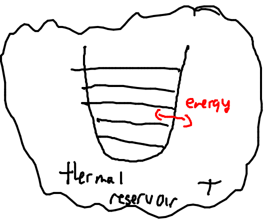


Consider oscillator & reservoir together

$$\Omega = \Omega_0 \, \Omega_R$$

Ω: # of microstates in combined system

Ω_0: # of microstates in oscillator

Ω_R: " " " " reservoir

The probability that the harmonic oscillator is in ground state $E = E_0$ is proportional to # microstates of the combined system given that oscillator is in its ground state.

if oscillator is in its ground state, $\Omega_0 = 1$

$$\Omega = 1\,\Omega_R$$

$$S = k \ln \Omega \longrightarrow \Omega = e^{S/k}$$

Consider two oscillator states A & B,

suppose $E(A) < E(B)$

$E_R(A) > E_R(B)$ because energy is conserved

$\longrightarrow \Omega_R(A) > \Omega_R(B)$

$\longrightarrow P(A) > P(B)$ lower energy states are more likely

$$\frac{P(A)}{P(B)} = \frac{\Omega_R(A)}{\Omega_R(B)} = \frac{e^{S_R(A)/k}}{e^{S_R(B)/k}} = e^{[S_R(A) - S_R(B)]/k}$$

$$dS_R = \frac{1}{T}\,dU_R = -\frac{1}{T}\,dU_0$$

$$S_R(A) - S_R(B) = -\frac{1}{T}\big(E(A) - E(B)\big)$$

$$\frac{P(A)}{P(B)} = e^{-[E(A) - E(B)]/kT} = \frac{e^{-E(A)/kT}}{e^{-E(B)/kT}}$$

$$\boxed{P(A) = \frac{1}{Z}\, e^{-E(A)/kT}}$$ for any system in contact with a thermal reservoir T

- Z is a normalization constant $\sum_{\substack{\text{all}\\ \text{states}\\ s}} \frac{1}{Z} e^{-E(s)/kT} = 1$

  ridiculously useful

  partition function $Z(T)$ independent of state $Z = \sum_s e^{-E(s)/kT}$

- $e^{-E/kT}$ Boltzmann factor for a given state

  $P(A) \sim e^{-E(A)/kT}$

  if energy increases by kT

  probability reduced by $1/e$ (to 37% of original)

  kT: characteristic energy scale

  @ 300 K, $kT \approx \frac{1}{40}$ eV

e.g. hydrogen atom

-3.4eV —

-13.6eV —

$\Delta E = 10.2$eV

@ 300 K, $\Delta E = 400kT$

$P_{exc} \sim e^{-400} = 2\times10^{-174}$

@ 3000 K, $\Delta E = 40kT$

$P_{exc} \sim e^{-40} = 4\times10^{-18}$

for 1 mol H, ~10,000 excited ones

$$Z = \sum_s e^{-E_s/kT}$$ sum of all Boltzmann factors

$$Z = \sum_s e^{-E_s/kT}$$ sum of all Boltzmann factors

$$= \sum_s e^{-\beta E_s} \qquad \beta = \frac{1}{kT}$$

If ground state is $E = 0$,

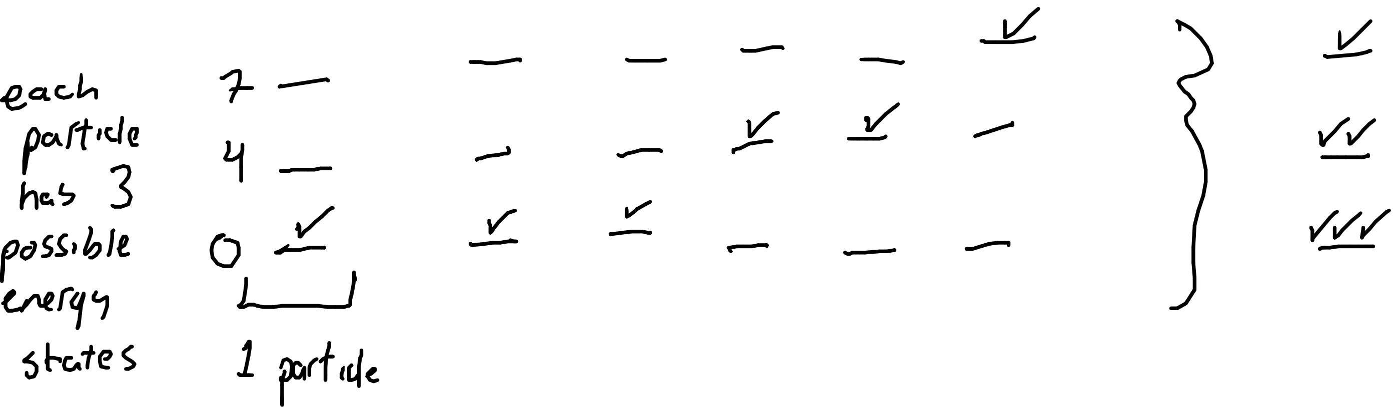
$$Z = 1 + \sum_{\text{excited}} e^{-\beta E_s} \leftarrow \text{all} < 1$$

$$\Omega = 1 + \sum_{\text{excited}} 1 \qquad 0 \leq Z \leq \Omega$$

Ω is a count of all microstates

Z is a weighted count of all microstates, weighted by $e^{-\beta E}$

Average Energy



$$\langle E \rangle = \frac{0+0+0+4+4+7}{6} = \frac{3(0)+2(4)+1(7)}{3+2+1}$$

$$= \frac{3}{6}(0) + \frac{2}{6}(4) + \frac{1}{6}(7)$$

probabilities of given energy state

$$\langle E \rangle = \sum_s P_s E_s \qquad \text{In general } \langle X \rangle = \sum_s P_s X_s$$

in contact with a thermal reservoir

$$\langle X \rangle = \frac{1}{Z} \sum_s X_s e^{-\beta E_s}$$

e.g. $\langle 1 \rangle = \frac{1}{Z} \sum_s 1 e^{-\beta E_s} = \frac{1}{Z} \sum_s e^{-\beta E_s} = \frac{1}{Z} Z = 1$

$$\langle E \rangle = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}$$

Neat trick: $E_s e^{-\beta E_s} = -\frac{\partial}{\partial \beta} e^{-\beta E_s}$

$$\langle E \rangle = \frac{1}{Z} \sum_s -\frac{\partial}{\partial \beta} e^{-\beta E_s}$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s e^{-\beta E_s}$$

$$\boxed{\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial Z} \frac{\partial Z}{\partial \beta}$$