7.D.2. Systems of Indistinguishable Particles

Identical particles are particles with the same inherent physical attributes such as rest mass, electric charge, spin, etc.

Indistinguishable particles are particles whose identities cannot be determined by measurement.

In classical physics, all particles are distinguishable.
In quantum mechanics, identical particles that can come to close proximity with each other become indistinguishable owing to the uncertainty principle.

Thus, indistinguishable particles must be identical but identical particles need not be indistinguishable. For example, atoms of the same species are indistinguishable in an ideal gas, but they are distinguishable when confined to the sites of a crystal lattice.

Note that although indistinguishability is a quantum mechanical phenomenon, it can affect macroscopic systems; to wit, the Gibbs' paradox.

Basic properties of systems of indistinguishable particles are discussed in detail in Appendix B. Here, we shall quote those results freely.

Consider a set of N free, and hence indistinguishable, identical particles. The momentum (and energy) eigenfunctions for a single particle are the plane waves

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \langle \boldsymbol{r} \mid \boldsymbol{k} \rangle$$

where $\hbar \boldsymbol{k} = \boldsymbol{p}$ is the momentum of the particle at position $\boldsymbol{r}$. For the set of N particles,

$$\psi_{\boldsymbol{k}_1,\dots,\boldsymbol{k}_N}(\boldsymbol{r}) = \langle \boldsymbol{r}_1 \mid \boldsymbol{k}_1 \rangle \dots \langle \boldsymbol{r}_N \mid \boldsymbol{k}_N \rangle$$
$$\equiv \langle \boldsymbol{r}_1 \dots \boldsymbol{r}_N \mid \boldsymbol{k}_1 \dots \boldsymbol{k}_N \rangle \qquad (7.52a)$$

where

$$\mid \boldsymbol{k}_1 \dots \boldsymbol{k}_N \rangle \equiv \mid \boldsymbol{k}_1 \rangle \otimes \dots \otimes \mid \boldsymbol{k}_N \rangle \qquad (7.52)$$
$$\langle \boldsymbol{r}_1 \dots \boldsymbol{r}_N \mid \equiv \langle \boldsymbol{r}_1 \mid \otimes \dots \otimes \langle \boldsymbol{r}_N \mid$$

are the direct product of the single particle eigenstates. Comparison with (7.52a) shows that $\mid \boldsymbol{k}_j \rangle$ is the state for the j^{th} particle.

Indistinguishability means that physical properties (or expectation values given by matrix elements of operators) must be invariant under the permutation of particles. This in turn means the wave functions must be symmetric or antisymmetric under such permutations. Thus, the basis states (7.52) should be replaced by

$$\mid \boldsymbol{k}_1 \dots \boldsymbol{k}_N \rangle^{(\pm)} = \frac{1}{\sqrt{C_{\boldsymbol{k}}}} \sum_P (-)^P \left| \boldsymbol{k}_{P[1} \dots \boldsymbol{k}_{N]} \right\rangle \qquad (7.53)$$

where P is any one of the $N!$ permutations of the subscripts $(1, \dots, N)$, and

$$C_{\boldsymbol{k}} = \frac{N!}{n_{\boldsymbol{k}_1}! \dots n_{\boldsymbol{k}_N}!} = \text{number of distinctive permutations in } (\boldsymbol{k}_1 \dots \boldsymbol{k}_N). \qquad (7.53a)$$
$$= \text{number of terms in the sum in (7.53).}$$

with

$$n_{\boldsymbol{k}_j} = \text{number of } \boldsymbol{k}\text{'s with the same value as } \boldsymbol{k}_j.$$

such that

$$\sum_{j=1}^{N} n_{\boldsymbol{k}_j} = N$$

Now, except for the case where all $\boldsymbol{k}_j$ are distinct, the choice of $\{n_{\boldsymbol{k}_j}\}$ is not unique. For example,

$$(\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3) = (\boldsymbol{a}, \boldsymbol{a}, \boldsymbol{b})$$

can be interpret as

$$(n_{\boldsymbol{k}_1}, n_{\boldsymbol{k}_2}, n_{\boldsymbol{k}_3}) = (2, 0, 1) \quad \text{or} \quad (0, 2, 1)$$

To avoid confusion, we shall adopt the convention that the non-zero $n_{\boldsymbol{k}_j}$ has the smallest j.

