Physics of Electronics:

3. Collection of Particles in Gases and Solids

July – December 2008

Contents overview

- The hydrogen atom.
- The exclusion principle.
- Assemblies of classical particles.
- Collection of particles obeying the exclusion principle.

The Hydrogen Atom

- Electron in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - SE in polar coordinates:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2m}{\hbar^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)\Psi=0$$

  - Full solution by separation of variables assuming:

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\left\{\begin{array}{l} \dfrac{1}{R}\dfrac{d}{dr}\left(r^2\dfrac{dR}{dr}\right)-\dfrac{2mr^2}{\hbar^2}[V(r)-E]=l(l+1); \\[2ex] \dfrac{1}{\Theta}\left[\sin\theta\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right)\right]+l(l+1)\sin^2\theta=m^2; \\[2ex] \dfrac{1}{\Phi}\dfrac{d^2\Phi}{d\phi^2}=-m^2. \end{array}\right.$$

The Hydrogen Atom

- Electron in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  - Azimuth part:

$$\Phi(\phi) = e^{im\phi}.$$

  - Polar part:

$$\Theta(\theta) = A P_l^m(\cos\theta), \qquad m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l.$$

  - Radial part:

$$R_{nl}(r) = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho), \qquad l = 0, 1, 2, \ldots, n-1.$$

  - Total w.v. and energy:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_l^m(\theta, \phi), \quad E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots.$$

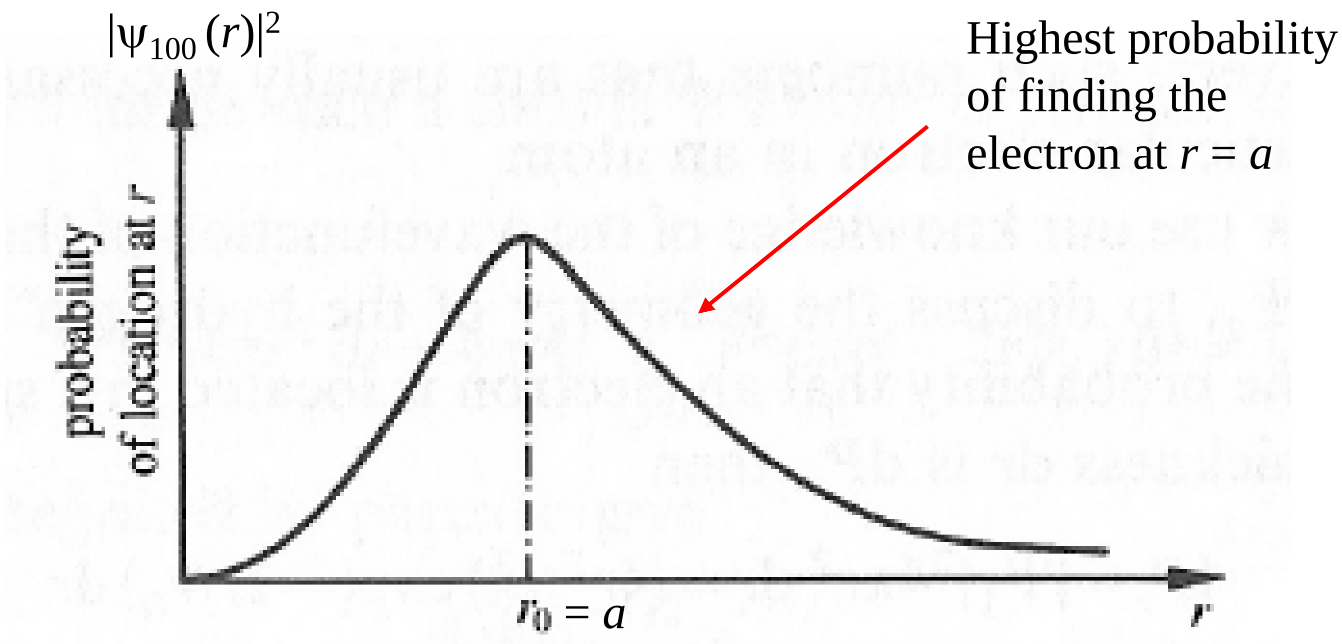
The Hydrogen Atom

- Electron moving in the electric field of the nucleus:

$$V = -e^2/(4\pi\epsilon_0 r)$$

  – The ground state (level with lowest energy) is:

