EE 403/503
Introduction to Plasma Processing

The kinetic Theory of Gases

Velocity Distribution

Dr. Kasra Etemadi
September 21, 2011

Outline

1- Velocity Distribution

2-Reaction Rate and Equilibrium (Saha Equation)

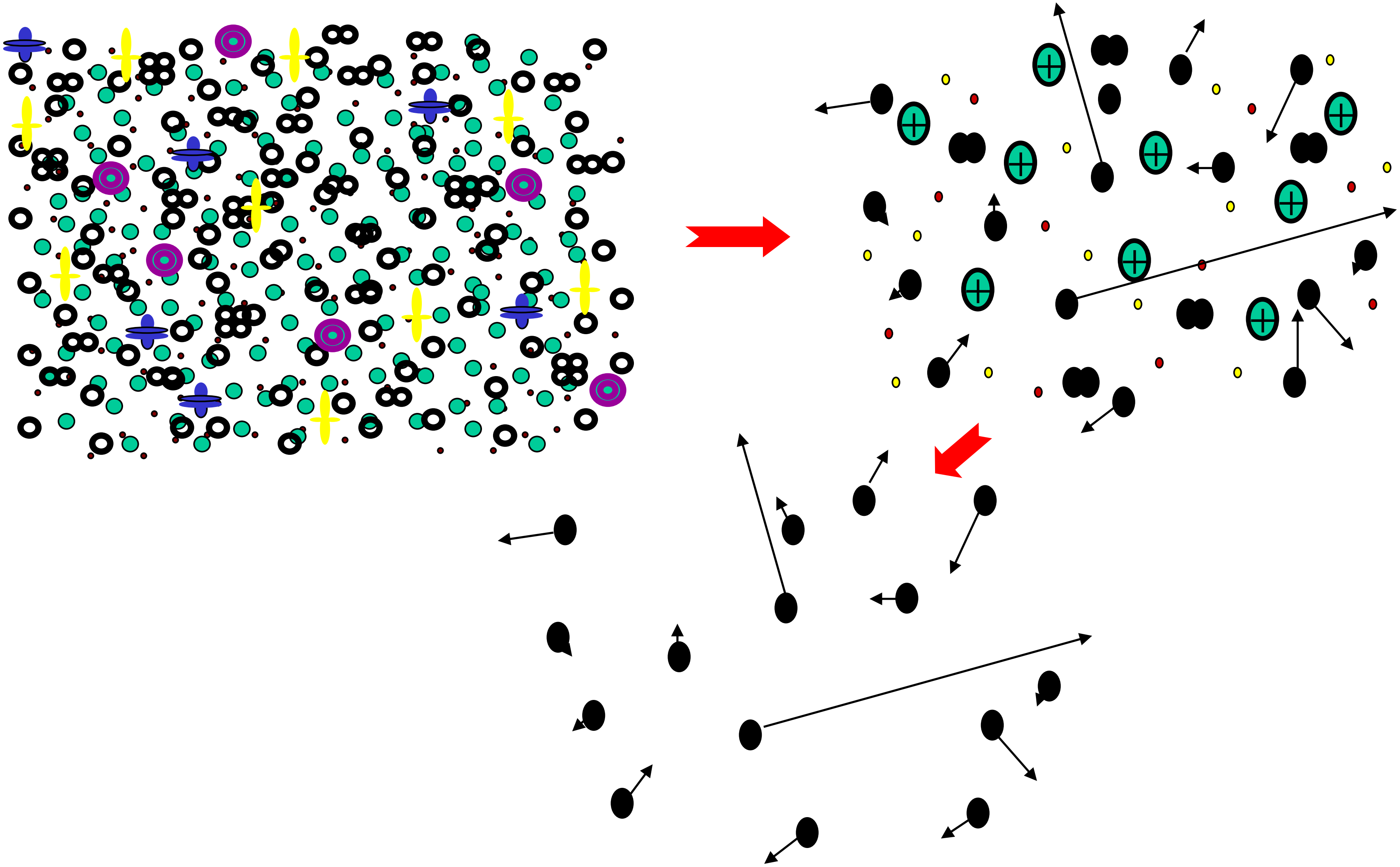
3-E3

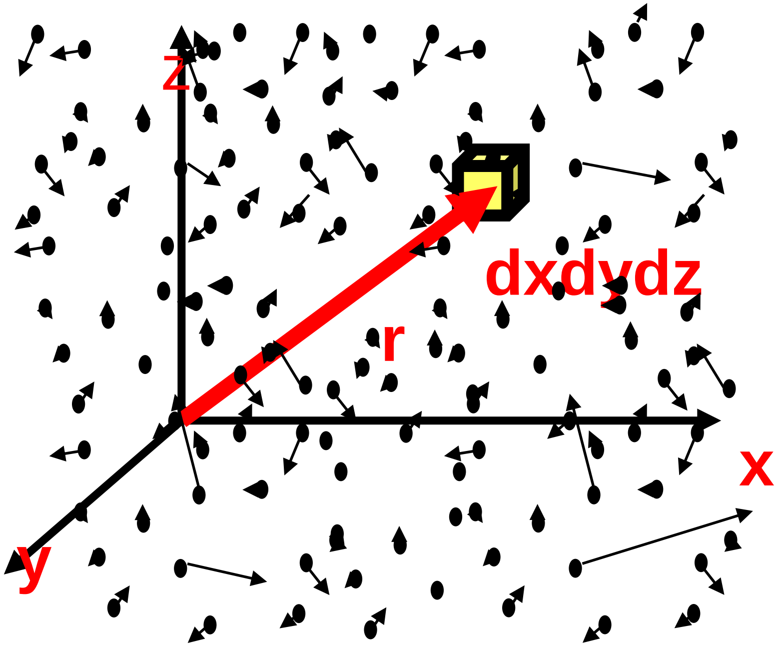
4- Boltzmann Distribution

5- Radiation (Planck’s Function)