Note that for the antisymmetric case,

$$|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(-)} = 0 \qquad \text{if any two of the } \boldsymbol{k}_j\text{'s are equal.}$$

Hence, we can set

$$n_{\boldsymbol{k}_j}! = 1 \qquad \forall\ j = 1, \ldots, N$$

$$\rightarrow \quad C_{\boldsymbol{k}} = N!$$

From the orthonormality of the 1-particle eigenstates

$$\langle \boldsymbol{k} \,|\, \boldsymbol{k}' \rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'}$$

we get

$$^{(\pm)}\langle \boldsymbol{k}_1' \ldots \boldsymbol{k}_N' \,|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(\pm)} = \delta_{\boldsymbol{k}_1 \boldsymbol{k}_1'} \ldots \delta_{\boldsymbol{k}_N \boldsymbol{k}_N'} \qquad (7.53b)$$

since there are $C_{\boldsymbol{k}}$ orthonormal terms in $|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(\pm)}$.

Since the trace is the sum of the diagonal matrix elements with respect to a set of complete orthonormal basis, we have

$$\mathrm{Tr}_N \hat{\rho} = \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \frac{1}{C_{\boldsymbol{k}}}\ ^{(\pm)}\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,|\, \hat{\rho} \,|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(\pm)} = 1 \qquad (7.51a)$$

where the factor $C_{\boldsymbol{k}}^{-1}$ is inserted to ensure the contribution of each distinct $|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(\pm)}$ is counted only once in the multiple sums.

In Ex.7.3, we shall show that [see (7c)]

$$\left\langle \boldsymbol{k}_{P[1} \ldots \boldsymbol{k}_{N]} \,\middle|\, e^{-\beta \hat{H}_N} \,\middle|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} = \left\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,\middle|\, e^{-\beta \hat{H}_N} \,\middle|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} \qquad \forall\ P$$

Thus, each term in $^{(\pm)}\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,|$ gives the same matrix element in (7.51a), which can therefore be written as

$$\mathrm{Tr}_N \hat{\rho} = \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \frac{1}{\sqrt{C_{\boldsymbol{k}}}} \langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,|\, \hat{\rho} \,|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \rangle^{(\pm)} = 1 \qquad (7.51)$$

Similarly,

$$Z_N = \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \frac{1}{C_{\boldsymbol{k}}}\ ^{(\pm)}\left\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,\middle|\, e^{-\beta \hat{H}_N} \,\middle|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} \qquad (7.51b)$$

$$= \sum_{\boldsymbol{k}_1 \ldots \boldsymbol{k}_N} \frac{1}{\sqrt{C_{\boldsymbol{k}}}} \left\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \,\middle|\, e^{-\beta \hat{H}_N} \,\middle|\, \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} \qquad (7.51c)$$

Identical particles whose wave functions are symmetric (antisymmetric) with respect to particle permutations are called bosons (fermions).

Ex. 7.3.

Compute the partition function $Z_3(T)$ for an ideal gas of 3 identical particles in a cubic box of volume $V = L^3$.

Assume the walls of the box are completely impenetrable.
Neglect spin and all other internal degrees of freedom.

What approximations can be made at high temperatures and low densities?

Answer

For a single particle in the box, we have

$$\hat{H}_1 = \frac{1}{2m}\hat{\boldsymbol{p}}^2$$

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = A\sin(k_x x)\sin(k_y y)\sin(k_z z) \qquad (1)$$

where A is a normalization constant and

$$\boldsymbol{k} = (k_x, k_y, k_z) = \frac{\pi}{L}\boldsymbol{n}$$

$$= \frac{\pi}{L}(n_x, n_y, n_z) \qquad n_j = 1, 2, 3, \ldots \qquad \forall\ j = x, y, z \qquad (2)$$

Hence,

$$Z_1(T) = \sum_{\boldsymbol{k}} \left\langle \psi_{\boldsymbol{k}} \,\middle|\, e^{-\beta \hat{H}_1} \,\middle|\, \psi_{\boldsymbol{k}} \right\rangle$$

$$= \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\beta}{2m}\left(\hbar\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)\right] \qquad (3)$$

For $V \to \infty$, we have

$$\sum_{\boldsymbol{k}} \approx \int \frac{d^3k}{\Delta k_x \Delta k_y \Delta k_z} = \left(\frac{L}{\pi}\right)^3 \int d^3k$$

where

$$\Delta k_j = \frac{\pi}{L}\Delta n_j = \frac{\pi}{L} = \text{spacing of } k_j$$

(3) thus becomes, for $V \to \infty$,

$$Z_1(T) = \left(\frac{L}{\pi}\right)^3 \int_0^{\infty} dk_x \int_0^{\infty} dk_y \int_0^{\infty} dk_z \exp\left[-\frac{\beta\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)\right]$$

$$= \left(\frac{L}{2\pi}\right)^3 \int d^3k \exp\left(-\frac{\beta\hbar^2}{2m}k^2\right)$$

$$= \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m\pi}{\beta\hbar^2}\right)^{3/2}$$

$$= \frac{V}{\lambda_T^3} \qquad (4)$$

where

$$\lambda_T = \sqrt{\frac{2\pi\beta\hbar^2}{m}} = \frac{h}{\sqrt{2\pi m k_B T}} \qquad (5)$$

is the thermal wavelength.

