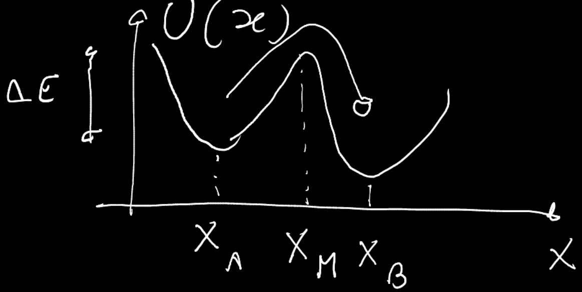
First exit time from a metastable state τ



Arrhenius formula $\tau \sim \exp\left(+\frac{\Delta E}{k_B T}\right)$

Kramers formula $\rightarrow$ prefactors

Fokker-Planck formalism: Chapman-Kolmogorov equation (continuous) $(d=1)$

$$W(x_0,t_0|x,t+\Delta t) = \int dy\, W(x_0,t_0|y,t)\cdot W(y,t|x,t+\Delta t)$$

F-P eq. for W: forward Kolmogorov equation

$$\frac{\partial W(x_0,t_0|x,t)}{\partial t} = -\frac{\partial}{\partial x}\Big(a(x,t)\,W(x_0,t_0|x,t)\Big) + \frac{1}{2}\frac{\partial^2}{\partial x^2}\Big(b(x,t)\,W(x_0,t_0|x,t)\Big)$$

Backward Kolmogorov equation (appendix E Kramers-Moyal expansion)

$$\frac{\partial W(x_0,t_0|x,t)}{\partial t_0} = -a(x_0,t_0)\frac{\partial}{\partial x_0}\Big[W(x_0,t_0|x,t)\Big] - \frac{1}{2}b(x_0,t_0)\frac{\partial^2}{\partial x_0^2}\Big[W(x_0,t_0|x,t)\Big]$$

escape time (first exit time) from $I=[x_1,x_2]$
with at least one absorbing boundary $(x_2 \rightarrow p(x_2,t)=0)$

NO REENTRANCE

$$\longrightarrow \boxed{\mathbb{P}_{x_0}(t) = \int_{x_1}^{x_2} W(x_0,t_0|y,t)\,dy}$$

$P_{x_0}(t)$ decreases with t; $P_{x_0}(t_0) = \underbrace{\int_{x_1}^{x_2} \delta(y - x_0)\,dy}_{=1}$

$P_{x_0}(t) \xrightarrow[t \to \infty]{} 0$

$\boxed{\text{CDF}}$ — $P_{x_0}(t)$ = prob. that the exit time $T_I(x_0) > t$

$\pi(t)$ = corresponding PDF for the random variable $T_I(x_0)$

$$\boxed{\pi(t) = -\frac{d P_{x_0}(t)}{dt} \qquad P_{x_0}(t) = \int_t^{+\infty} \pi(\tau)\,d\tau}$$

$$\boxed{\langle T_I \rangle = \int_{t_0}^{+\infty} \tau\, \pi(\tau)\,d\tau} = \boxed{t_0 + \int_{t_0}^{+\infty} P_{x_0}(\tau)\,d\tau}$$

$\lim_{t \to \infty} t\, P_{x_0}(t) = 0$

Backward K eq.

$$\frac{\partial W(x_0, t_0 / y, t)}{\partial t} = a(x_0) \frac{\partial W(x_0, t_0 / y, t)}{\partial x_0} + D \frac{\partial^2}{\partial x_0^2}\left[W(x_0, t_0 / y, t)\right]$$

$\left(\frac{\partial W}{\partial t_0} = -\frac{\partial W}{\partial t} \right)$

time translation invariance (W depends on $t - t_0$)

$\int_{x_1}^{x_2} dy$

$$\partial P_{x_0}(t) / \partial t = a(x_0) \frac{\partial}{\partial x_0} P_{x_0}(t) + D \frac{\partial^2}{\partial x_0^2} P_{x_0}(t)$$

from now $x_0 \to x$ (x = starting position)

