Problem 1 (**25**=5+15+5 marks)
For a certain rubber band of length L that consists of n moles of rubber, the differential of the internal energy U is

$$\mathrm{d}U = T\,\mathrm{d}S + \tau\,\mathrm{d}L + \mu\,\mathrm{d}n\,,$$

where T, S, τ, μ are the temperature, entropy, tension, and chemical potential, respectively.

(a) Show that

$$U(S, L, n) = T(S, L, n)S + \tau(S, L, n)L + \mu(S, L, n)n\,.$$

(b) The equation of state $TS = 3\tau L$ holds for this rubber band. It is also known that $\tau L^{1/2}$ does not change if both S and n are kept constant (no heat transfer, no particle exchange). Find $U(S, L, n)$ up to a multiplicative constant.

(c) Confirm that the equation in part (a) holds for this $U(S, L, n)$.

Problem 2 (**25**=15+10 marks)
The so-called Berthelot gas has the equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^2\,RT} \quad \text{with} \quad a, b > 0\,,$$

where, as usual, p, T, v, and R are pressure, temperature, molar volume, and gas constant, respectively. Above a critical temperature T_{cr}, this gives a pressure that decreases monotonically as the molar volume increases. For temperatures T below T_{cr}, the Maxwell construction identifies a range $v^{(1)} \le v \le v^{(2)}$, in which the pressure does not depend on v. For given material constants a and b, this co-existence pressure $\overline{p}(T)$ is a function of temperature T. At the critical temperature, we have the critical pressure, $\overline{p}(T_{\mathrm{cr}}) = p_{\mathrm{cr}}$, and the corresponding critical molar volume v_{cr}.

(a) Find T_{cr}, p_{cr}, and v_{cr} in terms of a and b. What is the value of $p_{\mathrm{cr}}v_{\mathrm{cr}}/T_{\mathrm{cr}}$?

(b) For temperatures T just below the critical temperature, $T_{\mathrm{cr}} - T \ll T_{\mathrm{cr}}$, the co-existence pressure is well approximated by

$$\overline{p}(T) = p_{\mathrm{cr}}\left(\frac{xT}{T_{\mathrm{cr}}} - (x-1)\right).$$

Determine the number x.

Problem 3 (**25**=15+10 marks)
Note: A homework exercise dealt with the link between the partition functions of the canonical and grand canonical ensembles. This problem concerns the link between the microcanonical and the canonical ensembles.

A thermodynamical system is described by entropy S or temperature $T = 1/(k_{\mathrm{B}}\beta)$ together with other extensive variables X. As usual, we denote the count of microstates with energy E by $\Omega(E, X)$ and the canonical partition function by $Q(\beta, X)$.

(a) Show that, for given $Q(\beta, X)$,

$$\Omega(E, X) = Q(\beta, X)\mathrm{e}^{\beta E} \quad \text{with } \beta \text{ such that } EQ(\beta, X) = -\frac{\partial Q(\beta, X)}{\partial \beta}\,.$$

(b) What, in turn, is $Q(\beta, X)$ for known $\Omega(E, X)$?

Problem 4 (**25**=15+10 marks)
For ideal gases, we know from lecture that the average occupation number is

$$\langle n_j \rangle = \frac{1}{\mathrm{e}^{\beta(\varepsilon_j - \mu)} \pm 1} \quad \left\{ \begin{matrix} \text{for fermions} \\ \text{for bosons} \end{matrix} \right\},$$

where ε_j is the jth single-particle energy and μ is the chemical potential. In the boson case, assume that the temperature is sufficiently high that there is no Bose-Einstein condensation.

(a) What is the corresponding expression for the correlation $\langle n_j n_{j'} \rangle - \langle n_j \rangle \langle n_{j'} \rangle$?

(b) Find the corresponding fluctuation $\langle \delta N^2 \rangle$ in the total number of particles, and verify that it is consistent with the general expression (page 85 in the lecture notes)

$$\langle \delta N^2 \rangle = \left(\frac{\partial \langle N \rangle}{\partial (\beta\mu)} \right)_{V,\beta}\,.$$