Midterm solutions (2024)

1. Recall that $p = -\left(\frac{\partial A}{\partial V}\right)_T$, where A is the Helmholtz free energy.

Then $A = -RT \log(V-b) - \frac{a}{V} + \underbrace{F(T)}_{\text{some function of } T}$.

The entropy is given by $S = -\left(\frac{\partial A}{\partial T}\right)_V = R \log(V-b) - F'(T)$.

But then $U = A + TS = -RT \cancel{\log}(V-b) -$

$- \frac{a}{V} + F(T) + RT \cancel{\log}(V-b) - TF'(T) =$

$= -\frac{a}{V} + F(T) - TF'(T)$.

Finally, $C_V = \left(\frac{\partial U}{\partial T}\right)_V = F'\cancel{(T)} - F'\cancel{(T)} -$

$-TF''(T) = -TF''(T)$, a function of T alone as desired.

$\boxed{\text{QED}}$

(2.) Recall that in a photon gas,

$$\log Q = -2 \sum_{\vec{k}} \log(1 - e^{-\beta\hbar c|\vec{k}|}) =$$

$$= -\frac{2V(4\pi)}{(2\pi)^3} \int_0^\infty dk\, k^2 \log(1 - e^{-\beta\hbar c k}).$$

Thus,

(1) $$a = -\beta^{-1} \log Q \times \frac{1}{V} = \frac{1}{\beta\pi^2} \int_0^\infty dk\, k^2 \log(1 - e^{-\beta\hbar c k}).$$

$\uparrow$

Helmholtz free
en. per unit V

Likewise, the total number of photons per unit volume is given by

(2) $$n = \frac{2(4\pi)}{(2\pi)^3} \int_0^\infty dk \frac{k^2}{e^{\beta\hbar c k} - 1} = \frac{1}{\pi^2} \int_0^\infty dk \frac{k^2}{e^{\beta\hbar c k} - 1}.$$

Using $x = \beta\hbar c k$, we obtain

$$n = \frac{1}{\pi^2} \int_0^\infty \frac{dx}{\beta\hbar c} \frac{x^2}{(\beta\hbar c)^2} \frac{1}{e^x - 1} =$$

$$= \frac{1}{\pi^2(\beta\hbar c)^3} \int_0^\infty dx \frac{x^2}{e^x - 1} \quad \text{for Eq. (2)}.$$

For Eq. (1), we have

$$a = \frac{1}{\beta\pi^2}\,\frac{1}{(\beta\hbar c)^3}\int_0^\infty dx\, x^2 \log(1-e^{-x}) \overset{\text{by parts}}{=}$$

$$= -\frac{1}{3\beta\pi^2}\,\frac{1}{(\beta\hbar c)^3}\int_0^\infty dx\, \frac{x^3}{e^x-1}.$$

$$\frac{x^3}{3}\log(1-e^{-x})\Big|_0^\infty = 0$$

The entropy <u>per unit volume</u> is given by $\tilde{S} = -\left(\frac{\partial a}{\partial T}\right)_V =$

$$= \frac{4T^3k_B^4}{(3\pi^2)(\hbar c)^3}\int_0^\infty dx\, \frac{x^3}{e^x-1}.$$

Then $S = \frac{\tilde{S}}{n} = \frac{4k_B}{\cancel{\beta^3}(3\cancel{\pi^2})\cancel{(\hbar c)^3}}\cancel{\pi^2}\cancel{(\beta\hbar c)^3}\times$

$$\times \frac{\int_0^\infty dx\, \frac{x^3}{e^x-1}}{\int_0^\infty dx\, \frac{x^2}{e^x-1}} = \frac{4k_B}{3}\,\frac{\int_0^\infty dx\, \frac{x^3}{e^x-1}}{\int_0^\infty dx\, \frac{x^2}{e^x-1}}.$$

Finally, use $\int_0^\infty dx\, \frac{x^n}{e^x-1} = \underbrace{\zeta(n+1)}_{\text{Riemann zeta f'n}}\,\underbrace{\Gamma(n+1)}_{\text{gamma f'n}} =$

$= n!\,\zeta(n+1):$

$$S = \frac{4}{3} k_B \frac{3!\,\zeta(4)}{2!\,\zeta(3)} = 4 k_B \frac{\zeta(4)}{\zeta(3)} = \underline{\underline{4 k_B \frac{\sum_{n=1}^{\infty} n^{-4}}{\sum_{n=1}^{\infty} n^{-3}}}},$$

where the last step used

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}.$$

$\boxed{\text{QED}}$