MANY PARTICLE SYSEMS

PRACTICE PROBLEMS 5 – SOLUTIONS

1(a) For distinguishable particles, Maxwell - Boltzmann statistics apply. Label the particles A and B, and the energy levels by ε and 2ε. The possible states are:

ε	2ε	TOTAL ENERGY
A B	–	2ε
–	AB	4ε
A	B	3ε
B	A	3ε

$$Z = e^{-2\varepsilon/k_BT} + e^{-4\varepsilon/k_BT} + 2e^{-3\varepsilon/k_BT}$$

$$= \left(e^{-\varepsilon/k_BT} + e^{-2\varepsilon/k_BT}\right)^2$$

$$= Z_1^{\,2}$$

where Z_1 is the single particle canonical partition function. The alternative way to solve this is to note the for Maxwell - Boltzmann statistics with two identical particles,

$$Z = (Z_1)^2$$

and $Z_1 = e^{-\varepsilon/k_B T} + e^{-2\varepsilon/k_B T}$ as a single particle can occupy energy levels ε_1 and ε_2.

(b) Modified Maxwell - Boltzmann statistics: we first treat the particles as distinguishable, and then try to correct for overcounting of states by dividing by $N!$. In this case, $N = 2$.

So $Z \approx \frac{1}{2!} (Z_1)^2$

result from Maxwell Boltzmann stats

$$= \frac{1}{2!} \left(e^{-\varepsilon/k_B T} + e^{-2\varepsilon/k_B T} \right)^2$$

$$= \frac{1}{2} e^{-2\varepsilon/k_B T} + \frac{1}{2} e^{-4\varepsilon/k_B T}$$

$$+ e^{-3\varepsilon/k_B T}$$

(c) Bose - Einstein statistics

ε	2ε	TOTAL ENERGY
AA	—	2ε
—	AA	4ε
A	A	3ε

$$Z_{BE} = e^{-2\varepsilon/k_BT} + e^{-4\varepsilon/k_BT} + e^{-3\varepsilon/k_BT}.$$

Note that only the third term in this expression is correctly reproduced by modified Maxwell - Boltzmann statistics, because the particles are in different energy levels, and the order $\dfrac{\varepsilon \quad 2\varepsilon}{A \quad B}$ or $\dfrac{\varepsilon \quad 2\varepsilon}{B \quad A}$ correspond to two different states if the particles are distinguishable.

(d) Fermi - Dirac statistics: two identical particles cannot occupy a given energy level

ε	2ε	TOTAL ENERGY
A	A	3ε

$$Z_{FD} = e^{-3\varepsilon/k_BT}$$

(e) $\bar{E} = \sum_n' E_n P_n = \sum_n' E_n \dfrac{e^{-E_n/k_BT}}{Z}$.

- For case (c)

$$\bar{E} = \frac{\left(2\varepsilon e^{-2\varepsilon/k_BT} + 4\varepsilon e^{-4\varepsilon/k_BT} + 3\varepsilon e^{-3\varepsilon/k_BT}\right)}{\left(e^{-2\varepsilon/k_BT} + e^{-4\varepsilon/k_BT} + e^{-3\varepsilon/k_BT}\right)}$$

- For case (d)

$$\bar{E} = \frac{3\varepsilon e^{-3\varepsilon/k_BT}}{e^{-3\varepsilon/k_BT}} = 3\varepsilon$$

- $S = -\dfrac{\partial F}{\partial T}$

$$= -\frac{\partial}{\partial T}\left(-k_BT \ln Z\right)$$

$$= k_B \ln Z + k_BT \frac{1}{Z}\frac{\partial Z}{\partial T}.$$

For (d), $Z_{FD} = e^{-3\varepsilon/k_BT}$

$$\Rightarrow S = k_B\left(\frac{-3\varepsilon}{k_BT}\right) + k_BT \frac{1}{e^{-3\varepsilon/k_BT}} \cdot \frac{3\varepsilon}{k_BT^2} e^{-3\varepsilon/k_BT}$$

$$= -\frac{3\varepsilon}{T} + \frac{3\varepsilon}{T}$$

$$= 0$$

(9) $S = k_B \ln \Omega(E)$ where $\Omega(E)$ is the number of energy eigenstate of energy E.

Even though the system is in contact with a heat reservoir, the Pauli exclusion principle means there is only one energy eigenstate, with $E = 3\varepsilon$.

So $S = k_B \ln 1 = 0$

This is a general result - if a system of particles has only one energy eigenstate, the entropy is zero.

