

## 1. Prove the following relation for the occupation number $n_{i}$ due to

Boltzmann distribution $n_{i}=\sum_{i} \frac{N}{Z} e^{\varepsilon_{i} / K T}$
Solution
Let the number of allowed states associated with the energy $\varepsilon_{i}$ be $g_{i}$. Let us first calculate the number of ways of putting $\mathrm{n}_{1}$ particles of N particles in one box, then $\mathrm{n}_{2}$ out of $\mathrm{N}-\mathrm{n}_{1}$ in second, and so on until we have exhausted all of the particles. The number of ways of choosing $n_{1}$ particles out of N particles is given by

$$
\begin{equation*}
\mathrm{W}_{1}=\frac{\mathrm{N}!}{\left(\mathrm{N}-\mathrm{n}_{1}\right)!\mathrm{n}_{1}!} \tag{1}
\end{equation*}
$$

and the number of choosing $\mathrm{n}_{2}$ out of $\mathrm{N}-\mathrm{n}_{1}$ is:

$$
\begin{equation*}
\mathrm{W}_{2}=\frac{\left(\mathrm{N}-\mathrm{n}_{1}\right)!}{\left(\mathrm{N}-\mathrm{n}_{1}-\mathrm{n}_{2}\right)!\mathrm{n}_{2}!} \tag{r}
\end{equation*}
$$

and the number of ways of achieving this arrangement is

$$
\begin{align*}
& \begin{array}{l}
\mathrm{W}=\mathrm{W}_{1} \cdot \mathrm{~W}_{2} \cdots \\
= \\
=\frac{\mathrm{N}!}{\left(\mathrm{N}-\mathrm{n}_{1}\right)!\mathrm{n}_{1}!} \cdot \frac{\left(\mathrm{N}-\mathrm{n}_{1}\right)!}{\left(\mathrm{N}-\mathrm{n}_{1}-\mathrm{n}_{2}\right)!\mathrm{n}_{2}!} \cdots \\
\mathrm{n}_{1}!\mathrm{n}_{2}!\cdots \\
\mathrm{W}=\mathrm{N}!\prod_{\mathrm{i}} \frac{\mathrm{~g}_{\mathrm{i}} \mathrm{n}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}}
\end{array} \\
& \begin{aligned}
\ln \mathrm{W} & =\ln \mathrm{N}!+\sum_{\mathrm{i}}\left(\mathrm{n} \ln \mathrm{~g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}!\right) \\
& =\mathrm{N} \ln \mathrm{~N}+\sum_{\mathrm{i}}\left(\mathrm{n} \ln \mathrm{~g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}\right)
\end{aligned}
\end{align*}
$$

To obtain the most probable distribution, we maximize Eq. (3) with $\mathrm{dN}=0:$

$$
\begin{aligned}
& \delta \ln \mathrm{W}=\sum_{\mathrm{i}}\left(\ln \mathrm{~g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}-\frac{\mathrm{n}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}}\right) \delta \mathrm{n}_{\mathrm{i}}=0 \\
& \quad \delta \ln \mathrm{~W}=\sum_{\mathrm{i}}\left(\ln \mathrm{~g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}-1\right) \delta \mathrm{n}_{\mathrm{i}}=0
\end{aligned}
$$

but

$$
\begin{align*}
& \delta \mathrm{N}=\sum_{\mathrm{i}} \delta \mathrm{n}_{\mathrm{i}}=0  \tag{4}\\
& \delta \mathrm{U}=\sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} \delta \mathrm{n}_{\mathrm{i}}=0 \tag{5}
\end{align*}
$$

multiply Eq. (4) by $\alpha+1$ and Eq. (5) bt -B and add the resulting equations to each other:

$$
\begin{equation*}
\sum_{\mathrm{i}}\left(\ln \mathrm{~g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}+\alpha-\beta \varepsilon_{\mathrm{i}}\right) \delta \mathrm{n}_{\mathrm{i}}=0 \tag{6}
\end{equation*}
$$

Since $\mathrm{n}_{\mathrm{i}}$ is vary independent,

$$
\ln \mathrm{g}_{\mathrm{i}}-\mathrm{n} \ln \mathrm{n}_{\mathrm{i}}+\alpha-\beta \varepsilon_{\mathrm{i}}=0
$$

or

$$
\begin{equation*}
\ln \frac{\mathrm{g}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}}+\alpha-\beta \varepsilon_{\mathrm{i}}=0 \tag{7}
\end{equation*}
$$

