

Solution to Exercise 2.1-2 "Do the Math for the Formation Entropy"

Illustration

We start with

$$F = kT \sum_j \frac{\hbar \omega_j}{kT} + \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right)$$

Next we must do the differentiation, i.e. form $\partial F / \partial T$:

$$S = - \frac{\partial}{\partial T} \left[kT \sum_j \frac{\hbar \omega_j}{kT} + \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) \right]$$

One can go straight ahead, of course. But here comes a little helpful trick: Multiply skillfully by T/T and re-sort; you get

$$\begin{aligned} &= - \frac{\partial}{\partial T} \left[k \sum_j \frac{\hbar \omega_j}{k} + T \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) \right] \\ &= - k \sum_j \frac{\partial}{\partial T} \left[T \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) \right] \\ &= - k \sum_j \left[\ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) + T \cdot \frac{- \exp \left(- \frac{\hbar \omega_j}{kT} \right) \frac{\hbar \omega_j}{kT^2}}{1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right)} \right] \\ &= k \sum_j \left[- \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) + \frac{\exp \left(- \frac{\hbar \omega_j}{kT} \right) \frac{\hbar \omega_j}{kT}}{1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right)} \right] \\ &= k \sum_j \left[- \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) + \frac{\exp \left(- \frac{\hbar \omega_j}{kT} \right) \frac{\hbar \omega_j}{kT}}{1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right)} \cdot \frac{\exp \left(\frac{\hbar \omega_j}{kT} \right)}{\exp \left(\frac{\hbar \omega_j}{kT} \right)} \right] \\ &= k \sum_j \left[- \ln \left(1 - \exp \left(- \frac{\hbar \omega_j}{kT} \right) \right) + \frac{\frac{\hbar \omega_j}{kT}}{\exp \left(\frac{\hbar \omega_j}{kT} \right) - 1} \right] \end{aligned}$$

Now we need to resort to approximations

First we realize that whenever $\hbar \cdot \omega / 2\pi \ll kT$, then

$$\exp \left(- \frac{\hbar \omega_j}{kT} \right) \approx 1 - \frac{\hbar \omega_j}{kT}$$

This takes care of the first term.

The second term needs a somewhat more sophisticated approach. Substituting x for $\hbar \cdot \omega / 2\pi \cdot kT$, we can use a simple expansion formula, stop after the second term and re-insert the result. This gives

$$\begin{aligned} \lim_{x \rightarrow 0} \frac{x}{\exp(x) - 1} &= \frac{x}{\left[1 + x + \frac{x^2}{2} + \dots \right] - 1} = \frac{x}{x + \frac{x^2}{2} + \dots} = \frac{1}{1 + \frac{x}{2} + \dots} = 1 \\ \Rightarrow S &\approx k \sum_j \left[- \ln \left[1 - \left(\frac{\hbar \omega_j}{kT} \right) \right] + 1 \right] = k \sum_j \left[- \ln \left(\frac{\hbar \omega_j}{kT} \right) + 1 \right] \approx - k \sum_j \ln \left(\frac{\hbar \omega_j}{kT} \right) \end{aligned}$$

That's as far as one can go. Now use ω' for the circle frequencies of the crystal with a vacancy and form $S_F = S' - S$

$$S_F = S' - S = - k \sum_j \ln \left(\frac{\hbar \omega_j'}{kT} \right) + k \sum_j \ln \left(\frac{\hbar \omega_j}{kT} \right) = k \sum_j \ln \left(\frac{\hbar \omega_j'}{\hbar \omega_j} \right) = k \sum_j \ln \left(\frac{\omega_j'}{\omega_j} \right)$$

q.e.d.