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

Illustration

- We start with

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

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

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

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

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

- Now we need to resort to approximations

  - First we realize that whenever **h ·ω/2π << k*T***, then

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

  - This takes care of the first term.
  - The second term needs a somewhat more sophisticated approach. Substituting ***x*** for **h · ω/2π · k*T***, we can use a simple expansion formula, stop after the second term and re-insert the result. This gives

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

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

$$s_F = S' - S = -k\sum_i \ln\left(\frac{\hbar\omega_i'}{kT}\right) + k\sum_i \ln\left(\frac{\hbar\omega_i}{kT}\right) = k\sum_i \ln\left(\frac{\frac{\hbar\omega_i}{kT}}{\frac{\hbar\omega_i'}{kT}}\right) = k\sum_i \ln\left(\frac{\omega_i}{\omega_i'}\right)$$

  - *q.e.d.*