MASSACHUSETTS INSTITUTE OF TECHNOLOGY

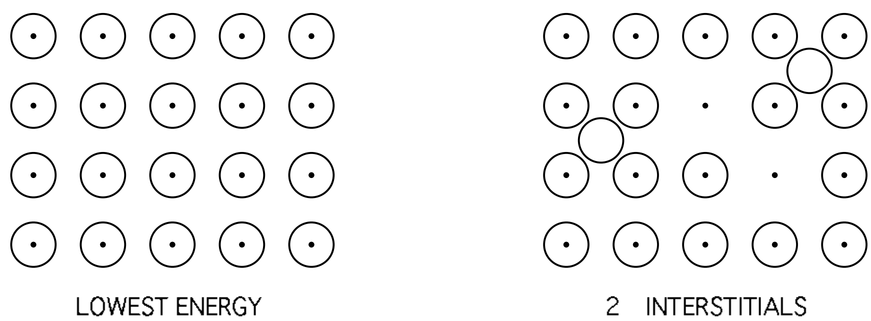
Physics Department

8.044 Statistical Physics I — Spring Term 2013

Interstitial Atoms

An Example Using the Microcanonical Ensemble

Consider a monatomic crystal which, in its lowest energy configuration, has N atoms located on N lattice sites. Higher energy configurations are possible in which some of the atoms are displaced to interstitial sites somewhere between the lattice sites.



Model

N total atoms
N lattice sites
M interstitial sites, all identical ($M \sim N$)
n atoms in interstitial sites
ϵ excess energy of atom when in interstitial site

This model assumes that every interstitial atom has the same excess energy. Physically, this will only be true if all the interstitial sites are identical. In a perfect 3-dimensional lattice there are usually several *geometrically* different interstitial lattice positions. Neglecting these geometrical differences, there will still be differences based on *occupation* effects. The energy of an atom in a given interstitial site will depend on whether the adjacent lattice sites are occupied or vacant, and on whether neighboring interstitial sites are occupied or vacant. Of course, the smaller the ratio of n to N, the smaller the chance that a lattice site will be vacant or a interstitial site occupied. Thus the model we have chosen is one that works best when $n << N$ or M, and we will use this limit to simplify some of our results.

Problem Find the number of atoms in interstitial sites as a function of temperature, $n(T)$.

Finding the Entropy First find the number of different possible configurations Ω consistent with the stipulation that the energy of the system (the excess energy above that of the ground state) is E. Note that in our model $E = \epsilon n$, so there is a one to one correspondence between E and n. Either can be used as the independent variable which specifies the macroscopic state of the system. Ω is the product of the number of ways of choosing the $N - n$ vacant lattice sites and the number of ways of choosing the n occupied interstitial sites.

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

The expression for the entropy follows from its definition in terms of Ω and some algebra.

$$\begin{aligned} S &= k \ln \Omega \\ &= k[N \ln N - n \ln n - (N-n)\ln(N-n) + M \ln M - n \ln n - (M-n)\ln(M-n) \\ &\quad \underbrace{-N + n + (N-n) - M + n + (M-n)}_{0}] \end{aligned}$$

The Temperature To find the temperature we need to take the derivative $(\partial S/\partial E)_N$ but there is no need to rewrite S in terms of E first. Rather, we use our known dependence of n on E in a simpler way.

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S}{\partial n}\right)_N \left(\frac{\partial n}{\partial E}\right)_N = \left(\frac{\partial S}{\partial n}\right)_N \frac{1}{\epsilon} \\ &= \frac{k}{\epsilon} \frac{\partial}{\partial n}[\cdots \text{from above} \cdots]_N \\ &= \frac{k}{\epsilon}\left(-1 - \ln n + 1 + \ln(N-n) - 1 - \ln n + 1 + \ln(M-n)\right) \\ &= -\frac{k}{\epsilon}\left(2 \ln n - \ln(N-n) - \ln(M-n)\right) \end{aligned}$$

Equation of State Now all one needs to do is invert the previous equation to obtain $n(T)$.

$$\begin{aligned} -\frac{\epsilon}{kT} &= 2\ln n - \ln(N-n) - \ln(M-n) \\ \exp[-\epsilon/kT] &= \frac{n^2}{(N-n)(M-n)} \approx \frac{n^2}{NM} \quad \text{since} \quad n << N, M \\ n(T) &\approx \sqrt{NM}\exp[-\epsilon/2kT] \end{aligned}$$

Note that n

1) decreases exponentially with ϵ,
2) increases exponentially with T,
3) at fixed ϵ and T, increases with increasing M.

The first two items are not hard to understand physically. The last can be interpreted as follows. The increasing phase space available to the atoms due to increasing M draws the atoms off of their lattice sites even when ϵ and T are fixed. In short, this is an entropy effect.

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