Pathria & Beale, Chapter 5

Problem 5.5

In the approximation in which the correlation between every pair of identical particle is taken into account, the partition function is

$$Z_N(V,T) = \frac{1}{N!}\int \frac{d^3r_1\, d^3p_1}{(2\pi\hbar)^3} \cdots \int \frac{d^3r_N\, d^3p_N}{(2\pi\hbar)^3}$$

$$\times \exp\left(-\beta\left[\sum_{n=1}^{N} \frac{1}{2m}\vec{p}_n^{\,2} + \sum_{n_1<n_2} v_\pm(|\vec{r}_{n_1}-\vec{r}_{n_2}|)\right]\right)$$

$$= \frac{1}{N!}\left(\frac{1}{(2\pi\hbar)^3}\int d^3p \, \exp(-\beta p^2/2m)\right)^N$$

$$\times \int d^3r_1 \cdots \int d^3r_N \, \exp\left(-\beta \sum_{n_1<n_2} v_\pm(|\vec{r}_{n_1}-\vec{r}_{n_2}|)\right)$$

where the potential for $\begin{pmatrix}\text{bosons}\\ \text{fermions}\end{pmatrix}$ is

$$v_\pm(r) = -kT \log\left(1 \pm e^{-2\pi r^2/\lambda_T^2}\right)$$

The Boltzmann factor for the potential is

$$e^{-\beta v_\pm(r)} = 1 \pm e^{-2\pi r^2/\lambda_T^2}$$

The partition function becomes

$$Z_N(V,T) = \frac{1}{N!}\left(\frac{1}{\lambda_T^3}\right)^N \int d^3r_1 \cdots \int d^3r_N \prod_{n_1<n_2}\left(1 \pm e^{-2\pi|\vec{r}_{n_1}-\vec{r}_{n_2}|^2/\lambda_T^2}\right)$$

If the product is expanded, the integral over a position vector $\vec{r}_n$ will be V if $\vec{r}_n$ does not appear in any of the exponential factor and it will be order λ_T^3 otherwise. The first correction comes from terms with only one exponential factor

$$Z_N(V,T) \simeq \frac{1}{N!}\left(\frac{1}{\lambda_T^3}\right)^N \int d^3r_1 \cdots \int d^3r_N \left(1 \pm \sum_{n_1<n_2} e^{-2\pi|\vec{r}_{n_1}-\vec{r}_{n_2}|^2/\lambda_T^2}\right)$$

$$= \frac{1}{N!}\left(\frac{1}{\lambda_T^3}\right)^N \left[V^N \pm \frac{N(N-1)}{2} V^{N-2} \int d^3r_1 \int d^3r_2\, e^{-2\pi|\vec{r}_1-\vec{r}_2|^2/\lambda_T^2}\right]$$

The remaining integral can be evaluated by changing variables to $\vec{R} = \frac{\vec{r}_1+\vec{r}_2}{2}$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$:

$$\int d^3r_1 \int d^3r_2\, e^{-2\pi|\vec{r}_1-\vec{r}_2|^2/\lambda_T^2} = \int d^3R \int d^3r\, e^{-2\pi r^2/\lambda_T^2}$$

$$= V\left(\frac{\lambda_T^2}{2}\right)^{3/2}$$

The partition function reduces to

$$Z_N(V,T) = \frac{1}{N!}\left(\frac{1}{\lambda_T^3}\right)^N V^N \left[1 \pm \frac{N^2}{2}\frac{1}{\sqrt{8}}\frac{\lambda_T^3}{V}\right]$$

The Helmholtz free energy, including the first order correction, is

$$F = -T \log Z_N$$

$$= -T\left[N \log\left(\frac{V}{\lambda_T^3}\right) - \log N! + \log\left(1 \pm \frac{N^2}{4\sqrt{2}}\frac{\lambda_T^3}{V}\right)\right]$$

