<u>**The Photon Gas**</u>

General Considerations

• *Goal:* Consider the quantized electromagnetic field in a box of volume V, in thermal equilibrium at temperature T. As a thermodynamical system we have a gas of photons, but the number N is not fixed; photons can be absorbed and emitted by the walls. Notice that in a real system this equilibrium description is often not a very good approximation because there are no photon-photon interactions (for our purposes), and the photon interactions with matter (the walls) play a central role in establishing equilibrium, but they are strongly dependent on the material photons interact with. We would like to calculate $\bar{E}$ and the energy density $u = \bar{E}/V$, the p and S equations of state, and the black-body spectrum (Planck's radiation law).

• *States:* Photons are spin-1 massless particles whose 1-particle quantum states are specified by the pair $\alpha = (\mathbf{k}, \gamma)$. In a box of volume $V = L_1 L_2 L_3$ with periodic boundary conditions, the allowed values for the wave vector components are $k_i = 2\pi n_i / L_i$, $n_i \in \mathbf{Z}$ for $i = 1, 2, 3$, while the polarization has two values we can label $\gamma = \pm 1$. We will use the Fock representation and label general states in the total Hilbert space by the occupation numbers for each $(\mathbf{k}, \gamma)$, $| N_{\mathbf{k}_1, \gamma_1}, N_{\mathbf{k}_2, \gamma_2}, ..., N_{\mathbf{k}_j, \gamma_j}, ... \rangle$, where each $N_{\mathbf{k}_j, \gamma_j} = 0, 1, 2, ...$

• *Hamiltonian:* Photons are, to an excellent approximation, non-interacting particles. The single-particle mode $(\mathbf{k}, \gamma)$ has energy $\epsilon_\alpha = \epsilon_k = \hbar\omega$ with $\omega = ck$, so the Hamiltonian operator can be written as

$$\hat{H} = \sum_{\mathbf{k},\gamma} \hbar\omega \, \hat{N}_{\mathbf{k},\gamma} = \sum_{\mathbf{k},\gamma} \hbar\omega \, \hat{a}_{\mathbf{k},\gamma}^\dagger \hat{a}_{\mathbf{k},\gamma} \ ,$$

where $\hat{N}_\alpha = \hat{a}_\alpha^\dagger \hat{a}_\alpha$ is the number operator for the mode α, and $\hat{a}_\alpha^\dagger$ and $\hat{a}_\alpha$ the creation and annihilation operators for a photon in that mode, respectively. This is like the Hamiltonian for an infinite set of oscillators.

• *Partition function:* Summing over all Fock states, the canonical partition function becomes

$$Z = \mathrm{tr}\, e^{-\beta\hat{H}} = \sum_{\{N_{\mathbf{k},\gamma}\}} e^{-\beta \Sigma_{\mathbf{k},\gamma} \hbar\omega N_{\mathbf{k},\gamma}} = \prod_{\mathbf{k},\gamma} \sum_{N_{\mathbf{k},\gamma}} e^{-\beta\hbar\omega N_{\mathbf{k},\gamma}} = \prod_{\mathbf{k},\gamma} \frac{1}{1 - e^{-\beta\hbar\omega}} \ .$$

Although N is not fixed we have not used the grand canonical ensemble, but we would obtain the same results using Z_g with $\mu = 0$. Notice that for a photon γ has $g_s = 2$ values (the two polarizations), and since ω does not depend on γ the product over its values simply gives the square of the argument of the product.

Thermodynamics

• *Density of states:* The calculation is similar to the one for massive bosons, but now the single-particle energy is $\epsilon = c\hbar k$ so $k = \omega/c$. If $f(\epsilon)$ is any slowly-varying function of the energy, then

$$\sum_\alpha f(\epsilon_\alpha) \approx \sum_\gamma \int_{\mathbb{R}^3} \mathrm{d}^3 n \, f(\epsilon(n)) = \frac{g_s V}{8\pi^3} \int_{\mathbb{R}^3} \mathrm{d}^3 k \, f(\epsilon(k)) = \frac{g_s V}{2\pi^2} \int_0^\infty \mathrm{d}k \, k^2 f(\omega(k)) = \frac{g_s V}{2\pi^2 c^3} \int_0^\infty \mathrm{d}\omega \, \omega^2 f(\omega) \ .$$

Equating this to $\int_0^\infty \mathrm{d}\omega \, g(\omega) f(\omega)$ and setting $g_s = 2$ we can read off $g(\omega) = (V/\pi^2 c^3)\, \omega^2$. $\qquad \triangleright g(\epsilon) \propto \epsilon^2$.

