Lecture 16

Equilibrium and Chemical Potential

- Free Energy and Chemical Potential
- Simple defects in solids

Reference for this Lecture:
Elements Ch 11

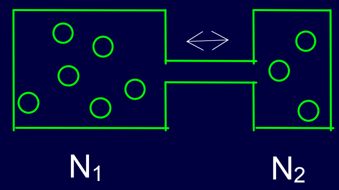
Reference for Lecture 17:
Elements Ch 12

Free Energy, Equilibrium and Chemical Potential

Last time: Free energy $F_{sys} = U_{sys} - T_{reservoir}S_{sys}$

This is the maximum available work we can get from a system that is connected to a reservoir (environment) at temperature $T_{reservoir}$.

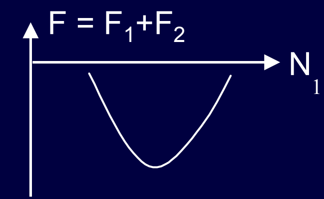
Equilibrium corresponds to maximum $S_{tot} = S_{reservoir} + S_{small\ system}$.
When we calculate ΔS, we only need to know the temperature of the reservoir. In minimizing F (equivalent to maximizing S_{tot}) we don't have to deal explicitly with $S_{reservoir}$.



Consider exchange of material (particles) between two containers. These are two small systems in equilibrium with a reservoir (not shown) at temperature T. In equilibrium, $dF/dN_1 = 0$:

$$\frac{dF}{dN_1} = \frac{dF_1}{dN_1} + \frac{dF_2}{dN_1} = \frac{dF_1}{dN_1} - \frac{dF_2}{dN_2} = 0$$

$$\frac{dF_1}{dN_1} = \frac{dF_2}{dN_2}$$



The derivative of free energy with respect to particle number is so important that we define a special name and symbol for it:

$$\mu_i \equiv \frac{dF_i}{dN_i}$$

The chemical potential of subsystem "i"

For two subsystems exchanging particles, the equilibrium condition is: $\mu_1 = \mu_2$

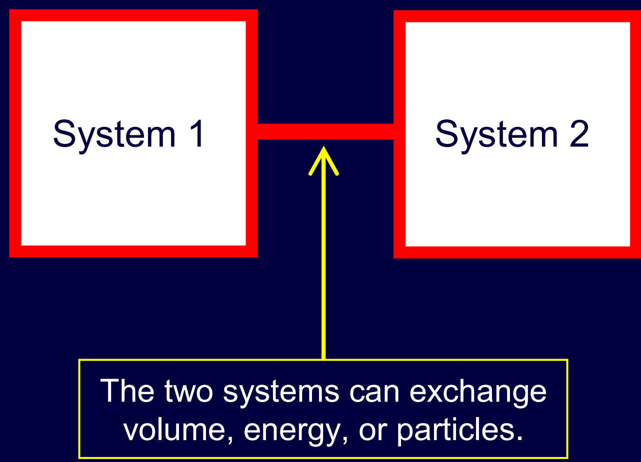
Maximum Total Entropy ⟶ Minimum Free Energy ⟶ Equal chemical potentials

Why Bother with Yet Another Definition?

Answer:
It makes the various equilibrium conditions look the same:

Exchange of:

- Volume: $\dfrac{d\sigma_1}{dV_1} = \dfrac{d\sigma_2}{dV_2}$ $\quad p_1 = p_2$
- Energy: $\dfrac{d\sigma_1}{dU_1} = \dfrac{d\sigma_2}{dU_2}$ $\quad T_1 = T_2$
- Particles: $\dfrac{dF_1}{dN_1} = \dfrac{dF_2}{dN_2}$ $\quad \mu_1 = \mu_2$



Why does the last equation use dF/dn, instead of $d\sigma/dN$? Remember that there is a thermal reservoir (not shown). When particles are exchanged, the reservoir's entropy might change. (It might gain or lose energy.) That's what F takes care of.

Equilibrium and Chemical Potential

Recall the situation when systems can exchange energy. The definition of temperature: 1/T = dS/dU (holding V and N fixed) tells us that temperatures are equal in thermal equilibrium. Otherwise we could increase S by exchanging some energy.

