ordinary LDB $\Rightarrow \frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)}$

(sys. exchanging therm. energy w/ env. at temp T) $\Rightarrow$ ESS $p_n^s = \frac{e^{-\beta E_n}}{Z}$

$\Downarrow$

$J_{nm}^s = 0$

To get NESS we need to modify LDB:

end result: $\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m - W_{nm})}$

"work" done on sys. during $m \to n$ trans.

conservative work

$W = \int \vec{F} \cdot d\vec{x} = U_{end} - U_{start}$

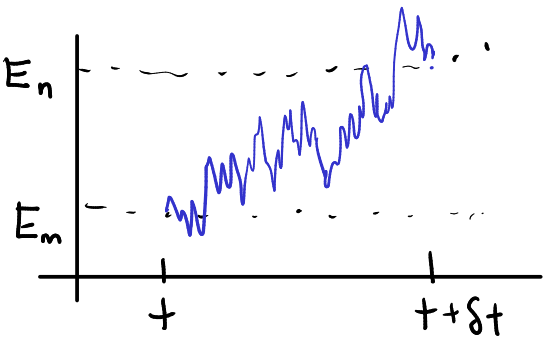
$\vec{F} = -\nabla U$

where $W_{nm} \neq \Phi_n - \Phi_m$ for any func. Φ_n

work has to be non-conservative (at least in part)

How to get this extra term?

recall:



$\Omega_{nm}\delta t \propto$ prob. that env. takes us from $E_m \to E_n$ in time δt (donates $E_n - E_m$ in energy)

$$\Rightarrow \frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}}$$

here: $Q_{nm} = E_n - E_m$

Q_{nm}: how much ther. energy we need from env. during $m \to n$ trans $\equiv$ "heat"

$$\beta = \frac{1}{k_B T}$$

imagine we have "help" from another energy source, in which case:

$$Q_{nm} = E_n - E_m - W_{nm}$$

"work": energy from another (non-therm.) source

$W_{nm} > 0$: help work into sys.

$W_{nm} < 0$: hurt work output from sys.

} during $m \to n$ trans.

$W_{nm} = 0$: transition does not couple to any other energy source

general LDB:

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}} = e^{-\beta(E_n - E_m - W_{nm})}$$