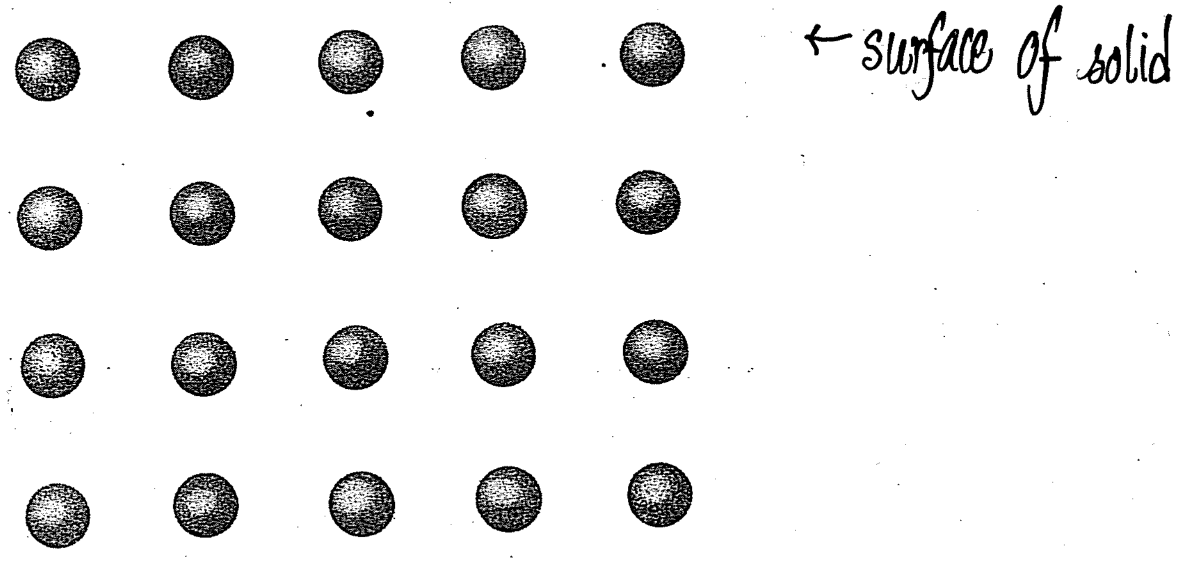
Appendix A: The Schottky Defect in Solids

T=0 Atoms in a solid form a regular array

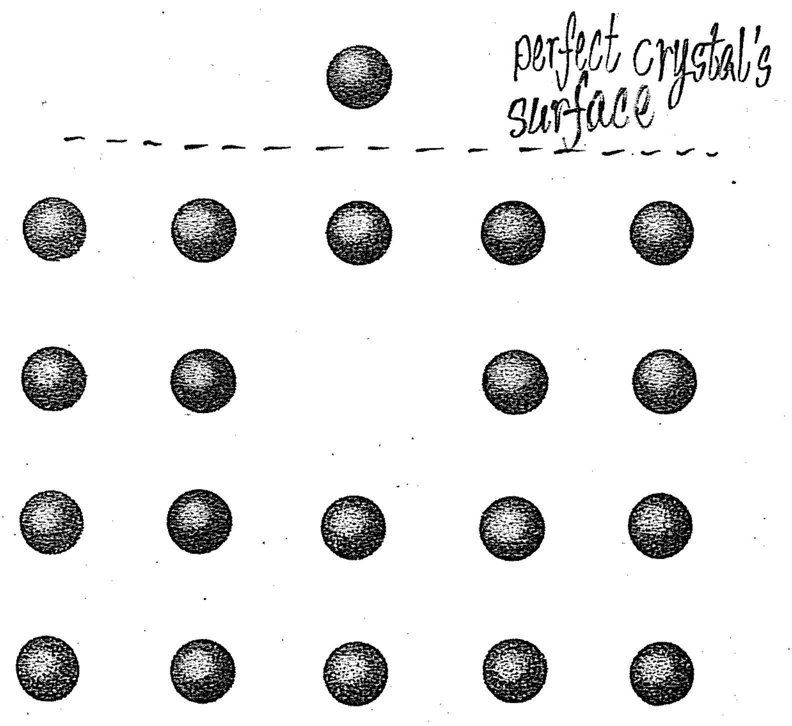


T≠0 Many things could happen!

[vibrations, atoms moved to intersitial sites, etc.]

Schottky Defects: (1935)

- Atoms displaced from lattice sites
  ⇒ create vacancies (empty sites)
  and atoms migrate to surface of crystal
  ["point defects"]



1 Schottky defect

T = 0K, no defects or n = # Schottky defects = 0

T≠0, what is $n(T)$?

