FYS2160 Termodynamikk og statistisk fysikk
Oblig 3

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Denne obligen inneholder 4 sider.

Exercise 1

a) In a crystal with N atoms and n vacancies, there are in total $N+n$ spots where the atoms can take place. The multiplicity is therefore

$$\Omega(N,n) = \binom{N+n}{n} = \frac{(N+n)!}{n!N!} \tag{1}$$

b) The entropy can then be written using the Boltzmann formula:

$$\begin{aligned} S &= k\ln\Omega \\ &= k\ln\binom{N+n}{n} \\ &= k\ln\left(\frac{(n+N)!}{n!N!}\right) \\ &= k\left[\ln((N+n)!) - \ln(n!) - \ln(N!)\right] \end{aligned} \tag{2}$$

c) Using Stirling's approximation:

$$\ln(x!) \approx \ln\sqrt{2\pi x} + x\ln x - x \approx x\ln x - x, \tag{3}$$

where in the last transition the assumption of large x were made (OK since we are assuming $N >> 1$), we can rewrite eq. (2):

$$\begin{aligned} S &\approx k\left[(N+n)\ln(N+n) - (N+n) - n\ln n + n - N\ln N + N\right] \\ &= k\left[(N+n)\ln(N+n) - n\ln n - N\ln N\right] \\ &= k\left[(N+n)\ln\left(N\left(1+\frac{n}{N}\right)\right) - n\ln n - N\ln N\right] \\ &= k\left[(N+n)\left(\ln N + \ln\left(1+\frac{n}{N}\right)\right) - n\ln n - N\ln N\right] \end{aligned} \tag{4}$$

Using Taylor expansion we get, for small x:

$$\ln(1+x) = x + O(x^2)$$

Using this under the assumption $n << N$, we can simplify eq. (4) to

$$S \approx kn\left[\ln\left(\frac{N}{n}\right)+\frac{n}{N}+1\right] \tag{5}$$

d) From the definition of temperature, we have that

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{6}$$

when the number of particles N and the volume V is held constant. To free atoms in the crystal so that there are n vacancies, requires energy equal to

$$U=\epsilon_0+n\Delta\epsilon \Rightarrow n=\frac{U-\epsilon_0}{\Delta\epsilon}$$

Plugging this back into eq. (5) and using eq. (6), we get

$$\begin{aligned}\frac{1}{T}&=\frac{\partial}{\partial U}\left(k\frac{U-\epsilon_0}{\Delta\epsilon}\left(\ln\left(\frac{N\Delta\epsilon}{U-\epsilon_0}\right)+\frac{U-\epsilon_0}{N\Delta\epsilon}+1\right)\right)\\&=\frac{k}{\Delta\epsilon}\ln\left(\frac{N\Delta\epsilon}{U-\epsilon_0}\right)\\&=\frac{k}{\Delta\epsilon}\ln\frac{N}{n}\\\Rightarrow T&=\frac{\Delta\epsilon}{k}\left(\ln\frac{N}{n}\right)^{-1}\end{aligned}$$

e) From the previous task, we have

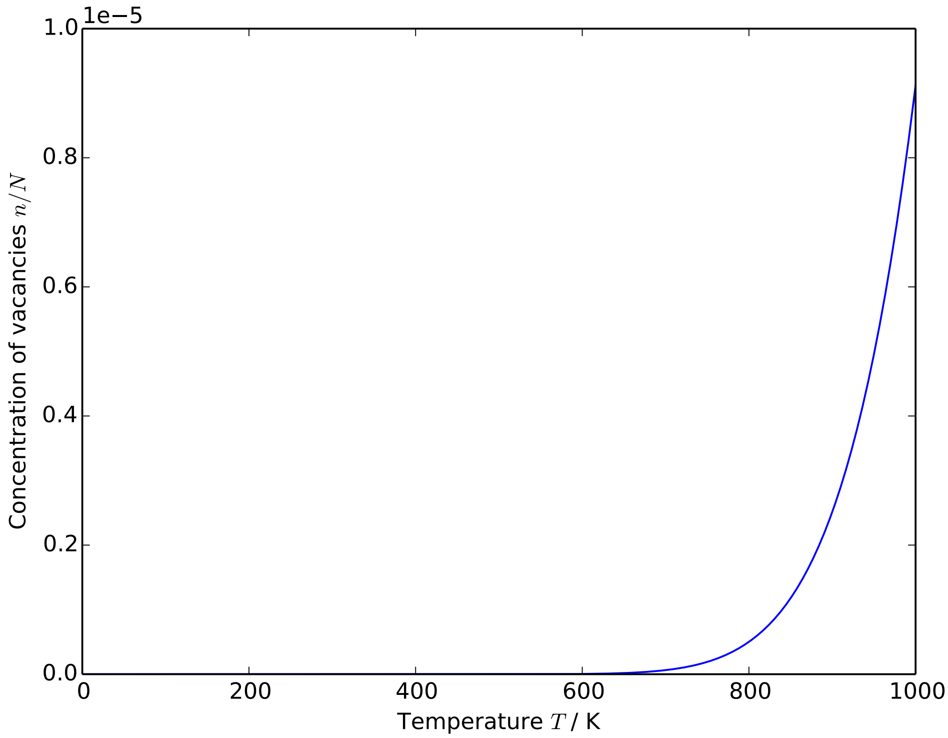
$$T=\frac{\Delta\epsilon}{k}\left(\ln\frac{N}{n}\right)^{-1}$$