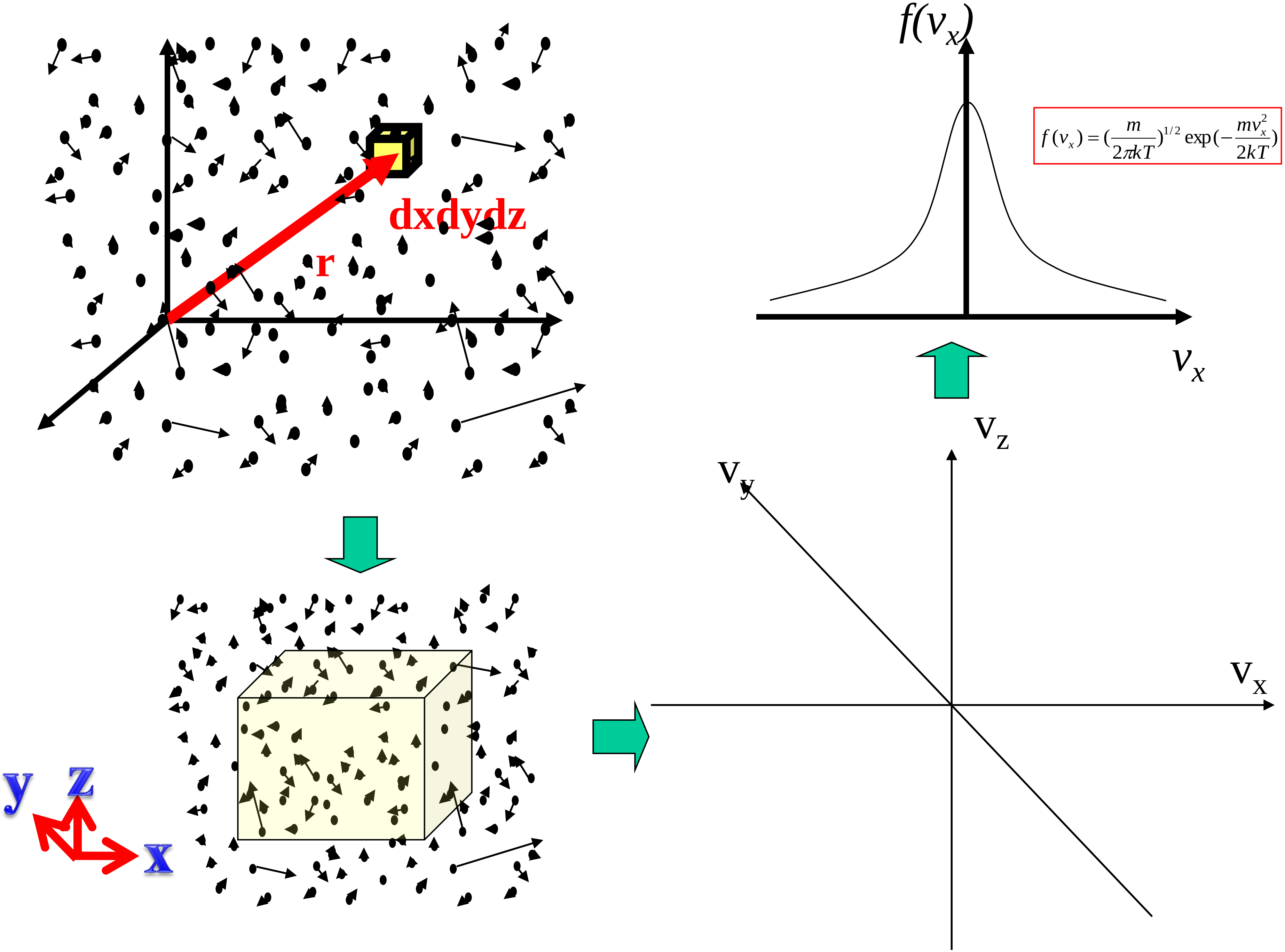
6- E4

Maxwellian Velocity Distribution

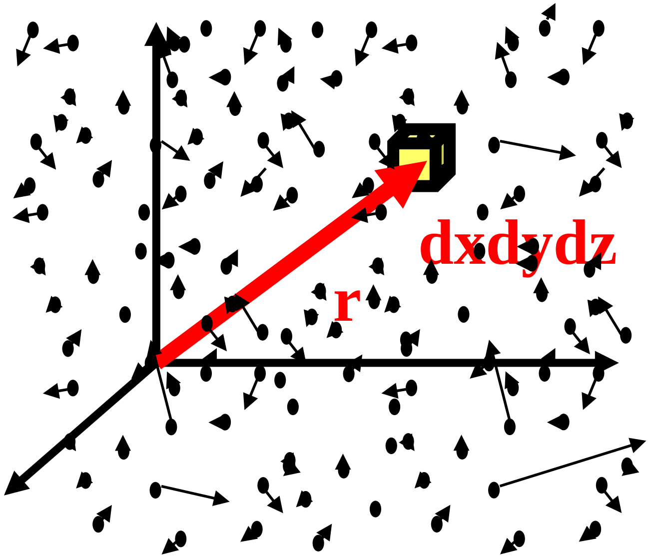


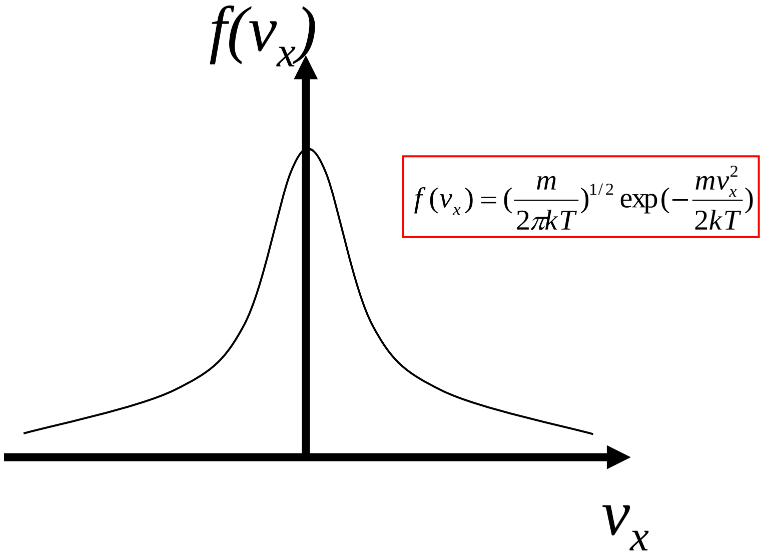


Applets



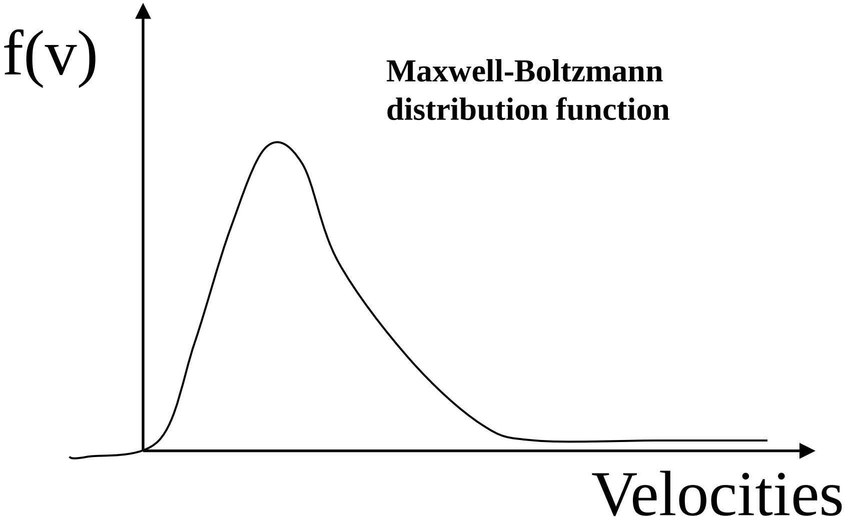
$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right)$$





$$f(v_x) = (\frac{m}{2\pi kT})^{1/2} \exp(-\frac{mv_x^2}{2kT})$$

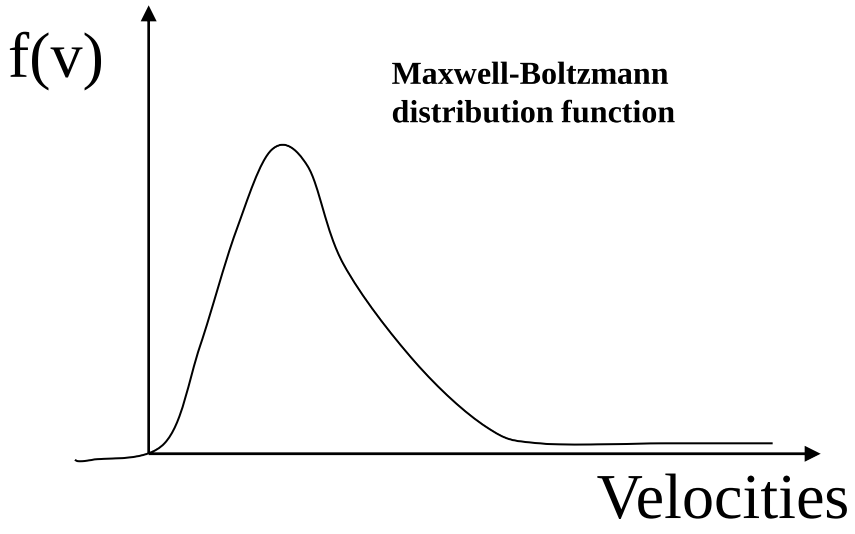
$$\underline{f(v) = f_x(v) \,.\, f_y(v) \,.\, f_z(v)}$$



$$f(v) = 4\pi(\frac{m}{2\pi kT})^{3/2} v^2 \exp(-\frac{mv^2}{2kT})$$

Distribution Functions f (r, v)