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}.$$



Spin & Exclusion Principle

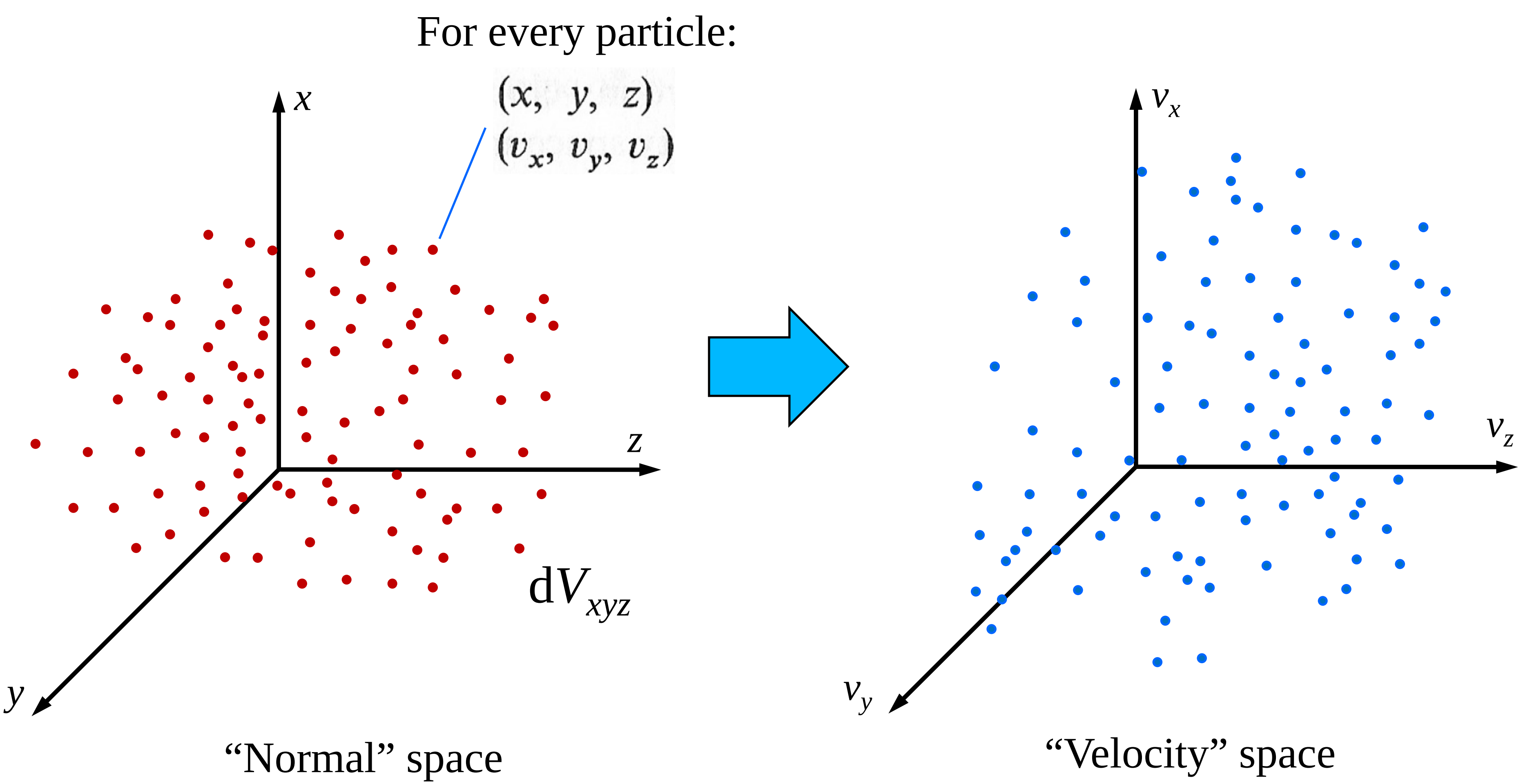
- It exist another quantum number describing the electron in an atom: SPIN number. It represents the rotation of the electron over its own axis. It can be obtained by solving the relativistic SE.
- Therefore, an electron inan atom is completely specified by 4 quantum numbers:

$$(n, l, m, s).$$

- The exclusion principle says that no 2 electrons can have the same quantum numbers.

