

1 Free energy of a two state system (2+2+2+2 points)

Consider a system with two states, one at zero energy and one at energy ϵ .

- Find the free energy as a function of the temperature.
- Determine the internal energy of the system.
- What is the entropy of the system?
- Evaluate σ for very large temperatures.

2 Harmonic oscillator (2+2+2 points)

The partition function of a harmonic oscillator is: $Z = \frac{1}{1 - e^{-\hbar\omega_n/\tau}}$

- Calculate the average energy of the system.
- Determine the free energy of the system.
- Evaluate the entropy of the system.

3 Free energy of a photon gas (2+1+4 points)

- Show that the partition function of a photon gas is given by

$$Z = \prod_n \frac{1}{1 - e^{-\hbar\omega_n/\tau}}, \text{ where the product runs over all possible modes of the}$$

electromagnetic field characterized by their frequencies ω_n .

- Write down the free energy of the system as a sum.
- If one converts the sum to an integral and integrates by parts, one finds

$$F = -\frac{\pi^2 V \tau^4}{45 \hbar^3 c^3}.$$

Use this expression to calculate the entropy and the internal energy of the photon gas.

4 Proof (3 points)

Prove the Maxwell relation: $\left(\frac{\partial \tau}{\partial V}\right)_\sigma = -\left(\frac{\partial p}{\partial \sigma}\right)_V$

using second partial derivatives of the internal energy. (Hint: Note that $\tau = (\partial U / \partial \sigma)_V$ and use the definition of pressure as the rate of change of energy with volume.)

1) Free energy of a two-state system

$$Z = \sum_s e^{-\epsilon_s/\tau} = 1 + e^{-\epsilon/\tau}$$

$$a) F = -\tau \log Z = -\tau \log(1 + e^{-\epsilon/\tau})$$

$$b) U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \frac{1}{1 + e^{-\epsilon/\tau}} e^{-\epsilon/\tau} \left(\frac{\epsilon}{\tau^2} \right)$$

$$= \frac{\epsilon}{e^{\epsilon/\tau} + 1}$$

$$c) \sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V = \log(1 + e^{-\epsilon/\tau}) + \tau \frac{e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} \left(\frac{\epsilon}{\tau^2} \right)$$

$$= \log(1 + e^{-\epsilon/\tau}) + \frac{\epsilon/\tau}{e^{\epsilon/\tau} + 1}$$

$$\text{As } \tau \rightarrow \infty \quad \sigma_{\tau \rightarrow \infty} = \log(1+1) + \frac{0}{2} = \underline{\underline{\log 2}}$$

3) Harmonic Oscillator

$$Z = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

a) Average energy: $\langle \epsilon \rangle = U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \frac{\tau^2}{Z} \frac{\partial Z}{\partial \tau}$

$$\begin{aligned} &= \frac{\tau^2}{(1 - e^{-\hbar\omega/\tau})} \cdot (-1) \cdot \frac{1}{(1 - e^{-\hbar\omega/\tau})^2} \cdot (-\hbar\omega) \cdot \frac{1}{\tau^2} e^{-\hbar\omega/\tau} \\ &= \frac{-\hbar\omega e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} \\ &= \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \end{aligned}$$

b) Free energy: $F = -\tau \log Z = \underline{\underline{\tau \log(1 - e^{-\hbar\omega/\tau})}}$

c) Entropy: $\sigma = \frac{1}{\tau} (U - F)$

$$= \frac{\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} - \log(1 - e^{-\hbar\omega/\tau})$$

3) a) Partition function of photon gas:
$$Z_\omega = \sum_{s=0}^{\infty} e^{-\epsilon_s/\tau} = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}$$

$$= \sum_{s=0}^{\infty} (e^{-\hbar\omega/\tau})^s = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

This is the partition function for a photon of frequency ω , so the total partition function is the product of these:

$$Z = \prod_{\omega} Z_{\omega} = \prod_n \frac{1}{1 - e^{-\hbar\omega_n/\tau}}$$

3) b)
$$F = - \frac{\pi^2 V \tau^4}{45 \hbar^3 c^3}$$

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_V = + \frac{\pi^2 V}{45 \hbar^3 c^3} 4 \tau^3 = \underline{\underline{\frac{4\pi^2 V}{45 \hbar^3 c^3} \tau^3}}$$

$$F = U - \tau \sigma \Rightarrow U = F + \tau \sigma$$

$$= \frac{\pi^2 V}{45 \hbar^3 c^3} \tau^4 (+1 + 4) = \underline{\underline{\frac{\pi^2 V}{15 \hbar^3 c^3} \tau^4}}$$

b)
$$F = -\tau \log Z = -\tau \log \prod_n \left(\frac{1}{1 - e^{-\hbar\omega_n/\tau}} \right) = +\tau \sum_n \log(1 - e^{-\hbar\omega_n/\tau})$$