Homework #2

Solutions

1. For the two 10-particle two-state systems described in lecture, suppose the total energy to be shared between the two objects is $E = E_A + E_B = 4$. What is the distribution of energies that gives the highest multiplicity?

Solution:

We can write

$$W(E_A) = \left(\frac{10!}{E_A!\,(10 - E_A)!}\right)\left(\frac{10!}{(4 - E_A)!\,(10 - 4 + E_A)!}\right)$$

The possibilities are

E	**W(E)**
0	210
1	1200
2	2025
3	1200
4	210

Thus, the highest multiplicity occurs , in this case, when the energy is divided equally between the two objects.

2. For a simple one-component system, the 1st Law of Thermodynamics can be written

$$dE = TdS - pdV$$

using what you know from thermodynamics (i.e. what you learned in PChem class) show

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V = -p$$

Solution:

The total differential

$$dE = TdS - pdV$$

implies that the partial derivative $(\partial E/\partial V)_T$ is given by

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Substituting the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

into the equation for $(\partial E/\partial V)_T$ yields

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

which is rearranged to obtain

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V = -p$$

3. One can obtain an analogous expression from statistical mechanics

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{\beta} + \beta\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_{V} = -\langle p\rangle$$

where $\langle E\rangle$ is the average energy and $\langle p\rangle$ is the average pressure using the probability distribution function $P_i = e^{-\beta E_i}/Q$ and $Q = \sum_j e^{-\beta E_j}$. To derive the above expression first obtain expressions for $\langle E\rangle$ and $\langle p\rangle$. Note that for each state j

$$p_j = -\left(\frac{\partial E_j}{\partial V}\right)_T$$

Differentiate the expression for $\langle E\rangle$ with respect to V (keeping β fixed) to obtain

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{\beta} = -\langle p\rangle + \beta\langle Ep\rangle - \beta\langle E\rangle\langle p\rangle$$

Similarly, one can differentiate $\langle p\rangle$ with respect to β (keeping V fixed) to obtain

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_{V} = \langle E\rangle\langle p\rangle - \langle Ep\rangle$$

Verify these last two expressions and combine them to obtain the top expression.

Solution:

Begin with the equations for the average energy $\langle E\rangle$

$$\langle E\rangle = \frac{\sum_i E_i e^{-\beta E_i}}{Q}$$

the average pressure $\langle p\rangle$

$$\langle p\rangle = \frac{\sum_i p_i e^{-\beta E_i}}{Q} = \frac{\sum_i -\left(\frac{\partial E_i}{\partial V}\right)_{\beta} e^{-\beta E_i}}{Q}$$

and the average of the product of energy and pressure $\langle Ep\rangle$

$$\langle Ep \rangle = \frac{\sum_i -E_i \left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i}}{Q}$$

Next we take the partial derivative of $\langle E \rangle$ with respect to V at constant β

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta = \left(\frac{\partial \left({}^{1}\!/_{Q}\right)}{\partial V}\right)_\beta \sum_i E_i e^{-\beta E_i} + \frac{1}{Q}\left(\frac{\partial\left(\sum_i E_i e^{-\beta E_i}\right)}{\partial V}\right)_\beta$$

which simplifies to

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta = -\frac{1}{Q^2}\left(\frac{\partial\left(\sum_i e^{-\beta E_i}\right)}{\partial V}\right)_\beta \sum_i E_i e^{-\beta E_i} + \frac{1}{Q}\left[\sum_i \left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i} + \sum_i E_i \left(\frac{\partial\left(e^{-\beta E_i}\right)}{\partial V}\right)_\beta\right]$$

then to

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta = \frac{1}{Q^2}\left(\sum_i e^{-\beta E_i}\beta\left(\frac{\partial E_i}{\partial V}\right)_\beta\right)\left(\sum_i E_i e^{-\beta E_i}\right) + \frac{1}{Q}\sum_i \left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i} - \frac{1}{Q}\sum_i E_i \beta \left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i}$$

