Statistical physics

Classical stat. phys.
Maxwell – Boltzmann distribution

System of large number of particles
e.g. $1 cm^3$ gas in normal state $\sim 3 \cdot 10^{19}$ molecules
Description of motion of each particle ↓
Purpose: description of possible states of the system
and their respective probabilities

Statistical equilibrium

N particles $E_1, E_2 \ldots$ possible energy states of particles
(continuous or discreet)

In E_i state n_i particles

$N = \sum_i n_i$

$U = \sum_i n_i E_i$ full energy of the system

Assumption: interaction of the particles can be taken into account with an average potential $E_i \to E_i + E_{i\,ave}$ $(= E_i)$

Closed system: $U = \text{const}$, but due to the interaction (e.g. collision) of particles the individual particles change their states ⤳

$\{n_1, n_2, \ldots\} = \{n_i\}$ distribution changes

$\exists$ a distribution with highest probability

$\{n_i\}_p \equiv$ corresponds to the statistical equilibrium

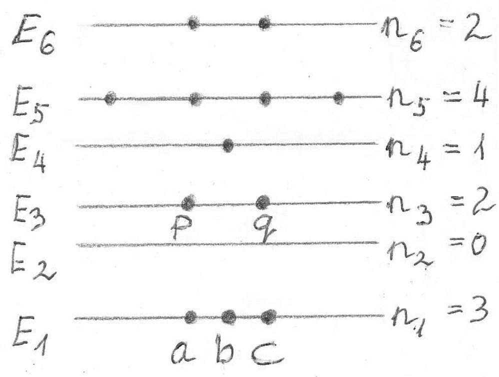
We search for $\{n_i\}_p \Rightarrow$ macroscopic quantities can be derived from it

n_i fluctuates around $\{n_i\}_p$ but this has no macroscopically observable effect.

Maxwell - Boltzmann distribution

System of identical and indistinguishable particles

first: assume distinguishability



Assumptions:

1. Probability of filling $\forall$ energy state is identical
2. Probability of an $\{n_i\}$ distribution is proportional to the number of its realization possibilities

("a" at E_1 "p" at E_3 is different from "a" at E_3 and "p" at E_1 due to distinguishability of the particles)

From the N particles we can select n_1 particles to the E_1 state in

$$\binom{N}{n_1} = \frac{N!}{n_1!\,(N-n_1)!} \quad \text{ways (number of combinations)}$$

After this we can select n_2 particles from $(N-n_1)$ to the E_2 state

$$\binom{N-n_1}{n_2} \quad \text{ways}$$

So for $\forall E_i$ an $\{n_i\}$ configuration can be selected in

$$P = \frac{N!}{n_1!\,(N-n_1)!} \cdot \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \cdot \ldots = \frac{N!}{n_1!\,n_2!\,n_3!\ldots}$$

ways.

According to 2. P = probability of the $\{n_i\}$ distribution

When assumpt. 1. $\forall$ i probability of getting to E_i is g_i

(g_i = degree of degeneracy of E_i)

$$P = \frac{N!\, g_1^{n_1} g_2^{n_2} \cdot g_3^{n_3} \cdot}{n_1!\,n_2!\ldots} = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

– Now when the particles are indistinguishable

$\rightsquigarrow$ $N!$ permutation gives the same distribution

$$P = \frac{g_1^{n_1} g_2^{n_2} \ldots}{n_1!\,n_2!\ldots} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

The most probable distribution (stat. equilibr.)

P_{max} $(dP=0)$ additional conditions: $\sum_i dn_i = 0$

(U and N are constant) $\sum_i E_i dn_i = 0$

$n_i = g_i e^{-\alpha - \beta E_i}$

Def.: partition function $Z = \sum_i g_i e^{-\beta E_i}$ $N = \sum_i n_i = e^{-\alpha} \underbrace{\sum_i g_i e^{-\beta E_i}}_{Z}$

$e^{-\alpha} = \frac{N}{Z} \rightsquigarrow$ $\underline{n_i = \frac{N}{Z} g_i e^{-\beta E_i}}$ Maxwell-Boltzmann distribution

Average of energy dependent physical quantities

$F_{ave} = \frac{1}{N} \sum_i n_i F(E_i) \overset{\text{in stat. equil.}}{=} \frac{1}{Z} \sum_i g_i F(E_i) e^{-\beta E_i}$