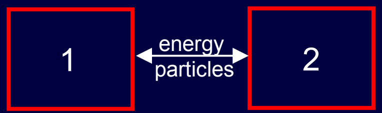
We also know what happens when the systems are out of equilibrium (unequal T). Because high T means a small derivative, energy flows from the hot system to the cold one.

Let's look at the situation when we have particle exchange.

From the definition of chemical potential, we have already seen that in thermal and particle equilibrium, the chemical potentials are equal: $\mu_1 = \mu_2$.

$$\mu \equiv \left.\frac{\partial F}{\partial N}\right|_{V,T}$$

Out of equilibrium ($\mu_1 > \mu_2$):
The larger μ system has a larger dF/dN, so particles flow from high μ to low μ.



Note that $d\mu/dN$ (= d^2F/dN^2) must be positive, or equilibrium isn't stable.

The Path Ahead...

Having considered thermal equilibrium when volume and energy exchanged,

now we'll consider systems in which particles can be exchanged (or "created").

Minimization of total free energy will allow us to understand a wide variety of different physical processes.

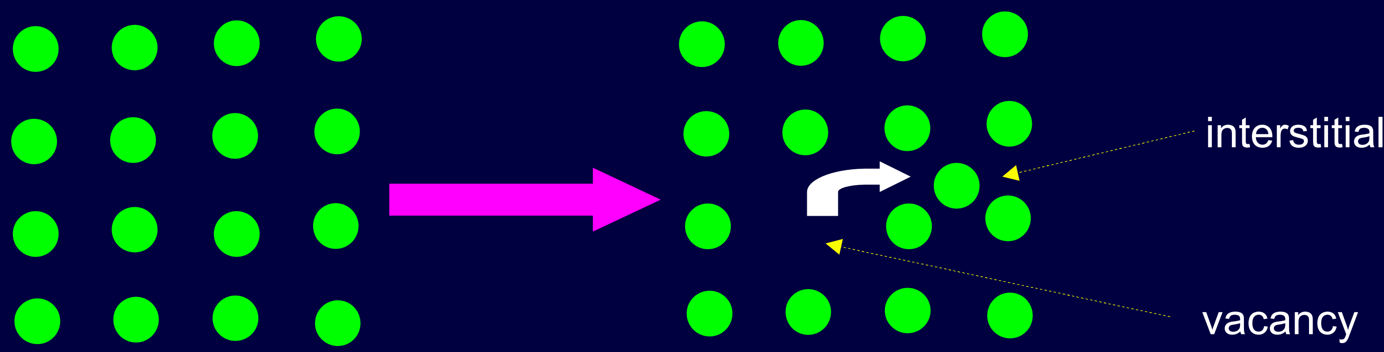
Some examples:

- Particles can move from place to place.
- Particles can combine into new types (*e.g.*, chemical reactions).
- This will lead to the concept of "chemical equilibrium".
- And lots and lots of applications...

Let's start with a concrete example.

F-minimum example:

Defects in Crystal Lattices



In a perfect crystal at low temperatures, the atoms are arranged on a lattice like the one shown at the left. Consider M atoms on lattice sites, where M is a very large number, about 10^{22} for a mm-sized crystal.

As the crystal is heated up the atoms jiggle around, and some atoms will jump to “interstitial” sites, leaving a “vacancy” behind.

There is an energy cost Δ to form each interstitial-vacancy pair (“I-V pair”) like the one shown above, i.e., there is an energy difference Δ between an I-V pair and a normally occupied site.

By minimizing the Free energy of N ‘I-V pairs’, we will calculate the average number of defects that form at a temperature T.

ACT 1

As we let the temperature of the solid $\rightarrow 0$,
what fraction of the atoms will sit at the interstitial sites?

a) none b) half c) all

Solution

As we let the temperature of the solid → 0,
what fraction of the atoms will sit at the interstitial sites?

a) none   b) half   c) all

Because it costs energy to create an interstitial-vacancy pair, at low temperature the decrease in F due to entropy gain (increasing the number of available sites) will be smaller than the increase in F due to the energy cost. Therefore, the free energy will be minimized by "staying at home".

$$F = U - TS$$

As $T \to 0$, the TS term becomes unimportant

Defects in Crystal Lattices (2)

Suppose we have M possible vacancy sites, and M possible interstitial sites (essentially one per atom).