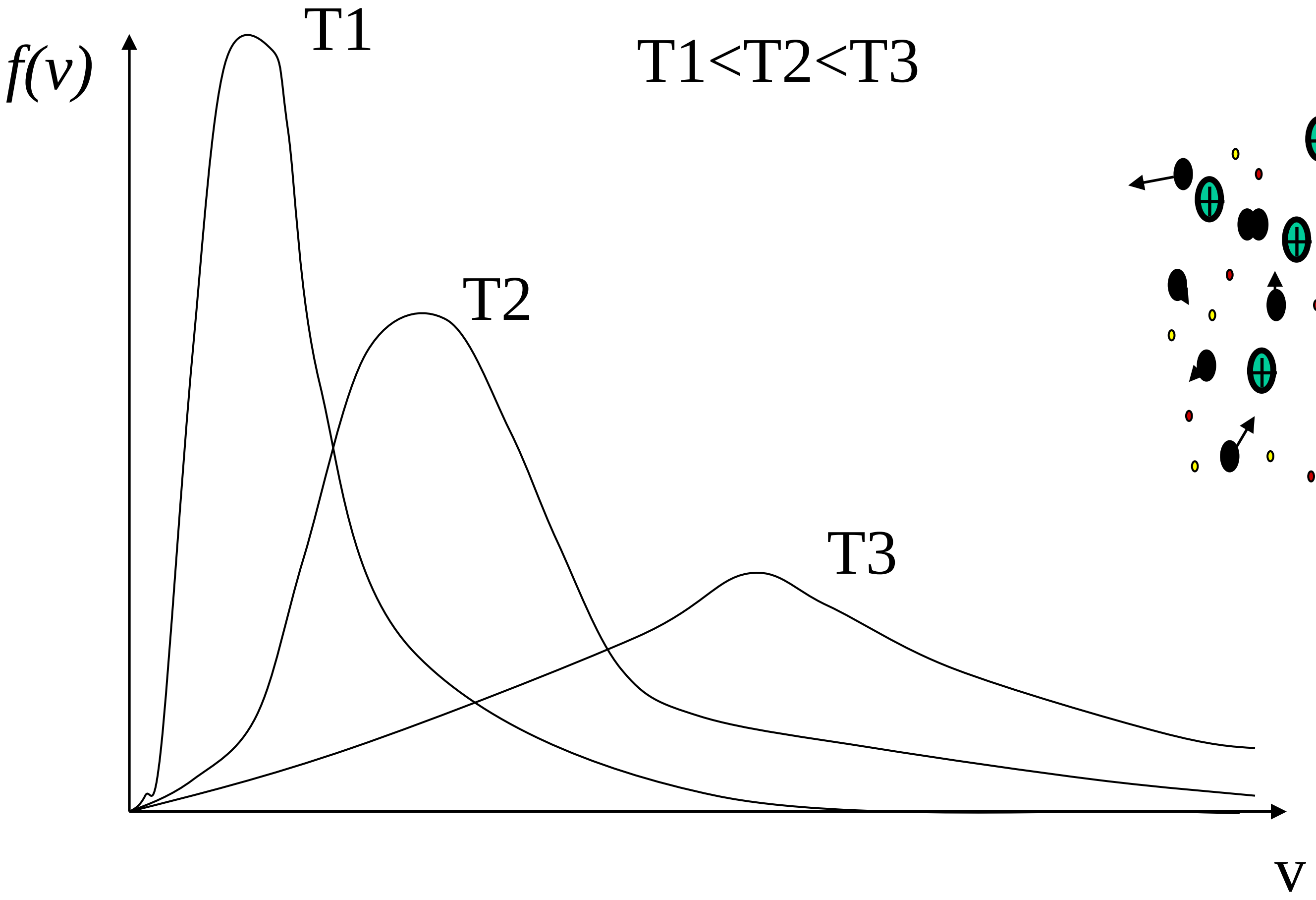
$\int f(r, v)\,drdv=1$ normalized

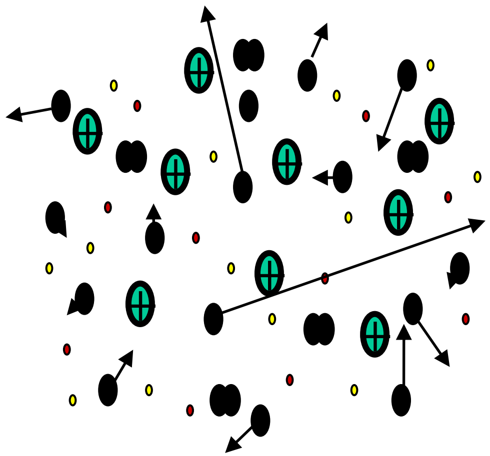


$$f(v) = 4\pi(\frac{m}{2\pi kT})^{3/2} v^2 \exp(-\frac{mv^2}{2kT})$$

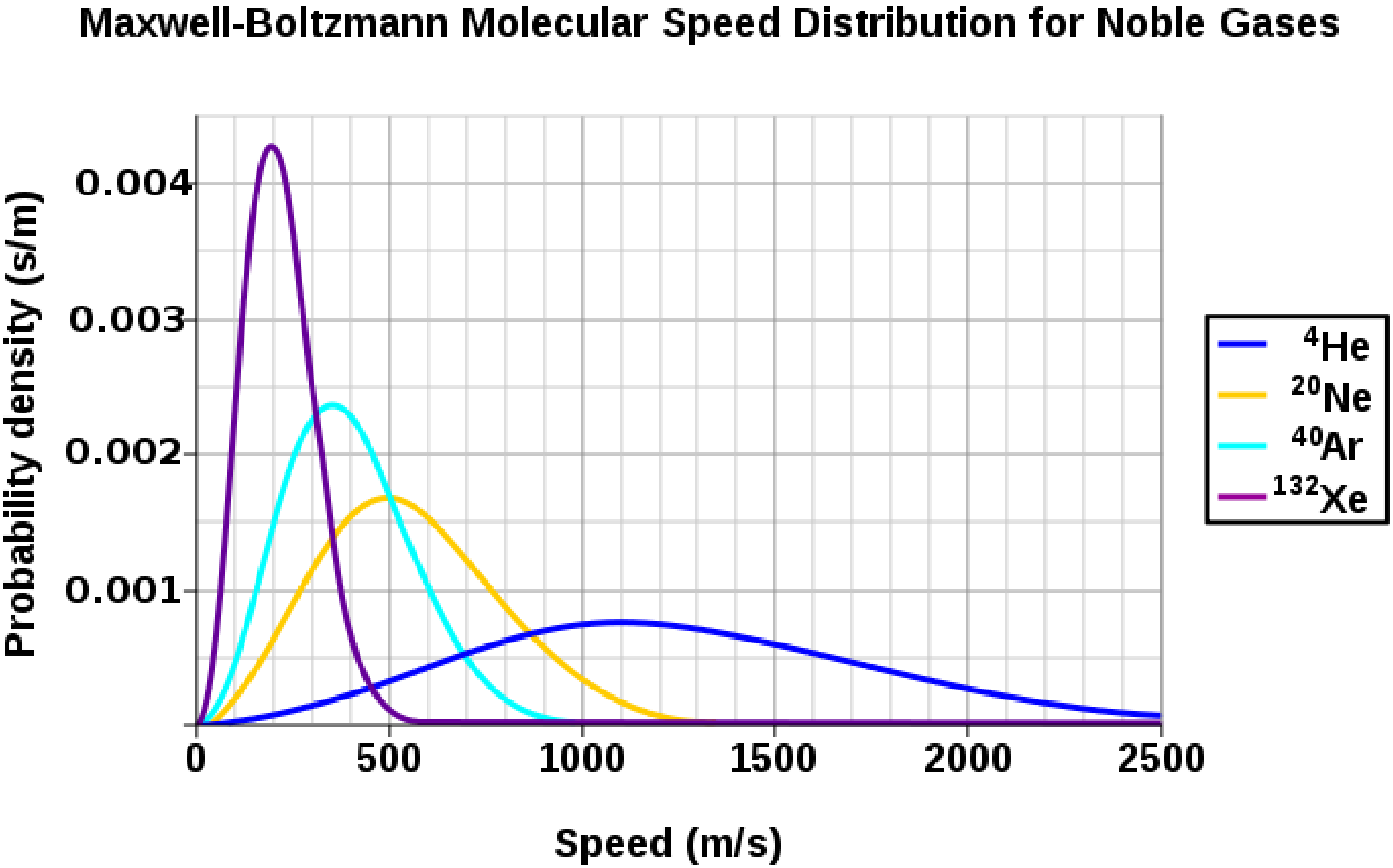
- $n(r) = \int n_{total} \,.\, f(r, v)\, dv$	Number Densities
- $\langle v(r) \rangle = \int n_{total} \,.\, v \,.\, f(r, v)\, dv$	Average Velocities
- $\langle p(r) \rangle = \int n_{total} \,.\, mv \,.\, f(r, v)\, dv$	Average Momentum
- $\langle E(r) \rangle = \int n_{total} \,.\, \frac{1}{2} mv^2 \,.\, f(r, v)\, dv$	Average Energy