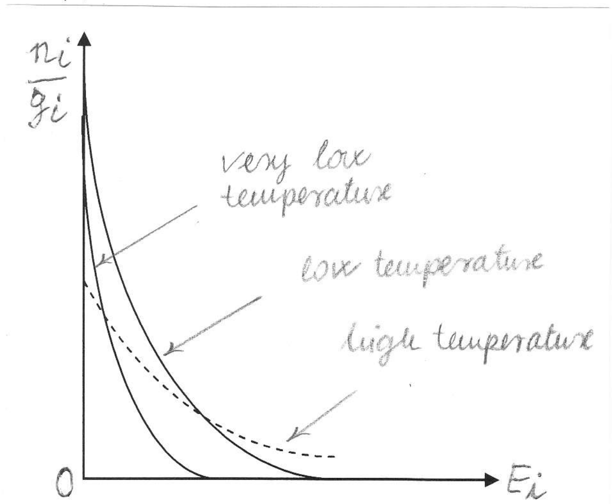
What is β?

Def. $\beta = \frac{1}{kT}$ $k = 1{,}38 \cdot 10^{-23}$ J/°K Boltzmann constant

T = temperature (°K)

$Z = \sum_i g_i e^{-\frac{E_i}{kT}}$

$n_i = \frac{N}{Z} g_i e^{-\frac{E_i}{kT}}$ $\longrightarrow$



The total energy is

$U = \frac{N}{Z} \sum_i g_i E_i e^{-\beta E_i} =$

$= \frac{N}{Z} \frac{d}{d\beta}\left(\sum_i g_i e^{-\beta E_i}\right) =$

$= -\frac{N}{Z} \frac{dZ}{d\beta} = -N \frac{d}{d\beta}(\ln Z)$ but $d\beta = -\frac{dT}{kT^2} \rightsquigarrow$

$U = k N T^2 \frac{d}{dT}(\ln Z)$.

Average energy of a particle $E_{ave} = kT^2 \frac{d}{dT} \ln Z$

$\rightsquigarrow$ the temperature of the system in statistical equilibrium depends on the average energy of the particles and on the structure of the system (Z)

E.g. population of the energy levels

$$E_j,\ E_i \quad \Delta E \qquad \frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-\frac{E_j-E_i}{kT}} = \frac{g_j}{g_i} e^{-\frac{\Delta E}{kT}}$$

Gas molecules in thermal equilibrium, n_j/n_i

	ΔE [eV]	100°K	300°K	1000°K
mol. rotational levels	10^{-4}	0,989	0,996	0,999
mol. vibration levels	$5\cdot10^{-2}$	$3\cdot10^{-3}$	$1,5\cdot10^{-1}$	$5,6\cdot10^{-1}$
electron excitation	3	$3\cdot10^{-164}$	$8\cdot10^{-49}$	$8\cdot10^{-16}$

E.g. ideal gas /one-atomic molecules, kinetic energy only/

$E_i = \frac{1}{2} m v_i^2$ not quantized $\quad Z = \int g(E)\, e^{-E/kT} dE$

$g(E)dE$ number of molecular states between E and $E+dE$ (different velocities)

We have seen at the potential box: $g(E) = \frac{4\pi V (2m^3)^{1/2}}{h^3} E^{1/2} \rightarrow$

$$Z = \frac{V(2\pi m kT)^{3/2}}{h^3} \rightsquigarrow \underline{E_{ave} = \frac{3}{2}kT}, \quad U = N\cdot E_{ave} = \frac{3}{2}kTN$$