We want to know N, the number of interstitial-vacancy pairs at temperature T.

We want to minimize F(N) as a function of N. Call F(0)=0 for convenience.

$$F(N) = U(N) - TS(N)$$

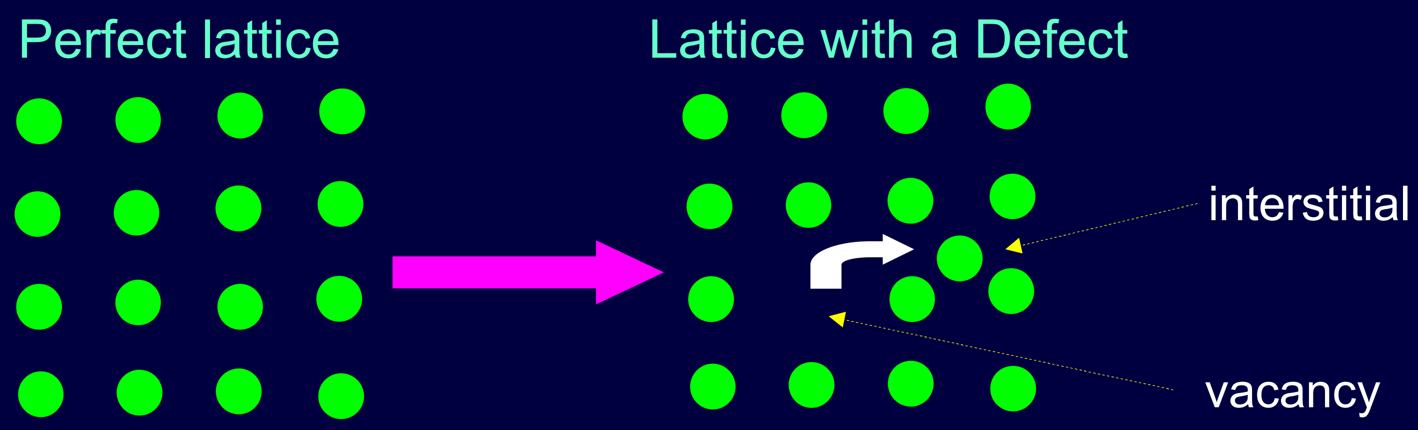
$$U(N) = N\,\Delta$$

Need energy Δ for each institial-vacancy pair

How to calculate S(N) ?

Assume the crystal's vibrational entropy is not much changed by making an interstitial. S is then due to the number of places each vacancy could be, and the number of places each interstitial could be.

Defects in Crystal Lattices (3)



Entropy of I-V pair: $S(N) = k \ln \Omega$

ways to put N identical particles in M cells = $M^N/N!$ (single occupancy, dilute limit)
But there is no correlation between the position of a vacancy and the position of an interstitial. Therefore, the total number of accessible states $\Omega = \Omega_I \Omega_V = (M^N/N!)^2$.

Entropy: $$S(N) = k \ln \Omega = k \ln \left(\frac{M^N}{N!} \right)^2 = 2k \left(N \ln M - \ln N! \right)$$ typo!

Free energy: $$F(N) = U(N) - TS(N) = N\Delta - 2kT \left(N \ln M - \ln N! \right)$$

In equilibrium: $$\frac{dF(N)}{dN} = 0$$

Stirling's Approximation

It will often be necessary to calculate d(ln N!)/dN.

We'll use a well known approximation for N!, known as Stirling's Approximation*:

$$\ln N! \approx N \ln N - N$$

Try some numbers:

N	ln N!	≈	N lnN	-	N		
10	15.1	≈	23.0	-	10	=	13.0
50	148.5	≈	195.6	-	50	=	145.6
1000	?	≈	6908	-	1000	=	5908

$$\frac{d(\ln N!)}{dN} \approx \frac{d}{dN}\left(N \ln N - N\right) = \ln N + \frac{N}{N} - 1 = \ln N$$

The derivative is only defined for large N.