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$





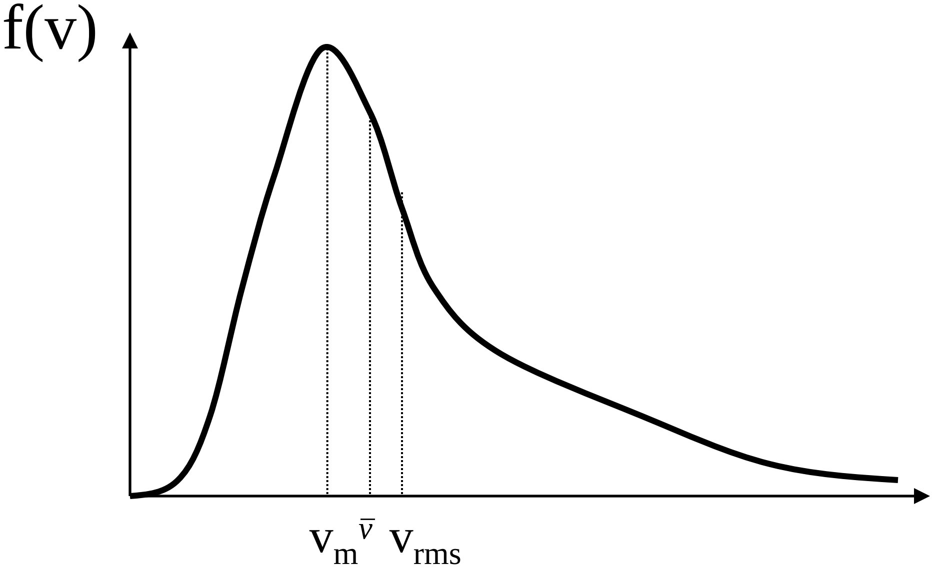
Maxwell-Boltzmann distribution function


Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases
Probability density (s/m)
0.004
0.003
0.002
0.001
0
500
1000
1500
2000
2500
Speed (m/s)
^{4}He
^{20}Ne
^{40}Ar
^{132}Xe

$$\boxed{f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)}$$

$$\bar{v}_{v_2-v_1} = \int_{v_1}^{v_2} v f(v)\,dv \quad\Longrightarrow\quad \bar{v} = \int_0^{\infty} v f(v)\,dv = \sqrt{\frac{8kT}{\pi m}}$$

$$v_{rms,v_2-v_1} = \left(\int_{v_1}^{v_2} v^2 f(v)\,dv\right)^{1/2} \quad\Longrightarrow\quad v_{rms} = \left(\int_0^{\infty} v^2 f(v)\,dv\right)^{1/2} = \left(\frac{3kT}{m}\right)^{1/2}$$



$$v_m = (\frac{2kT}{m})^{1/2}$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

$$v_{rms} = (\frac{3kT}{m})^{1/2}$$

Energy Distribution Function

$$f(w) = 2\pi \frac{w^{1/2}}{(\pi kT)^{3/2}} \exp(-\frac{w}{kT})$$

$$\overline{w} = \int_0^\infty wf(w)dw = \frac{3}{2}kT$$

$W=1/2mv^2$

E3

Find the fraction N_v/N of the total number of particles N having speeds above a given speed V in a system of particles described by the Maxwell-Boltzmann distribution.

Solution:

$$\boxed{f(v)=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}v^2\exp\left(-\frac{mv^2}{2kT}\right)}$$

$$du=\sqrt{\frac{m}{2kT}}dv$$

$$\frac{N_V}{N}=\frac{1}{N}\int_V^\infty dn_v=\int_V^\infty f(v)dv=4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_V^\infty v^2e^{-mv^2/2kT}dv$$

$$dn_v=Nf(v)dv$$

$$u^2=\frac{mv^2}{2kT}$$

$$\frac{N_V}{N}=\frac{4}{\sqrt{\pi}}\int_U^\infty u^2e^{-u^2}du$$

$$\frac{N_V}{N} = \frac{4}{\sqrt{\pi}} \int_U^\infty u^2 e^{-u^2}\, du$$

$$U = \sqrt{\frac{m}{2kT}}V$$

$$\frac{N_V}{N} = \frac{4}{\sqrt{\pi}}\{[-\frac{1}{2}ue^{-u^2}]_U^\infty + \frac{1}{2}\int_U^\infty e^{-u^2}du\} = \frac{4}{\sqrt{\pi}}\{\frac{1}{2}Ue^{-U^2} + \frac{1}{2}\int_0^\infty e^{-u^2}du - \frac{1}{2}\int_0^U e^{-u^2}du\}$$

See Equation Sheet II

$$\frac{N_V}{N} = \frac{4}{\sqrt{\pi}}\{\frac{1}{2}Ue^{-U^2} + \frac{1}{2}\frac{\sqrt{\pi}}{2} - \frac{1}{2}\int_0^U e^{-u^2}du\} = \frac{2}{\sqrt{\pi}}Ue^{-U^2} + 1 - \underbrace{\frac{2}{\sqrt{\pi}}\int_0^U e^{-u^2}du}_{erf(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}dx}$$

Error function

$$\boxed{\frac{N_V}{N} = 1 + \frac{2}{\sqrt{\pi}}Ue^{-U^2} - erf(U)}$$

The fraction N_v/N of the total number of particles N having speeds above a given speed V in a system of particles described by the Maxwell-Boltzmann distribution.

$$\boxed{\frac{N_V}{N} = 1 + \frac{2}{\sqrt{\pi}} U e^{-U^2} - erf(U)}$$

Error Function

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$$

x	erf(x)
0	0
0.2	0.2227
0.4	0.4284
0.6	0.6039
0.8	0.7421
1.0	0.8427
1.2	0.9103
1.4	0.9523
1.6	0.9763
1.8	0.9891
2.0	0.9953
2.2	0.9981
2.4	0.9993
2.6	0.9998
2.8	0.9999

$$U = \sqrt{\frac{m}{2kT}} V$$

EE 403/503
Introduction to Plasma Processing

The kinetic Theory of Gases

(Reaction Rate, Equilibrium)

Dr. Kasra Etemadi
September 21, 2011

Chemical Kinetics:

Definition

At what rate does a chemical reaction undergo changes under a given set of conditions?

Reaction Rate: **a A + b B → products**

Kinetic order determined experimentally

$$Rate = k\left[A\right]^{m}\left[B\right]^{n} = -\frac{d\left[A\right]}{dt}$$

Rate constant ~ T
& chemical potential

Concentrations

Total order = m + n

Chemical Equilibrium

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{backward}}$$

Example:

$CH_4 + H_2O$ -------> $3\ H_2 + CO_2$

The law of Mass Action will be:

$$K_{eq} = [H_2][CO_2]/[CH_4][H_2O]$$

$$aA + bB + \cdots \Leftrightarrow pP + qQ + \cdots$$

$$K_{eq} = \frac{Z^p Z^q \cdots}{Z^a Z^b \cdots} \exp(-\frac{\Delta\varepsilon_0}{kT})$$

The Saha Equation

(see page 135)

It describes the relationship between the electron, ion, and neutral number densities $e + A^{+} \rightarrow A^{:}$

$$\frac{n_e n_{ion}}{n_a} = \frac{(2\pi m_e kT)^{3/2}}{h^3} \frac{2Z_{ion}}{Z_a} \exp(\frac{-e\chi_a}{kT})$$

n_e	number density of electrons	n_{ion}	number density of ions
n_a	number density of atoms	m_e	mass of electron
k	Boltzmann constant	T	Temperature
h	Planck's constant	e	Electron charge
Z_{ion}	Partition function of ion		
Z_a	Partition function of atom		
χ_a	E_i-ΔE_i		
$E_{ionization}$	Ionization potential of neutral atoms		
$\Delta E_{ionization}$	Lowering of ionization potential		

$\Delta E_{ionization}$ Lowering of ionization potential

$$\Delta E_{ionization} = 6.96 \,.\, 10^{-13}\, n_e^{1/3} \quad [eV]$$

Unit of n_e is $[m^{-3}]$

$$\chi_a = E_{ionization} - \Delta E_{ionization}$$

Inglis & Teller Theory of Lowering of ionization Potential

(only for hydrogen atoms)