- We use the microcanonical approach

Physics: Inside crystal, atoms are of lower energy due to chemical bondings

ε = energy to create a Schottky defect [~1 eV]

N = # atoms in system

n = # Schottky defects

Assume $n \ll N$ (the answer justifies this assumption) (usually the case)

$\therefore E = n\varepsilon$ (macrostate described by $(E(n), N, V)$)

(i) Count microstates

- Move n out of N atoms to surface sites

$$W = W(E(n),N) = {}_N C_n = \frac{N!}{n!\,(N-n)!}$$

(ii) Boltzmann

$$S(E(n),N) = k \ln W = k \ln\left(\frac{N!}{n!\,(N-n)!}\right)$$

(iii)
$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{dS(n)}{dn}\overbrace{\frac{dn}{dE}}^{\frac{dE}{dn}=\varepsilon} = \frac{1}{\varepsilon}\frac{dS(n)}{dn}$$

$$S(n) = k[\underbrace{\ln N!} - \underbrace{\ln n!} - \underbrace{\ln (N-n)!}]$$

Stirling's formula

$$= k[N\ln N - n\ln n - (N-n)\ln(N-n)]$$

$$\therefore \frac{dS(n)}{dn} = k[-\ln n + \ln(N-n)]$$

$$\boxed{\frac{1}{T} = \frac{k}{\varepsilon}\ln\frac{N-n}{n}}$$

Conceptually: this expresses temp. T of a crystal in terms of n and N [microcanonal ensemble]

$$\boxed{\frac{n}{N} = \frac{1}{e^{\varepsilon/kT}+1}}$$

$$\underbrace{\varepsilon \sim 1}\text{eV}, \quad \overset{}{kT} \sim \frac{1}{40}\text{eV} \Rightarrow e^{\varepsilon/kT} \sim e^{40} >> 1$$

energy for creating a defect

room temp

$$\therefore \boxed{n = N e^{-\varepsilon/kT}}$$ hence $n \ll N$ is justified

This can be thought of as giving the defect concentration $\frac{n}{N}$ in a crystal which is in thermal equilibrium at temp. T [i.e., system in heat bath].

Remarks:

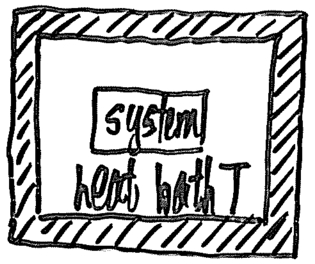
(a) $T \to 0$, $e^{-\varepsilon/kT} \to 0 \Rightarrow n = 0$ (0K) [no defects]

(b) $T \sim$ room temp $\Rightarrow \frac{n}{N} \approx 10^{-17}$ (a tiny fraction)
[but $N \sim 10^{22-23}/\text{cm}^3$ for solids]

(c) $e^{-\varepsilon/kT}$ ("Boltzmann factor")
- appears often in statistical physics
- $\left\{\begin{array}{l}\varepsilon \sim \text{energy scale of the problem}\\ kT \sim \text{thermal energy}\end{array}\right.$

stat. phy. ⇒ competition between two energies

(d) can get the same result by considering



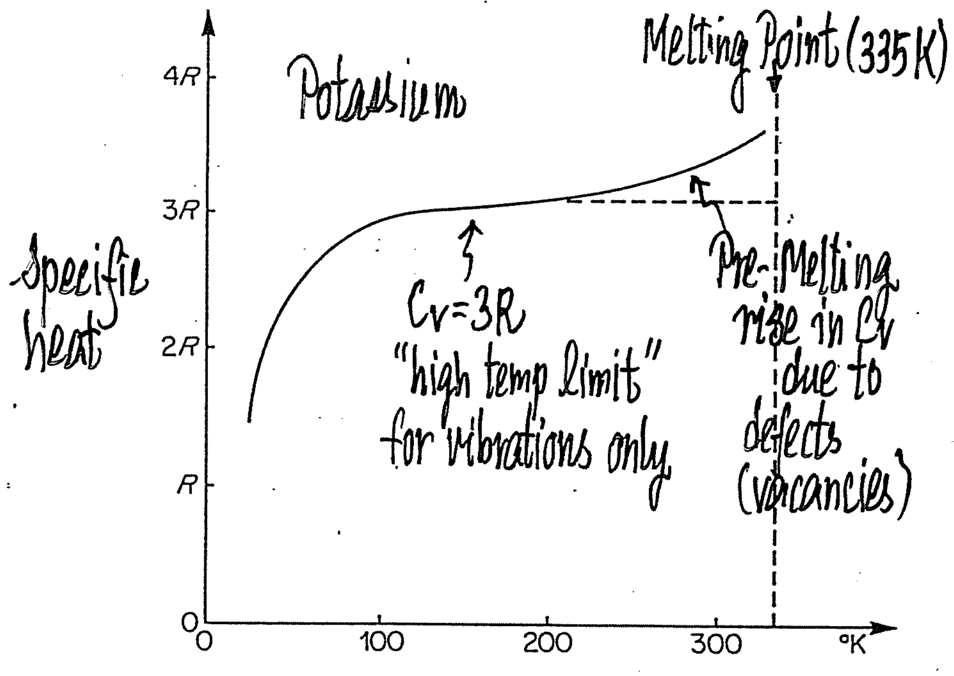
"canonical ensemble"
(Ch. V)

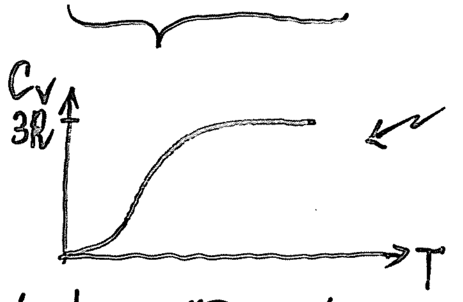
(e) These defects formation leads to experimentally observable features at temperatures where a solid is going to melt ("pre-melting phenomena"), e.g. a rise in heat capacity before reaching the melting temperature.

