General Considerations

• *Goal:* Consider the electromagnetic field in a box of volume V, in thermal equilibrium at temperature T. From the point of view of thermodynamics, since the field consists of photons, we have a gas of photons, but the number N is not fixed because photons can be absorbed and emitted by the walls of the box. We would like to obtain (i) the equation of state, and (ii) the black-body spectrum (Planck's radiation law).
• *States:* We will start from the quantum partition function. The system consists of photons, spin-1 massless particles, whose 1-particle states are specified by the pair $(\mathbf{k}, \epsilon)$, where in a box of volume $V = L_1 L_2 L_3$ with periodic boundary conditions the allowed values of k_i are $2\pi n_i/L_i$, for $i = 1, 2, 3$; $\epsilon = \pm 1$ is the polarization. General states in the total Hilbert space, using the Fock representation, are labelled by the occupation numbers for each $(\mathbf{k}, \epsilon)$, $|\, n_{\mathbf{k}_1,\epsilon_1}, n_{\mathbf{k}_2,\epsilon_2}, ..., n_{\mathbf{k}_j,\epsilon_j}, ...\rangle$, where each $n_{\mathbf{k}_j,\epsilon_j} = 0, 1, 2, ...$
• *Hamiltonian:* Photons are, to an excellent approximation, non-interacting particles. The single-particle mode $(\mathbf{k}, \epsilon)$ has energy $E_k = \hbar\omega$, with $\omega = ck$, so

$$\hat{H} = \sum_{\mathbf{k},\epsilon} \hbar\omega\, \hat{N}_{\mathbf{k},\epsilon} = \sum_{\mathbf{k},\epsilon} \hbar\omega\, \hat{a}^\dagger_{\mathbf{k},\epsilon} \hat{a}_{\mathbf{k},\epsilon}\ .$$

• *Partition function:* Summing over all Fock states,

$$Z = \mathrm{tr}\, \mathrm{e}^{-\beta\hat{H}} = \sum_{\{n_{\mathbf{k},\epsilon}\}} \mathrm{e}^{-\beta\Sigma_{\mathbf{k},\epsilon}\hbar\omega n_{\mathbf{k},\epsilon}} = \prod_{\mathbf{k},\epsilon} \sum_{n_{\mathbf{k},\epsilon}} \mathrm{e}^{-\beta\hbar\omega n_{\mathbf{k},\epsilon}} = \Big(\prod_{\mathbf{k}} \frac{1}{1-\mathrm{e}^{-\beta\hbar\omega}}\Big)^2$$

Thermodynamics

• *Free energy:* From the general expression, with $x := \beta\hbar\omega$ and integrating by parts in one step,

$$F = -k_{\rm B}T \ln Z = 2\, k_{\rm B}T \sum\nolimits_{\mathbf{k}} \ln(1-\mathrm{e}^{-\beta\hbar\omega}) \approx \frac{V\,(k_{\rm B}T)^4}{\pi^2(\hbar c)^3} \int_0^\infty \mathrm{d}x\, x^2 \ln(1-\mathrm{e}^{-x})$$
$$= \frac{V\,(k_{\rm B}T)^4}{\pi^2(\hbar c)^3} \Big(-\frac{1}{3}\int_0^\infty \frac{\mathrm{d}x\, x^3}{\mathrm{e}^x - 1}\Big) = -\frac{V\,(k_{\rm B}T)^4}{\pi^2(\hbar c)^3}\,(2\,\zeta(4)) = -\frac{V\,(k_{\rm B}T)^4}{\pi^2(\hbar c)^3}\,\frac{\pi^4}{15} = -\frac{4\sigma}{3c}\,VT^4\ ,$$

where $\sigma := \pi^2 k_{\rm B}^4/60\hbar^3c^2$ is the Stefan-Boltzmann constant.
• *Entropy:* From the general expression,

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

• *Energy and specific heat:* From the general expressions,

$$\bar{E} = F + TS = \frac{4\,\sigma}{c}\,VT^4\ , \qquad \text{so} \qquad u = \frac{4\,\sigma}{c}\,T^4\ , \qquad \text{and} \qquad c_V = \frac{T}{V}\,\frac{\partial S}{\partial T}\Big|_V = \frac{16\,\sigma}{c}\,T^3\ .$$

• *Pressure and equation of state:* From the general expression,

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

Spectrum

• *Idea:* From the general expression for the mean occupation number of each energy state, for bosons, we want to obtain the mean energy density of radiation at temperature T in a frequency interval $\mathrm{d}\omega$.
• *Planck spectrum:* Recall that, for a gas of bosons, $\langle n_{\mathbf{k},\lambda}\rangle = 1/(\mathrm{e}^{\beta\epsilon_k} - 1)$. Then the number of occupied states within d^3p in a volume V is

$$\mathrm{d}N = \langle n_{\mathbf{k},\lambda}\rangle\, \frac{2V}{(2\pi\hbar)^3}\,\mathrm{d}^3p = \langle n_{\mathbf{k},\lambda}\rangle\, \frac{V}{\pi^2\hbar^3}\,p^2\,\mathrm{d}p = \frac{V}{\pi^2c^3}\,\frac{\omega^2\,\mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega}-1}\ ,$$

and the spectrum is given by Planck's law,

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

Relevant Sections:
[Phys 731, pp 16b-18b]; Chandler, pp 90-92; Halley, ?; Reif, pp 373-387; Schwabl, pp 197-205.