• *Free energy:* If we start with the general expression for F in terms of the partition function, $F = -k_\mathrm{B} T \ln Z$, use the density of states, define $x := \beta\hbar\omega$, and integrate by parts in one step, we get

$$F = k_\mathrm{B} T \sum_{\mathbf{k},\gamma} \ln(1 - e^{-\beta\hbar\omega}) \approx k_\mathrm{B} T \int_0^\infty \mathrm{d}\omega \, g(\omega) \ln(1 - e^{-\beta\hbar\omega}) = \frac{V(k_\mathrm{B} T)^4}{\pi^2 (\hbar c)^3} \int_0^\infty \mathrm{d}x \, x^2 \ln(1 - e^{-x})$$

$$= \frac{V(k_\mathrm{B} T)^4}{\pi^2 (\hbar c)^3} \left(-\frac{1}{3} \int_0^\infty \frac{\mathrm{d}x \, x^3}{e^x - 1} \right) = -\frac{V(k_\mathrm{B} T)^4}{\pi^2 (\hbar c)^3} \left(2\,\zeta(4) \right) = -\frac{V(k_\mathrm{B} T)^4}{\pi^2 (\hbar c)^3} \frac{\pi^4}{45} = -\frac{4\sigma}{3c} V T^4 \ ,$$

where $\sigma := \pi^2 k_\mathrm{B}^4 / 60\hbar^3 c^2$ is the Stefan-Boltzmann constant and the Riemann zeta function is

$$\zeta(x) = \frac{1}{\Gamma(x)} \int_0^\infty \mathrm{d}u \, \frac{u^{x-1}}{e^u - 1} = \sum_{n=1}^\infty \frac{1}{n^x} \ , \quad \text{with} \quad \zeta(4) = \frac{\pi^4}{90} \ .$$

- *Entropy:* From the general expression as a derivative of the Helmholtz free energy,

$$S = -\frac{\partial F}{\partial T}\Big|_V = \frac{16\,\sigma}{3\,c}\,VT^3\ .$$

- *Energy and specific heat:* Inverting the expression for F in terms of $\bar{E}$ we get the Stefan-Boltzmann law,

$$\bar{E} = F + TS = \frac{4\,\sigma}{c}\,VT^4\ , \qquad \text{or} \qquad u = \frac{4\,\sigma}{c}\,T^4\ ,$$

which leads to a heat capacity that vanishes like T^3 as $T \to 0$,

$$C_V = T\,\frac{\partial S}{\partial T}\Big|_V \text{ or } \frac{\partial \bar{E}}{\partial T}\Big|_V = \frac{16\,\sigma}{c}\,VT^3\ .$$

- *Pressure equation of state:* From the general expression,

$$p = -\frac{\partial F}{\partial V}\Big|_T = \frac{4\,\sigma}{3\,c}\,T^4\ , \quad \text{so} \quad \bar{E} = 3\,pV\ , \qquad \text{or} \qquad u = 3\,p\ .$$

Photon Spectrum ("Black bodies are not black")

- *Idea:* From the general expression for the mean occupation number of each energy state for bosons, and the density of states for massless free particles in terms of energy or angular frequency ω, we want to obtain the mean energy density $u(\omega)\,\mathrm{d}\omega$ of radiation at temperature T in a frequency interval $\mathrm{d}\omega$.

- *Planck spectrum:* Recall that the mean occupation number of a single-particle state labelled by $\alpha \leftrightarrow (\mathbf{k}, \gamma)$ for a boson gas (using $\mu = 0$) and the density of states for particles of energy $\epsilon = cp = c\hbar k$ and two polarization states inside a volume V are, in terms of the angular frequency ω,

$$\bar{N}_{\omega,\gamma} = \frac{1}{e^{\beta\hbar\omega} - 1}\ , \qquad g(\omega) = \frac{V\omega^2}{\pi^2 c^3}\ .$$

Then the number of photons occupying states in an interval $\mathrm{d}\omega$ around ω inside a volume V is

$$\mathrm{d}\bar{N}_\omega = \bar{N}_{\omega,\gamma}\,g(\omega)\,\mathrm{d}\omega = \frac{V}{\pi^2 c^3}\,\frac{\omega^2\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1}\ .$$

Planck's law gives the amount of energy in photons in an energy interval $\mathrm{d}\omega$, and it is then given by

$$u(\omega)\,\mathrm{d}\omega = \hbar\omega\,\frac{\mathrm{d}\bar{N}_\omega}{V} = \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1}\ .$$

- *Laws of black-body radiation:* The energy density $u(\omega)$ peaks at a maximum frequency ω_{max} which scales with temperature [plot]. If we use the dimensionless variable $x := \beta\hbar\omega$ in $u(\omega)$, we can write

$$u(\omega)\,\mathrm{d}\omega = \frac{\hbar}{\pi^2 c^3}\left(\frac{k_{\mathrm{B}}T}{\hbar}\right)^4 \frac{x^3\,\mathrm{d}x}{e^x - 1}\ .$$

This means that (i) as T varies, the peak of this curve always occurs at the same value of x, so that ω_{max}/T is a constant, and $\omega_{\mathrm{max}} \propto T$ (Wien's displacement law), and (ii) the energy in each interval $\mathrm{d}x$ is proportional to T^4, consistently with the result above for the integrated energy density u (Stefan-Boltzmann law).

- *Mean number of photons:* Integrating the expression above for the mean number of photons in each frequency interval, we get for the mean total number

$$\bar{N} = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} = \frac{2\,V\zeta(3)}{\pi^2 c^3 (\beta\hbar)^3} \propto VT^3\ ,$$

where $\zeta(3) \approx 1.20205$.

Reading

- *Course textbook:* Kennett, § 9.1.
- *Other books:* Chandler, § 4.2; Mattis & Swendsen, § 5.5; Pathria & Beale, § 7.3; Plischke & Bergersen [Problem 2.7]; Reif, §§ 9.13–9.15; Schwabl, § 4.5.