A vacancy problem...

Problem:

A perfect atomic crystal has exactly one atom at each lattice site. Such a configuration is only stable at zero temperature.

At any finite temperature, due to the thermal fluctuations, various types of crystal imperfections develop. One of the simplest, called a vacancy, is an empty lattice point.

In this example we want to determine the temperature dependence of the density of vacancies. For this, we take the energy of the perfect crystal as zero and assume that the energy of the crystal with n vacancies is $n\varepsilon$.

We assume : $\underbrace{n \ll N}_{\frac{n}{N} \ll 1}$ (N: number of atoms $\underbrace{\text{in crystal}}_{\text{3D structure}}$).

N_s: number of sites on the surface of the perfect crystal $\rightsquigarrow$ perfect crystal $\rightsquigarrow$ 3D

surface $\rightsquigarrow$ 2D

N: total number of atoms in crystal

$\frac{N_s}{N} \ll 1$; $\frac{n}{N} \ll 1$; moreover : $\frac{n}{N} \gg \frac{N_s}{N}$

Goal: Calculate $\frac{n}{N}$ as a fct. of T.

Solution :

To think about this problem, let us start with a perfect crystal, i.e., N particles filling N sites (we are essentially considering the T=0 limit). Now, let us start to heat the system up.

At finite T, some particle ~~located~~ near the surface may move to surface, leaving behind a vacancy. The vacancy (or vacancies) can then move through the lattice.

Because, by our assumption, $n > N_s$, the surface thickness has to grow, i.e., new surface layers have to be created.

"New" imperfect crystal: $\underbrace{N \text{ occupied sites and } n \text{ vacancies}}_{\text{total of } N+n \text{ sites}}$.

means "finite T"

What is the number of possible configurations?

$$T = \frac{(N+n)!}{N!\,n!}$$

$$\Rightarrow S \underset{\text{def.}}{=} k \log T \underset{\text{Stirling}}{\approx} k\left[(N+n)\log(N+n) - N\log N - n\log n\right]$$

We also know : $E = \varepsilon n$

$$\text{and } T^{-1} = \frac{\partial S}{\partial E}$$

$$\text{Rewrite } T^{-1} = \frac{1}{\varepsilon}\frac{\partial S}{\partial n}$$

$$\Rightarrow \frac{\varepsilon}{kT} = \frac{1}{k}\frac{\partial S}{\partial n} = \log(N+n) - \log n = \log\frac{N+n}{n}$$

Rearrange: $$\frac{N+n}{n} = e^{\varepsilon/kT}$$

$$\Rightarrow \frac{n}{N} = \frac{1}{e^{\varepsilon/kT} - 1} \underset{\text{low } T}{\approx} e^{-\varepsilon/kT}$$

we demanded $\frac{n}{N} \ll 1$

$\Rightarrow e^{\varepsilon/kT} \gg 1$