Keeping only the first term in the expansion of the logarithm, the free energy reduces to

$$F = -NT\left[\log \frac{V}{\lambda_T^3} - \log N + 1 \pm \frac{N}{4\sqrt{2}} \frac{\lambda_T^3}{V}\right]$$

$$= -NT\left[\log \frac{V/N}{\lambda_T^3} + 1 \pm \frac{1}{4\sqrt{2}} \frac{\lambda_T^3}{V/N}\right]$$

The thermodynamic relation is

$$dF = -S\,dT - P\,dV + \mu\,dN$$

The pressure is therefore

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$= NT\left[\frac{1}{V} \pm \frac{1}{4\sqrt{2}}\left(-\frac{\lambda_T^3}{V^2/N}\right)\right]$$

$$= \frac{NT}{V}\left[1 \mp \frac{1}{4\sqrt{2}} \frac{\lambda_T^3}{V/N}\right]$$

This equation of state can be written

$$PV = NkT\left[1 \mp \frac{1}{4\sqrt{2}} \frac{\lambda_T^3}{V/N}\right]$$

where the sign is $-$ for bosons and $+$ for fermions.

Pathria & Beale, Chapter 6

Problem 6.1

The entropy S of an ideal gas in thermal equilibrium can be determined from the grand potential Φ of the grand canonical ensemble. The thermodynamic relation is

$$d\Phi = -S\,dT - P\,dV - N\,d\mu$$

This implies that the entropy is given by

$$S = -\frac{\partial}{\partial T}\Phi\Big|_{V,\mu}$$

The grand potential can be determined from the grand partition function:

$$\mathbb{Q} = e^{-\beta\Phi}$$

The logarithm of the grand partition function for an ideal gas of $\binom{\text{bosons}}{\text{fermions}}$ is given in Eq. (17) of Section 6.2 of Pathria and Beale (PB):

$$\log \mathbb{Q} = \mp \sum_i \log\left(1 \mp z e^{-\beta\epsilon_i}\right)$$

$$= \mp \sum_i \log\left(1 \mp e^{-\beta(\epsilon_i - \mu)}\right)$$

where the sum is over single-particle states and ϵ_i is its energy. The entropy is

$$S = -\frac{\partial}{\partial T}\left(-T\log Q\right)_{V,\mu}$$

$$= \log Q + T\frac{\partial}{\partial T}\left(\log Q\right)_{V,\mu}$$

$$= \log Q - \beta\frac{\partial}{\partial \beta}\left(\log Q\right)_{V,\mu}$$

$$= \mp\sum_i \log\left(1 \mp e^{-\beta(\epsilon_i-\mu)}\right)$$

$$\pm\sum_i \frac{1}{1\mp e^{-\beta(\epsilon_i-\mu)}}\left(\pm\beta(\epsilon_i-\mu)e^{-\beta(\epsilon_i-\mu)}\right)$$

We wish to express this in terms of the average occupation number $\langle n_i\rangle$ of the single-particle state i, which is given in Eq. (22) of Section 6.2 of PB:

$$\langle n_i\rangle = \frac{1}{\frac{1}{z}e^{\beta\epsilon_i}\mp 1}$$

$$= \frac{e^{-\beta(\epsilon_i-\mu)}}{1\mp e^{-\beta(\epsilon_i-\mu)}}$$

We can solve for $e^{\beta(\epsilon_i-\mu)}$:

$$e^{-\beta(\epsilon_i-\mu)} = \frac{\langle n_i\rangle}{1\pm\langle n_i\rangle}$$

