Ex2311: Imperfect lattice with defects

Submitted by: Gabi Socolovsky

The problem:

A perfect lattice is composed of N atoms on N sites. If n of these atoms are shifted to interstitial sites (i.e. between regular positions) we have an imperfect lattice with n defects. The number of available interstitial sites is M and is of order N. Every atom can be shifted from lattice to any defect site. The energy needed to create a defect is ω. The temperature is T. Define $x \equiv e^{-\omega/T}$.

(a) Write the expression for the partition function $Z(x)$ as a sum over n.
(b) Using Stirling approximation (see note) determine what is the most probable n, and write for it the simplest approximation assuming $x \ll 1$.
(c) Explian why your result for $\bar{n}$ merely reproduces the law of mass action.
(d) Evaluate $Z(x)$ using a Gaussian integral.
(e) Derive the expressions for the entropy and for the specific heat.
(f) What would be the result if instead of Gaussian integration one were taking only the largest term in the sum?

Note: Regarding n as a continuous variable the derivative of $\ln(n!)$ is approximately $\ln(n)$.

The solution:

(a) For n defects the total energy is given by

$$E_n = n\omega \tag{1}$$

The number of arrangements for n defects:

$$g_n = \binom{N}{n}\binom{M}{n} \tag{2}$$

where $\binom{N}{n}$ is the number of possibilities to choose n atoms from the lattice, and $\binom{M}{n}$ is the number of possible arrangements of these n atoms in the interstitial sites. Thus the partition function becomes:

$$Z(x) = \sum_{n=0}^{N} \binom{N}{n}\binom{M}{n} e^{-n\omega/T} = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!}\frac{M!}{n!(M-n)!}x^n \tag{3}$$

Notice that since M can be smaller or larger than N, the correct upper limit is $\min(N, M)$. However, we neglect the difference between N and M since they have the same order of magnitude.

(b) In order to find the most probable n we can rewrite $Z(x)$ in the following form

$$Z(x) = \sum_{n=0}^{N} e^{-f_n(x)} \tag{4}$$

where

$$f_n(x) = -n\ln(x) - \ln\left(\frac{N!}{n!(N-n)!}\right) - \ln\left(\frac{M!}{n!(M-n)!}\right) \tag{5}$$

and find which element dominates $Z(x)$.
We will regard n as a continuous variable, and find the minima of $f(n,x)$ -

$$\frac{\partial f(n,x)}{\partial n} = -\ln(x) + 2\ln(n) - \ln(N-n) - \ln(M-n) = 0 \tag{6}$$

$$\frac{n^2}{(N-n)(M-n)} = x \tag{7}$$

by taking the $x \ll 1$ assumption we get

$$\bar{n} = \sqrt{MN}e^{-\frac{\omega}{2T}} \tag{8}$$

(c) This problem resembles a case with chemical reactions, where we have four different particles - A, B, C and D. Each particle represents a different component in the original problem: A - filled site, B - empty interstitial site, C - empty site, D - filled interstitial site.
The reaction is $A+B \rightleftharpoons C+D$, which can be interpreted as the transfer of an atom from a site, to an interstitial site, and vice versa. If we treat n as the reaction parameter, the number of particles for A, B, C and D will be $N-n$, $M-n$, n and n, respectively. Therefore, we get the law of mass action

$$\frac{n^2}{(N-n)(M-n)} = e^{-\frac{\omega}{T}} \tag{9}$$

where ω is the required energy for this chemical reaction. If we take the assumption that $\omega \gg T$ we get

$$\bar{n} = \sqrt{MN}e^{-\frac{\omega}{2T}} \tag{10}$$

(d) Since n is a continuous variable, our partition function is now an integral over n. In addition we expand the integrand around $\bar{n}$ up to second order in the exponent -

$$Z(x) = \int_0^\infty e^{-f(n,x)}dn \approx \int_0^\infty e^{-f(\bar{n},x)-\frac{1}{2}f''(\bar{n},x)(n-\bar{n})^2}dn = \sqrt{\frac{\pi}{2f''(\bar{n},x)}}e^{-f(\bar{n},x)} \tag{11}$$

where the prime sign denotes a derivative with respect to n, and $f''(\bar{n},x) = \frac{2}{\bar{n}}$. In addition, the first derivative vanishes as a result of expanding $f(n,x)$ around its minima.

(e) Using the partition function, we get the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = \frac{1}{2}\ln\left(\frac{\pi}{4}\right) + \frac{1}{2}\ln\left(\sqrt{MN}\right) + \bar{n}\left(2+\frac{\omega}{T}\right) \tag{12}$$

where we used that $\frac{\partial f}{\partial \bar{n}} = 0$. Therefore, we find the specific heat

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{\bar{n}}{2}\left(\frac{\omega}{T}\right)^2 \tag{13}$$

(f) Taking only the largest term in the sum we have

$$Z(x) = e^{-f(\bar{n},x)} \tag{14}$$

This is the same as Eq. (11) but without the prefactor. Hence, the entropy is equal to the one found in Eq. (12), albeit without the constant terms

$$S = \bar{n}\left(2+\frac{\omega}{T}\right) \tag{15}$$

Therefore, the specific heat stays the same

$$C_V = \frac{\bar{n}}{2}\left(\frac{\omega}{T}\right)^2. \tag{16}$$