Assemblies of Classical Particles

- Consider a gas of N neutral molecules



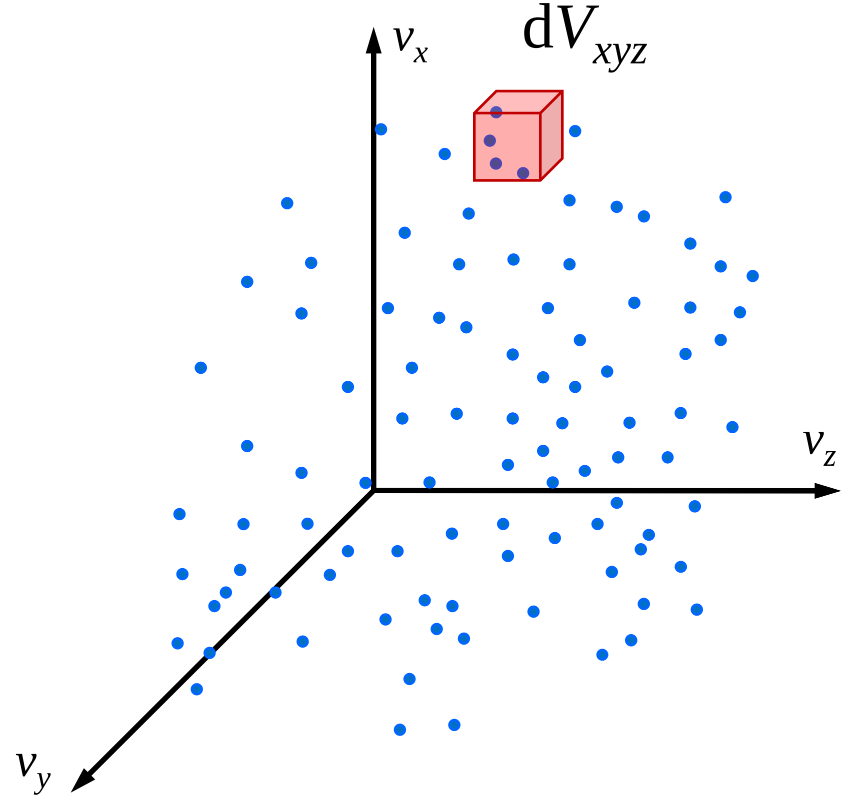
Assemblies of Classical Particles

- Consider a gas of N neutral molecules

The number of particles in dV_{xyz} is

$$dN_{xyz} = P(v^2)\,dv_x\,dv_y\,dv_z$$

where $P(v^2)$ is the density of particles having a speed v (i.e. density of points in v-space).



"Velocity" space

Assemblies of Classical Particles

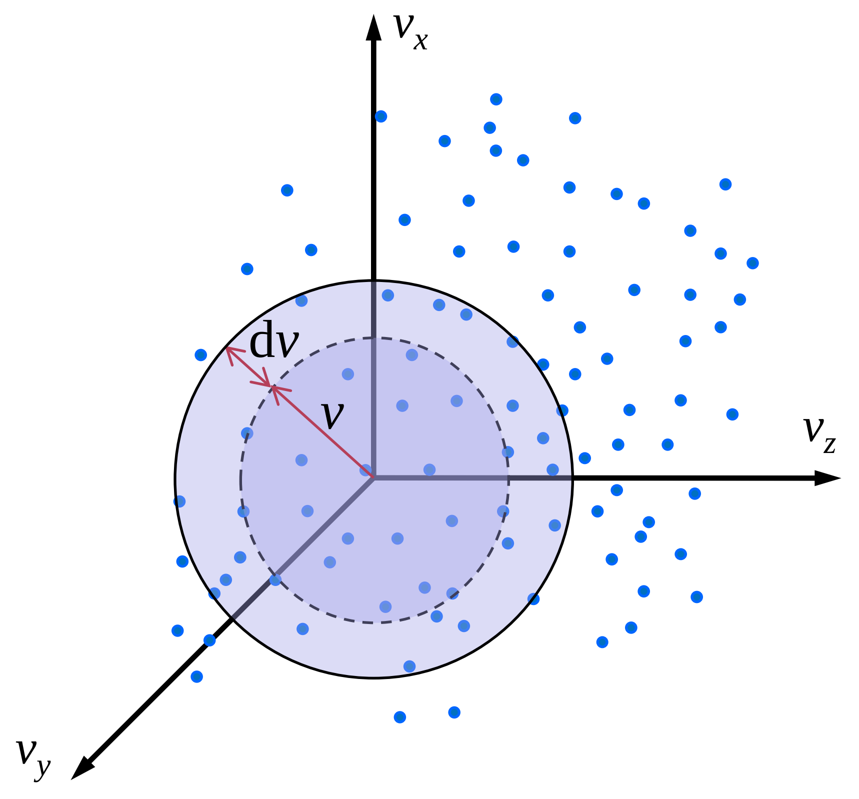
- Consider a gas of N neutral molecules

The number of particles in a shell of thickness dv is

$$dN_v = P(v^2)4\pi v^2\, dv$$

Total number of particles is:

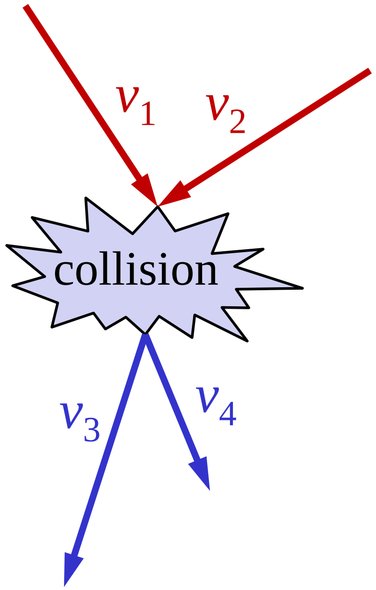
$$\int_0^\infty dN_v = \int_0^\infty P(v^2)4\pi v^2\, dv = N$$



"Velocity" space

Assemblies of Classical Particles

- The distribution function (distribution of speeds):
  - To find $P(v^2)$ let's consider collisions inside this gas



collision probability $\propto P(v_1^2) \times P(v_2^2)$

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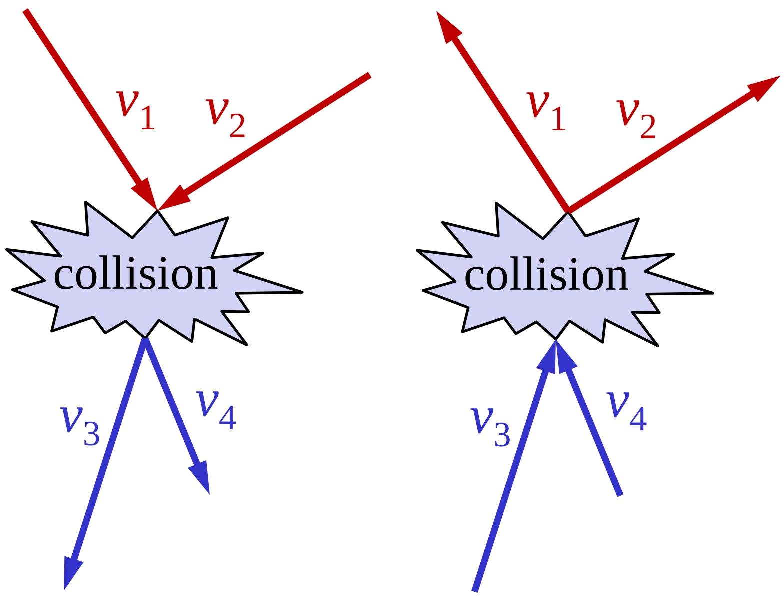


collision probability $\propto P(v_1^{\,2}) \times P(v_2^{\,2})$

collision probability $\propto P(v_3^{\,2}) \times P(v_4^{\,2})$

Collision and reversed collision:

$$P(v_1^2)P(v_2^2)=P(v_3^2)P(v_4^2)$$

Energy conservation:

$$v_1^2+v_2^2=v_3^2+v_4^2$$

$$P(v^2)=A\ \exp(-\beta v^2)$$

Assemblies of Classical Particles

- The distribution function (distribution of speeds):
  - To find $P(v^2)$ let's consider collisions inside this gas

$$P(v^2) = A\ \exp(-\beta v^2)$$

  - Constants A and β are found from:

Total number of particles: $N = 4\pi A \int_0^\infty \exp(-\beta v^2) v^2\, \mathrm{d}v$

Definition of T: $\underbrace{\int_0^\infty \tfrac{1}{2}(M\, v^2)\, [A \exp(-\beta\, v^2)]\, 4\pi v^2\, \mathrm{d}v}_{\text{Mean kinetic energy}} = \tfrac{3}{2} NkT$