Rearranging, we get

$$\Rightarrow n=Ne^{-\Delta\epsilon/(kT)} \tag{7}$$

f) From eq. (7), it is evident that in the limit when $T\to 0$, $n\to 0$ which was the behaviour we wanted.

g) Assuming $\Delta\epsilon = 1$ eV, the concentration of vacancies n/N is plotted in fig. 1



Figur 1: Concentration of vacancies n/N in the crystal as a function of temperature.

h) The heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

Again, using that the total energy needed to make n vacancies is $U = \epsilon_0 + n\Delta\epsilon$. Then $n = (U - \epsilon_0)/\Delta\epsilon$ as above. Eq. (7) then becomes

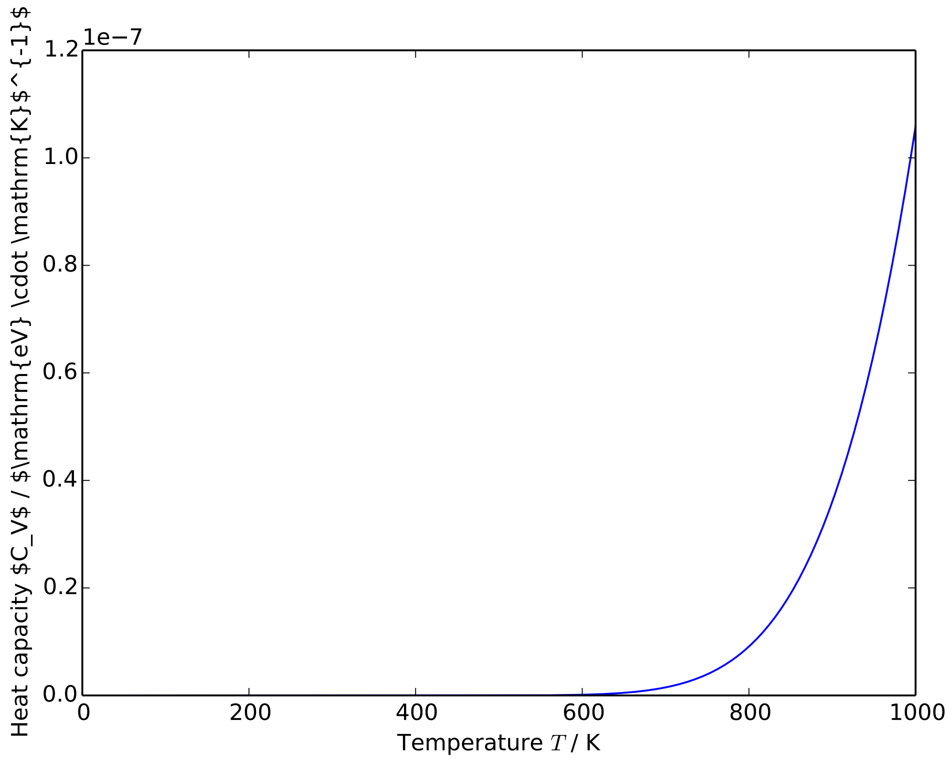
$$\begin{aligned}\frac{U-\epsilon_0}{\Delta\epsilon} &= Ne^{-\Delta\epsilon/(kT)} \\ U &= \Delta\epsilon N e^{-\Delta\epsilon/(kT)} + \epsilon_0\end{aligned}$$

so the expression for the specific heat capacity is

$$\begin{aligned}C_V &= \left(\frac{\partial U}{\partial T}\right)_{N,V} \\ &= \Delta\epsilon N e^{-\Delta\epsilon/(kT)} \cdot \frac{\Delta\epsilon}{kT^2} \\ &= \frac{\Delta\epsilon^2 N}{kT^2} e^{-\Delta\epsilon/(kT)}\end{aligned}$$

Fig. 2 shows a plot of this in the temperature range from $T = 0$ to $T = 1000$ K. The heat capacity seems to be very high at high temperatures compared to lower temperatures.

Whether or not this is a true behaviour is not easy to say without any experimental data, however, the expression for the heat capacity was derived under the assumption of $n << N$ - i.e. low temperatures. 1000K may not be a very low temperature.



Figur 2: Specific heat capacity of the crystal as a function of temperature

Exercise 2

a)

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