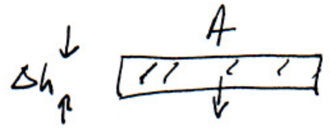
The Boltzmann Distribution for Potential Energy

Suppose the atmosphere is an ideal gas,

$$PV = Nk_BT \Rightarrow P = nk_BT, \quad n = N/V.$$

We also know that the pressure, in equilibrium, equals the weight of the air above:



$$mgn\,\Delta h A = \Delta P A \qquad \frac{dP}{dh} = -mgn$$

$$\frac{dn}{dh} = -\frac{mg}{kT}\,n$$

$$n = n_0 e^{-mgh/kT}$$

Correspondingly, the probability density that a given atom is at height h is

$$\rho(h) = Ce^{-mgh/kT} = e^{-(\text{Potential Energy of } \cancel{\text{the}} \text{ atom})/kT}$$

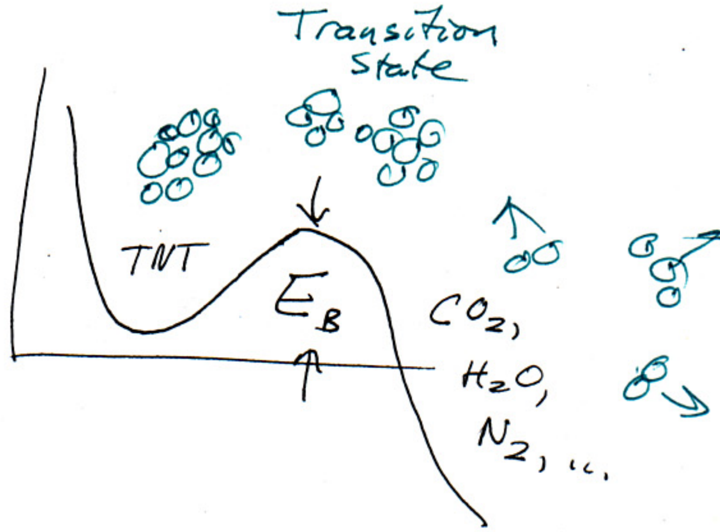
Boltzmann Distribution: In general, for a small subsystem (or an open system) in equilibrium, with total energy $E(\vec{x},\vec{p})$,

$$\rho(\vec{x},\vec{p}) \propto e^{-E(\vec{x},\vec{p})/kT}$$

Applications:

Arrhenius Law:

Chemical reaction,
unstable molecule,
energy barrier E_B



- Probability of Sitting At transition state $\sim e^{-E_B/kT}$

- Rate of Spontaneous Reaction

$$= (\text{velocity across barrier})\, e^{-E_B/kT}$$

$$\propto e^{-E_B/kT}$$