2 (a) The probability of occupancy of the energy eigenstate with energy ε_i $(i=1,2)$ is

$$P_i = \frac{e^{-\varepsilon_i/k_B T}}{Z}$$

with $Z = e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T}$.

The mean energy is

$$\bar{E} = \sum_i \varepsilon_i \, e^{-\varepsilon_i/k_B T}$$

$$= \varepsilon_1 \frac{e^{-\varepsilon_1/k_B T}}{Z} + \varepsilon_2 \frac{e^{-\varepsilon_2/k_B T}}{Z}.$$

$$= \frac{\left(\varepsilon_1 e^{-\varepsilon_1/k_B T} + \varepsilon_2 e^{-\varepsilon_2/k_B T}\right)}{\left(e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T}\right)}$$

(b) $\varepsilon_2 - \varepsilon_1$ is the energy required to produce a transition from the groundstate to the excited state $(\varepsilon_1 \rightarrow \varepsilon_2)$.

$k_B T$ is a measure of the average thermal energy available.

- High temperature regime:

average thermal energy >> the energy required to produce a transition from the groundstate to excited state

$\Rightarrow \quad k_B T >> \varepsilon_2 - \varepsilon_1$

$$\Rightarrow \quad \frac{(\varepsilon_2 - \varepsilon_1)}{k_B T} << 1$$

- Low temperature regime:

average thermal energy << energy required to produce a transition from the groundstate to the excited state

$\Rightarrow \quad k_B T << \varepsilon_2 - \varepsilon_1$

$$\Rightarrow \quad \frac{(\varepsilon_2 - \varepsilon_1)}{k_B T} >> 1.$$

(c) $$\bar{E} = \frac{(\varepsilon_1 e^{-\varepsilon_1/k_BT} + \varepsilon_2 e^{-\varepsilon_2/k_BT})}{e^{-\varepsilon_1/k_BT} + e^{-\varepsilon_2/k_BT}}$$

$$= \frac{e^{-\varepsilon_1/k_BT}\left(\varepsilon_1 + \varepsilon_2 e^{-(\varepsilon_2-\varepsilon_1)/k_BT}\right)}{e^{-\varepsilon_1/k_BT}\left(1 + e^{-(\varepsilon_2-\varepsilon_1)/k_BT}\right)}$$

$$= \frac{\left(\varepsilon_1 + \varepsilon_2 e^{-(\varepsilon_2-\varepsilon_1)/k_BT}\right)}{\left(1 + e^{-(\varepsilon_2-\varepsilon_1)/k_BT}\right)}$$

<u>High temperature limit</u>

$$\frac{(\varepsilon_2 - \varepsilon_1)}{k_BT} << 1$$

$$\Rightarrow e^{-(\varepsilon_2-\varepsilon_1)/k_BT} \simeq 1 - \frac{(\varepsilon_2-\varepsilon_1)}{k_BT}$$

$$\Rightarrow \bar{E} \simeq \frac{\varepsilon_1 + \varepsilon_2\left(1 - \frac{(\varepsilon_2-\varepsilon_1)}{k_BT}\right)}{1 + 1 - \frac{(\varepsilon_2-\varepsilon_1)}{k_BT}}$$

$$\simeq \frac{\varepsilon_1 + \varepsilon_2}{2} \quad \text{since } \frac{(\varepsilon_2-\varepsilon_1)}{k_BT} << 1$$

Low temperature limit :

$$\frac{(\varepsilon_2 - \varepsilon_1)}{k_B T} >> 1$$

$$\Rightarrow \quad e^{-(\varepsilon_2 - \varepsilon_1)/k_B T} << 1$$

$$\Rightarrow \quad \overline{E} \approx \frac{\varepsilon_1}{1} = \varepsilon_1$$

(d) High temperature limit :

There is a lot of thermal energy available

$\Rightarrow$ the system is readily knocked from the groundstate to the excited state

$\Rightarrow$ both states have approximately equal probability to be occupied

$$\Rightarrow \quad \overline{E} \approx \frac{1}{2}\varepsilon_1 + \frac{1}{2}\varepsilon_2$$

Low temperature limit

There is little thermal energy available

$\Rightarrow$ the probability of excitation of the system from the groundstate energy ε_1 to the excited state energy ε_2 is low

$\Rightarrow$ the system is very likely to be in the groundstate with energy ε_1

$$\Rightarrow \quad \overline{E} \approx \varepsilon_1$$