Solving Eq. (7) for $n_{i}$ gives
$\mathrm{n}_{\mathrm{i}}=\frac{\mathrm{N}}{\mathrm{Z}} \mathrm{g}_{\mathrm{i}} \mathrm{e}^{-\beta \varepsilon_{\mathrm{i}}}$
2. (a) Find the relation between the partition function $Z$ and thermodynamic functions $\mathbf{U}, \mathbf{S}$, and $\mathbf{F}$.
$\qquad$

## (a) Relation between Z and U

Since

$$
\mathrm{Z}=\sum_{\mathrm{i}} \mathrm{~g}_{\mathrm{i}} \mathrm{e}^{\varepsilon_{\mathrm{i}} / \mathrm{KT}}
$$

differentiate Z with respect to T , holding V constant,

$$
\begin{aligned}
\left(\frac{\partial \mathrm{Z}}{\partial \mathrm{~T}}\right)_{\mathrm{V}} & =\sum_{\mathrm{i}} \mathrm{~g}_{\mathrm{i}}\left(\frac{\varepsilon_{\mathrm{i}}}{\mathrm{KT}^{2}}\right) \mathrm{e}^{\varepsilon_{\mathrm{i}} / \mathrm{KT}} \\
& =\frac{1}{\mathrm{KT}^{2}} \sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} \mathrm{~g}_{\mathrm{i}} \mathrm{e}^{\varepsilon_{\mathrm{i}} / \mathrm{KT}} \\
& =\frac{1}{\mathrm{KT}^{2}} \frac{\sum_{\mathrm{i}} \mathrm{n}_{\mathrm{i}} \varepsilon_{\mathrm{i}}}{\sum_{\mathrm{i}} \mathrm{n}_{\mathrm{i}}} \mathrm{~g}_{\mathrm{i}} \mathrm{e}^{\varepsilon_{\mathrm{i}} / \mathrm{KT}} \\
& =\frac{\mathrm{ZU}}{\mathrm{NKT}^{2}}
\end{aligned}
$$

It follow that

$$
\begin{equation*}
\mathrm{U}=\mathrm{NKT}^{2}\left(\frac{\partial \ln \mathrm{Z}}{\partial \mathrm{~T}}\right)_{\mathrm{V}} \tag{8}
\end{equation*}
$$

and U may be calculated once $\ln \mathrm{Z}$ is known as a function of T and V .

## (b) Relation between $Z$ and $S$

The entropy $S$ is related to the order or distribution of the particles, through the relation:

$$
\mathrm{S}=\mathrm{K} \ln \mathrm{~W}
$$

but

$$
\ln \mathrm{W}=-\sum_{\mathrm{i}} \mathrm{n}_{\mathrm{i}} \ln \frac{\mathrm{n}_{\mathrm{i}}}{\mathrm{~g}_{\mathrm{i}}}+\mathrm{N} \ln \mathrm{~N}
$$

Hence

$$
\mathrm{S}=\mathrm{K} \ln \mathrm{~W}=\mathrm{K}\left[-\sum_{\mathrm{i}} \mathrm{n}_{\mathrm{i}} \ln \frac{\mathrm{n}_{\mathrm{i}}}{\mathrm{~g}_{\mathrm{i}}}+\mathrm{N} \ln \mathrm{~N}\right]
$$

By using the relation

$$
\mathrm{n}_{\mathrm{i}}=\frac{\mathrm{N}}{\mathrm{Z}} \mathrm{~g}_{\mathrm{i}} \mathrm{e}^{-\varepsilon_{\mathrm{i}} / K \mathrm{KT}}
$$

we have

$$
\frac{n_{i}}{g_{i}}=\frac{N}{Z} e^{-\varepsilon_{i} / K T}
$$

then

$$
\begin{align*}
\mathrm{S} & =\mathrm{K} \ln \mathrm{~W}=\mathrm{K}\left[-\mathrm{N} \ln \mathrm{~N}+\mathrm{N} \ln \mathrm{Z}+\frac{\mathrm{U}}{\mathrm{KT}}+\mathrm{N} \ln \mathrm{~N}\right]  \tag{9}\\
& =\mathrm{NKT} \ln \mathrm{Z}+\frac{\mathrm{U}}{\mathrm{~T}}
\end{align*}
$$

and S may be calculated once ln Z is known as a function of T and V .