*This is not Robert Stirling ("Stirling engine") but James Stirling, Scottish mathematician.

Defects in Crystal Lattices (4)

By minimizing the Free energy of N interstitial-vacancy pairs, we determine the average number of defects that form at temperature T:

(from a previous slide)

$$F(N) = U(N) - TS(N) = N\Delta - 2kT\left(N\ln M - \ln N!\right)$$

Minimize F:

$$\frac{dF}{dN} = \Delta - 2kT\ln M + 2kT\ln N = \Delta - 2kT(\ln\frac{M}{N}) = 0$$

Solve for the fraction N/M = # defects ÷ lattice sites:

$$2kT(\ln\frac{N}{M}) = -\Delta$$

$$\boxed{\frac{N}{M} = e^{-\Delta/2kT}}$$

This looks like a Boltzmann factor: an exponential temperature dependence.

$$\boxed{\frac{n}{n_c} = e^{-\Delta/2kT}}$$

with $n = \frac{N}{V} = \text{pair density}$, $n_c = \frac{M}{V} = \text{cell density}$

Notice the 2 in the Boltzmann factor. It came from squaring the ($M^N/N!$) number of positional states, because there are 2 movable objects, vacancy and interstitial.

As we predicted before, as T → 0 the fraction of interstitial-vacancy pairs is exponentially suppressed.

Act 2

We just saw the fraction of interstitial-vacancy pairs is given by $\frac{N}{M} = e^{-\frac{\Delta}{2kT}}$

1. Suppose the energy cost to create such a pair is 1 eV. If we want to keep the fraction of vacancies less than 1%, what is the maximum temperature $T_{1\%}$ we should heat the material to?

a) 100 °C b) 1000 °C c) 10,000 °C

2. Suppose that for some reason the vacancy and interstitial sites were always right next to each other. How would this 'safe' temperature $T_{1\%}$ change?

a) $T_{1\%}$ will decrease b) $T_{1\%}$ will increase c) $T_{1\%}$ will stay the same

Solution

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a) 100 °C   **b) 1000 °C**   c) 10,000 °C

$$e^{-\frac{\Delta}{2kT_{1\%}}} = 0.01 \Rightarrow \frac{\Delta}{2kT_{1\%}} = -\ln(0.01) = 4.6$$

$$\Rightarrow T_{1\%} = \frac{\Delta/2}{4.6k} = \frac{0.5\text{eV}}{4.6(8.6\times 10^{-5}\,\text{eV/K})} = 1264\text{ K}$$

Interpretation: As we raise the temperature higher, the material is literally coming apart.

2. Suppose that for some reason the vacancy and interstitial sites were always right next to each other. How would this 'safe' temperature $T_{1\%}$ change?

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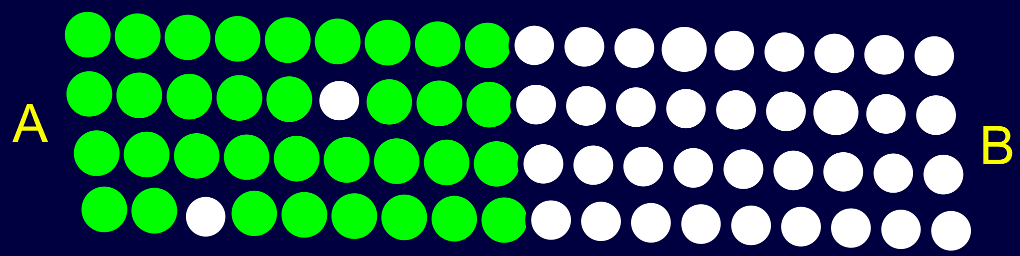
The 2 in the Boltzman factor came from the fact that the vacancy sites and interstitial locations were independent. If instead their locations are correlated, the allowable temperature will essentially double.

Related Example: Solid "Solutions"



Important for real devices
e.g., silicon-gold, tin-lead

In equilibrium, some A atoms are in the B crystal and vice versa.