Experimentally observable effects : Pre-melting behavior

- T=0 perfect crystal
- T≠0 (low temp.) $\underbrace{\text{vibrations of atoms about equil. positions}}_{\text{Contribute to } C_V \text{ (Einstein, Debye)}}$
- higher T (T ≲ Melting Point)

  $\underbrace{\text{vibrations}}_{\text{even for } T \approx \text{ melting pt, amplitude} \approx 10\% \text{ of lattice spacing}} + \underbrace{\overset{\text{very important in understanding materials}}{\text{Creating Vacancies}}}_{\boxed{\text{help understand what melting is!}}}$



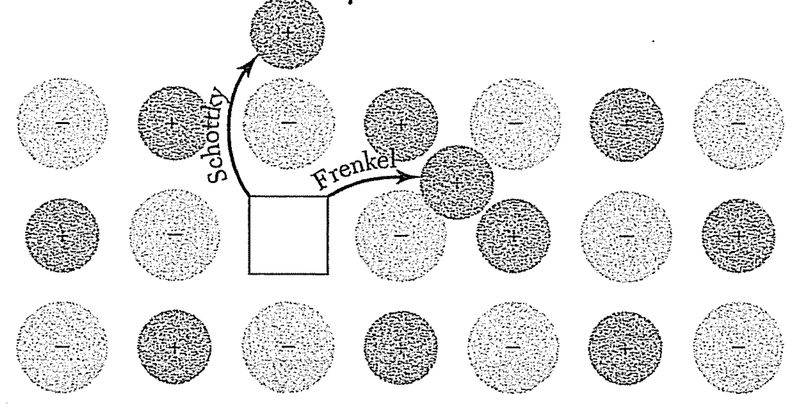


← Cv of solids due to atomic vibrations only (Einstein/Debye)

[See Flowers and Mendoza, "Properties of Matter"]

Defects are an important topic in Solid State Physics

Schottky defect



Frenkel Defect
Atom/Ion moves into interstitial sites

ionic crystal

[Picture taken from Kittel, "Introduction to Solid State Physics"]

$$n \approx \sqrt{\underset{\#\text{ ions}}{N}\;\underset{\#\text{ interstitial sites}}{N'}}\; e^{-\varepsilon/2kT}$$

ε = energy to move an atom to interstitial site

- Also, often a pair of +ion & −ion will be vacated in ionic crystals.

$$\underset{\#\text{ pairs of vacanies created}}{n} \approx N e^{-\varepsilon/2kT}$$

ε = energy of formation of a pair

- Diffusion of impurities in metal : $\overset{\text{diffusion coefficient}}{D} = D_0 e^{-\varepsilon/kT}$

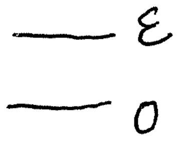
Same Math Form: kT (thermal energy) vs $\varepsilon\ \underbrace{(\text{energy scale set by physical process})}_{\text{an energy barrier}}$

Statistical Physics: $e^{-\varepsilon/kT}$

Important Remarks

- This defect problem is an example of a big class of problems — "Two-level" systems
- Each atom: stays in position [energy 0]
  excited to surface [energy ε]

Schematically,



} possible single-atom (single-particle) states

- From the general result (see p. IV-(A3))

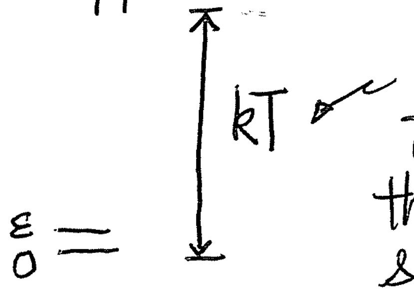
$$\frac{n}{N} = \frac{1}{e^{\varepsilon/kT}+1}$$

formally, the high-temperature limit is

$$\frac{n}{N} \to \frac{1}{2} \Rightarrow$$ temperature alone can at most excite half of the atoms!

Important physical sense!

[Don't ever think that temperature can put all particles to the upper state in a 2-level system!]



for kT >> ε, the two states look the same on the scale of kT!

- "Two-level" systems are just a representative of systems with particles having a bounded single-particle energy spectrum

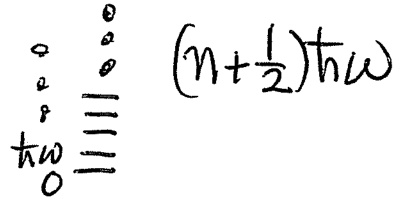
e.g.

etc.

e.g. magnetic moment in $\vec{B}$-field (Zeeman effect)

- Behavior very different from systems in which the single-particle energy spectrum is unbounded,

e.g. harmonic oscillator



and Ideal Gas