In[∘]:=
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Assuming[a > 0, ∫_{-∞}^{∞} e^(-a x^2) dx]
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Out[∘]= $\frac{\sqrt{\pi}}{\sqrt{a}}$

For a 2-particle ideal gas,

$$\hat{H}_2 = \frac{1}{2m}\left(\hat{\boldsymbol{p}}_1^2 + \hat{\boldsymbol{p}}_2^2\right)$$

and (7.51a) gives

$$Z_2(T) = \sum_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2} \frac{1}{C_{\boldsymbol{k}}} {}^{(\pm)}\left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} \qquad C_{\boldsymbol{k}} = \frac{2!}{n_{\boldsymbol{k}_1}!\, n_{\boldsymbol{k}_2}!} \qquad (6a)$$

Assuming $\boldsymbol{k}_1 \neq \boldsymbol{k}_2$, we have

$$\left| \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} = \frac{1}{\sqrt{2!}}\left(\left| \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle \pm \left| \boldsymbol{k}_2 \boldsymbol{k}_1 \right\rangle \right) \qquad C_{\boldsymbol{k}} = \frac{2!}{1! \times 1!} = 2! \qquad (6b)$$

$$\left| \boldsymbol{k}_1 \boldsymbol{k}_1 \right\rangle^{(\pm)} = \begin{cases} \left| \boldsymbol{k}_1 \boldsymbol{k}_1 \right\rangle \\ 0 \end{cases} \qquad C_{\boldsymbol{k}} = \frac{2!}{2! \times 0!} = 1$$

Since $\hat{H}_2$ is symmetric to particle permutations, we have

$$P\left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} = \left\langle \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \;\middle|\; e^{-\beta P(\hat{H}_2)} \;\middle|\; \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \right\rangle^{(\pm)}$$
$$= \left\langle \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} \qquad (7a)$$

On the other hand,

$$\left\langle \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \;\middle|\; e^{-\beta P(\hat{H}_2)} \;\middle|\; \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \right\rangle^{(\pm)} = \left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)}$$

since the two sides are related by a simple relabeling of all the particles, which cannot affect the values of any physical quantities. Putting this into (7a) gives

$$\left\langle \boldsymbol{k}_{P[1}\boldsymbol{k}_{2]} \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} = \left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle^{(\pm)} \qquad \forall\, P \qquad (7b)$$

which is easily generalized to

$$\left\langle \boldsymbol{k}_{P[1} \ldots \boldsymbol{k}_{N]} \;\middle|\; e^{-\beta \hat{H}_N} \;\middle|\; \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} = \left\langle \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \;\middle|\; e^{-\beta \hat{H}_N} \;\middle|\; \boldsymbol{k}_1 \ldots \boldsymbol{k}_N \right\rangle^{(\pm)} \qquad \forall\, P \quad (7c)$$

To check the validity of (7b), we 1st use

$$\left\langle \boldsymbol{k} \;\middle|\; \hat{H} \;\middle|\; \boldsymbol{k}' \right\rangle = \delta_{\boldsymbol{k}\boldsymbol{k}'} \frac{\hbar^2 \boldsymbol{k}^2}{2m} \qquad (7d)$$

evaluate (6a). Putting (6b) into (6a) gives

$$Z_2(T) = \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2} \frac{1}{(2!)^2}\left[\left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \right| \pm \left\langle \boldsymbol{k}_2 \boldsymbol{k}_1 \right| \right] e^{-\beta \hat{H}_2} \left[\left| \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle \pm \left| \boldsymbol{k}_2 \boldsymbol{k}_1 \right\rangle \right] + \delta_B \sum_{\boldsymbol{k}_1} \left\langle \boldsymbol{k}_1 \boldsymbol{k}_1 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_1 \right\rangle$$

where

$$\delta_B = \begin{cases} 1 & \text{for Bosons (or symmetric permutations)} \\ 0 & \text{for Fermions (or anti − symmetric permutations)} \end{cases}$$

