Thermal Physics

Two degenerate energy levels

Problem 1.- Consider a physical system with two degenerate energy levels ε_1 and $\varepsilon_2 > \varepsilon_1$ and degeneracies g_1 and g_2

a) Find the entropy of the system as a function of temperature.
b) Check that when $\tau \to 0$ the entropy becomes $\log(g_1)$ and explain why this is physically reasonable.
c) What will be the average energy of the system when $\tau \to \infty$?

Solution:

The partition function for this system is: $Z = g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}$

The Helmholtz's free energy is: $F = -\tau \log(Z) = -\tau \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau})$

The entropy is calculated from the free energy as follows:

$$\sigma = -\frac{\partial F}{\partial \tau} = \frac{\partial\left(\tau \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau})\right)}{\partial \tau}$$

Taking the derivative:

$$\sigma = \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) + \tau \frac{\partial\left(\log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau})\right)}{\partial \tau}$$

Next, we apply the chain rule:

$$\sigma = \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) + \tau \frac{1}{g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}} \frac{\partial\left(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}\right)}{\partial \tau}$$

Once again, we apply the chain rule:

$$\sigma = \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) + \tau \frac{1}{g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}} \left(g_1 e^{-\varepsilon_1/\tau} \frac{\partial(-\varepsilon_1/\tau)}{\partial \tau} + g_2 e^{-\varepsilon_2/\tau} \frac{\partial(-\varepsilon_2/\tau)}{\partial \tau} \right)$$

Finally, the entropy is:

$$\sigma = \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) + \tau \frac{g_1 e^{-\varepsilon_1/\tau}\left(\frac{\varepsilon_1}{\tau^2}\right) + g_2 e^{-\varepsilon_2/\tau}\left(\frac{\varepsilon_2}{\tau^2}\right)}{g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}}$$

This expression can be simplified to give:

$$\sigma = \log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) + \frac{g_1\varepsilon_1 e^{-\varepsilon_1/\tau} + g_2\varepsilon_2 e^{-\varepsilon_2/\tau}}{\tau(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau})}$$

So, what happens to the entropy when the temperature is very low? Let us first analyze what happens to the second term in the entropy:

$$\frac{g_1\varepsilon_1 e^{-\varepsilon_1/\tau} + g_2\varepsilon_2 e^{-\varepsilon_2/\tau}}{\tau(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau})} = \frac{g_1\varepsilon_1 + g_2\varepsilon_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau}}{\tau(g_1 + g_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau})}$$

Since $\tau \to 0$, $-(\varepsilon_2 - \varepsilon_1)/\tau \to -\infty$, so the exponentials tend to zero when the temperature tends to zero. Then the second term tends to:

$$\frac{g_1\varepsilon_1 + g_2\varepsilon_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau}}{\tau(g_1 + g_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau})} \to \frac{g_1\varepsilon_1 + 0}{\tau(g_1 + 0)} = \frac{\varepsilon_1}{\tau}$$

Now, let us look at the first term:

$$\log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) = \log\left(e^{-\varepsilon_1/\tau}\left(g_1 + g_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau}\right)\right) = \log\left(e^{-\varepsilon_1/\tau}\right) + \log\left(g_1 + g_2 e^{-(\varepsilon_2-\varepsilon_1)/\tau}\right)$$

When $\tau \to 0$ the exponential that multiples g_2 becomes zero so we get:

$$\log(g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}) \to -\frac{\varepsilon_1}{\tau} + \log(g_1 + 0) = -\frac{\varepsilon_1}{\tau} + \log(g_1)$$

Putting these two results together we get when $\tau \to 0$:

$$\sigma \to -\frac{\varepsilon_1}{\tau} + \log(g_1) + \frac{\varepsilon_1}{\tau} = \log(g_1)$$

Is this result reasonable? Actually, yes, because when the temperature is very low the system will only occupy the lowest energy level, which has degeneracy g_1, so the entropy will be $\log(g_1)$. For the same reason at very high temperature the entropy should approach $\log(g_1 + g_2)$, which you can easily prove.

The average energy is calculated from the probabilities:

$$U = \langle \varepsilon \rangle = P_1\varepsilon_1 + P_2\varepsilon_2 = \frac{g_1 e^{-\varepsilon_1/\tau}\varepsilon_1 + g_2 e^{-\varepsilon_2/\tau}\varepsilon_2}{Z} = \frac{g_1 e^{-\varepsilon_1/\tau}\varepsilon_1 + g_2 e^{-\varepsilon_2/\tau}\varepsilon_2}{g_1 e^{-\varepsilon_1/\tau} + g_2 e^{-\varepsilon_2/\tau}}$$

Notice that when $\tau \to \infty$ the exponentials become equal to 1, so:

$$U \to \frac{g_1\varepsilon_1 + g_2\varepsilon_2}{g_1 + g_2}$$

You can also deduce this result without calculations. Just realize that at high temperature all the states will be equally likely, so U is an average over the energies with the degeneracies as weights (this is how GPA is calculated, the credits play the role of the degeneracies and the individual grades play the role of the energies).