Inserting this into the expression for the entropy, it becomes

$$S = \mp \sum_i \log\left(1 \mp \frac{\langle n_i \rangle}{1 \pm \langle n_i \rangle}\right)$$

$$- \sum_i \frac{1}{1 \mp \frac{\langle n_i \rangle}{1 \pm \langle n_i \rangle}} \frac{\langle n_i \rangle}{1 \pm \langle n_i \rangle} \log\left(\frac{\langle n_i \rangle}{1 \pm \langle n_i \rangle}\right)$$

$$= \mp \sum_i \log \frac{1}{1 \pm \langle n_i \rangle} - \sum_i \langle n_i \rangle \log\left(\frac{\langle n_i \rangle}{1 \pm \langle n_i \rangle}\right)$$

$$= \sum_i \left[\pm (1 \pm \langle n_i \rangle) \log (1 \pm \langle n_i \rangle) - \langle n_i \rangle \log \langle n_i \rangle \right]$$

The expression with $\binom{\text{upper}}{\text{lower}}$ signs agrees with the given expression for the entropy of $\binom{\text{bosons}}{\text{fermions}}$.

A general formula for the information entropy is

$$S = - \sum_i \sum_n p_i(n) \log p_i(n)$$

where $p_i(n)$ is the probability for the single-particle state i to have occupation number n.

For bosons, the expression for the probability $p_i(n)$ in terms of the average occupation numbers $\langle n \rangle_i$ is given in Eq (10) of PB Section 6.3:

$$p_i(n) = \frac{(\langle n \rangle_i)^n}{(1 + \langle n \rangle_i)^{n+1}}$$

The general formula for S gives

$$S = -\sum_i \sum_{n=0}^{\infty} \frac{(\langle n\rangle_i)^n}{(1+\langle n\rangle_i)^{n+1}} \log \frac{(\langle n\rangle_i)^n}{(1+\langle n\rangle_i)^{n+1}}$$

$$= -\sum_i \sum_{n=0}^{\infty} \frac{(\langle n\rangle_i)^n}{(1+\langle n\rangle_i)^{n+1}} \left[n \log \langle n\rangle_i - (n+1) \log (1+\langle n\rangle_i) \right]$$

$$= -\sum_i \left[\frac{\log \langle n\rangle_i - \log (1+\langle n\rangle_i)}{1+\langle n\rangle_i} \sum_{n=0}^{\infty} n \left(\frac{\langle n\rangle_i}{1+\langle n\rangle_i} \right)^n \right.$$

$$\left. - \frac{\log(1+\langle n_i\rangle)}{1+\langle n\rangle_i} \sum_{n=0}^{\infty} \left(\frac{\langle n\rangle_i}{1+\langle n\rangle_i} \right)^n \right]$$

$$= -\sum_i \left[\frac{\log \langle n\rangle_i - \log (1+\langle n\rangle_i)}{1+\langle n\rangle_i} \frac{\frac{\langle n\rangle_i}{1+\langle n\rangle_i}}{\left(1 - \frac{\langle n\rangle_i}{1+\langle n\rangle_i}\right)^2} \right.$$

$$\left. - \frac{\log(1+\langle n\rangle_i)}{1+\langle n\rangle_i} \cdot \frac{1}{1 - \frac{\langle n\rangle_i}{1+\langle n_i\rangle}} \right]$$

$$= -\sum_i \left[\left(\log \langle n\rangle_i - \log (1+\langle n\rangle_i) \right) \langle n\rangle_i - \log (1+\langle n\rangle_i) \right]$$

$$= \sum_i \left[(1+\langle n\rangle_i) \log (1+\langle n\rangle_i) - \langle n\rangle_i \log \langle n\rangle_i \right]$$

This agrees with the expression for the thermodynamic entropy for bosons.

For fermions, the expression for the probability $p_i(n)$ in terms of the average occupation number $\langle n\rangle_i$ is

$$\begin{aligned} p_i(n) &= 1 - \langle n\rangle_i \qquad && n = 0 \\ &= \langle n\rangle_i && n = 1 \end{aligned}$$

The general formula for S gives

$$S = -\sum_i \left((1 - \langle n \rangle_i) \log (1 - \langle n \rangle_i) + \langle n \rangle_i \log \langle n_i \rangle \right)$$

This agrees with the expression for the thermodynamic entropy of fermions