$$Z_2(T) = \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2} \frac{1}{4}\left[\left\langle \boldsymbol{k}_1 \boldsymbol{k}_2 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_1 \boldsymbol{k}_2 \right\rangle + \left\langle \boldsymbol{k}_2 \boldsymbol{k}_1 \;\middle|\; e^{-\beta \hat{H}_2} \;\middle|\; \boldsymbol{k}_2 \boldsymbol{k}_1 \right\rangle \right]$$
$$+ \delta_B \sum_{\boldsymbol{k}_1} \exp\left[-\frac{\beta \hbar^2}{2m}\left(2 k_1^2\right) \right]$$
$$= \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2} \frac{1}{2} \exp\left[-\frac{\beta \hbar^2}{2m}\left(\boldsymbol{k}_1^2 + \boldsymbol{k}_2^2 \right) \right] + \delta_B Z_1\left(\frac{T}{2}\right) \qquad \text{[(6b) used.]} \qquad (a)$$
$$= \frac{1}{2}\sum_{\boldsymbol{k}_1} \left\{ \exp\left(-\frac{\beta\hbar^2}{2m}\boldsymbol{k}_1^2 \right) \left[\sum_{\boldsymbol{k}_2} \exp\left(-\frac{\beta\hbar^2}{2m}\boldsymbol{k}_2^2 \right) - \exp\left(-\frac{\beta\hbar^2}{2m}\boldsymbol{k}_1^2 \right) \right] \right\} + \delta_B Z_1\left(\frac{T}{2}\right)$$
$$= \frac{1}{2}\sum_{\boldsymbol{k}_1} \exp\left(-\frac{\beta\hbar^2}{2m}\boldsymbol{k}_1^2 \right) \sum_{\boldsymbol{k}_2} \exp\left(-\frac{\beta\hbar^2}{2m}\boldsymbol{k}_2^2 \right) \pm \frac{1}{2} Z_1\left(\frac{T}{2}\right)$$
$$= \frac{1}{2} Z_1(T)^2 \pm \frac{1}{2} Z_1\left(\frac{T}{2}\right) \qquad (b)$$

Comparing with the result for distinguishable particles

$$Z_2(T) = Z_1(T)^2$$

we notice that (b) possess two new features

1. The Gibbs counting factor $\frac{1}{2}$ for the 1st term that resolves the Gibbs paradox.
2. The term $\pm\frac{1}{2}Z_1\left(\frac{T}{2}\right)$ commonly attributed to the "exchange-correlation" effects.

Next expand the $N=2$ version of (7.51c) to get

$$\begin{aligned}
Z_2(T) &= \sum_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2}\frac{1}{\sqrt{C_{\boldsymbol{k}}}}\left\langle \boldsymbol{k}_1\,\boldsymbol{k}_2 \,\middle|\, e^{-\beta\hat{H}_2} \,\middle|\, \boldsymbol{k}_1\,\boldsymbol{k}_2\right\rangle^{(\pm)} \\
&= \sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2}\frac{1}{\sqrt{2!}}\left\langle \boldsymbol{k}_1\,\boldsymbol{k}_2 \,\middle|\, e^{-\beta\hat{H}_2}\frac{1}{\sqrt{2!}}\left[\,\middle|\,\boldsymbol{k}_1\,\boldsymbol{k}_2\right\rangle \pm \left|\,\boldsymbol{k}_2\,\boldsymbol{k}_1\right\rangle\Big] \\
&\quad +\delta_B\sum_{\boldsymbol{k}_1}\left\langle \boldsymbol{k}_1\,\boldsymbol{k}_1 \,\middle|\, e^{-\beta\hat{H}_2} \,\middle|\, \boldsymbol{k}_1\,\boldsymbol{k}_1\right\rangle \\
&= \sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2}\frac{1}{2}\exp\left[-\frac{\beta\hbar^2}{2m}\left(\boldsymbol{k}_1^2+\boldsymbol{k}_2^2\right)\right]+\delta_B Z_1\left(\frac{T}{2}\right)
\end{aligned}$$

which is the same as (a), as promised.

The 3-particle Hamiltonian is

$$\hat{H}_3=\frac{1}{2m}\left(\hat{\boldsymbol{p}}_1^2+\hat{\boldsymbol{p}}_2^2+\hat{\boldsymbol{p}}_3^2\right)$$

so that (7.51c) becomes

$$Z_3(T)=\sum_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2}\sum_{\boldsymbol{k}_3}\frac{1}{\sqrt{C_{\boldsymbol{k}}}}\left\langle \boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3 \,\middle|\, e^{-\beta\hat{H}_3} \,\middle|\, \boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3\right\rangle^{(\pm)} \qquad (6)$$

$$C_{\boldsymbol{k}}=\frac{3!}{n_{\boldsymbol{k}_1}!\,n_{\boldsymbol{k}_2}!\,n_{\boldsymbol{k}_3}!}$$

