Derivation of Helmholtz free energy for the photon gas

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Here we discuss the thermodynamic properties of photon gas using the Helmholtz free energy.

The partition function:

$$\ln Z_C = \ln[\prod_{\boldsymbol{k}} Z_{C1}(\boldsymbol{k})] = \sum_{\boldsymbol{k}} \ln Z_{C1}(\boldsymbol{k})$$

The Helmholtz free energy:

$$\begin{aligned} F &= -k_B T \ln Z_C \\ &= k_B T \sum_{\nu} \ln(1 - e^{-\beta h\nu}) \\ &= k_B T \int_0^{\infty} d\omega D(\omega) \ln(1 - e^{-\beta\hbar\omega}) \\ &= k_B T \frac{V}{\pi^2 c^3} \int_0^{\infty} \omega^2 d\omega \ln(1 - e^{-\beta\hbar\omega}) \end{aligned}$$

where $D(\omega)$ is the density of states for ω and $\left(\omega + d\omega\right)$.

$$D(\omega)d\omega = \frac{2V}{(2\pi)^3} 4\pi k^2 dk$$

Note that $\omega = ck$

$$D(\omega)d\omega = \frac{2V}{(2\pi)^3} \frac{4\pi}{c^3} \omega^2 d\omega = \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

The above integral can be calculated as follows.

$$
\begin{aligned}
I &= \int_0^\infty d\omega\omega^2 \ln(1-e^{-\beta\hbar\omega}) \\
&= -\int_0^\infty d\omega \frac{\omega^3}{3} \frac{\beta\hbar e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\
&= -\frac{\beta h}{3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega}-1}
\end{aligned}
$$

We put $x = \beta\hbar\omega$. So we get the integral

$$
\begin{aligned}
I &= -\frac{\beta h}{3} \frac{1}{(\beta h)^4} \int_0^\infty \frac{x^3}{e^x-1} dx \\
&= -\frac{1}{3} \frac{1}{(\beta h)^3} \int_0^\infty \frac{x^3}{e^x-1} dx \\
&= -\frac{1}{3} \frac{1}{(\beta h)^3} \frac{\pi^4}{15}
\end{aligned}
$$

where

$$
\int_0^\infty \frac{x^3 dx}{e^x-1} = \frac{\pi^4}{15}.
$$

The Helmholtz free energy

$$
F = -\frac{V\pi^2}{45h^3c^3}(k_B T)^4.
$$

(b)

$$
\begin{aligned}
dF &= d(U-ST) \\
&= TdS - PdV + \mu dN - SdT - TdS \\
&= -PdV + \mu dN - SdT
\end{aligned}
$$

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

The internal energy:

$$U = -\frac{\partial}{\partial \beta}\ln Z_C = \frac{\partial}{\partial \beta}(\beta F) = -k_B T^2 \frac{\partial}{\partial T}(\frac{F}{k_B T})$$

or

$$\begin{aligned} U &= k_B T^2 \frac{V\pi^2 k_B{}^3}{45c^3\hbar^3}\frac{\partial}{\partial T}(T^3) \\ &= \frac{V\pi^2 k_B{}^4}{15c^3\hbar^3}T^4 \\ &= -3F \end{aligned}$$

The entropy:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{4V}{45}\frac{\pi^2 k_B{}^4}{c^3\hbar^3}T^3 = \frac{16\sigma_{SB}}{3c}VT^3$$

((**Note**))

$$F = U - ST = -3F - ST$$

$$S = -\frac{4F}{T}$$

The pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{1}{45}\frac{\pi^2 k_B{}^4}{c^3\hbar^3}T^4 = \frac{4\sigma_{SB}}{3c}T^4$$

Note that

$$PV = \frac{1}{45}\frac{V\pi^2 k_B{}^4}{c^3\hbar^3}T^4 = \frac{1}{3}U$$

The chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = 0$$

Note that

$$G = \mu N = F + PV = -\frac{1}{3}F + \frac{1}{3}F = 0$$

The Stefan-Boltzmann constant

$$\sigma_{SB} = \frac{\pi^2 k_B{}^4}{60\hbar^3 c^2} = 5.67036713 \text{ x } 10^{-8} \text{ W/(m}^2\text{K}^4\text{)}.$$

The energy density

$$u = \frac{U}{V} = \frac{\pi^2 k_B{}^4}{15\hbar^3 c^3} T^4 = \frac{4\sigma_{SB}}{c} T^4$$

The heat capacity

$$c_V = \frac{C}{V} = \frac{du}{dT} = \frac{4\pi^2 k_B{}^4}{15\hbar^3 c^3} T^3 = \frac{16}{c}\sigma_{SB} T^3$$

REFERENCES

H.S. Robertson, Statistical Thermodynamics (PTR Prentice Hall, 1993).