$$\log n^{*} = 3.11 - 0.133 \times \log n_{e}$$

n_e **Electron density [1/cm3]**

n^* **Energy level cut-off**

Pressure

Boltzmann’s Constant

Pressure

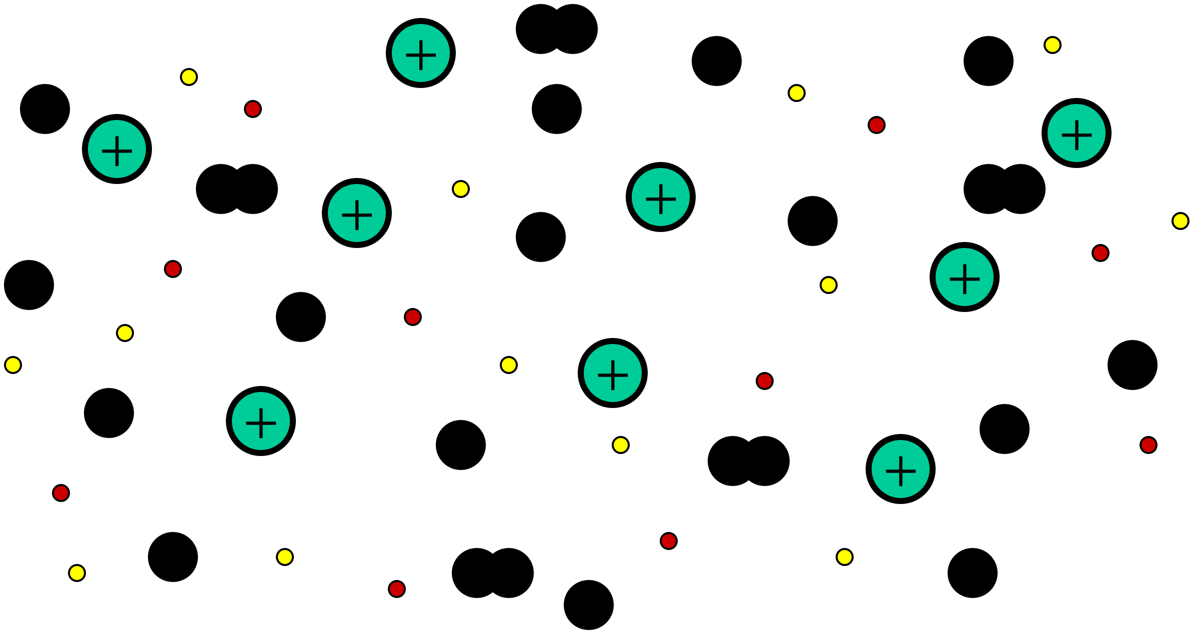
Temperature

$$P = n\,k\,T$$

Number Density of particles

1 atm = 760 Torr (mm Hg) = 101325 N/m^2 (Pascal)
1 bar = 10^5 Pa

k = 1.380 10^{-23} J/K Boltzmann’s constant



$$p = n\,k\,T = (n_e+n_{ion}+n_a)\,k\,T$$

For singly ionized plasma $p = (2n_e+n_a)\,k\,T$; $n_e = n_{ion}$

For multi-temperature plasmas $p = n_ekT_e + n_{ion}kT_i + n_akT_a$

$$\frac{n_e n_{ion}}{n_a} = f(T)$$

f(T) is Saha Equation; p and T are given

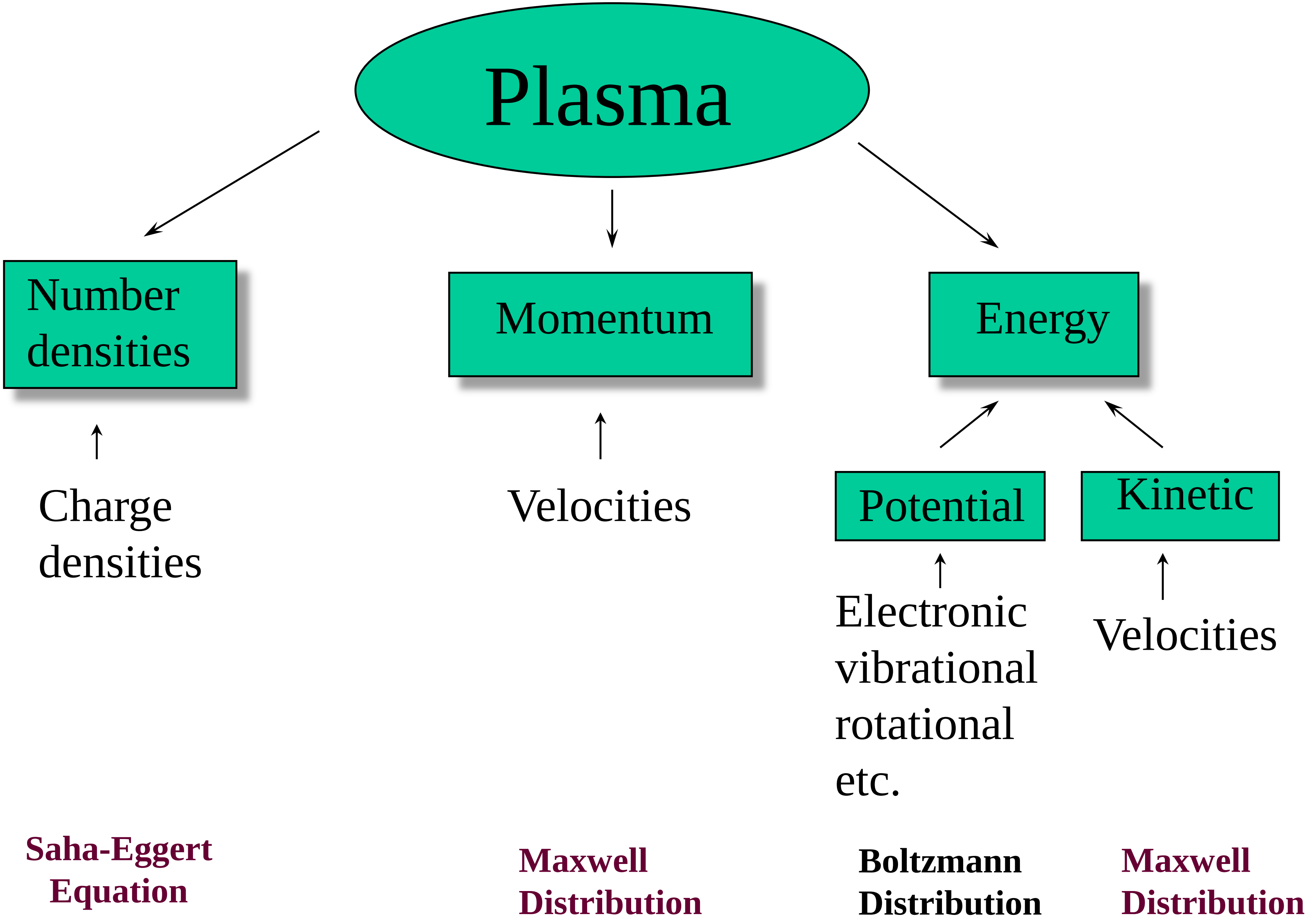
$$\left.\begin{array}{l} n_e=n_{ion} \longrightarrow n_a = \dfrac{n_e^2}{f(T)} \\ p=(2n_e+n_a)kT \end{array}\right\} \longrightarrow \boxed{n_e^2 + 2f(T)n_e - \frac{pf(T)}{kT} = 0}$$

Assume an initial value for n_e

n_e → find $\Delta E_{ionization}$ → Find χ_a → Solve Eq above → new n_e

New iteration

Equilibrium vs non-equlibrium



Plasma

Number densities

Momentum

Energy

Charge densities

Velocities

Potential

Kinetic

Electronic
vibrational
rotational
etc.

Velocities

Saha-Eggert Equation

Maxwell Distribution

Boltzmann Distribution

Maxwell Distribution

EE 403/503
Introduction to Plasma Processing

The kinetic Theory of Gases

(Boltzmann Distribution)