Assuming $\boldsymbol{k}_1\neq\boldsymbol{k}_2\neq\boldsymbol{k}_3$, we have

$$\begin{aligned}
\left|\boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3\right\rangle^{(\pm)} &= \frac{1}{\sqrt{3!}}\Big(\left|\boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3\right\rangle \pm \left|\boldsymbol{k}_1\,\boldsymbol{k}_3\,\boldsymbol{k}_2\right\rangle + \left|\boldsymbol{k}_3\,\boldsymbol{k}_1\,\boldsymbol{k}_2\right\rangle \qquad (7)\\
&\qquad \pm\left|\boldsymbol{k}_3\,\boldsymbol{k}_2\,\boldsymbol{k}_1\right\rangle + \left|\boldsymbol{k}_2\,\boldsymbol{k}_3\,\boldsymbol{k}_1\right\rangle \pm \left|\boldsymbol{k}_2\,\boldsymbol{k}_1\,\boldsymbol{k}_3\right\rangle\Big) \\
\left|\boldsymbol{k}_1\,\boldsymbol{k}_1\,\boldsymbol{k}_3\right\rangle^{(\pm)} &= \delta_B\frac{1}{\sqrt{3}}\Big(\left|\boldsymbol{k}_1\,\boldsymbol{k}_1\,\boldsymbol{k}_3\right\rangle + \left|\boldsymbol{k}_1\,\boldsymbol{k}_3\,\boldsymbol{k}_1\right\rangle + \left|\boldsymbol{k}_3\,\boldsymbol{k}_1\,\boldsymbol{k}_1\right\rangle\Big) \\
\left|\boldsymbol{k}_1\,\boldsymbol{k}_1\,\boldsymbol{k}_1\right\rangle^{(\pm)} &= \delta_B\left|\boldsymbol{k}_1\,\boldsymbol{k}_1\,\boldsymbol{k}_1\right\rangle
\end{aligned}$$

Together with

$$\sum_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2}=\sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2}+\sum_{\boldsymbol{k}_1}$$

$$\begin{aligned}
\sum_{\boldsymbol{k}_1}\sum_{\boldsymbol{k}_2}\sum_{\boldsymbol{k}_3} &= \sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2\neq\boldsymbol{k}_3}+\left(\sum_{\boldsymbol{k}_1\neq(\boldsymbol{k}_2=\boldsymbol{k}_3)}+\sum_{(\boldsymbol{k}_1=\boldsymbol{k}_3)\neq\boldsymbol{k}_2}+\sum_{(\boldsymbol{k}_1=\boldsymbol{k}_2)\neq\boldsymbol{k}_3}\right)+\sum_{\boldsymbol{k}_1=\boldsymbol{k}_2=\boldsymbol{k}_3} \\
&= \sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2\neq\boldsymbol{k}_3}+3\sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2}+\sum_{\boldsymbol{k}_1} \qquad [\text{ All } \boldsymbol{k}_j\text{'s are equivalent.}] \qquad (8a)
\end{aligned}$$

(6) becomes

$$\begin{aligned}
Z_3(T) &= \sum_{\boldsymbol{k}_1\neq\boldsymbol{k}_2\neq\boldsymbol{k}_3}\frac{1}{\sqrt{3!}}\left\langle \boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3 \,\middle|\, e^{-\beta\hat{H}_3}\right. \\
&\quad \times\frac{1}{\sqrt{3!}}\Big(\left|\boldsymbol{k}_1\,\boldsymbol{k}_2\,\boldsymbol{k}_3\right\rangle \pm \left|\boldsymbol{k}_1\,\boldsymbol{k}_3\,\boldsymbol{k}_2\right\rangle + \left|\boldsymbol{k}_3\,\boldsymbol{k}_1\,\boldsymbol{k}_2\right\rangle \pm \left|\boldsymbol{k}_3\,\boldsymbol{k}_2\,\boldsymbol{k}_1\right\rangle + \left|\boldsymbol{k}_2\,\boldsymbol{k}_3\,\boldsymbol{k}_1\right\rangle \pm \left|\boldsymbol{k}_2\,\boldsymbol{k}_1\,\boldsymbol{k}_3\right\rangle\Big)
\end{aligned}$$

$$+3\,\delta_B \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_3} \frac{1}{\sqrt{3}} \left\langle \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_3 \,\middle|\, e^{-\beta \hat{H}_3} \frac{1}{\sqrt{3}} \left(\middle| \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_3 \right\rangle + \left| \boldsymbol{k}_1\, \boldsymbol{k}_3\; \boldsymbol{k}_1 \right\rangle + \left| \boldsymbol{k}_3\, \boldsymbol{k}_1\; \boldsymbol{k}_1 \right\rangle \Big)$$