then to

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta = -\beta\left[\frac{\sum_i -\left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i}}{Q}\right]\left[\frac{\sum_i E_i e^{-\beta E_i}}{Q}\right] - \left[\frac{\sum_i -\left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i}}{Q}\right] + \beta\left[\frac{\sum_i -E_i\left(\frac{\partial E_i}{\partial V}\right)_\beta e^{-\beta E_i}}{Q}\right]$$

and finally to

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta = -\beta\langle E\rangle\langle p\rangle - \langle p\rangle + \beta\langle Ep\rangle$$

Next we take the partial derivative of $\langle p\rangle$ with respect to β at constant V

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = \left(\frac{\partial\left({}^{1}\!/_{Q}\right)}{\partial\beta}\right)_V \sum_i p_i e^{-\beta E_i} + \frac{1}{Q}\left(\frac{\partial\left(\sum_i p_i e^{-\beta E_i}\right)}{\partial\beta}\right)_V$$

which simplifies to

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = -\frac{1}{Q^2}\left(\frac{\partial\left(\sum_i e^{-\beta E_i}\right)}{\partial\beta}\right)_V \sum_i p_i e^{-\beta E_i} + \frac{1}{Q}\sum_i\left(\frac{\partial\left(p_i e^{-\beta E_i}\right)}{\partial\beta}\right)_V$$

In order to simplify this expression further we note that $E_i \equiv E_i$(N,V) is independent of β and

$$\left(\frac{\partial p_i}{\partial\beta}\right)_V = \frac{\partial}{\partial\beta}\left(-\left(\frac{\partial E_i}{\partial V}\right)_\beta\right)_V = \frac{\partial}{\partial V}\left(-\left(\frac{\partial E_i}{\partial\beta}\right)_V\right)_\beta = 0$$

Thus,

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = -\frac{1}{Q^2}\left[\sum_i\left(\frac{\partial\left(e^{-\beta E_i}\right)}{\partial\beta}\right)_V\right]\left[\sum_i p_i e^{-\beta E_i}\right] + \frac{1}{Q}\left[\sum_i p_i\left(\frac{\partial\left(e^{-\beta E_i}\right)}{\partial\beta}\right)_V\right]$$

which simplifies to

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = -\frac{1}{Q^2}\left[\sum_i -E_i e^{-\beta E_i}\right]\left[\sum_i p_i e^{-\beta E_i}\right] + \frac{1}{Q}\left[\sum_i -E_i p_i e^{-\beta E_i}\right]$$

then to

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = \left[\frac{\sum_i E_i e^{-\beta E_i}}{Q}\right]\left[\frac{\sum_i p_i e^{-\beta E_i}}{Q}\right] - \left[\frac{\sum_i E_i p_i e^{-\beta E_i}}{Q}\right]$$

and finally to

$$\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = \langle E\rangle\langle p\rangle - \langle Ep\rangle$$

Combining the partial derivatives $(\partial\langle E\rangle/\partial V)_\beta$ and $\beta(\partial\langle p\rangle/\partial\beta)_V$ yields

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_\beta + \beta\left(\frac{\partial\langle p\rangle}{\partial\beta}\right)_V = [-\beta\langle E\rangle\langle p\rangle - \langle p\rangle + \beta\langle Ep\rangle] + \beta[\langle E\rangle\langle p\rangle - \langle Ep\rangle] = -\langle p\rangle$$

4. Explain how one can use the results of problems 2 and 3 to show that $\beta \propto 1/T$.

Solution:

Compare the equations derived in problem 1

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V = -p$$

and problem 2

$$\left(\frac{\partial \langle E \rangle}{\partial V}\right)_\beta + \beta\left(\frac{\partial \langle p \rangle}{\partial \beta}\right)_V = -\langle p \rangle$$

