A slightly artificial example:

1d ideal polymer

Exactly like 1-d random walk

# of conformations with N steps, an lattice displacement x

$$\frac{N!}{\left(\frac{N+x}{2}\right)!\left(\frac{N-x}{2}\right)!}$$

Maximum at $x=0$

Physical distance $x = x\ell$, polymer length $L = N\ell$

for large N, x,

$$S = k_B \ln\left[N!/\left\{\left(\frac{N+x}{2}\right)!\left(\frac{N-x}{2}\right)!\right\}\right]$$

$$\simeq k_B\left[\text{const} - \frac{N+x}{2}\ln\frac{N+x}{2} + \frac{N+x}{2} - \frac{N-x}{2}\ln\frac{N-x}{2} + \frac{N-x}{2}\right]$$

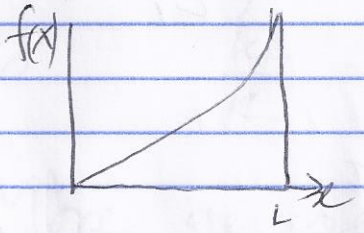
Force $f(x) = -T\frac{\partial}{\partial x}S = T\frac{1}{\ell}\frac{\partial}{\partial X}S$

$$= \frac{k_B T}{2\ell}\ln\frac{N-X}{N+X} = \frac{k_B T}{2\ell}\ln\frac{L-x}{L+x}$$

For $x \ll L$

$$f(x) = -\frac{k_B T}{\ell} x$$ (Entropic spring)

For x close to $+L$ $\quad f(x) = \frac{k_B T}{2\ell} \log_2\left(1 - \frac{x}{L}\right)$



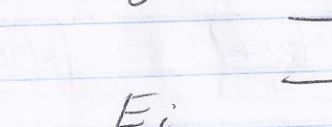
The logarithmic divergence at $x = L$ is a special feature of 1d. The divergence law would change for realistic models, but the qualitative features are the same.

Once more, every configuration has the same energy but it is entropy which drives the polymer force.

Force-extension curves for biopolymers teach us a lot about the nature of the polymer, as we will see later.

Two-state systems.

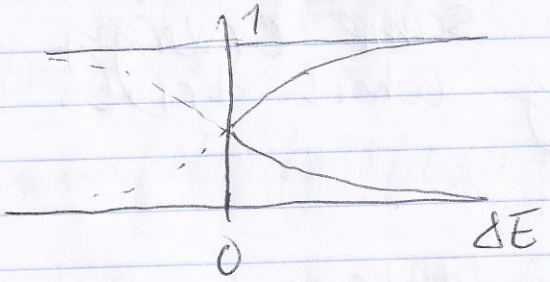
A system with only two microstates
N copies of the system. [Example: molecular transitions, spins, ...]



$$P_i \propto e^{-\frac{E_i}{k_B T}}$$

$$P_i = \frac{e^{-E_i/k_B T}}{e^{-E_1/k_B T} + e^{-E_2/k_B T}} \qquad E_2 - E_1 = \Delta E$$

$$P_1 = \frac{1}{1+e^{-\Delta E/k_B T}} \qquad P_2 = \frac{1}{1+e^{\Delta E/k_B T}}$$



Kinetics

$$\frac{dN_1}{dt} = -k_+ N_1(t) + k_- N_2(t)$$

$$\frac{dN_2}{dt} = k_+ N_1(t) - k_- N_2(t)$$

Note $N_1(t) + N_2(t) = N$ is fixed.

In the stationary state

$$\frac{N_2}{N_1} = e^{-\Delta E/k_B T}$$

Stationarity means $k_+ N_1 = k_- N_2$

So $$\frac{k_+}{k_-} = \frac{N_2}{N_1} = e^{-\Delta E/k_B T}$$

[More general version: Detailed Balance]

Approach to equilibrium:

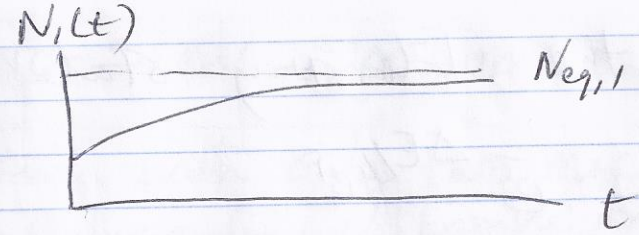
$$\frac{dN_1(t)}{dt} = -k_+ N_1(t) + k_- N_2(t)$$
$$= -k_+ N_1(t) + k_-(N - N_1(t))$$
$$= k_- N - (k_+ + k_-) N_1(t)$$

Solves to give

$$N_1(t) = -(N_{eq,1} - N_1(0)) e^{-t/\tau} + N_{eq,1}$$

where $N_{eq,1} = k_- N/(k_+ + k_-)$

and $1/\tau = k_+ + k_-$



τ is the relaxation time

For 'complex' two state systems with each state having many microstates [Example: protein unfolding]

$$P_1 \propto \sum_{i \in \text{State1}} e^{-\beta E_i} = e^{-\beta F_1} \qquad \left[\beta = \frac{1}{k_B T}\right]$$

$$P_2 \propto \sum_{j \in \text{State2}} e^{-\beta E_j} = e^{-\beta F_2}$$

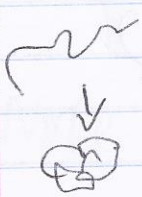
$F_{1,2}$'s are Helmholtz free energies.

$\Delta F = F_2 - F_1$

etc.

$$P_{1,2} = \frac{1}{1 + e^{\mp \Delta F/(k_B T)}}$$

In fact, with a constant pressure fluid around.



$$P_{1,2} = \frac{1}{1 + e^{\mp \Delta G/(k_B T)}}$$

Better derivation through chemical potentials