$$+\delta_B \sum_{\boldsymbol{k}_1} \left\langle \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_1 \,\middle|\, e^{-\beta \hat{H}_3} \,\middle|\, \boldsymbol{k}_1\, \boldsymbol{k}_1\, \boldsymbol{k}_1 \right\rangle$$

$$= \frac{1}{3!} \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2 \neq \boldsymbol{k}_3} \left\langle \boldsymbol{k}_1\, \boldsymbol{k}_2\; \boldsymbol{k}_3 \,\middle|\, e^{-\beta \hat{H}_3} \,\middle|\, \boldsymbol{k}_1\, \boldsymbol{k}_2\; \boldsymbol{k}_3 \right\rangle + \delta_B \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_3} \left\langle \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_3 \,\middle|\, e^{-\beta \hat{H}_3} \,\middle|\, \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_3 \right\rangle$$

$$+\delta_B \sum_{\boldsymbol{k}_1} \left\langle \boldsymbol{k}_1\, \boldsymbol{k}_1\; \boldsymbol{k}_1 \,\middle|\, e^{-\beta \hat{H}_3} \,\middle|\, \boldsymbol{k}_1\, \boldsymbol{k}_1\, \boldsymbol{k}_1 \right\rangle \qquad \text{[(6b) used.]}$$

$$= \frac{1}{3!} \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2 \neq \boldsymbol{k}_3} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(\boldsymbol{k}_1^2 + \boldsymbol{k}_2^2 + \boldsymbol{k}_3^2 \right) \right] \qquad \text{(c)}$$

$$+\delta_B \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_3} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(2\,\boldsymbol{k}_1^2 + \boldsymbol{k}_3^2 \right) \right] + \delta_B \sum_{\boldsymbol{k}_1} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(3\,\boldsymbol{k}_1^2 \right) \right]$$

(8a) gives

$$\sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2} = \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} - \sum_{\boldsymbol{k}_1}$$

$$\sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2 \neq \boldsymbol{k}_3} = \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} \sum_{\boldsymbol{k}_3} - 3 \sum_{\boldsymbol{k}_1 \neq \boldsymbol{k}_2} - \sum_{\boldsymbol{k}_1} = \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} \sum_{\boldsymbol{k}_3} - 3 \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} + 2 \sum_{\boldsymbol{k}_1}$$

so that (c) becomes

$$Z_3(T) = \frac{1}{3!} \Bigg\{ \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} \sum_{\boldsymbol{k}_3} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(\boldsymbol{k}_1^2 + \boldsymbol{k}_2^2 + \boldsymbol{k}_3^2 \right) \right]$$

$$- 3 \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_2} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(2\,\boldsymbol{k}_1^2 + \boldsymbol{k}_2^2 \right) \right] + 2 \sum_{\boldsymbol{k}_1} \exp\left(-\frac{\beta \hbar^2}{2\,m}\, 3\,\boldsymbol{k}_1^2 \right) \Bigg\}$$

$$+\delta_B \left\{ \sum_{\boldsymbol{k}_1} \sum_{\boldsymbol{k}_3} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(2\,\boldsymbol{k}_1^2 + \boldsymbol{k}_3^2 \right) \right] - \sum_{\boldsymbol{k}_1} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(3\,\boldsymbol{k}_1^2 \right) \right] \right\}$$

$$+\delta_B \sum_{\boldsymbol{k}_1} \exp\left[-\frac{\beta \hbar^2}{2\,m} \left(3\,\boldsymbol{k}_1^2 \right) \right]$$

$$= \frac{1}{3!} \left[Z_1(T)^3 - 3\, Z_1\left(\frac{T}{2}\right) Z_1(T) + 2\, Z_1\left(\frac{T}{3}\right) \right] + \delta_B \left[Z_1\left(\frac{T}{2}\right) Z_1(T) - Z_1\left(\frac{T}{3}\right) \right] + \delta_B\, Z_1\left(\frac{T}{3}\right)$$

$$= \frac{1}{3!} Z_1(T)^3 + \left(-\frac{1}{2} + \delta_B \right) Z_1\left(\frac{T}{2}\right) Z_1(T) + \frac{1}{3} Z_1\left(\frac{T}{3}\right)$$

$$= \frac{1}{3!} Z_1(T)^3 \pm \frac{1}{2} Z_1\left(\frac{T}{2}\right) Z_1(T) + \frac{1}{3} Z_1\left(\frac{T}{3}\right)$$

$$= \frac{1}{3!} \left[Z_1(T)^3 \pm 3\, Z_1\left(\frac{T}{2}\right) Z_1(T) + 2\, Z_1\left(\frac{T}{3}\right) \right] \qquad \text{(8b)}$$

