

# PHYS 301: Thermodynamics and Statistical Mechanics

## Solutions to Problem Set #9

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### Question 1: Gas of Photons

We are given a gas of photons at temperature  $T$  in a volume  $V$ . The occupancy of a state with energy  $E = \hbar\omega = pc$  is given by the Bose-Einstein distribution for particles with zero chemical potential ( $\mu = 0$ ):

$$\langle N \rangle_E = \frac{1}{e^{E/k_B T} - 1} \quad (1)$$

The number of states in an infinitesimal phase space volume is:

$$g(p) d^3x d^3p = 2 \frac{d^3x d^3p}{h^3} \quad (2)$$

where  $g(p)$  is the density of states, and where the factor of 2 accounts for the two independent polarization states of a photon.

**(a) Compute the average number of photons in the box and show it is proportional to  $T^3$**

The total average number of photons  $\langle N \rangle$  is the integral of the occupancy over all phase space:

$$\langle N \rangle = \int \langle N \rangle_E \left( 2 \frac{d^3x d^3p}{h^3} \right) \quad (3)$$

The spatial integral trivially gives the volume  $V$ . For the momentum integral, we use spherical coordinates ( $d^3p = 4\pi p^2 dp$ ) and substitute  $p = \hbar\omega/c$  and  $dp = (\hbar/c)d\omega$ :

$$\begin{aligned} \langle N \rangle &= \frac{2V}{h^3} \int_0^\infty \frac{1}{e^{\hbar\omega/k_B T} - 1} (4\pi p^2) dp \\ &= \frac{8\pi V}{(2\pi\hbar)^3} \int_0^\infty \frac{1}{e^{\hbar\omega/k_B T} - 1} \left( \frac{\hbar\omega}{c} \right)^2 \left( \frac{\hbar}{c} \right) d\omega \\ &= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2}{e^{\hbar\omega/k_B T} - 1} d\omega \end{aligned} \quad (4)$$

To evaluate this integral, we define a dimensionless variable  $x = \frac{\hbar\omega}{k_B T}$ . Then  $d\omega = \frac{k_B T}{\hbar} dx$ :

$$\begin{aligned} \langle N \rangle &= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{(x k_B T / \hbar)^2}{e^x - 1} \left( \frac{k_B T}{\hbar} \right) dx \\ &= \frac{V}{\pi^2 c^3 \hbar^3} (k_B T)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx \end{aligned} \quad (5)$$

The definite integral evaluates to  $2\zeta(3) \approx 2.404$ , where  $\zeta(s)$  is the Riemann zeta function. Thus:

$$\boxed{\langle N \rangle = \frac{2\zeta(3)V}{\pi^2(\hbar c)^3} (k_B T)^3} \quad (6)$$

Since  $V$ ,  $\hbar$ ,  $c$ , and  $k_B$  are constants, we have shown that  $\langle N \rangle \propto T^3$ .

### (b) What is the mean energy of a photon in the box?

The mean energy of a single photon,  $\bar{E}$ , is the total energy of the photon gas  $\langle E \rangle$  divided by the total number of photons  $\langle N \rangle$ . First, we compute the total average energy  $\langle E \rangle$  by inserting an extra factor of  $E = \hbar\omega$  into our integral:

$$\begin{aligned} \langle E \rangle &= \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\hbar\omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega \\ &= \frac{V\hbar}{\pi^2 c^3} \left( \frac{k_B T}{\hbar} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx \end{aligned} \quad (7)$$

The dimensionless integral is a standard result:  $\int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$ .

$$\langle E \rangle = \frac{\pi^2 V}{15(\hbar c)^3} (k_B T)^4 \quad (8)$$

Now we divide by the total number of photons found in part (a):

$$\begin{aligned} \bar{E} &= \frac{\langle E \rangle}{\langle N \rangle} = \frac{\frac{\pi^2 V}{15(\hbar c)^3} (k_B T)^4}{\frac{2\zeta(3)V}{\pi^2(\hbar c)^3} (k_B T)^3} \\ &= \frac{\pi^4}{30\zeta(3)} k_B T \end{aligned} \quad (9)$$

Using  $\pi^4 \approx 97.41$  and  $\zeta(3) \approx 1.202$ :

$$\boxed{\bar{E} \approx 2.701 k_B T} \quad (10)$$

### (c) What is the most likely energy of a photon in the box?

To find the most likely energy characteristic of the blackbody radiation, we must maximize the spectral energy density (the Planck function), which represents the energy per unit volume per unit energy interval.

