May 2005 Preliminary Exam, Statistical Mechanics 2

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Problem (Defects in a Cubic Crystal):

A cubic crystal contains N atoms. The atoms can exist at lattice sites or an atom may find itself displaced from its normal site into the center of one of the 8 adjacent unit cells as suggested by the figure. When an atom is displaced, its energy is increased by $\epsilon > 0$ over its energy at the normal lattice site. Suppose that the crystal is in equilibrium at temperature T. Assume $k_B T \ll \epsilon$ so the chance that two displaced atoms try to occupy the same cell is negligible. Calculate the partition function, the entropy, the energy (relative to the energy the crystal would have if all atoms were at their normal sites), and the number of atoms in displaced sites.

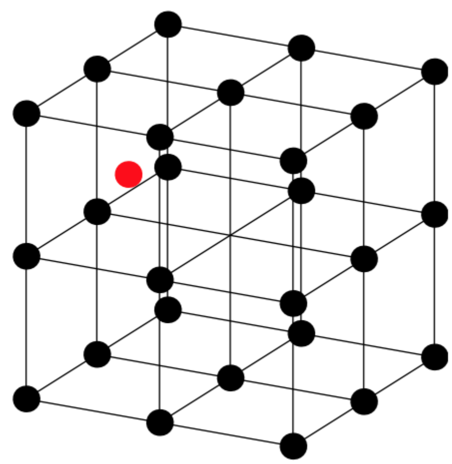

Figure 1: *Figure from M05T.2*

Solution:

For a single atom, there are 9 states: one where the atom is on its normal lattice site, and eight where the atom is displaced in one of the displaced body-centered positions. Therefore, for a single atom, the partition function is as follows:

$$Z_1 = \sum_i e^{-\beta\epsilon_i} = 1 + 8e^{-\beta\epsilon} \tag{1}$$

Each atom is identical, but distinguishable from the others because they all have distinct normal lattice sites. Therefore,

$$Z = Z_1^N = (1 + 8e^{-\beta\epsilon})^N \tag{2}$$

We can immediately use this result to get the free energy F of the system, which will help us find the entropy, as follows:

$$F = -\tau \log(Z) = -N\tau \log(Z_1) = -\frac{N}{\beta} \log\left(1 + 8e^{-\beta\epsilon}\right) \tag{3}$$

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N\left[\log\left(1+8e^{-\beta\epsilon}\right) + \tau\frac{8\beta^2\epsilon e^{-\beta\epsilon}}{1+8e^{-\beta\epsilon}}\right] = N\left[\log\left(1+8e^{-\beta\epsilon}\right) + \frac{8\beta\epsilon}{e^{\beta\epsilon}+8}\right] \tag{4}$$

σ goes to zero at low temperatures (perfect crystal) and $N\log(9)$ at high temperatures (9^N "equivalent" microstates), which makes sense. The energy of the system can also be derived from the partition function, as follows:

$$U = -\frac{\partial \log(Z)}{\partial \beta} = -N\frac{\partial \log(Z_1)}{\partial \beta} = -N\frac{-8\epsilon e^{-\beta\epsilon}}{1+8e^{-\beta\epsilon}} = \frac{8N\epsilon}{e^{\beta\epsilon}+8} \tag{5}$$

U goes to zero at low temperatures (no excitations) and $\frac{8}{9}N\epsilon$ at high temperatures (randomly on site or displaced), which makes sense.

Finally, we need the average number of atoms displaced. Each atom's state is independent from every other atom's state, so the average number of displaced atoms is N times the probability an atom is displaced:

$$\langle N\rangle = N\langle 1\rangle = N\frac{8e^{-\beta\epsilon}}{1+8e^{-\beta\epsilon}} = \frac{8N}{e^{\beta\epsilon}+8} \tag{6}$$

$\langle N\rangle$ goes to zero at low temperatures (no excitations) and $\frac{8}{9}N$ at high temperatures (randomly on site or displaced), which again makes sense.