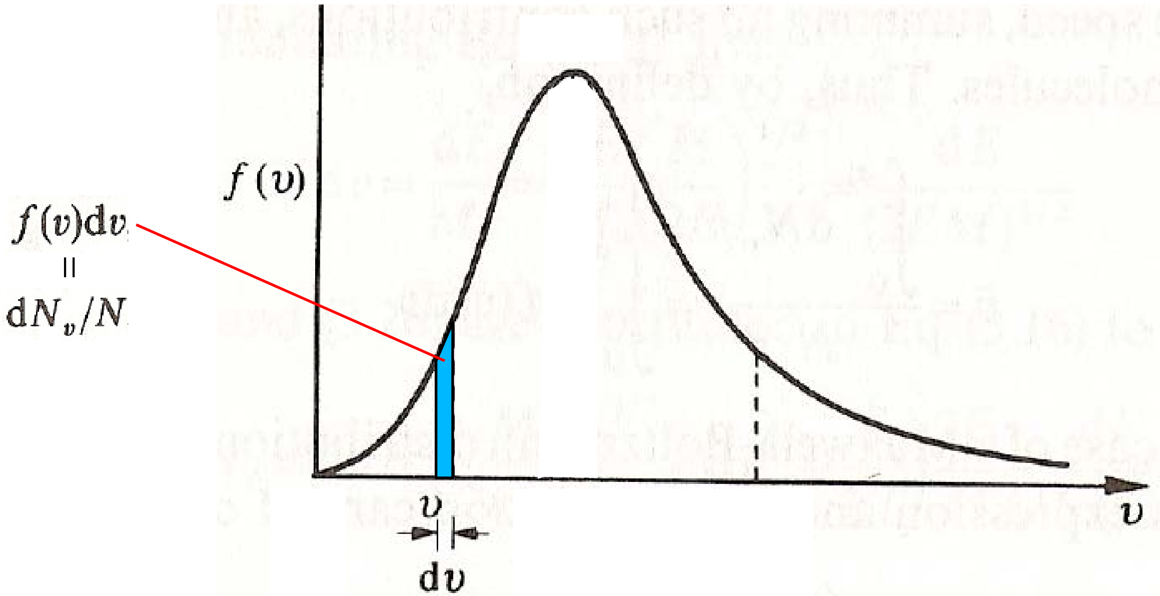
$$\Rightarrow \quad A = N\left(\frac{M}{2\pi kT}\right)^{3/2} \qquad \beta = M/(2kT)$$

Maxwell-Boltzmann Distribution Function

- Relation between MBDF $f(v)$ and $P(v^2)$:
  - Number of particles in a shell of thickness dv:

$$\left.\begin{aligned} \mathrm{d}N_v &= P(v^2)4\pi v^2\,\mathrm{d}v \\ \mathrm{d}N_v &= Nf(v)\,\mathrm{d}v \end{aligned}\right\} \Rightarrow \boxed{f(v) = 4\pi\left(\frac{M}{2\pi kT}\right)^{3/2}\exp\left(-\frac{Mv^2}{2kT}\right)v^2}$$

  - $f(v)$ gives the fraction of molecules (per unit volume) in a given speed range (per unit range of speed).



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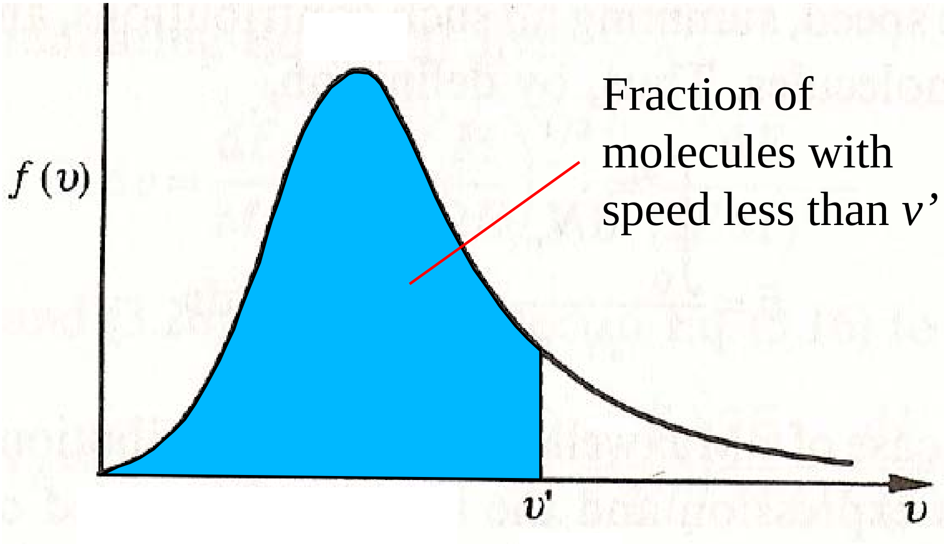
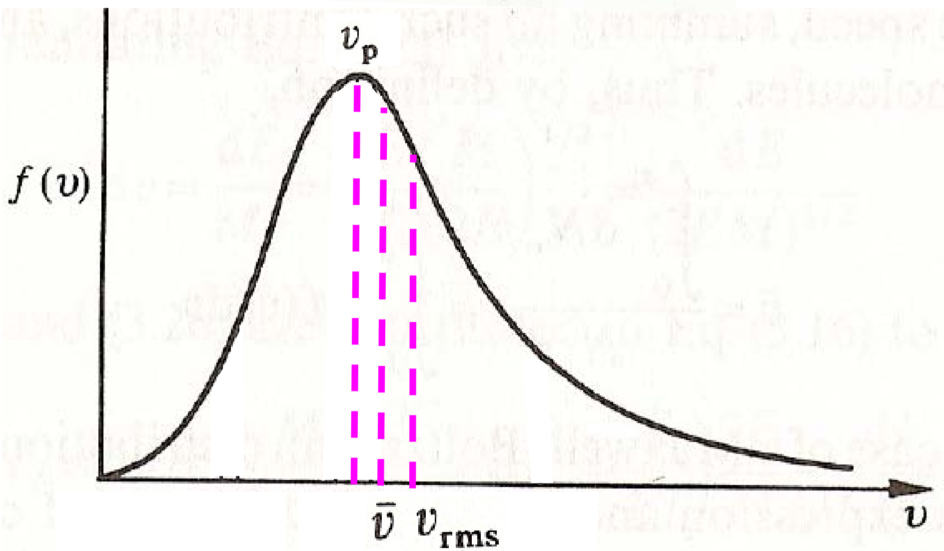


