E2311: Imperfect lattice (lattice with defects)

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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) determined what is the most probable n, and write for it the simplest approximation assuming $x \ll 1$.
(c) Evaluate $Z(x)$ using a Gaussian integral.
(d) Derive the expressions for the entropy and for the specific heat.

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

The solution:

(a) Each defect adds ω energy to the system. Therefore the total system energy is given by:

$$E(n) = n\omega$$

First let's calculate $g(n)$ number of possible rearrangements of n defects:

$$g(n) = \binom{N}{n}\binom{M}{n}$$

$\binom{N}{n}$ is a number of possibilites to choose n atoms from lattice and
$\binom{M}{n}$ is number of possible rearrangements of these n atoms between interstitial sites.

Thus partition function gets form:

$$Z = \sum_{n=0}^{min(N,M)} g(E)e^{-\beta E} = \sum_{n=0}^{min(N,M)} \binom{N}{n}\binom{M}{n} e^{-\beta n\omega} \tag{1}$$

(b) We are going to calculate dominant term in the sum (1). In oder to find it we differentiate expression under the sum by n, but first we rearange it a little:

$$\binom{N}{n}\binom{M}{n} e^{-\beta n\omega} = e^{-\beta n\omega + ln\binom{N}{n} + ln\binom{M}{n}} \approx$$

$$\approx e^{-\beta n\omega + NlnN - MlnM - 2nln(n) - (N-n)ln(N-n) - (M-n)ln(M-n)} \tag{2}$$

Here following relations have been used:

$\binom{N}{n} = \frac{N!}{n!(N-n)!}$

$lnN! \approx NlnN \quad (Stirling's\ approximation)$

We differentiate by n and equate to 0, after a little bit algebra we have:

$$\frac{n^2}{(N-n)(M-n)} = e^{-\beta\omega} \tag{3}$$

We have requested to approximate for $x \ll 1$, therefore

$$x \ll 1 \ \Rightarrow \ e^{-\omega/T} \ll 1 \ \Rightarrow \ \frac{n}{(N-n)} \frac{n}{(M-n)} \ll 1 \tag{4}$$

It is given then M is of order N, consequently:

$$\frac{n}{(N-n)} \ll 1 \; and \; \frac{n}{(M-n)} \ll 1$$

$$n \ll N - n \; and \; n \ll M - n$$

And, finally, we get following condition:

$$n \ll N \; and \; n \ll M \tag{5}$$

We use previous result (3) and the fact, that for small x equality $\frac{1}{1-x} \approx 1 + x$ holds to evaluate:

$$\frac{n^2}{(N-n)(M-n)} = \frac{\frac{n^2}{NM}}{(1-\frac{n}{N})(1-\frac{n}{M})} = \frac{n^2}{NM}(1+\frac{n}{N})(1+\frac{n}{M}) = \frac{n^2}{NM} + O(\frac{n}{N^3}) + O(\frac{n}{M^3})$$

And we have:

$$\frac{n^2}{NM} \approx e^{-\beta\omega} \ \Rightarrow \ n_{max} = \sqrt{NM} e^{-\frac{\beta\omega}{2}} \tag{6}$$

(c) We evaluate following relations by using (5) and the fact, that for small x equality $\ln(1+x) \approx x$ is true:

$$ln(N-n) = lnN + ln(1-\frac{n}{N}) \approx lnN - \frac{n}{N} \tag{7}$$

$$ln(M-n) \approx lnN - \frac{n}{M} \tag{8}$$

and we rearrange (2) a little in view of (7) and (8):

$$\binom{N}{n}\binom{M}{n} e^{-\beta n\omega} \approx e^{-\beta n\omega + NlnN - MlnM - 2nln(n) - (N-n)ln(N-n) - (M-n)ln(M-n)} \approx$$

$$\approx e^{-2nln(n) + 2n + nlnNM - \frac{n^2}{N} - \frac{n^2}{M} - \beta\omega n} \tag{9}$$

Thus, in order to calculate partition function we need to evaluate following sum:

$$\sum_{n=0}^{min(N,M)} e^{-2nln(n)+2n+nlnNM-\frac{n^2}{N}-\frac{n^2}{M}-\beta\omega n} = \sum_{n=0}^{min(N,M)} e^{-f(n)}$$

Where $f(n) \equiv 2nln(n) - 2n - nlnNM + \frac{n^2}{N} + \frac{n^2}{M} + \beta\omega n$

In order to evaluate the sum we change summation by integration:

$$\sum_{n=0}^{min(N,M)} e^{-f(n)} \approx \int_0^{min(N,M)} e^{-f(n)} \, dn \tag{10}$$

and use steepest descent method. We expand $f(n)$ by Teylor series about $n = n_{max}$ to second order:

$$f(n) \approx f(n_{max}) + \frac{1}{2}f''(n_{max})(n - n_{max})^2 \tag{11}$$

We rewrite (10) in view of (11):

$$Z = \int_{-\infty}^{\infty} e^{-f(n_{max})-\frac{1}{2}f(n_{max})(n-n_{max})^2}\, dn = e^{-f(n_{max})} \int_{-\infty}^{\infty} e^{-\frac{1}{2}f''(n_{max})(n-n_{max})^2}$$

We may choose limits of integration to be $\pm\infty$, because only terms about $n = n_{max}$ are significant.

Finally using Gaussian integral ($\int_{-\infty}^{\infty} e^{-\frac{(x-a)^2}{c^2}}\, dx = c\sqrt{\pi}$) we have:

$$Z = e^{-f(n_{max})}\sqrt{\frac{2\pi}{f''(n_{max})}} \tag{12}$$

Let us calculate $f(n_{max})$ and $f''(n_{max})$:

$$f(n_{max}) = -2n_{max} + \frac{n_{max}^2}{M} + \frac{n_{max}^2}{N} \tag{13}$$

$$f''(n_{max}) = \frac{2}{n_{max}} + \frac{2}{M} + \frac{2}{N} \tag{14}$$

$$Z = e^{2n_{max}-\frac{n_{max}^2}{M}-\frac{n_{max}^2}{N}}\sqrt{\frac{2\pi}{\frac{2}{n_{max}} + \frac{2}{M} + \frac{2}{N}}} \approx \sqrt{\pi n_{max}}e^{2n_{max}} \tag{15}$$

Here we have used (5) again.

(d) Entropy of perfect lattice is 0, because there is only one possible state, therefore all entropy in "defected" lattice is caused by difects existance.

In order to calculate the entropy at first we calculate Helmholtz free energy
we use (15):

$$F = -T ln Z \approx -T\left(ln\sqrt{\pi} + \frac{1}{2}ln(n_{max}) + 2n_{max}\right) \tag{16}$$

Thus we can calculate the entropy (when the dependence of n_{max} on T is taken into account):

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = ln\sqrt{\pi} + \frac{1}{2}ln\sqrt{NM} + n_{max}\left(2 + \frac{\omega}{T}\right) \tag{17}$$

And we can calculate a specific heat:

$$C_V = T(\frac{\partial S}{\partial T})_{N,V} = \frac{1}{2}\sqrt{NM}(\frac{\omega}{T})^2 e^{-\omega/2T} = \frac{n_{max}}{2}\left(\frac{\omega}{T}\right)^2 \tag{18}$$