Problem 1 (**20** marks)
For a system that can be characterized by entropy S, volume V, and particle number N, show that

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

How is this statement modified for the photon gas? Find the free energy of the photon gas, and then verify explicitly that the statement is true.

Problem 2 (**20** marks)
Consider an ideal gas composed of a single kind of molecules that rotate, vibrate, and have electronic excitations, such that the single-molecule energies are a sum $\varepsilon_k = \varepsilon^{(\mathrm{rot})}_{a_k} + \varepsilon^{(\mathrm{vib})}_{b_k} + \varepsilon^{(\mathrm{el})}_{c_k}$ of the respective contributions, where a_k, b_k, c_k jointly label the kth microstate. Show that the heat capacity C_V is a corresponding sum: $C_V = C^{(\mathrm{rot})}_V + C^{(\mathrm{vib})}_V + C^{(\mathrm{el})}_V$.
Hint: There is no need to distinguish between bosons and fermions, just consider Maxwell–Boltzmann statistics.

Problem 3 (**20** marks)
In lecture, we discussed the Debye model (Section 3.5 in the lecture notes). There is also the Einstein model, in which one assumes that a single frequency ω_0 is dominating,

$$g(\omega) = 3N\delta(\omega - \omega_0)\,.$$

In the Einstein model, then, what is the constant-volume specific heat at low temperatures? What is it at high temperatures?

Problem 4 (**40=10+10+10+10** marks)
Consider a model system of N constituents distributed over M sites with $M \gg N$. Each constituent has two internal states with energies $\pm\frac{1}{2}E_0$, and there is no interaction between the constituents.

(a) Find the canonical partition function $Q^{(M)}(\beta, N)$.

(b) In the canonical ensemble, what is the expected value of the energy, and what is the energy spread?

(c) Now consider the grand-canonical ensemble and find the partition function $Z^{(M)}(\beta, z)$.

(d) In the grand-canonical ensemble, what is the expected number of constituents, and what is its spread?
[Remember that $\langle N\rangle \ll M$. You may want to use this for simplifying some expressions although this is not really necessary here and not required.]