Maxwell-Boltzmann Distribution Function

- Average values:
  - Most probable velocity: $f'(v) = 0 \Rightarrow v_p = (2kT/M)^{1/2}$
  - Average velocity: $\bar{v} = \frac{\int_0^\infty dN_v v}{N} = \int_0^\infty v f(v)\, dv = 2\left(\frac{2kT}{\pi m}\right)^{1/2} = \frac{2}{\pi^{1/2}} v_p$
  - RMS velocity: $\overline{v^2} = \frac{\int_0^\infty dN_v v^2}{N} = \int_0^\infty v^2 f(v)\, dv \Rightarrow v_{rms} = (\overline{v^2})^{1/2} = (\sqrt{\tfrac{3}{2}})v_p$



Energy Distribution Function

- How the energy is distributed in the ensemble
  - The particles in the ensemble we have considered so far only have kinetic energy:

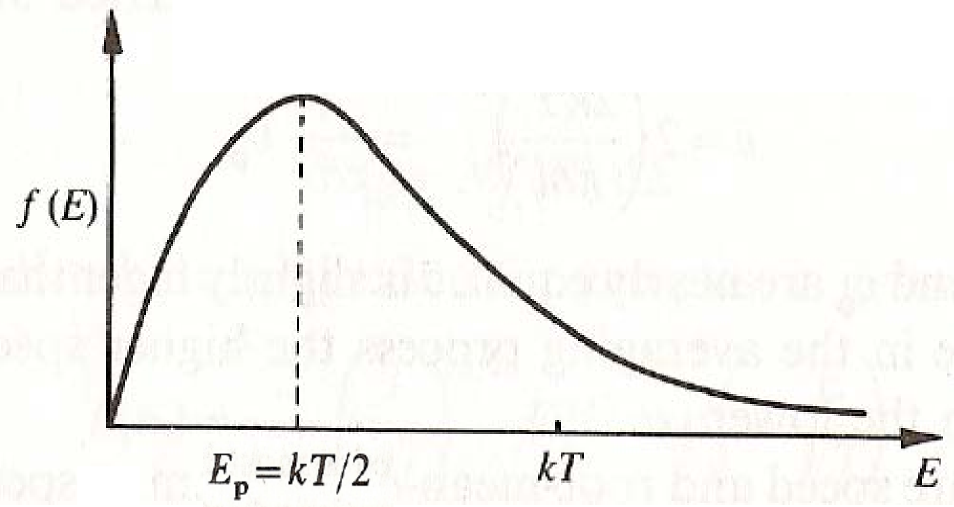
$$E = \frac{Mv^2}{2} \quad \Longrightarrow \quad \mathrm{d}v = \frac{\mathrm{d}E}{Mv} = \frac{\mathrm{d}E}{M}\left(\frac{M}{2E}\right)^{1/2} = \frac{\mathrm{d}E}{(2EM)^{1/2}}$$

  - Replacing in the expression for $\mathrm{d}N_v$:

$$\mathrm{d}N_E = 4\pi N\left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left(-\frac{E}{kT}\right)\frac{2E}{M}\frac{\mathrm{d}E}{(2EM)^{1/2}}$$

  - But $\mathrm{d}N_E = Nf(E)\,\mathrm{d}E$ then:

$$\boxed{f(E) = \frac{2}{\pi^{1/2}}\left(\frac{1}{kT}\right)^{3/2} E^{1/2} \exp\left(-\frac{E}{kT}\right)}$$



