

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.

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

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

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

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.