Using (4 & 5), we have

$$\lambda_{T/n} = \sqrt{n}\; \lambda_T \qquad\qquad Z_1\left(\frac{T}{n}\right) = \frac{V}{\lambda_{T/n}^3} = \frac{V}{n^{3/2}\, \lambda_T^3}$$

so that (8b) becomes

$$Z_3(T) = \frac{1}{3!} \left[\left(\frac{V}{\lambda_T^3} \right)^3 \pm 3 \left(\frac{V}{2^{3/2}\, \lambda_T^3} \right) \left(\frac{V}{\lambda_T^3} \right) + 2 \left(\frac{V}{3^{3/2}\, \lambda_T^3} \right) \right]$$

$$= \frac{1}{3!} \left(\frac{V}{\lambda_T^3} \right)^3 \left[1 \pm \frac{3}{2^{3/2}} \frac{\lambda_T^3}{V} + \frac{2}{3^{3/2}} \left(\frac{\lambda_T^3}{V} \right)^2 \right] \qquad \text{(8)}$$

At high temperatures and low densities,

$$\lambda_T << 1 \qquad \& \qquad V >> 1$$

so that (8) reduces to

$$Z_3(T) \approx \frac{1}{3!}\left(\frac{V}{\lambda_T^3}\right)^3 \tag{9}$$

Generalizing to the case of N particles, we get

$$Z_N(T) \approx \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N = \frac{1}{N!} Z_1(T)^N \tag{10}$$

which differs from the classical result by the Gibbs counting factor $\frac{1}{N!}$, thus resolving the Gibbs paradox.

--- Ex.7.3 ends --

(10) suggests that at high temperatures and low densities,

$$Z_N(T) \approx \frac{1}{N!} \sum_{k_1 \dots k_N} \left\langle \boldsymbol{k}_1 \dots \boldsymbol{k}_N \,\middle|\, e^{-\beta \hat{H}_N} \,\middle|\, \boldsymbol{k}_1 \dots \boldsymbol{k}_N \right\rangle \tag{7.54}$$

which is just the partition function of distinguishable particles multiplied by the Gibbs counting factor. This is called the semi-classical approximation, which takes into all quantum mechanical effects except those concerning indistinguishability (or particle exchange effects).

For a system of ideal gas of N non-interacting molecules, the Hamiltonian can be written as

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i$$

$$\hat{H}_i = \frac{\hat{\boldsymbol{p}}_i^2}{2m} + \hat{H}_{i\,(\text{rot})} + \hat{H}_{i\,(\text{vib})} + \hat{H}_{i\,(\text{elec})} + \hat{H}_{i\,(\text{nucl})} + \dots \tag{7.55a}$$

$= (\text{ kinetic + rotational + vibrational + electronic + nuclear + ... }) \text{ energy}$

where couplings between the various internal degrees of freedom are neglected.

(7.54) thus becomes

$$Z_N(T) \approx \frac{1}{N!} \mathrm{Tr}_N \left\{ \exp\left[-\beta \sum_{i=1}^{N} \left(\frac{\hat{\boldsymbol{p}}_i^2}{2m} + \hat{H}_{i\,(\text{rot})} + \hat{H}_{i\,(\text{vib})} + \hat{H}_{i\,(\text{elec})} + \hat{H}_{i\,(\text{nucl})} + \dots \right) \right] \right\} \tag{7.55}$$

In the absence of couplings, the internal Hamiltonians commute with each other, so that (7.55) simplifies to

$$Z_N(T) \approx \frac{1}{N!} \left[Z_{1\,(\text{tr})}\, Z_{1\,(\text{rot})}\, Z_{1\,(\text{vib})}\, Z_{1\,(\text{elec})}\, Z_{1\,(\text{nucl})} \dots \right]^N \tag{7.56}$$

where

$$Z_{1\,(\text{tr})} = \mathrm{Tr}_1 \exp\left(-\beta \frac{\hat{\boldsymbol{p}}^2}{2m} \right) \qquad Z_{1\,(\text{rot})} = \mathrm{Tr}_1 \exp\left(-\beta \hat{H}_{i\,(\text{rot})} \right) \quad \dots \tag{7.56a}$$

For a semiclassical ideal gas with no internal degrees of freedom,

$$Z_N(T) \approx \frac{1}{N!} \left[Z_{1\,(\text{tr})} \right]^N = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \qquad \text{[(4) of Ex.7.3 used.]}$$

$$\approx \left(\frac{e V}{N \lambda_T^3} \right)^N \qquad \text{[Stirling's formula used.]} \tag{7.57}$$

