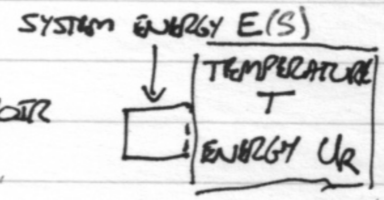
1] BOLTZMANN DISTRIBUTION

THIS IS THE PROBABILITY DISTRIBUTION OF A SYSTEM BEING IN SOME STATE, S, WITH ENERGY E(S) GIVEN THE WHOLE SYSTEM IS AT TEMPERATURE T.

EXAMPLE: A SIMPLE SYSTEM IS A HYDROGEN ATOM FOR WHICH THE ELECTRON CAN HAVE DIFFERENT ENERGIES:

$S_1 : -13.6\,eV$; $S_2 + 3P_2 : -3.4\,eV$; $S_3 + 3P_3 + 5D_3 : -1.5\,eV$

IF ISOLATED, THE ENERGY OF THE SYSTEM IS FIXED.
BUT, IF IN CONTACT WITH A (CONSTANT TEMPERATURE) RESERVOIR, THEN ANY STATE IS POSSIBLE, THOUGH LOWER ENERGY MORE LIKELY



SO, CONSIDER SYSTEM IN CONTACT WITH A RESERVOIR
LET E(S) BE ENERGY OF SYSTEM IN STATE S.
LET P(S) BE PROBABILITY OF SYSTEM IN STATE, S.
LET $\Omega_R(S)$ BE MULTIPLICITY OF RESERVOIR FOR SYSTEM IN STATE S

CONSIDER STATES S_1 AND S_2 WITH $E(S_1) < E(S_2)$
HENCE $\Omega_R(S_1) > \Omega_R(S_2)$ (LESS ENERGY IN SYSTEM ⇒ MORE IN RESERVOIR)
BECAUSE RESERVOIR MULTIPLICITY IS HIGHER WHEN SYSTEM IS IN STATE S_1, THIS STATE IS MORE LIKELY:

$$\frac{P(S_2)}{P(S_1)} = \frac{\Omega_R(S_2)}{\Omega_R(S_1)} \overset{\text{DEF}^{\text{N}}\text{ ENTROPY}}{=} \frac{e^{\frac{1}{k}S_R(S_2)}}{e^{\frac{1}{k}S_R(S_1)}} = e^{\frac{1}{k}[S_R(S_2) - S_R(S_1)]}$$

BECAUSE SYSTEM IS SMALL COMPARED WITH RESERVOIR, TEMPERATURE IS ~CONSTANT AND $S_R(S_2) - S_R(S_1) \approx dS_R \approx \frac{1}{T}dU_R = -\frac{1}{T}dE$
IN WHICH dE IS CHANGE OF SYSTEM ENERGY

i] (CONT'D)

So $\frac{P(S_2)}{P(S_1)} = e^{\frac{1}{k}[S_R(S_2) - S_R(S_1)]} \approx e^{-\frac{1}{kT}[E(S_2) - E(S_1)]}$

$\Rightarrow \frac{P(S_2)}{EXP[-E(S_2)/kT]} = \frac{P(S_1)}{EXP[-E(S_1)/kT]}$

BECAUSE S_1 AND S_2 ARE INDEPENDENT, BOTH RATIOS MUST BE CONSTANT, $\mathcal{C}$

$\Rightarrow P(S_i) = \mathcal{C}\, e^{-E(S_i)/kT}$ FOR EACH STATE S_i

SINCE P IS A PROBABILITY, $\sum_{S_i} P(S_i) = 1$

$\Rightarrow \mathcal{C} = \left[\sum_i e^{-E(S_i)/kT}\right]^{-1}$

DEFINE $Z = \sum_S e^{-E(S)/kT}$ THE "<u>PARTITION FUNCTION</u>"

$\Rightarrow P(S) = \frac{1}{Z} e^{-E(S)/kT}$ IS THE "<u>BOLTZMANN DISTRIBUTION</u>"

THE TERM $e^{-E/kT}$ IS THE "BOLTZMANN FACTOR"

EXAMPLE: SUPPOSE SYSTEM HAS ONLY 2 STATES WITH ENERGY $E_1 = 0\,eV$ AND $E_2 = 2eV$

- So AT $T = 300K$, $kT = 1.38\times10^{-23}\frac{J}{K} \times 300K \times \frac{1}{1.60\times10^{-19} J/eV} = 0.0259 eV$
  $\Rightarrow Z = e^0 + e^{-2/0.0259} \simeq 1 + 2.51\times10^{-34}$
  $\Rightarrow$ 0eV ENERGY STATE EXTREMELY LIKELY
- AT $T = 30000K$, $kT = 2.59\,eV$
  $\Rightarrow Z = e^0 + e^{-2/2.59} = 1 + 0.461$
  $\Rightarrow$ PROBABILITY OF 0eV STATE IS $\frac{1}{1.461} \simeq 0.68$
  AND PROBABILITY OF 2eV STATE IS $\frac{0.461}{1.461} \simeq 0.32$

NOTE: IF TWO ENERGIES ARE E_0 AND $E_0 + 2eV$

$\Rightarrow Z = e^{E_0/kT} + e^{(E_0+2)/kT} = e^{E_0/kT}[1 + e^{2/kT}]$

$\Rightarrow P(S_1) = e^{E_0/kT}/[e^{E_0/kT}(1 + e^{2/kT})] = 1/(1 + e^{2/kT})$ AS BEFORE

