

Problem 1

Kittel & Kroemer, Chapter 3, problem 1 [Free energy of a two state system]

(a): 1 point

Find an expression for the free energy as a function of τ of a system with two states, one at energy 0 and one at energy ϵ .

The easiest way to go about this is to first calculate the partition function Z , and then use $F = -\tau \ln Z$. So:

$$Z \equiv \sum_s e^{-\epsilon_s/\tau} = 1 + e^{-\epsilon/\tau}.$$

Then

$$F = -\tau \ln Z = -\tau \ln(1 + e^{-\epsilon/\tau}).$$

(a): 1 point

(b): 1 point

From the free energy, find expressions for the energy and entropy of the system. The entropy is plotted in Figure 3.11.

For entropy we can take a derivative:

$$\begin{aligned} \sigma &= -(\partial F / \partial \tau)_V = \ln(1 + e^{-\epsilon/\tau}) + \frac{\tau e^{-\epsilon/\tau}}{1 + e^{-\epsilon/\tau}} \frac{\epsilon}{\tau^2} \\ &= \ln(1 + e^{-\epsilon/\tau}) + \frac{1}{1 + e^{\epsilon/\tau}} \frac{\epsilon}{\tau}. \end{aligned}$$

For the energy, we can use the definition $F \equiv U - \tau \sigma$ and solve for U :

$$\begin{aligned} U &= F + \tau \sigma = -\tau \ln(1 + e^{-\epsilon/\tau}) + \tau \ln(1 + e^{-\epsilon/\tau}) + \frac{\tau}{1 + e^{\epsilon/\tau}} \frac{\epsilon}{\tau} \\ &= \frac{\epsilon}{1 + e^{\epsilon/\tau}}. \end{aligned}$$

We can identify this as what we would get if we calculated $\langle \epsilon \rangle \equiv U = \sum_s \epsilon_s e^{-\epsilon_s/\tau} / Z$. Either way works!

(b): 1 point

Problem 2

Adapted from: Kittel & Kroemer, Chapter 3, problem 3 [Free energy of a harmonic oscillator]

A one-dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $\epsilon_s = s\hbar\omega$, where s is a positive integer or zero, and ω is the classical frequency of the oscillator. We have chosen the zero of the energy at the state $s = 0$.

(a): 1 point

Find the partition function for this system. The answers for (b), (c), and (d) in this problem will follow from this starting point. Note: do not leave your answer as an infinite sum! See if you can work out an exact expression for Z .

We can calculate:

$$\begin{aligned} Z &\equiv \sum_s e^{-\epsilon_s/\tau} = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} \\ &= 1 + e^{-\hbar\omega/\tau} + e^{-2\hbar\omega/\tau} + \dots \\ &= 1 + e^{-\hbar\omega/\tau} (1 + e^{-\hbar\omega/\tau} + e^{-2\hbar\omega/\tau} + \dots) \\ &= 1 + e^{-\hbar\omega/\tau} Z. \end{aligned}$$

(a): 1 point

We can now solve explicitly for Z :

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

(b): 1 point

Show that for a harmonic oscillator the free energy is

$$F = \tau \ln[1 - e^{-\hbar\omega/\tau}]$$

Note that at high temperatures such that $\tau \gg \hbar\omega$ we may expand the argument of the logarithm to obtain $F \simeq \tau \ln(\hbar\omega/\tau)$.

We can calculate:

$$\begin{aligned} F &= -\tau \ln Z = -\tau \ln \left(\frac{1}{1 - e^{-\hbar\omega/\tau}} \right) \\ &= \tau \ln[1 - e^{-\hbar\omega/\tau}] \end{aligned}$$

(b): 1 point

(c): 1 point

Find the internal energy U .

The internal energy U is given by

$$\begin{aligned} U &= \tau^2 (\partial \ln Z / \partial \tau) = \tau^2 \frac{\partial}{\partial \tau} \ln \left(\frac{1}{1 - e^{-\hbar\omega/\tau}} \right) \\ &= -\tau^2 \frac{\partial}{\partial \tau} \ln (1 - e^{-\hbar\omega/\tau}) \\ &= \tau^2 \frac{e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} \frac{\hbar\omega}{\tau^2} \\ &= \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}. \end{aligned}$$

(c): 1 point

(d): 1 point

Show that the entropy is

$$\sigma = \frac{\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} - \ln[1 - e^{-\hbar\omega/\tau}].$$

Here we can use $F \equiv U - \tau\sigma$ and solve for σ , which immediately gives us our result:

$$\sigma = (U - F)/\tau = \frac{\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} - \ln[1 - e^{-\hbar\omega/\tau}]$$

(d): 1 point

(e): 1 point

Compare your answer for U to what you obtained in problem 3 of Homework 2, where you calculated the energy of N harmonic oscillators. Is the answer you obtained there equal to N times the answer you obtained for U in this problem? Write it down, and explain how they are related.

In that problem, we found

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

for N harmonic oscillators. Yes, this is N times the answer we obtained for U in this problem; in this problem, we calculated the *average* energy U of a single oscillator in contact with a reservoir at temperature τ ; if we had N independent such oscillators, the total average energy would be NU .

(e): 1 point

(f): 1 point

Compare your answer for σ to what you obtained in problem 3 of Homework 2. They look different, because one is a function of U while the other is a function of τ . Show that they are the same (except for the factor of N) by substituting $U(\tau)$ into the expression for σ you obtained in Homework 2.