The Helmholtz energy (7.44) becomes

$$A = -k_B T \ln Z_N = -N k_B T \left(1 + \ln \frac{V}{N \lambda_T^3} \right)$$

$$= -N k_B T - N k_B T \ln\left[\frac{V}{N} \left(\frac{h^2}{2\pi m k_B T} \right)^{-3/2} \right] \qquad [\,(5) \text{ of Ex.7.3 used.}\,] \qquad (7.58)$$

which gives the entropy as

$$S = -\left(\frac{\partial A}{\partial T} \right)_{V,N} = N k_B + N k_B \ln\left[\frac{V}{N} \left(\frac{h^2}{2\pi m k_B T} \right)^{-3/2} \right] + \frac{3}{2} N k_B$$

$$= \frac{5}{2} N k_B + N k_B \ln\left[\frac{V}{N} \left(\frac{h^2}{2\pi m k_B T} \right)^{-3/2} \right] \qquad (7.59)$$

which is just the Sackur-Tetrode equation given in Ex.2.4 of §2.F.2.

Ex.7.4.

A cubic box of volume $V = L^3$ contains an ideal gas of N identical atoms, each of spin $s = \frac{1}{2}$ and magnetic moment

$$\boldsymbol{\mu} = -g\,\mu_B\,\boldsymbol{s}$$

where $g \approx 2$ is the g-factor for electron spin and $\mu_B = \frac{e\hbar}{2 m_e c}$ is the Bohr magneton.

A magnetic field $\boldsymbol{B}$ is applied to the system.

(a) Compute the partition function for this system.

(b) Compute the internal energy and heat capacity.

(c) What is the magnetization?

Answer (a)

Since there is no interactions between the particles, (7.56) applies so that

$$Z_N = \frac{1}{N!} [\,Z_{1\,(\text{tr})}\,]^N\,[\,Z_{1\,(\text{mag})}\,]^N \qquad (1)$$

$$= \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N [\,Z_{1\,(\text{mag})}\,]^N \qquad [\,(4) \text{ of Ex.7.3 used.}\,] \qquad (1a)$$

Using the 1-particle magnetic Hamiltonian

$$H_{(\text{mag})} = -\boldsymbol{\mu}\cdot\boldsymbol{B} = g\,\mu_B\,\boldsymbol{s}\cdot\boldsymbol{B} \approx \mu_B\,\sigma\,B \qquad \sigma = \pm 1$$

we get

$$Z_{1\,(\text{mag})} = \sum_{\sigma=\pm 1} \exp(-\beta\,\mu_B\,\sigma\,B) = 2\cosh(\beta\,\mu_B\,B) \qquad (2)$$

so that (1a) becomes

$$Z_N = \frac{1}{N!} \left(\frac{2V}{\lambda_T^3} \right)^N \cosh^N(\beta\,\mu_B\,B) \qquad (3)$$

Answer (b)

$$U = \langle H \rangle = \frac{1}{Z_N} \mathrm{Tr}_N\!\left(\hat{H}\,e^{-\beta \hat{H}} \right) = -\frac{1}{Z_N} \frac{\partial}{\partial \beta} \mathrm{Tr}_N\!\left(e^{-\beta \hat{H}} \right) = -\frac{\partial}{\partial \beta} \ln Z_N$$

$$= -\frac{\partial}{\partial \beta} \left[-3N \ln \lambda_T + N \ln\cosh(\beta\,\mu_B\,B) \right]$$

$$= \frac{3N}{\lambda_T} \frac{\partial \lambda_T}{\partial \beta} - N \frac{\sinh(\beta\,\mu_B\,B)}{\cosh(\beta\,\mu_B\,B)} \mu_B\,B$$

$$= \frac{3N}{2\beta} - N\mu_B B \tanh(\beta\mu_B B) \qquad [\ \lambda_T \propto \sqrt{\beta} \ \rightarrow\ \frac{\partial \lambda_T}{\partial \beta} = \frac{\lambda_T}{2\beta}\ ]$$

$$= \frac{3}{2} N k_B T - N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right) \qquad (4)$$

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_B = \left(\frac{\partial U}{\partial T}\right)_B$$

$$= \frac{3}{2} N k_B + N k_B \left(\frac{\mu_B B}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu_B B}{k_B T}\right) \qquad (5)$$

Answer (c)

$$M = -\left(\frac{\partial A}{\partial B}\right)_T = k_B T\left(\frac{\partial \ln Z_N}{\partial B}\right)_T \qquad [\ (7.44)\ \text{used.}\ ]$$

$$= k_B T \frac{\partial}{\partial B}\left[N \ln\cosh(\beta\mu_B B)\right]_T$$

$$= N\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \qquad (6)$$