If we assume $E = \langle E \rangle$ and $p = \langle p \rangle$ then we rewrite the second equation as

$$\left(\frac{\partial E}{\partial V}\right)_\beta + \beta\left(\frac{\partial p}{\partial \beta}\right)_V = -p$$

Now the discrepancy between the two equations is in the second term and for the two equations to be equal

$$-T\left(\frac{\partial p}{\partial T}\right)_V = \beta\left(\frac{\partial p}{\partial \beta}\right)_V$$

the partial derivative

$$\left(\frac{\partial p}{\partial \beta}\right)_V = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial \beta}\right)$$

Thus,

$$-T\left(\frac{\partial p}{\partial T}\right)_V = \beta\left(\frac{\partial p}{\partial \beta}\right)_V = \beta\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial \beta}\right)$$

and

$$-T = \beta\left(\frac{\partial T}{\partial \beta}\right)$$

which yields the differential equation

$$\frac{\partial T}{\partial \beta} = -\frac{T}{\beta} \quad or \quad \frac{\partial \beta}{\partial T} = -\frac{\beta}{T}$$

Since $\beta \equiv \beta(T)$ a general solution to this equation has the form

$$\beta(T) \propto \frac{1}{T}$$

and the formal solution is

$$\beta(T) = \frac{1}{kT}$$

5. Show that the Boltzmann distribution can be used to determine the relative population (to the ground state population n_0) such that

$$\frac{n_i}{n_0} = e^{-\beta E_i}$$

Solution:

The probability of being in the state with energy E_i is given by

$$p_i = \frac{e^{-\beta E_i}}{\sum_{j=0}^{N} e^{-\beta E_j}} = \frac{n_i}{N}$$

If we assume the state $E_0 = 0$ then

$$\frac{p_i}{p_0} = \frac{\frac{n_i}{N}}{\frac{n_0}{N}} = \frac{\frac{e^{-\beta E_i}}{\sum_{j=0}^{N} e^{-\beta E_j}}}{\frac{e^{-\beta E_0}}{\sum_{j=0}^{N} e^{-\beta E_j}}} = \frac{e^{-\beta E_i}}{e^{-\beta E_0}} = e^{-\beta E_i}$$

and we have

$$\frac{n_i}{n_0} = e^{-\beta E_i}$$

6. One can derive the Gibbs entropy formula using the Boltzmann entropy formula, the average energy obtained from the Boltzmann distribution function and both equations for the Helmholtz free energy (i.e. A = E – TS and A = - kT lnQ). Derive the formula

$$S = -k \sum_i P_i ln P_i$$

Solution:

Begin with the equation for the Helmholtz free energy

$$A = E - TS$$

which can be solved for S

$$S = \frac{E}{T} - \frac{A}{T} = \frac{E}{T} + \frac{kTlnQ}{T} = k\beta E + klnQ = \frac{k\beta}{Q}\sum_i E_i e^{-\beta E_i} + klnQ$$

We then rewrite this equation as

$$S = \frac{k}{Q}\left[\beta \sum_i E_i e^{-\beta E_i} + QlnQ\right] = \frac{k}{Q}\left[\beta \sum_i E_i e^{-\beta E_i} + lnQ \sum_i e^{-\beta E_i}\right]$$

and further simplify to obtain

$$S = -\frac{k}{Q}\sum_i \left[-\beta E_i e^{-\beta E_i} - e^{-\beta E_i} lnQ\right] = -\frac{k}{Q}\sum_i e^{-\beta E_i}[-\beta E_i - lnQ]$$

We rearrange this equation to obtain

$$S = -\frac{k}{Q}\sum_i e^{-\beta E_i} ln\left(\frac{e^{-\beta E_i}}{Q}\right) = -k\sum_i \frac{e^{-\beta E_i}}{Q} ln\left(\frac{e^{-\beta E_i}}{Q}\right) = -k\sum_i P_i ln P_i$$