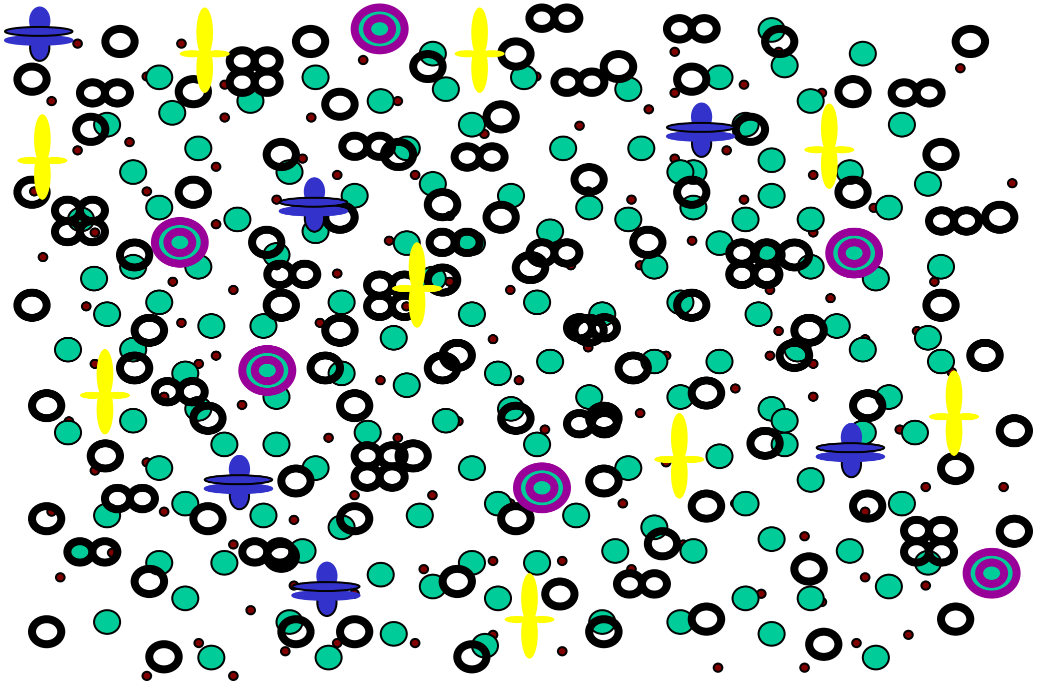
Dr. Kasra Etemadi
September 21, 2011

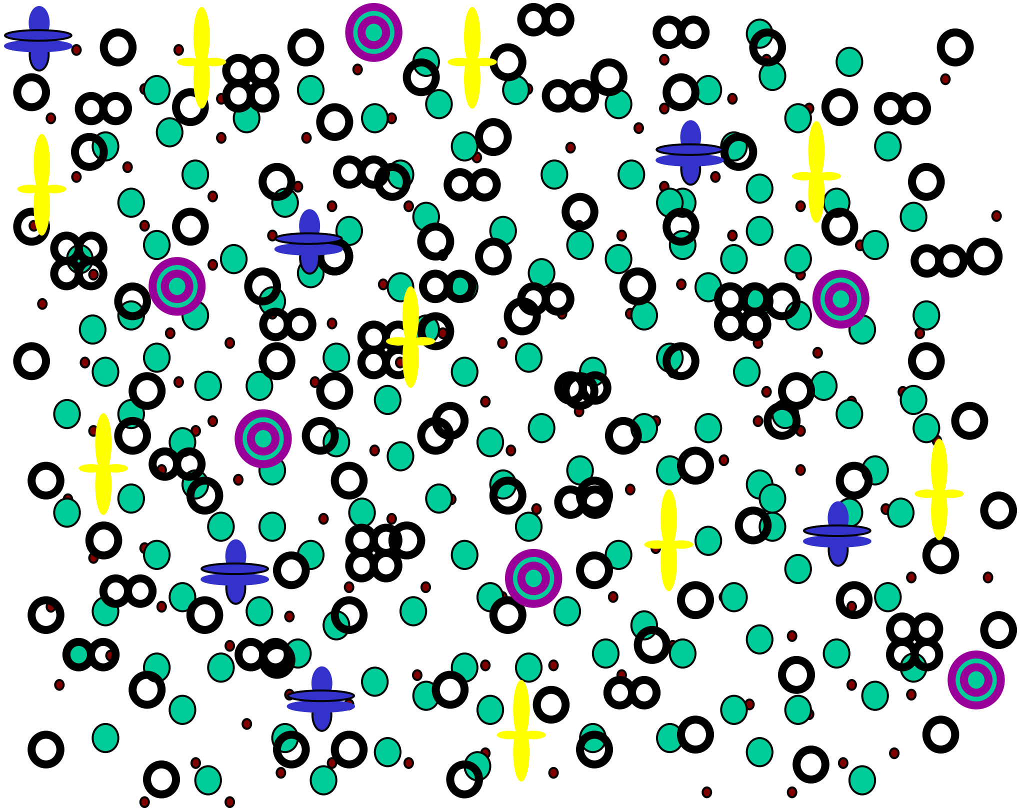
1- Kinetic Theory of Gases

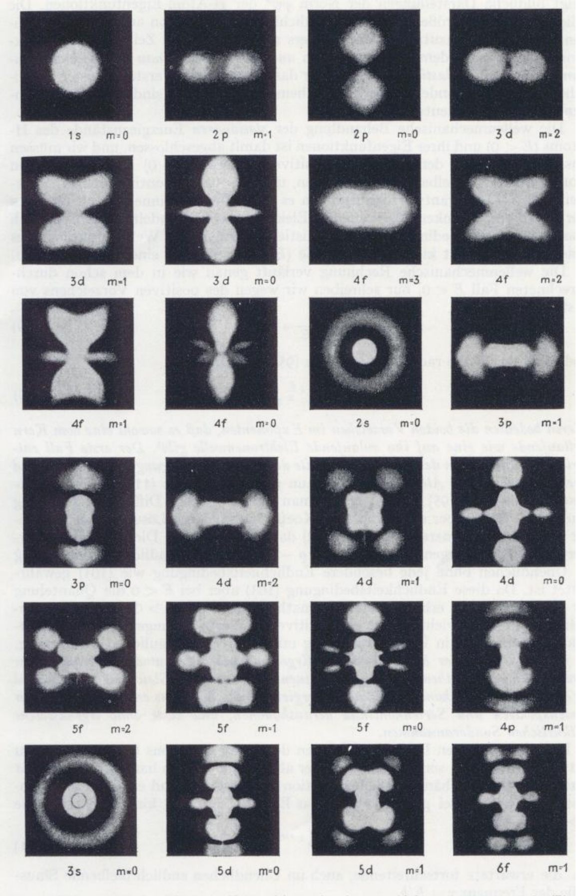
$$f(v_x) = (\frac{m}{2\pi kT})^{1/2} \exp(-\frac{mv_x^2}{2kT})$$

2- Boltzmann Distribution

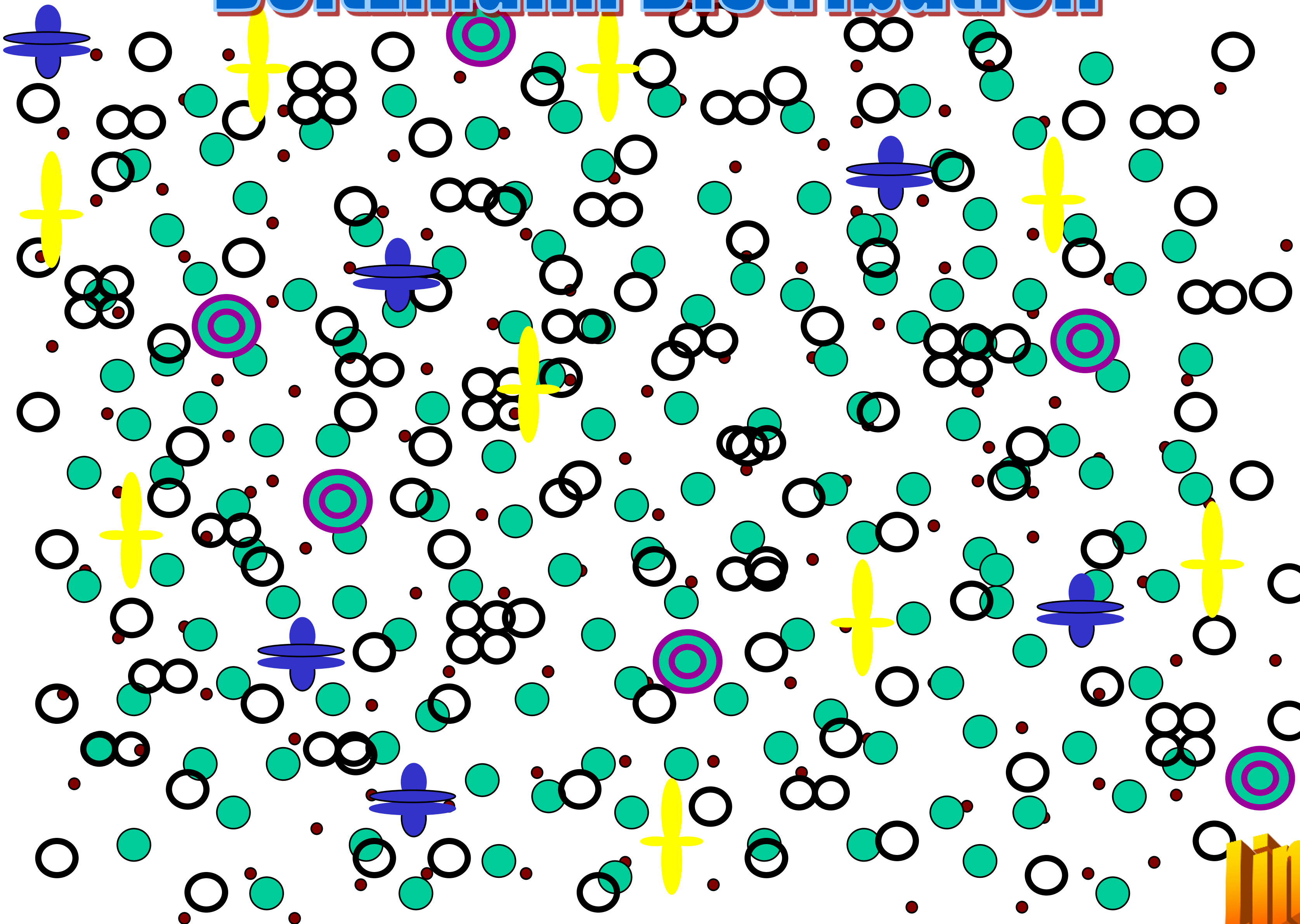
$$n_i = \frac{g_i}{Z_a} n_a \exp(\frac{-E_i}{kT})$$