On the previous homework we found

$$\sigma_N(U) = N \ln(1 + U_N/N\hbar\omega) + \frac{U_N}{\hbar\omega} \ln(1 + N\hbar\omega/U_N).$$

Plugging in $U_N = \frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1}$, we have

$$\begin{aligned} \sigma_N(\tau) &= N \ln \left(1 + \frac{1}{e^{\hbar\omega/\tau} - 1} \right) + \frac{N}{e^{\hbar\omega/\tau} - 1} \ln(1 + (e^{\hbar\omega/\tau} - 1)) \\ &= N \ln \left(1 + \frac{1}{e^{\hbar\omega/\tau} - 1} \right) + \frac{N\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} \\ &= N \ln \left(\frac{e^{\hbar\omega/\tau} - 1}{e^{\hbar\omega/\tau} - 1} + \frac{1}{e^{\hbar\omega/\tau} - 1} \right) + \frac{N\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} \\ &= N \ln \left(\frac{e^{\hbar\omega/\tau}}{e^{\hbar\omega/\tau} - 1} \right) + \frac{N\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} \\ &= N \ln \left(\frac{1}{1 - e^{-\hbar\omega/\tau}} \right) + \frac{N\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1} \\ &= -N \ln(1 - e^{-\hbar\omega/\tau}) + \frac{N\hbar\omega/\tau}{e^{\hbar\omega/\tau} - 1}. \end{aligned}$$

This is N times the entropy we found for the single oscillator, as expected.

(f): 1 point

Problem 3

In this problem you will connect the “fundamental” quantities σ, τ we have been working with, with the “conventional” quantities S and T .

Consider a block of copper at a temperature $T = 300$ K.

(a): 1 point

How much heat energy (in Joules) would you have to add to the block to double the number of accessible quantum states in the copper? (Assume that the block is thermally isolated from its surroundings, except for the heat you are adding. Also assume that the amount of heat you are adding is small enough that the temperature of the copper remains constant throughout the process.)

Doubling the number of accessible quantum states means that the multiplicity g is doubling. This means that the entropy will change by $\Delta\sigma = \ln(g_f/g_i) = \ln 2$.

$$Q = \tau\Delta\sigma = k_B T \ln 2 = 2.87 \times 10^{-21} \text{ J.}$$

(a): 1 point

(b): 1 point

By how much will the block’s entropy S increase when the heat is added? (Note that your answer should have units of J/K.)

We can calculate:

$$\Delta S = k_B \Delta\sigma = 0.96 \times 10^{-23} \text{ J/K.}$$

(b): 1 point

Problem 4

Consider a system with 3 quantum states, labeled by index $n = 0, 1, 2$, with respective energies $\epsilon_0 = 0$, $\epsilon_1 = a$, and $\epsilon_2 = 3a$. The system is in thermal equilibrium with a reservoir at temperature τ .

(a): 1 point

What is the probability of finding the system in the $n = 1$ state?

We are in the canonical distribution, and can use the Boltzmann factor to find this:

$$P(1) = \frac{e^{-\epsilon_1/\tau}}{Z} = \frac{e^{-a/\tau}}{1 + e^{-a/\tau} + e^{-3a/\tau}}.$$

(a): 1 point

(b): 1 point

What is the average energy of the system? (You could use a general formula, but it is easier to work directly from the Canonical distribution function.)

We can calculate:

$$\langle \epsilon \rangle \equiv \sum_s \epsilon_s P_s = \frac{ae^{-a/\tau} + 3ae^{-3a/\tau}}{1 + e^{-a/\tau} + e^{-3a/\tau}}.$$

(b): 1 point

(c): 1 point

Make a table showing the numerical values of the probabilities for the system to be in each of the 3 states for the following specific values of the temperature: $\tau = 0$, $\tau = a$, and $\tau = 100a$. (Your table should have $3 \times 3 = 9$ entries.) Notice what happens when the temperature is very high.

	$P(0)$	$P(1)$	$P(2)$
$\tau = 0$	1	0	0
$\tau = a$	0.705	0.259	0.035
$\tau = 100a$	0.338	0.334	0.328

(c): 1 point

This illustrates a feature of the Boltzmann distribution: when the temperature is low compared to the energy spacing, the system is very likely to be found in the ground state; when the temperature is high compared to the energy spacing, the system is roughly equally-likely to be found in each state.

Problem 5

Consider an N -particle system thermally isolated from its surroundings. The multiplicity g depends on the energy U as $g(U) = e^{\sqrt{NU/U_0}}$, where U_0 is a constant with dimensions of energy.

(a): 1 point

Find expressions for the entropy σ and the temperature τ in terms of N , U , and U_0 .

We can calculate:

$$\begin{aligned}\sigma(U) &\equiv \ln G(U) = \ln e^{\sqrt{NU/U_0}} \\ &= \sqrt{NU/U_0},\end{aligned}$$

and

$$1/\tau \equiv (\partial\sigma/\partial U)_N = \frac{1}{2}\sqrt{\frac{N}{UU_0}},$$

so

$$\tau = 2\sqrt{\frac{UU_0}{N}}$$

(a): 1 point

(b): 1 point

Find expressions for the energy U and entropy σ in terms of τ , N , and U_0 .

Using our expression for temperature and solving for U , we can see that

$$U = \frac{N\tau^2}{4U_0}.$$

We can now replace U in our expression for entropy:

$$\sigma(\tau) = \sqrt{\frac{N^2\tau^2}{4U_0^2}} = \frac{N\tau}{2U_0}.$$

(b): 1 point

(c): 1 point

Let $N = 6.02 \times 10^{23}$ and $U_0 = 10^{-20}$ J. If the temperature is $T = 300$ K, calculate numerical values (with correct units) for the energy U , entropy S , and free energy F of the system.

Plugging in numbers, we find

$$\begin{aligned}U &= 258 \text{ J} \\ S &= 1.72 \text{ J/K} \\ F &= U - TS = -258 \text{ J}\end{aligned}$$

(This equal-and-opposite result for U and F is simply a coincidence.)

(c): 1 point