A system of N atoms can be in the ground state (minimum energy state) or in an excited state. For convenience, we set the zero of energy exactly in between, so the energies of the two states of an atom are ±ε/2. The atoms are isolated from the outside world. There are only weak couplings between the atoms, sufficient to bring them into internal equilibrium but without other effects.

(a) Microcanonical entropy. If the net energy is $E$ (corresponding to a number of excited atoms $m = E/\epsilon + N/2$), what is the microcanonical entropy $S(E)$ of our system? Simplify your expression using Stirlings formula, $\log n! \approx n \log n - n$.

(b) Negative temperature. Find the temperature, using your simplified expression from part (a). What happens to the temperature when $E > 0$. (Having the energy $E > 0$ is a kind of population inversion. Population inversion is the driving mechanism for lasers).

(c) Canonical ensemble. Take one of our atoms and couple it to a heat bath of temperature $k_B T = 1/\beta$. Write explicit formulae for $Z$, $\langle E \rangle$, and $S$ in the canonical ensemble.

(d) What happens to $\langle E \rangle$ in the limit $T \to \infty$. Is it possible to get into the negative temperature regime discussed in part (b)?

(e) Find the entropy of the canonical ensemble for $N$ atoms using the result for a single atom in part (c). Using the approximate form of the microcanonical ensemble from part (a) and the temperature from part (b), show that the canonical and microcanonical ensembles agree.

Suppose that there are $N$ independent, distinguishable molecules and each molecule can be in one of a set of energy states $\epsilon_n$, $n = 0, 1, 2, \ldots$. The corresponding partition function is

$$Z_N = \sum_{n_1, \ldots, n_N} e^{-\beta(\epsilon_{n_1} + \ldots + \epsilon_{n_N})} = q^N$$

where $q = \sum_n e^{-\beta \epsilon_n}$.

(a) Show that the average total energy is given by

$$\langle A \rangle = N \sum_n \epsilon_n \eta_n, \quad \eta_n = \frac{e^{-\beta \epsilon_n}}{q}$$

where $\eta_n$ is the fraction of molecules in state $\epsilon_n$.

(b) Show that the entropy is given by

$$S = -k_B N \sum_n \eta_n \log \eta_n$$
(c) Using parts (a) and (b) show that the pressure

\[ p = -\left( \frac{\partial E}{\partial V} \right)_{S,N} = -N \sum_n \eta_n \frac{\partial \epsilon_n}{\partial V} \]

and the specific heat

\[ C_V \equiv T \left( \frac{\partial S}{\partial T} \right)_{V,N} = N \sum_n \epsilon_n \frac{\partial \eta_n}{\partial T} \]

Evaluate the latter to obtain the result

\[ C_V = N \frac{\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2}{k_B T^2} \]

(c) Calculate \( q, E, C_V \) in the case where the energy states of a molecule are given by

\[ \epsilon_n = (n + 1/2) \hbar \nu, \quad n = 0, 1, 2, \ldots \]

(These correspond to the energy states of a quantum harmonic oscillator with natural frequency \( \nu \)). Determine the behavior of \( E, C_V \) in the small \( T \) and high \( T \) limits.

[3.3] Consider a vertical column of an ideal gas of \( N \) particles in equilibrium at temperature \( T \). Assume that the column has uniform cross-sectional area \( A \). Taking into account the potential energy due to gravity, the energy of a particle with momentum \( p = (p_x, p_y, p_z) \) and position \( r = (x, y, z) \) is \( p^2/2m + mgz \) where \( m \) is the mass of each particle, \( z \) is height above the ground and \( g \) is the gravitational constant. Since the gas particles are noninteracting, the momentum and position of each particle is drawn independently from the single–particle Boltzmann distribution

\[ \rho(r, p) = q^{-1} \exp \left( -\frac{\beta p^2}{2m} - \beta mgz \right) \]

where \( q \) is the single molecule partition function

\[ q = \frac{1}{h^3} \int \exp \left( -\frac{\beta p^2}{2m} - \beta mgz \right) d^3p \]

(a) Using the single–particle Boltzmann distribution, show that the particle density \( n(z) \) varies with height above the ground according to

\[ n(z) = \frac{mgN}{k_BT A} e^{-\beta mgz} \]
(b) Let \( P(z) \) be the gas pressure at a height \( z \). By considering the balance between pressure and gravitational forces acting on a thin column of gas between \( z \) and \( z + \delta z \), derive the equation
\[
\frac{dP(z)}{dz} = -mg n(z)
\]
Hence, deduce that the pressure at a given height obeys the ideal gas law.

(c) Calculate \( \langle v_z \rangle \) and \( \langle v_z^2 \rangle \) using the single–particle Boltzmann distribution, where \( v_z = p_z/m \) is the vertical particle velocity. Explain why these averages are independent of height \( z \).

(d) What do cold mountain tops imply about the earth’s atmosphere?

[3.4] Starting from the entropy written as \( S = S(T,V) \) for fixed \( N \) and differentiating with respect to \( T \) at fixed pressure \( p \), use Maxwell relations to prove that
\[
C_p - C_V = \frac{T}{V \kappa_T} \left( \frac{\partial V}{\partial T} \right)_p^2
\]
where
\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V, \quad C_p = T \left( \frac{\partial S}{\partial T} \right)_p, \quad \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T
\]