## (c) Relation between Z and F

The property of the system is defined by its Helmholtz function F which is given by:

$$
\mathrm{F}=\mathrm{U}-\mathrm{TS}
$$

This equation can be evaluated in terms of the partition function Z. By using the entropy S, Eq. (8), we get

$$
\begin{align*}
& \mathrm{F}=\mathrm{U}-\mathrm{T}\left(\mathrm{NK} \ln \mathrm{Z}+\frac{\mathrm{U}}{\mathrm{~T}}\right) \\
& \mathrm{F}=-\mathrm{NKT} \ln \mathrm{Z} \tag{10}
\end{align*}
$$

and F may be calculated once $\ln \mathrm{Z}$ is known as a function of T and V .
2. Prove the following relation for the occupation number $n_{i}$ due to

```
Fermi-Dirac statistics, \(n_{i}=\frac{g_{i}}{e^{\left(\varepsilon_{i}-\varepsilon_{F}\right) / K T}+1}\)
```

Solution
Let the number of allowed states associated with the energy $\varepsilon_{i}$ be $g_{i}$. Let us first calculate the number of ways of putting $n_{1}$ particles of N particles in one box, then $n_{2}$ out of $\mathrm{N}-\mathrm{n}_{1}$ in second, and so on until we have exhausted all of the particles. The number of ways of choosing $\mathrm{n}_{1}$ particles out of N particles is given by

$$
\begin{equation*}
\mathrm{W}=\prod_{\mathrm{i}} \frac{\mathrm{~g}_{\mathrm{i}}!}{\mathrm{n}_{\mathrm{i}}!\left(\mathrm{g}_{\mathrm{i}}-\mathrm{n}_{\mathrm{i}}\right)!} \tag{1}
\end{equation*}
$$

$$
\ln \mathrm{W}=\sum_{\mathrm{i}}\left[\left(\ln \mathrm{~g}_{\mathrm{i}}!-\ln \mathrm{n}_{\mathrm{i}}!-\ln \left(\mathrm{g}_{\mathrm{i}}-\mathrm{n}_{\mathrm{i}}\right)!\right]\right.
$$

To obtain the most probable distribution, we maximize Eq. (3) with $\mathrm{dN}=0$ :

$$
\delta \ln \mathrm{W}=\sum_{\mathrm{i}} \ln \frac{\mathrm{~g}_{\mathrm{i}}-\mathrm{n}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}} \delta \mathrm{n}_{\mathrm{i}}=0
$$

but

$$
\begin{align*}
& \delta \mathrm{N}=\sum_{\mathrm{i}} \delta \mathrm{n}_{\mathrm{i}}=0  \tag{4}\\
& \delta \mathrm{U}=\sum_{\mathrm{i}} \varepsilon_{\mathrm{i}} \delta \mathrm{n}_{\mathrm{i}}=0 \tag{5}
\end{align*}
$$

multiply Eq. (4) by $-\alpha$ and Eq. (5) bt -B and add the resulting equations to each other:

$$
\begin{equation*}
\sum_{\mathrm{i}}\left[\ln \left(\frac{\mathrm{~g}_{\mathrm{i}}-\mathrm{n}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}}\right)-\alpha-\beta \varepsilon_{\mathrm{i}}\right] \delta \mathrm{n}_{\mathrm{i}}=0 \tag{6}
\end{equation*}
$$

Since $\mathrm{n}_{\mathrm{i}}$ is vary independent,

$$
\ln \left(\frac{\mathrm{g}_{\mathrm{i}}-\mathrm{n}_{\mathrm{i}}}{\mathrm{n}_{\mathrm{i}}}\right)-\alpha-\beta \varepsilon_{\mathrm{i}}=0
$$

Solving Eq. (7) for $\mathrm{n}_{\mathrm{i}}$ gives

$$
\mathrm{n}_{\mathrm{i}}=\frac{\mathrm{g}_{\mathrm{i}}}{\mathrm{e}^{\left(\alpha+\beta \varepsilon_{\mathrm{i}}\right)}+1}
$$