2] BOLTZMANN STATISTICS

AVERAGE ENERGY IS $\bar{E} = \frac{1}{Z} \sum_s E(s)\, e^{-E(s)/kT}$

WITH $Z = \sum_s e^{-E(s)/kT} = \sum_s e^{-\beta E(s)}$ WITH $\beta \equiv \frac{1}{kT}$

NOTE $\frac{\partial Z}{\partial \beta} = \sum_s -E(s)\, e^{-\beta E(s)}$

SO $\boxed{\bar{E} = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)}$

LIKEWISE CAN COMPUTE STANDARD DEVIATION ABOUT THIS MEAN:

$$\sigma_E^2 = \sum_s (E(s) - \bar{E})^2\, P(s) \qquad \text{WITH } P(s) = e^{-E(s)/kT}$$

$$= \ldots = \sum_s E^2 P(s) - \bar{E}^2$$

$$\Rightarrow \sigma_E = \left(\overline{E^2} - \bar{E}^2\right)^{1/2}$$

AS WITH MEAN, NOTE $\frac{\partial^2 Z}{\partial \beta^2} = \sum E(s)^2 e^{-\beta E(s)}$

$$\Rightarrow \overline{E^2} = \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right) = \frac{1}{Z}\frac{\partial}{\partial \beta}\left(-Z\bar{E}\right) = -\frac{\partial \bar{E}}{\partial \beta} - \frac{1}{Z}\frac{\partial Z}{\partial \beta}\bar{E} = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

$$\text{SO } \sigma_E = \left(\overline{E^2} - \bar{E}^2\right)^{1/2} = \left(-\frac{\partial \bar{E}}{\partial \beta}\right)^{1/2}$$

CONVENIENTLY, THIS CAN BE REWRITTEN IN TERMS OF HEAT CAPACITY:

$$C \equiv \frac{\partial \bar{E}}{\partial T} = \frac{\partial \bar{E}}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} \overset{\beta = \frac{1}{kT}}{=} -\frac{1}{kT^2}\frac{\partial \bar{E}}{\partial \beta}$$

SO $\boxed{\sigma_E = \left(-\frac{\partial \bar{E}}{\partial \beta}\right)^{1/2} = \sqrt{kT^2 C} = kT\sqrt{C/k}}$

3] APPLICATION TO PARAMAGNETISM

$\Uparrow B$ $\quad \uparrow$ 'UP' ENERGY $\underbrace{-\mu B}_{E_1}$ $\quad \downarrow$ 'DOWN' ENERGY $\underbrace{+\mu B}_{E_2}$

($\mu B \sim 5.8 \times 10^{-5}$ eV, $kT = 0.025$ AT 300K)

$$\text{SO} \quad Z = \sum_s e^{-\beta E(s)} = e^{\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

$$\text{So} \quad P_\uparrow = e^{+\beta\mu B}/(2\cosh\beta\mu B), \quad P_\downarrow = e^{-\beta\mu B}/(2\cosh\beta\mu B)$$

($\mu B \ll kT \Rightarrow P_\uparrow \approx \frac{1}{2}(1+\frac{\mu B}{kT})$; $P_\downarrow \approx \frac{1}{2}(1-\frac{\mu B}{kT})$; $\mu B \gg kT \Rightarrow P_\uparrow \approx 1 - e^{-\frac{2\mu B}{kT}}$, $P_\downarrow \approx e^{-\frac{2\mu B}{kT}}$)

$\Rightarrow$ AVERAGE ENERGY IS $\bar{E} = \sum E(s) P(s) = -\mu B P_\uparrow + \mu B P_\downarrow$

$$\Rightarrow \bar{E} = -\mu B (e^{\beta\mu B} - e^{-\beta\mu B})/(2\cosh\beta\mu B)$$
$$= -\mu B (2\sinh\beta\mu B)/(2\cosh\beta\mu B)$$
$$= -\mu B \tanh\beta\mu B \quad (\approx -(\mu B)^2/kT)$$

(ALTERNATELY $\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{2\cosh\beta\mu B}\left(2\mu B \sinh(\beta\mu B)\right) = -\mu B \tanh(\beta\mu B)$)

So, FOR N DIPOLES, ENERGY IS

$$U = N\bar{E} = -N\mu B \tanh(\beta\mu B) \overset{\beta = \frac{1}{kT}}{=} -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

(SAME RESULT FOUND BY FINDING S FROM MULTIPLICITIES)

FOR MAGNETIZATION $\bar{\mu} = \sum \mu(s) P(s) = \mu P_\uparrow + (-\mu) P_\downarrow$

$$= \mu \tanh(\beta\mu B)$$

So, FOR N DIPOLES, MAGNETIZATION IS

$$M = N\bar{\mu} = N\mu \tanh(\beta\mu B) = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

HEAT CAPACITY: $C_1 = -\frac{1}{kT^2}\frac{\partial \bar{E}}{\partial \beta} = -\frac{1}{kT^2}\left(-(\mu B)^2 \operatorname{sech}^2(\beta\mu B)\right) = \frac{(\mu B)^2}{kT^2}\operatorname{sech}^2\left(\frac{\mu B}{kT}\right)$

FOR N DIPOLES $\quad C = +Nk\left(\frac{\mu B}{kT}\right)^2 \operatorname{sech}^2\left(\frac{\mu B}{kT}\right)$

STANDARD DEVIATION $\quad \sigma_E = kT\left[C_1/k\right]^{1/2} = kT\left[\left(\frac{\mu B}{kT}\right)\operatorname{sech}\left(\frac{\mu B}{kT}\right)\right] = \mu B \operatorname{sech}\left(\frac{\mu B}{kT}\right)$

(FOR $kT \gg \mu B \Rightarrow \sigma_E \approx \mu B$)