$t_0 = 0$

Integrate over t $\int_0^{+\infty} dt$ $\quad P_x(0) = 1$

$\hookrightarrow$ eq. for $\langle T_I(x)\rangle$ $\quad P_x(+\infty) = 0$

$$\boxed{a(x)\frac{\partial}{\partial x}\langle T_I(x)\rangle + D\frac{\partial^2}{\partial x^2}\langle T_I(x)\rangle = -1}$$

General solution $\Phi(x) = \exp\left[\frac{1}{D}\int_{\bar{x}}^{x} a(y)\,dy\right]$

$$\boxed{\frac{d}{dx}\left[\Phi(x)\frac{d}{dx}\langle T_I(x)\rangle\right] = -\frac{1}{D}\Phi(x)}$$

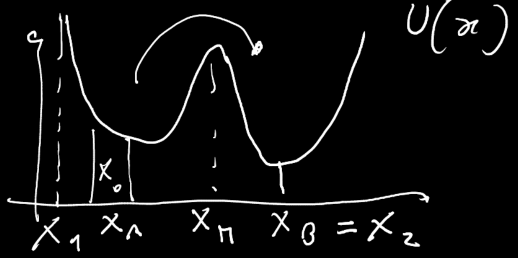
$$\frac{d\langle T_I(x)\rangle}{dx} = -\frac{1}{D}\frac{1}{\Phi(x)}\int_{X_1}^{x} dy\,\Phi(y)$$ 1st integration

Reflecting boundary at x_1 $\longrightarrow$ $\left.\frac{d\langle T_I(x)\rangle}{dx}\right|_{x=x_1} = 0$

$$\langle T_I(x)\rangle = -\frac{1}{D}\int_{X_2}^{x}\frac{dy}{\Phi(y)}\int_{x_1}^{y} dz\,\Phi(z)$$ 2nd integration

Absorbing boundary at x_2 $\longrightarrow$ $\langle T_I(x_2)\rangle = 0$

$$a(x) = v_0(x) = \frac{F(x)}{\tilde{\gamma}} = -\frac{1}{\tilde{\gamma}}\frac{dU}{dx}$$



$$\Phi(x) = \exp\left[-\frac{1}{D\tilde{\gamma}}\left(U(x) - U(\bar{x})\right)\right]$$

$$\rightarrow \boxed{\langle T(x)\rangle = \frac{1}{D}\int_x^{x_B} dy\,\exp\left(\frac{U(y)}{T}\right)\int_{x_1}^{y} dz\,\exp\left(-\frac{U(z)}{T}\right)}$$

So far: exact equation

y dependence of $\underbrace{\exp\left(\frac{U(y)}{T}\right)}\underbrace{\int_{x_1}^{y} dz\, \exp\left(-\frac{U(z)}{T}\right)}$

dominated by $\exp\left(\frac{U(x_M)}{T}\right)$ for $y \sim x_M$

(provided $\Delta E \gg U(x_A) - U(x_B)$) $y \approx x_M$

$$\langle T_I(x)\rangle \approx \frac{1}{D}\underbrace{\int_{x}^{x_B} dy\, \exp\left(\frac{U(y)}{T}\right)}\cdot\underbrace{\int_{x_1}^{x_M} dz\, \exp\left(-\frac{U(z)}{T}\right)}$$

Both integrals evaluated as Gaussian integrals

$$U(x) = U(x_M) - \tfrac{1}{2}\alpha_2 (y - x_M)^2 \qquad \alpha_2 = -U''(x_M) > 0$$

$$\approx \exp\left(\frac{U(x_M)}{T}\right)\int_{x\to-\infty}^{x_B\to+\infty} dy\, \exp\left(-\frac{\alpha_2}{2T}(y-x_M)^2\right)$$

$$\approx \sqrt{\frac{2\pi T}{\alpha_2}}\exp\left(\frac{U(x_M)}{T}\right)$$

$$\approx \sqrt{\frac{2\pi T}{\alpha_1}}\exp\left(-\frac{U(x_A)}{T}\right)$$

$$\alpha_1 = U''(x_A) > 0$$

$$\langle T_I(x)\rangle \simeq \frac{2\pi}{\sqrt{\alpha_1\alpha_2}}\frac{T}{D} \,!\, \exp\left(\frac{\Delta U}{T}\right)$$

$$\Delta U = U(x_M) - U(x_A)$$