Ben Sauerwine
Practice for Qualifying Exams

Problem Source: **CMU August 2002 Qualifying Exam**

Consider N identical but distinguishable very weakly interacting five-state quantum subsystems with energy levels shown as in figure 1.

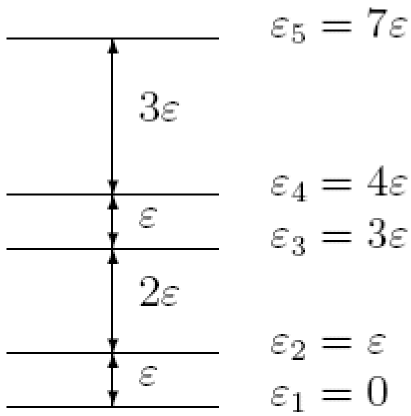

Figure 1: Energy level diagram of a five-state quantum system.

(a) What is the ratio of the fraction of systems in state ε_4 to those in state ε_2 for $k_B T = \frac{\varepsilon}{2}$? A numerical answer is required.

Throughout these solutions, let $\beta = \frac{1}{k_B T}$

Using the canonical ensemble, I have (for one particle)

$$Z(\beta) = e^0 + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} + e^{-7\beta\varepsilon}$$
$$Z\left(\frac{2}{\varepsilon}\right) = 1 + e^{-2} + e^{-6} + e^{-8} + e^{-14}$$

However, the proportion in state ε_4 is

$$P(\varepsilon_4, \beta) = \frac{e^{-8}}{Z\left(\frac{2}{\varepsilon}\right)}$$

and the proportion in ε_2 is

$$P(\varepsilon_2, \beta) = \frac{e^{-2}}{Z\left(\frac{2}{\varepsilon}\right)}$$

so that

$$\frac{P(\varepsilon_4,\beta)}{P(\varepsilon_2,\beta)} = \frac{e^{-8}}{e^{-2}} = e^{-6}$$

(b) How high, in units of $\frac{\varepsilon}{k_B}$, must the temperature T be so that the minimum ratio of the population of any state to the population of any other state having a lower energy equals 0.99? In other words, what is the minimum temperature needed to guarantee that all states will be equally populated to within 1%? A numerical answer is required.

I notice that the lowest ratio will be: $\frac{P(\varepsilon_5,\beta)}{P(\varepsilon_1,\beta)} = e^{-7\beta\varepsilon}$. Then, I want the temperature such that $0.99 = e^{-7\beta\varepsilon}$:

$$\ln 0.99 = -7\frac{1}{k_B T}\varepsilon$$

$$\ln 0.99 = \frac{1}{T}\frac{\varepsilon}{k_B}$$

$$T = -\frac{7}{\ln 0.99}\frac{\varepsilon}{k_B}$$

Thanks to LC for correcting an error on this problem.

(c) Derive a formula for the internal energy U of the entire system of particles. For a very high temperature, say $T > 1000\frac{\varepsilon}{k_B}$, approximately what is the value of U? A numerical answer in units of $N\varepsilon$ is required.

The expected energy of a single particle is given by

$$\langle E\rangle = \frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \frac{\varepsilon e^{-\beta\varepsilon} + 3\varepsilon e^{-3\beta\varepsilon} + 4\varepsilon e^{-4\beta\varepsilon} + 7\varepsilon e^{-7\beta\varepsilon}}{e^0 + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} + e^{-7\beta\varepsilon}}$$

$$U = N\langle E\rangle = N\frac{\varepsilon e^{-\beta\varepsilon} + 3\varepsilon e^{-3\beta\varepsilon} + 4\varepsilon e^{-4\beta\varepsilon} + 7\varepsilon e^{-7\beta\varepsilon}}{e^0 + e^{-\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} + e^{-7\beta\varepsilon}}$$

At a very high temperature, the states are all equally populated for maximum entropy. This being the case,

$$U = N\langle E\rangle = N\varepsilon\left(\frac{1}{5}+\frac{3}{5}+\frac{4}{5}+\frac{7}{5}\right) = 3N\varepsilon$$

(d) For T=0, what is the entropy S of the entire system of particles? What is the justification for your answer?

Consider momentarily the microcanonical ensemble, where $S = k_B \ln \Omega$, where omega counts the number of states. At this temperature, all of the particles are in the lowest quantum state and therefore the counting function gives one. $S = k_B \ln 1 = 0$.

(e) For a very high temperature, say $T > 1000\frac{\varepsilon}{k_B}$, approximately what is the entropy S of the entire system of particles? A numerical answer in units of Nk_B is required.

Note that using the Helmholtz free energy $A \equiv -\frac{1}{\beta}\ln Z$,

$$S \equiv -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -Nk_B\langle \ln P_i \rangle = -Nk_B \sum_i P_i \ln P_i$$

At the highest-temperature possible, each state has equal occupation. In that case,

$$S = -Nk_B 5\left[\frac{1}{5}\ln\frac{1}{5}\right] = Nk_B \ln 5$$

(f) Consider the heat capacity C_V at constant volume of the entire system of particles. Develop an approximate formula (the first non-vanishing term) for C_V that is valid at very low temperatures, $T << \frac{\varepsilon}{k}$, and sketch this result versus T. What is the asymptotic value of C_V for high temperatures, say $T > 1000\frac{\varepsilon}{k_B}$? Justify your result.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left(\frac{\partial U}{\partial \beta}\right)_{N,V}\left(\frac{\partial \beta}{\partial T}\right) = -\frac{1}{k_B T^2}\left(\frac{\partial U}{\partial \beta}\right)_{N,V} = -k_B\beta^2\left(\frac{\partial U}{\partial \beta}\right)_{N,V}$$

(We could find no good way to do the expansion for the first part of this problem.)

At very large temperatures, I notice from part c that the internal energy is bounded above and so at large temperatures $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \to 0$.