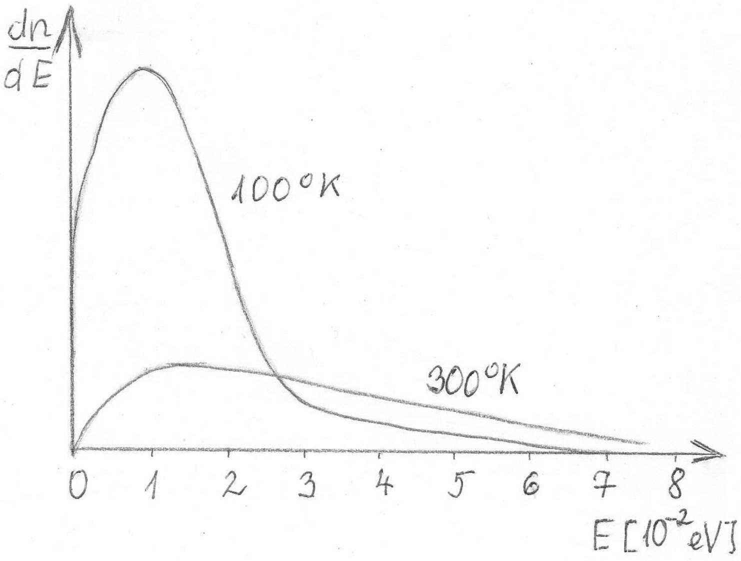
The distribution instead of n_i

$$dn = \frac{N}{Z} e^{-\frac{E}{kT}} g(E)\,dE$$

$$\frac{dn}{dE} = \frac{2\pi N}{(\pi kT)^{3/2}} E^{1/2} e^{-\frac{E}{kT}}$$

(independent of mass!)

Distribution by velocity



Maxwell - Boltzmann distribution: does not take into account limitations on the population of the E_i states. Restrictions of quantum mechanics

High temperatures and low densities:

V distribution - is equivalent with Maxwell-Boltzmann

Statistical physics II.

Quantum statistics

Fermi-Dirac & Bose-Einstein stat.

Electromagnetic radiation

E4

Quantum statistics

Restrictions on the number of particles that can occupy the same state with any given energy.

~> Distribution function changes.

Particles: identical and indistinguishable

2 cases

1. Exclusion principle ✓ ~> antisymmetric wavefunction
   → Fermi-Dirac stat. fermions

2. Exclusion principle ✗ ~> symmetric wavefunction
   → Bose-Einstein stat. bosons

We look for the distribution of statistical equilibrium (most probable distr.)

1. Fermi-Dirac distribution

Particles with half spin (e.g. electrons)

$g_i \equiv$ the number of different quantum states with E_i energy $\equiv$ maximum number of fermions that can have E_i energy without violation of the exclusion principle, i.e.:

$$n_i \le g_i$$

E.g. in a central force field $g_i = \sum_{l=0}^{n-1} 2(2l+1)$

→ When filling up the E_i states

1. particle g_i different states available

2. particle $g_i - 1$ — " — — " — — " —

For n_i particles there are

$$g_i(g_i-1)\ldots(g_i-n_i+1) = \frac{g_i!}{(g_i-n_i)!}$$

arrangements on the g_i states

But since the particles are indistinguishable the number of different distributions is

$$\frac{g_i!}{n_i!\,(g_i-n_i)!}$$

Number of realizations for $\forall$ levels:

$$P = \prod_i \frac{g_i!}{n_i!\,(g_i-n_i)!} \quad \text{for a } \{n_i\} \text{ distribution}$$

This is the probability of the $\{n_i\}$ distribution

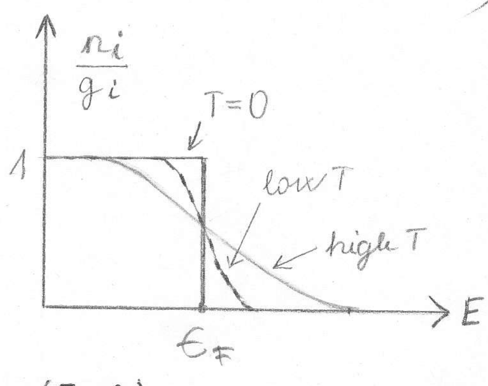
Most probable distribution (stat. equilibr.) $\rightarrow P_{max}$

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i}+1} \qquad \text{Fermi-Dirac distribution}$$

$\beta = \frac{1}{kT}$ $\quad \sum_i n_i = N \rightsquigarrow \alpha$

Def.: $\alpha = -\frac{\epsilon_F}{kT}$ $\quad \epsilon_F$ = Fermi energy (e.g. electrons in metals)

$$n_i = \frac{g_i}{e^{-(E_i-\epsilon_F)/kT}+1}$$



T=0: Due to the exclusion principle $\forall$ atoms are not in ground state but fill up all the energy levels up to $E=\epsilon_F$ $(n_i = g_i)$

