M00T.3

Solution to M00T.3 - Defects in a Crystal

a) We treat the on-site atoms and the defect atoms as two systems which can exchange energy and particle number. This leads us to write down a total partition function as the product of the partition function for each system. We also include a chemical potential in both subsystem partition functions. Then:

\[ Z = (1 + z)^N (1 + z e^{\beta \epsilon})^{N_i} \]

where \( z = e^{\beta \mu} \). Using the standard relation between the partition function and free energy, we find:

\[ F = -kT \ln(Z) = -kT [N \ln(1 + z) + N_i \ln(1 + z e^{\beta \epsilon})] \]

So \( f = F/N = -kT [\ln(1 + z) + \rho \ln(1 + z e^{\beta \epsilon})] \)

We also conclude that the chemical potential must satisfy the relation:

\[ N = N \left[ \frac{z}{1 + z} + \rho \frac{z}{e^{\beta \epsilon} + z} \right] \]

b) \( n(T) = K/N \), where \( K = N \rho \frac{z}{e^{\beta \epsilon} + z} \). So:

\[ n(T) = \rho \frac{z}{e^{\beta \epsilon} + z} \]

c) We need to write out \( z \) explicitly to find its behavior at large and small temperatures. The solution to the above equation for \( z \) is:

\[ z = \frac{1 - \rho + \sqrt{(1 - \rho)^2 + 4 \rho e^{\beta \epsilon}}}{2 \rho} \]
For $T \to \infty$, $z \to \rho^{-1}[1 + \frac{\epsilon}{T} + \frac{\rho}{1+\rho} + \ldots]$. Then:

$$n = \frac{\rho}{1+\rho} - \frac{\epsilon}{T} \left(\frac{\rho}{1+\rho}\right)^2 + \ldots$$

For $T \to 0$, $z \to \rho^{-1/2} e^{2\beta \epsilon} + \ldots$ and:

$$n = \sqrt{\rho} e^{-2\beta \epsilon} + \ldots$$

d) $S = -k \ln(Z)$, so we can write it as:

$$S = -k[N \ln(1 + z) + N_i \ln(1 + ze^{\beta \epsilon})]$$

Finally, $C = \frac{dE}{dT}$, but $E = \epsilon n(T)$. So:

$$C = \frac{\beta^2 \epsilon}{\rho} e^{\beta \epsilon} z^{-1} n^2 \left[1 - \frac{e^{\beta \epsilon}}{\sqrt{(1-z)^2 + 4\rho e^{\beta \epsilon}}}\right]$$