From part (a), the number of photons in the energy range  $dE$  is proportional to  $\frac{E^2}{e^{E/k_B T} - 1}$ . The total energy in this range,  $u(E)dE$ , is found by multiplying by the photon energy  $E$ :

$$u(E) \propto E \cdot n(E) \propto \frac{E^3}{e^{E/k_B T} - 1} \quad (11)$$

To find the peak of this distribution, we define the dimensionless variable  $x = \frac{E}{k_B T}$  and maximize the function  $f(x) = \frac{x^3}{e^x - 1}$  by setting its derivative to zero:

$$\begin{aligned} \frac{df}{dx} &= \frac{3x^2(e^x - 1) - x^3 e^x}{(e^x - 1)^2} = 0 \\ \implies 3x^2(e^x - 1) - x^3 e^x &= 0 \end{aligned} \quad (12)$$

Assuming  $x \neq 0$ , we divide by  $x^2$ :

$$\begin{aligned} 3(e^x - 1) - xe^x &= 0 \\ (3 - x)e^x &= 3 \end{aligned} \tag{13}$$

This is a well-known transcendental equation. Its non-trivial numerical solution is  $x \approx 2.821$ .

Substituting  $x = \frac{E}{k_B T}$  back into this result, we find the energy at which the Planck spectrum peaks:

$$\boxed{E_{peak} \approx 2.821 k_B T} \tag{14}$$

This result is the energy-domain formulation of **Wien's displacement law**, showing that the peak energy of blackbody radiation shifts linearly with the absolute temperature.

**(d) Show that the partition function for this gas of photons is given by the specified integral**

We can treat the electromagnetic field inside the box as a collection of independent quantum harmonic oscillators, where each oscillator corresponds to a specific photon frequency mode (and polarization state)  $i$ .

For a single mode with frequency  $\omega_i$ , the system can contain  $n_i = 0, 1, 2, \dots$  photons. The energy of this single mode is  $E_{n_i} = n_i \hbar \omega_i$  (ignoring the constant zero-point energy, which simply shifts the reference point).

The partition function for this single independent mode,  $Z_i$ , is the sum over all possible number of photons  $n_i$ :

$$\begin{aligned} Z_i &= \sum_{n_i=0}^{\infty} e^{-\beta(n_i \hbar \omega_i)} \\ &= \sum_{n_i=0}^{\infty} \left( e^{-\beta \hbar \omega_i} \right)^{n_i} \end{aligned} \tag{15}$$

This is a standard geometric series of the form  $\sum x^n = \frac{1}{1-x}$ . Summing it yields:

$$Z_i = \frac{1}{1 - e^{-\beta \hbar \omega_i}} \tag{16}$$

Because the photons are non-interacting, the different frequency modes are completely independent of one another. The total partition function  $Z$  for the entire gas of photons is simply the product of the partition functions of all the individual modes:

$$Z = \prod_i Z_i = \prod_i \left( \frac{1}{1 - e^{-\beta \hbar \omega_i}} \right) \tag{17}$$

To compute thermodynamic quantities, we always need the natural logarithm of the partition function. Taking the natural log turns the product over states into a sum over states:

$$\begin{aligned} \ln Z &= \ln \left( \prod_i \frac{1}{1 - e^{-\beta \hbar \omega_i}} \right) \\ &= \sum_i \ln \left( \frac{1}{1 - e^{-\beta \hbar \omega_i}} \right) \\ &= - \sum_i \ln \left( 1 - e^{-\beta \hbar \omega_i} \right) \end{aligned} \tag{18}$$

For a macroscopic volume  $V$ , the allowed frequency modes are incredibly dense, allowing us to convert the discrete sum over states  $i$  into an integral over continuous phase space. Using the density of states established in part (a) (which includes the factor of 2 for polarization):

$$\sum_i \longrightarrow \int \left( 2 \frac{d^3x d^3p}{h^3} \right) = \frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 d\omega \quad (19)$$

Substituting this continuous integral operator into our expression for  $\ln Z$ :

$$\boxed{\ln Z = -\frac{V}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \ln \left( 1 - e^{-h\omega/k_B T} \right)} \quad (20)$$

This completes the derivation.