Homework #4 Solutions

Question 1a) K+K Chapter 3, Problem 1. The free energy can be obtained from the partition function using the formula $F = -\tau \log Z$ where $Z = e^0 + e^{-\varepsilon/\tau}$. Hence

$$F = -\tau \log(1 + e^{-\varepsilon/\tau})$$

1b) Entropy is related to the free energy by $\sigma = -\frac{\partial F}{\partial \tau}\big|_V$. Note that the energy levels are a property of the system and cannot depend on temperature. Since volume is held fixed we conclude that in this differentiation ε is fixed.

$$\sigma = \log(1 + e^{-\varepsilon/\tau}) + \frac{\tau\varepsilon}{\tau^2(1 + e^{-\varepsilon/\tau})} e^{-\varepsilon/\tau}$$

Energy is given by $U = F + \tau\sigma = -\tau \log(1 + e^{-\varepsilon/\tau}) + \tau \log(1 + e^{-\varepsilon/\tau}) + \frac{\varepsilon e^{-\varepsilon/\tau}}{1+e^{-\varepsilon/\tau}}$

$$U = \frac{\varepsilon}{1 + e^{\varepsilon/\tau}}$$

which agrees with Eq.(14) on page 62.

Question2a) K+K Chapter 3, Problem 3. We calculate the partition function first and use the standard relation to get the free energy.

$$Z = \sum_{s=0}^{\infty} e^{-\varepsilon_s/\tau} = \sum_{s=0}^{\infty} \left(e^{-\hbar\omega/\tau}\right)^s$$

where we have used the fact that $\varepsilon_s = s\hbar\omega$. This sum can be performed exactly using

$$\frac{1}{1-x} = \sum_{s=0}^{\infty} x^s$$

This formula is only valid for $x < 1$. In our case $x = e^{-\hbar\omega/\tau}$ satisfies this condition since both τ and $\hbar\omega$ are positive. Hence

$$Z = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

From this we get the free energy $F = -\tau \log Z = \tau \log\left[1 - e^{-\hbar\omega/\tau}\right]$.

2b) To find the entropy we differentiate F wrt τ keeping V fixed. Note that fixed V corresponds to fixed energy levels, hence $\hbar\omega$ is fixed.

$$\sigma = -\frac{\partial F}{\partial \tau}\bigg|_V = -\log\left[1 - e^{-\hbar\omega/\tau}\right] + \frac{(\hbar\omega/\tau)}{e^{\hbar\omega/\tau} - 1}$$

Question 3) K+K Chapter 3, Problem 4. We start by making the following observation

$$< (\varepsilon - < \varepsilon >)^2 > = < \varepsilon^2 > -2 < \varepsilon >^2 + < \varepsilon >^2 = < \varepsilon^2 > - < \varepsilon >^2$$

Another observation is that the averages of the powers of energy can be obtained by differentiating the partition function with respect to τ:

$$\begin{aligned}\frac{\partial Z}{\partial \tau} &= \frac{1}{\tau^2}\sum_n \varepsilon_n e^{-\varepsilon_n/\tau} = \frac{Z}{\tau^2} < \varepsilon >= \frac{Z}{\tau^2}U \\ \frac{\partial}{\partial \tau}\left(\tau^2 \frac{\partial Z}{\partial \tau}\right) &= \frac{1}{\tau^2}\sum_n \varepsilon_n^2 e^{-\varepsilon_n/\tau} = \frac{Z}{\tau^2} < \varepsilon^2 >\end{aligned}$$

Now we can verify Eq.(89)

$$\begin{aligned}\tau^2\left(\frac{\partial U}{\partial \tau}\right)_V &= \tau^2 \frac{\partial}{\partial \tau}\left(\frac{1}{Z}\times \tau^2 \frac{\partial Z}{\partial \tau}\right) = \tau^2\left[\frac{1}{Z}\times\frac{Z}{\tau^2} < \varepsilon^2 > - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \tau}\right)^2\right] \\ &= < \varepsilon^2 > - < \varepsilon >^2\end{aligned}$$

Question 4) Start with the Fundamental Thermodynamic Relation:

$$dU(\sigma, V) = \tau d\sigma - pdV$$

Use $d(\tau\sigma) = \tau d\sigma + \sigma d\tau$ to get

$$d(U - \tau\sigma) = -\sigma d\tau - pdV$$

Let $F(\tau, V) = U - \tau\sigma$ be the Helmholtz free energy. Now instead do a Legendre transformation on the pdV term of the Fundamental relation

$$d(pV) = pdV + Vdp$$

$$d(U + pV) = \tau d\sigma + Vdp$$

Let $H(\sigma, p) \equiv U + pV$ be the entalphy. So

$$dH = \tau d\sigma + Vdp$$