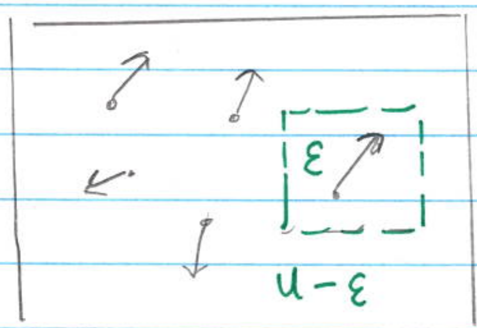
The Boltzman Factor

- This is based on Sect. 4.6. We will return to Chapter 4 later. Our goal is to give only an initial understanding

- Consider a system with total energy U



- System has energy U
- Subsystem has energy ε
- Rest has energy $U-\varepsilon$

- Pick a <u>small</u> subsystem which is independent of the larger system except through the exchange of energy. In the case of an ideal gas, each molecule is independent of all others, and can be considered an independent subsystem

- What is the probability that the subsystem will have energy ε?

For instance, it is possible, though extremely unlikely, that the one molecule (subsystem) will have all of the energy of the gas.

- The probability to find the subsystem with energy ε is

$$\boxed{P(\varepsilon) \propto e^{-\varepsilon/k_B T} \leftarrow \text{Boltzmann factor}}$$

- We get tired of writing $1/k_B T$ so define $\beta \equiv 1/k_B T$, i.e.

$$P(\varepsilon) = C e^{-\beta \varepsilon} \qquad \beta \equiv \frac{1}{k_B T}$$

- If you have some set of microscopic states $i = 1 \ldots N$, then since $\sum_i C e^{-\beta \varepsilon_i} = 1$ (since the sum of probabilities is one) we have

$$P(\text{state } r) = \frac{e^{-\beta \varepsilon_r}}{\sum_i e^{-\beta \varepsilon_i}}$$

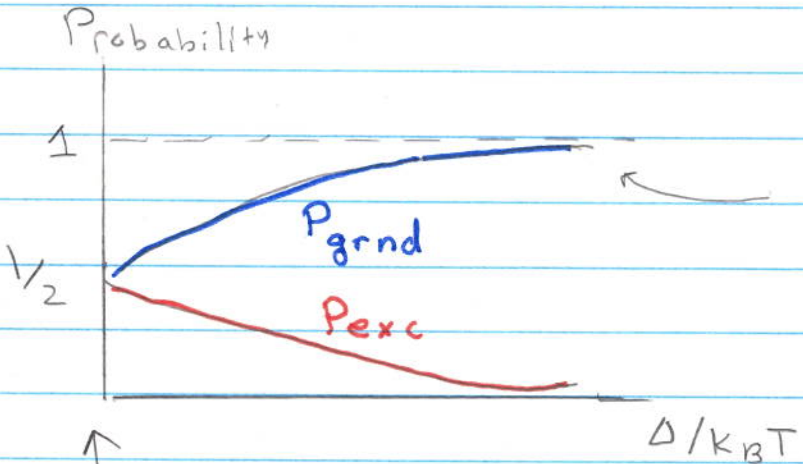
probability to find the subsytem in state r with energy ε_r

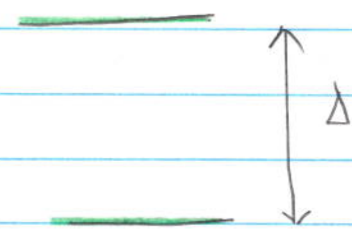
Ex 1

Consider an "atom" consisting of a ground state with energy 0, and an excited state of energy Δ. At temperature T determine the probability to be in the ground and excited state

$$P_{ground} = \frac{e^{-\beta 0}}{e^{-\beta 0} + e^{-\beta \Delta}} = \frac{1}{1 + e^{-\beta \Delta}}$$

$$P_{excit} = \frac{e^{-\beta \Delta}}{e^{-\beta 0} + e^{-\beta \Delta}} = \frac{e^{-\beta \Delta}}{(1 + e^{-\beta \Delta})}$$





small Δ compared to k_BT, the system can easily jump from ground to excited and back and thus $P \simeq 1/2$

For large Δ compared to k_BT the system does not have enough thermal energy to jump to the higher state and thus all the atoms are in the ground state, $P_{\text{grnd}} \simeq 1$