Exercise 3.11

In this exercise we extend the derivation of the canonical ensemble to more general ensembles. We'll basically follow the arguments Chandler presents on page 63, but our system will be able to exchange both energy E and some other extensive variable X with the bath.

So the idea here is that we have a system embedded in a very large bath. We're interested in the probability of a given state, ν, which is characterized by a particular energy E_ν and a particular value of the other extensive variable X_ν. If the system is in state ν, then the total energy is $E = E_\nu + E_B$ and the total X is $X = X_\nu + X_B$, where the B subscript indicates the value for the bath.

Since the total E and total X are constant, the number of microstates Ω for the system plus bath, given that the system is in state ν, can be written in terms of the number of microstates for the bath. In this case, Ω depends on both E_B and X_B. So the number of microstates for the total system plus bath, given that our system is in state ν, is $\Omega(E_B, X_B) + \Omega(E - E_\nu, X - X_\nu)$.

To get the probability of our state ν, we refer to the basic postulate of statistical mechanics: all microstates are equally possible. This means that the probability of being in state ν is proportional to the number of microstates of the total system plus bath in which the system is given by ν, *i.e.*,

$$P_\nu \propto \Omega(E - E_\nu, X - X_\nu) \tag{1}$$

Following Chandler, we rewrite this as the exponential of the natural logarithm, and expand the quantity in the exponent as a Taylor series in the perturbation to the total number of microstates induced by enforcing that the system be in state ν:

$$\begin{aligned} P_\nu &\propto \exp(\ln(\Omega(E - E_\nu, X - X_\nu))) \qquad (2) \\ &\approx \exp\left(\ln(\Omega(E, X)) - E_\nu \frac{\partial \ln(\Omega)}{\partial E} - X_\nu \frac{\partial \ln(\Omega)}{\partial X} + \mathcal{O}(\Delta^2)\right) \qquad (3) \end{aligned}$$

where $\mathcal{O}(\Delta^2)$ indicates second (and higher) derivatives of the logarithm.

If we think of our restriction that the system be in state ν as a perturbation, it is clear that the effect of the perturbation gets smaller and smaller and the bath gets larger relative to the system. So as we approach the infinite bath limit, we're justified in truncated the Taylor expansion at first-order.

Now we recall that $\ln(\Omega) = S/k_\mathrm{B}$. So now we have

$$P_\nu \propto \exp\left(-\frac{1}{k_\mathrm{B}}\left(E_\nu \frac{\partial S}{\partial E} + X_\nu \frac{\partial S}{\partial X}\right)\right) \tag{4}$$

where we've removed the term $\ln(\Omega(E, X))$, which is independent of the state ν, by absorbing it into the total proportionality constant.

Now we use the entropy differential as given by Chandler on page 69:

$$\frac{1}{k_\mathrm{B}} \mathrm{d}S = \beta \mathrm{d}E + \xi \mathrm{d}X \tag{5}$$

This is simply a different (and specialized) way of writing the entropy differential we have used in previous chapters,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E - \frac{\mathbf{f}}{T}\mathrm{d}\mathbf{X} \tag{6}$$

It gives us the results

$$\frac{1}{k_\mathrm{B}}\frac{\partial S}{\partial E} = \beta \tag{7}$$

$$\frac{1}{k_\mathrm{B}}\frac{\partial S}{\partial X} = \xi \tag{8}$$

which we can put into our probability to obtain

$$P_\nu \propto \exp\left(-\beta E_\nu - \xi X_\nu\right) \tag{9}$$

All that is left for us now is to determine the constant of proportionality. Since this is a probability, the sum over all possible states ν should be 1. So the reciprocal proportionality constant Ξ is

$$\Xi = \sum_\nu \exp\left(-\beta E_\nu - \xi X_\nu\right) \tag{10}$$

and the probability is

$$P_\nu = \exp\left(-\beta E_\nu - \xi X_\nu\right)/\Xi \tag{11}$$

Just as Chandler said it should be. $\square$