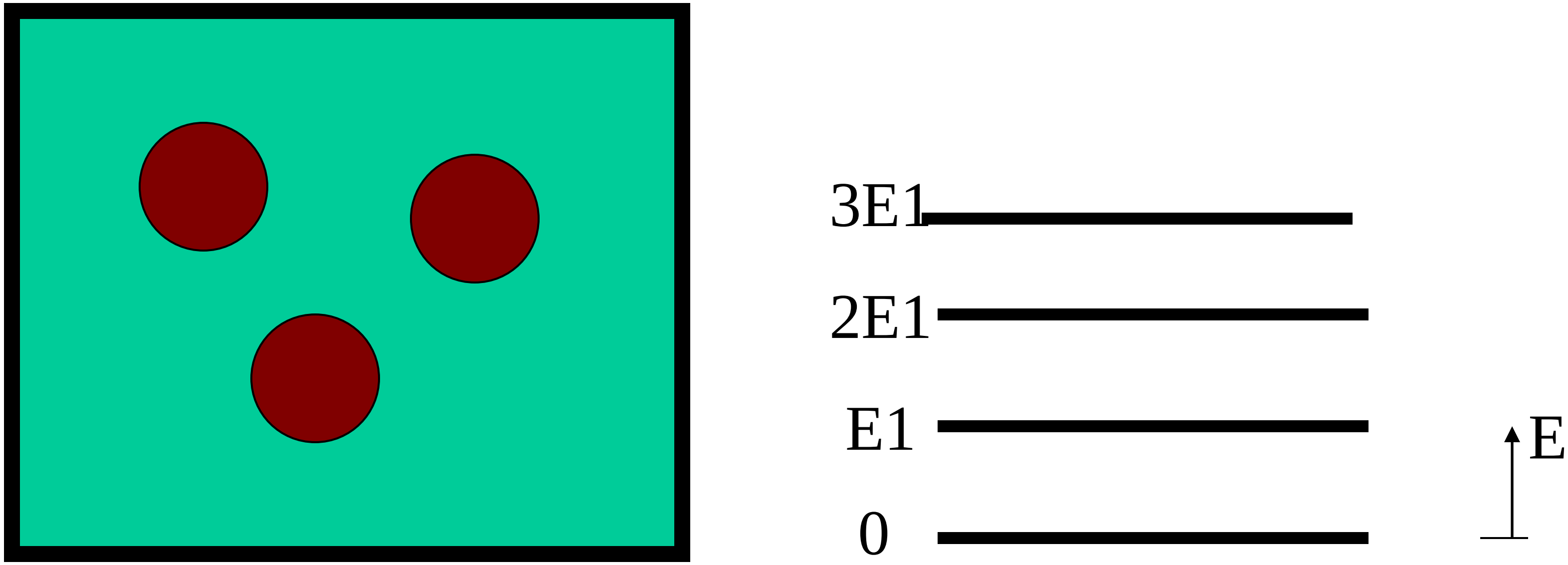

1s m=0
2p m=1
2p m=0
3d m=2
3d m=1
3d m=0
4f m=3
4f m=2
4f m=1
4f m=0
2s m=0
3p m=1
3p m=0
4d m=2
4d m=1
4d m=0
5f m=2
5f m=1
5f m=0
4p m=1
3s m=0
5d m=0
5d m=1
6f m=1

Boltzmann Distribution

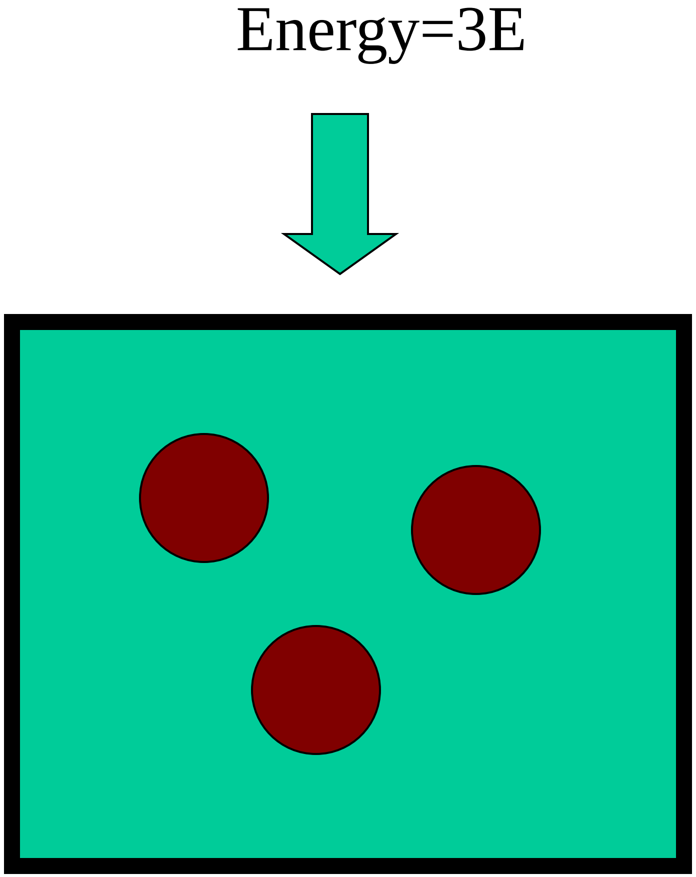


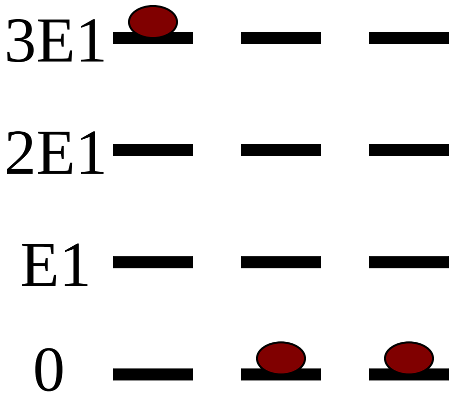
Link1

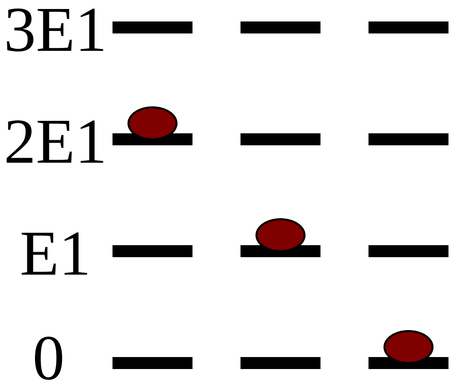
Consider a system with three particles (e.g. H) each having four equidistance energy levels.