Assume:

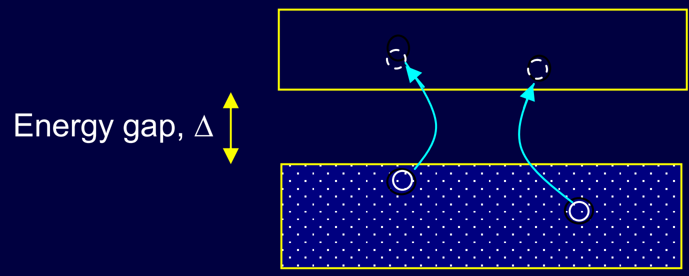
- There are M "A" sites, N of which are occupied by "B" atoms. N << M.
- The only entropy is due to site counting (ignore vibrations, *etc.*)
- The energy increase when a "B" goes to an "A" site is Δ.

Let's call the chemical potential of the B atoms in their own crystal 0, by choosing a convenient zero for energy. Then, in equilibrium, the chemical potential of the B's in A must also be zero:

$$\mu = 0 = \left.\frac{\partial F}{\partial N}\right|_{V,T} = \left.\frac{\partial U}{\partial N}\right|_{V,T} - T\left.\frac{\partial S}{\partial N}\right|_{V,T} = \Delta - kT\ln\left(\frac{M-N}{N}\right). \text{ So, if } N \ll M: \quad \frac{N}{M} = e^{-\Delta/kT}$$

$$S = k\ln\left(\frac{M!}{N!(M-N)!}\right)$$

Electrons in Semiconductors



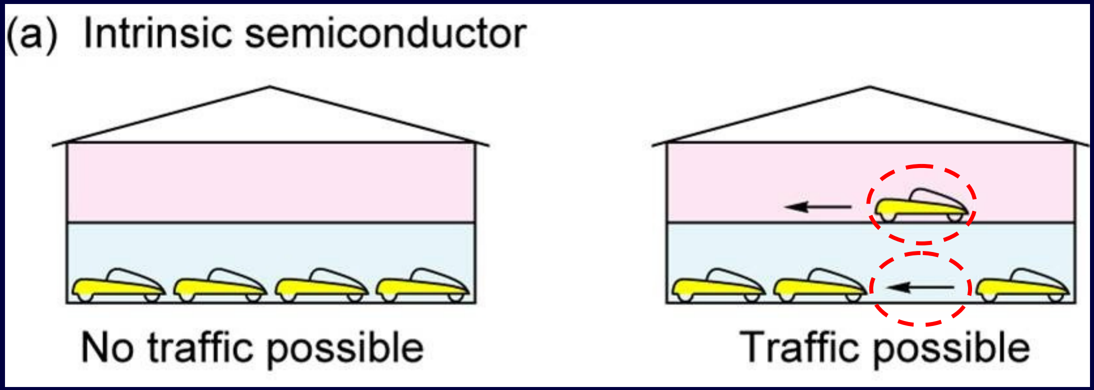
In many materials, electrons cannot have every conceivable energy. There is a low energy range (the "valence band") and a high energy range (the "conduction band"). A "gap" of disallowed energies separates them. (The reason for the gap is a Physics 214 topic.)

At T = 0, every valence band state is occupied. (S=0. Why?) At T ≠ 0, electrons are thermally excited from the valence band to the conduction band. How many determines the electrical conductivity.

The activated free electrons and the "holes" (unfilled states) left behind act as two ideal gases. We can compute the density of thermally excited electrons (and holes) by minimizing $F_{electron} + F_{hole}$.

We simplify the problem by assuming that excitation from valence to conduction band always requires the same energy, *i.e.*, every conduction state has energy Δ more than every valence state. This avoids having to do integrals.

Electrons in Semiconductors (2)



Conduction electron

Hole

This is Shockley's* cartoon of an intrinsic semiconductor. At T = 0, the cars (electrons) can't move. If some are raised to the upper level (the conduction band) then motion becomes possible.

The vacant spaces on the lower level are "holes". Motion of the cars on the lower level is more simply described by pretending that the holes are the objects that move.

An intrinsic semiconductor is one in which the number of electrons equals the number of valence band states, so that at T = 0 every state is filled, and no electrons are left over.

*John Bardeen, Walter Brattain, and William Shockley invented the transistor in 1947.

Next Time

Applications of free energy

- Semiconductors
- Law of atmospheres, revisited