$E > \epsilon_F$ empty $(n_i = 0)$

$$\lim_{T\to 0} e^{\frac{(E_i-\epsilon_F)}{kT}} = \begin{cases} 0 & E_i-\epsilon_F<0 \\ 1 & E_i-\epsilon_F>0 \end{cases}$$

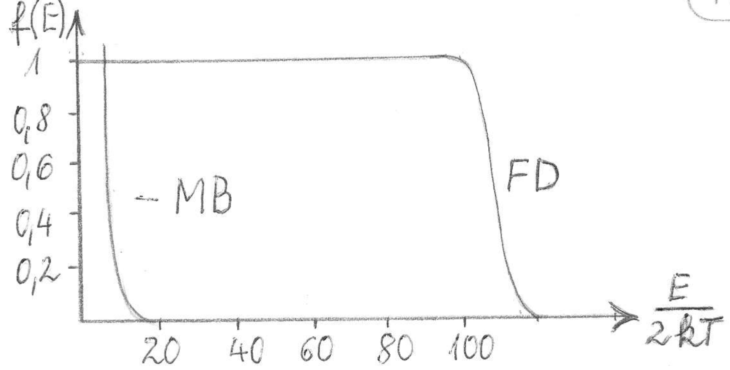
(For Maxw.-Boltzm. $\Rightarrow$ T=0 $\forall$ particles in ground state!)

T > 0 but $kT \ll \epsilon_F \rightsquigarrow$ Population of states near to ϵ_F changes only, due to the exclusion principle

$\Theta_F = \epsilon_F/k$ – Fermi temperature

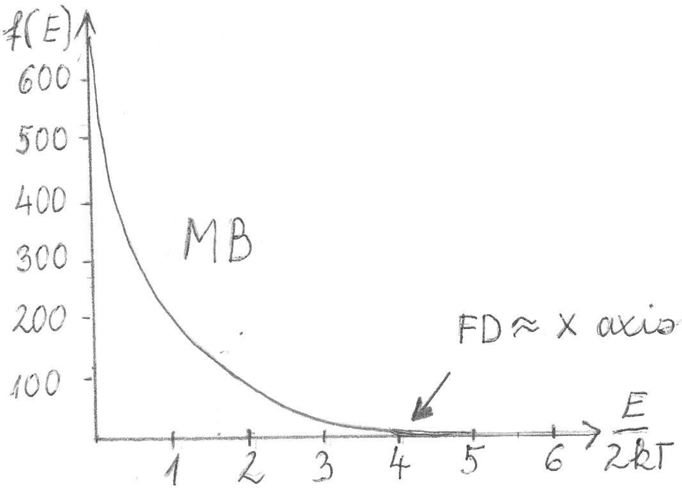
(electrons in metals $\Theta_F \approx 10^4\,{}^\circ K$)

Comparision of Maxwell-Boltzmann and Fermi-Dirac distribution at $T=10^{-2}\cdot\Theta_F$



$$f(E)=\frac{n_i}{g_i}(E)=$$

$$=\frac{1}{e^{\frac{(E-E_F)}{kT}}+1}$$



Total energy of N fermions at T≈0

$$U=\int E\,dN=\int E\frac{dn}{dE}dE=\int_0^{E_F}E\frac{dn}{dE}dE$$

$$T=0 \quad dn/dE=g(E)=\text{density of states}=\frac{8\pi V(2m^3)^{1/2}}{h^3}\cdot E^{1/2}$$

$$U=\frac{8\pi V(2m^3)^{1/2}}{h^3}\int_0^{E_F}E^{3/2}dE=\frac{16\pi V(2m^3)^{1/2}}{5h^3}E_F^{5/2}$$

For an ideal gas $U=\frac{3}{2}kNT$ $\quad T=0 \rightsquigarrow U=0$!

E.g. free electrons /conduction electrons/ in metals

No. of electrons between E and E+dE

$$dn=\frac{g(E)\,dE}{e^{(E-E_F)/kT}+1}=\frac{8\pi V(2m^3)^{1/2}}{h^3}\,\frac{E^{1/2}dE}{e^{(E-E_F)/kT}+1}$$

$$N=\int dn=\int_0^{E_F}\frac{dn}{dE}dE \rightsquigarrow .$$

$$! \; \underline{E_F=\frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}} \leftarrow$$

Depends on the electron density

$$U=\frac{3}{5}N\cdot E_F$$

E_F for metals tipically few eV