J09T.1 - The Partition Function

Problem

A system A is in thermal equilibrium with a bath at temperature T. The thermal average of a physical quantity q is

$$\langle q \rangle = \sum_r q_r P_r \,,$$

where P_r, the probability that A occupies the state r of energy E_r, is given by

$$P_r = \frac{e^{-\beta E_r}}{Z} \,,$$

where $\beta = 1/k_B T$, and the partition function $Z = \sum_r e^{-\beta E_r}$.

a) Show that the energy is given by

$$\langle E \rangle = -\frac{\partial \log Z}{\partial \beta} \,.$$

b) When the volume V of A is increased by dV at constant temperature, the energy of each state increases by $(\partial E_r/\partial V)dV$. The work done by A is $dW = -\langle \partial E_r/\partial V \rangle dV$. Show that the pressure p is given by

$$\langle p \rangle = \frac{1}{\beta}\frac{\partial \log Z}{\partial V} \,.$$

c) The free energy is defined as $F = E - TS$ with $S = -k_B \langle \log P \rangle$ the entropy. Derive an expression for F in terms of Z.

d) When observed over a long time, E fluctuates about $\bar{E} \equiv \langle E \rangle$. The average magnitude of the fluctuations is given by the variance $\langle (E - \bar{E})^2 \rangle$. Calculate the variance in terms of $\log Z$.