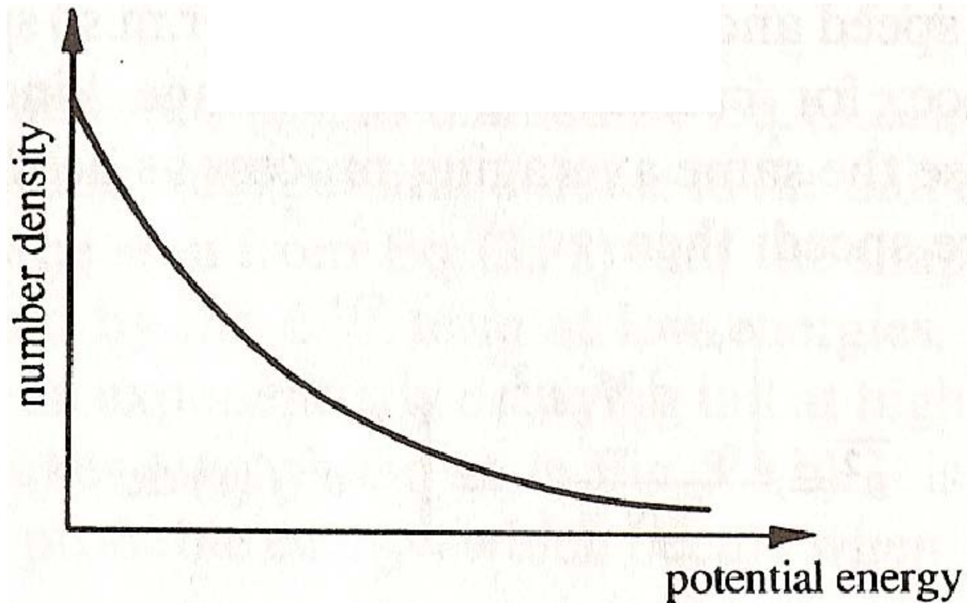
Boltzmann Distribution Function

- How the energy is distributed in the ensemble
  - We now consider that the particles in the ensemble not only have KE but also PE (gravitational or electrical field).

$$f(E) \propto \exp(-E/kT) \propto \exp[-(\mathrm{KE}+\mathrm{PE})/kT]$$

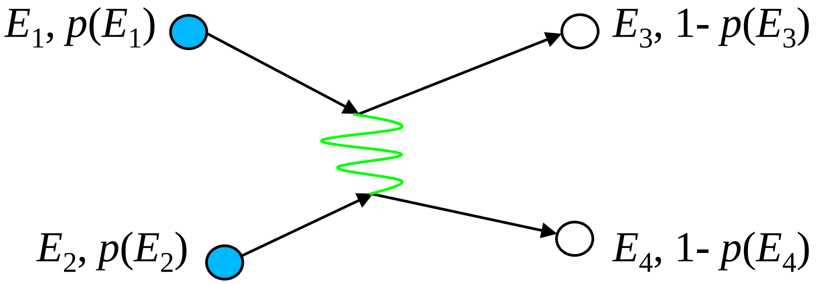
  - If the PE depends on the position so does the density of the ensemble:

$$n_2/n_1 = \exp[-e(V_2 - V_1)/kT]$$



Fermi-Dirac Distribution

- Ensembles obeying exclusion principle
  - Two quantum particles (E_1, E_2) interact and end up in two states (E_3, E_4) previously empty:



$$p(E_1)p(E_2)[1-p(E_3)][1-p(E_4)]$$

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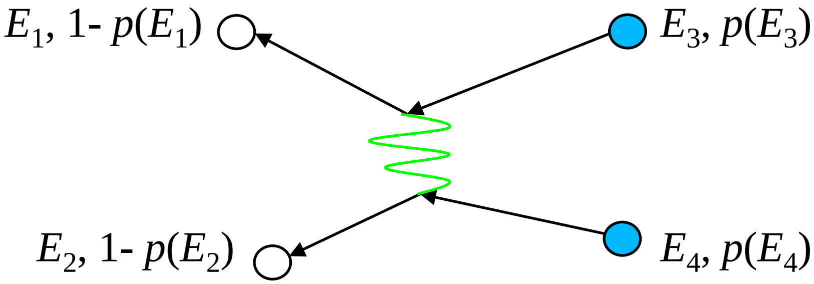

$$p(E_1)p(E_2)[1-p(E_3)][1-p(E_4)]$$
$$\parallel$$
$$p(E_3)p(E_4)[1-p(E_1)][1-p(E_2)]$$

