) dx' dx$$

$$k_{on} = \frac{1}{\int_0^{x_0} \exp\left(-\frac{u(x)}{k_B T}\right) \cdot \int_x^{x_0} \exp\left(\frac{u(x')}{k_B T}\right) dx' dx}$$

Simple case  $u(x) = 0$

$$k_{on} = \frac{D}{\frac{1}{2} x_0^2} = \frac{2D}{x_0^2}$$

Recall  $k_{on} = \frac{1}{\tau_{on}}$

$$\Rightarrow \tau_{on} = \frac{x_0^2}{2D}$$



$$u(x) = -x \cdot F \Rightarrow E_b = -x_0 \cdot F$$

$$\tau_{on} = \frac{1}{D} \int_0^{x_0} \exp\left(\frac{x \cdot F}{k_B T}\right) \int_x^{x_0} \exp\left(-\frac{x' F}{k_B T}\right) dx' dx$$

$$\tau_{on} = \frac{1}{D} \cdot \int_0^{x_0} \exp\left(\frac{x F}{k_B T}\right) \frac{-F}{k_B T} \left[ \exp\left(\frac{E_b}{k_B T}\right) - \exp\left(-\frac{x F}{k_B T}\right) \right] dx$$

$$\tau_{on} = \left(\frac{k_B T}{E_b}\right)^2 \frac{x_0^2}{D} \left[ -1 + \exp\left(\frac{E_b}{k_B T}\right) + \frac{E_b}{k_B T} \right]$$

Limit  $E_b \gg k_B T$

$$= \left(\frac{k_B T}{E_b}\right)^2 \frac{x_0^2}{D} \cdot \exp\left(\frac{E_b}{k_B T}\right) \Leftrightarrow k_{on} = \left(\frac{E_b}{k_B T}\right)^2 \frac{D}{x_0^2} \cdot \exp\left(-\frac{E_b}{k_B T}\right)$$

Kramers Rate in 1D literature

$$u(A+\delta) = u(A) + \frac{1}{2} u''(A) \cdot \delta^2$$

Expansion



$$\int_0^{x_0} \exp\left(-\frac{u(x)}{k_B T}\right) dx \approx \int_{-\infty}^{\infty} \exp\left(-\frac{u(A)}{k_B T}\right) \cdot \exp\left(-\frac{u''(A) \cdot \delta^2}{2 k_B T}\right) d\delta$$

$$\int_x^{x_0} \exp\left(\frac{u(x)}{k_B T}\right) dx \approx \int_{-\infty}^{\infty} \exp\left(\frac{u(B)}{k_B T}\right) \cdot \exp\left(-\frac{u''(B) \cdot \delta^2}{2 k_B T}\right) d\delta$$

$$k_{on} = \frac{D}{\int_0^{x_0} \exp\left(-\frac{u(x)}{k_B T}\right) \int_x^{x_0} \exp\left(\frac{u(x')}{k_B T}\right) dx' dx} \approx \frac{D}{\exp\left(\frac{\Delta u}{k_B T}\right) \cdot \sqrt{\frac{\pi}{u''(A) \cdot 2 k_B T}} \cdot \sqrt{\frac{\pi}{u''(B) \cdot 2 k_B T}}}$$

$$k_{on, Kramers} = \frac{D}{2\pi k_B T} \cdot \sqrt{u''(A) \cdot |u''(B)|} \cdot \exp\left(-\frac{\Delta u}{k_B T}\right)$$