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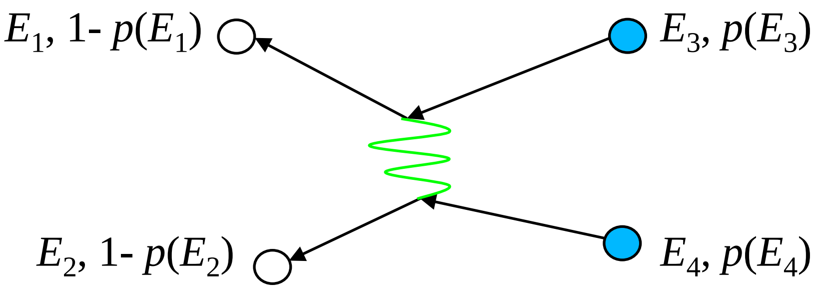


$$p(E_1)p(E_2)[1-p(E_3)][1-p(E_4)]$$
$$\|$$
$$p(E_3)p(E_4)[1-p(E_1)][1-p(E_2)]$$

$$\left(\frac{1}{p(E_1)}-1\right)\left(\frac{1}{p(E_2)}-1\right)=\left(\frac{1}{p(E_3)}-1\right)\left(\frac{1}{p(E_4)}-1\right)$$

$$\boldsymbol{E_1 + E_2 = E_1 + E_2}$$

$$[1/p(E)]-1 = A\ \exp(\beta E)$$
$$p(E) = 1/[1 + A\exp(\beta E)]$$

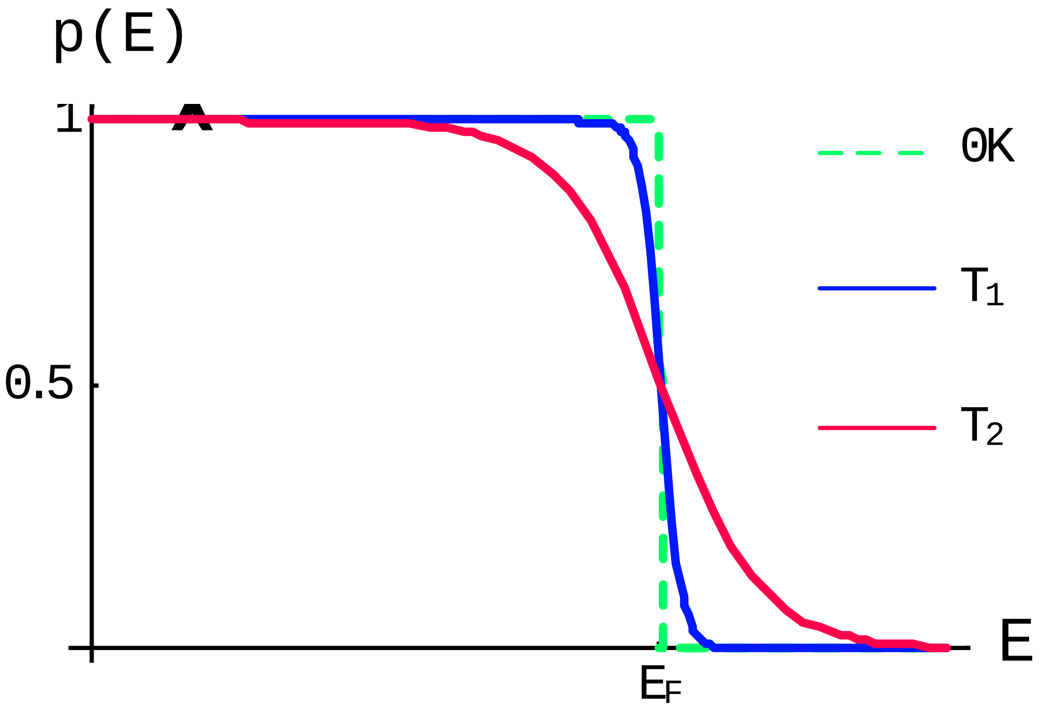
  - When $E \rightarrow \infty$ it reduces to the Boltzmann distribution:

$$p(E) \simeq A\ \exp(-\beta E) \qquad \beta = 1/kT$$

Fermi-Dirac Distribution

- Ensembles obeying exclusion principle
  - The constant A is redefined through E_F and can be found via normalization:

$$A = \exp\left(-E_F / kT\right) \quad \Rightarrow \quad \boxed{p(E) = \frac{1}{1+\exp\left[(E-E_F)/kT\right]}}$$



Note that for T = 0, $p(E)$ reduces to a step function. It means that all the states with energies $E \le E_F$ are occupied and those above, are empty. When T > 0, some states below E_F are emptied and some are occupied due to thermal energy.

Conclusions

- We have studied how to describe assemblies of particles.
- This description is made through a distribution function $f(E)$.
- The distribution function depends on what kind of "physics" the particles follow:
  - Classical particles: Boltzmann distribution.
  - Quantum particles complying exclusion principle: Fermi distribution.
  - Quantum particles NOT complying exclusion principle: Bose distribution.