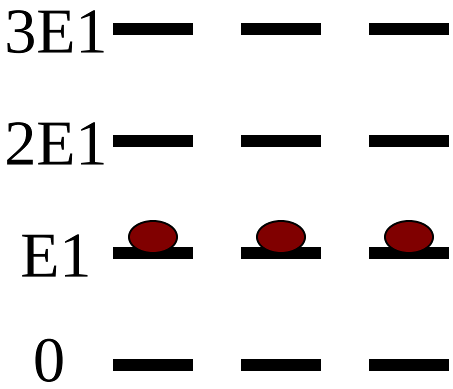


We introduce an energy equivalent to 3E in the Box




3E1
2E1
E1
0


3E1
2E1
E1
0


3E1
2E1
E1
0

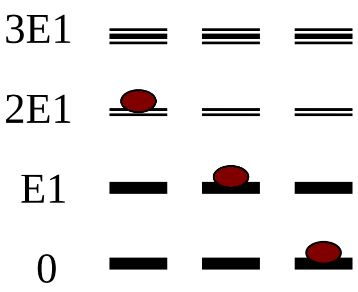
Boltzmann Distribution

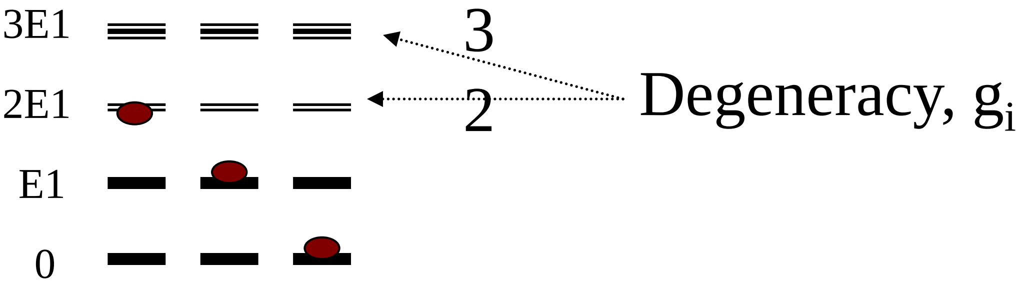
$$n_i = \frac{g_i}{Z_a} n_a \exp(\frac{-E_i}{kT})$$

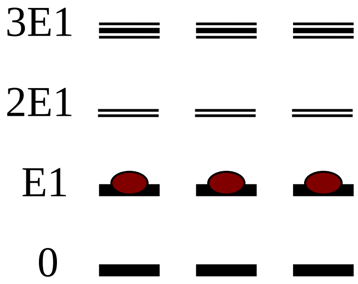
n_i	Number densityof atom in ith energy state
E_i	Energy state of the ith energy level
g_i	Degeneracy
Z_a	Partition function
n_a	Total number of atoms
T	Temperature
k	Boltzmann Constant

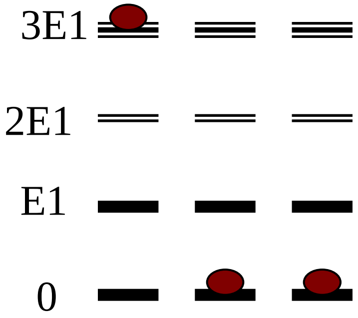
Partition Function

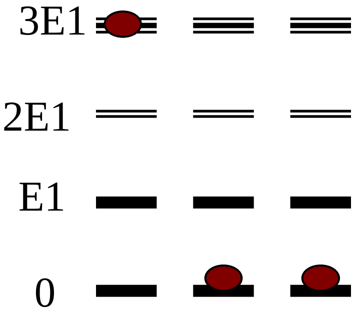
$$Z_a = \sum_{i=1}^{n_{ionization}} g_i \exp\left(\frac{-E_i}{kT}\right)$$

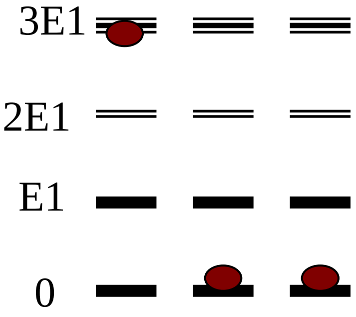

3E1
2E1
E1
0


3E1
2E1
E1
0
3
2
Degeneracy, g_i


3E1
2E1
E1
0

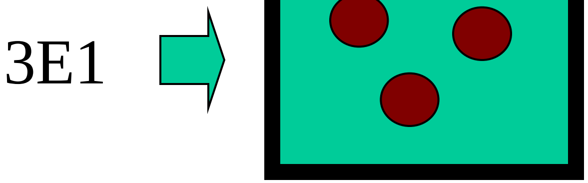

3E1
2E1
E1
0


3E1
2E1
E1
0

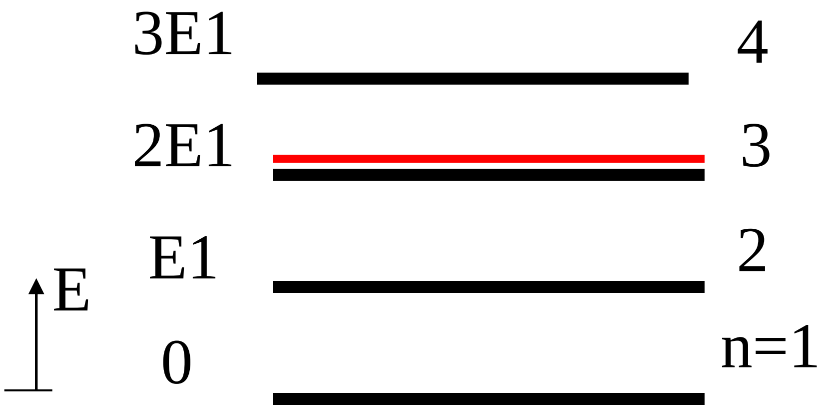

3E1
2E1
E1
0

Example

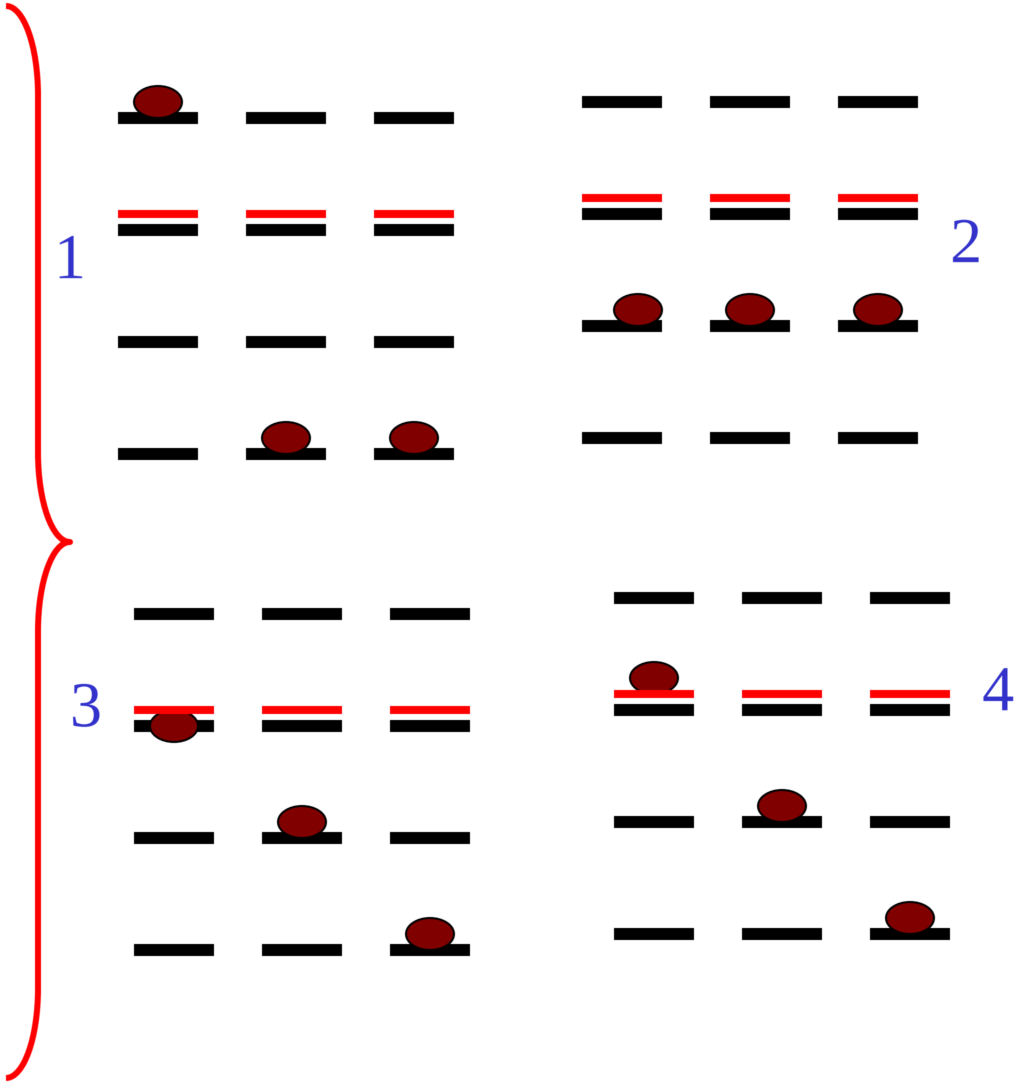
System of three particles



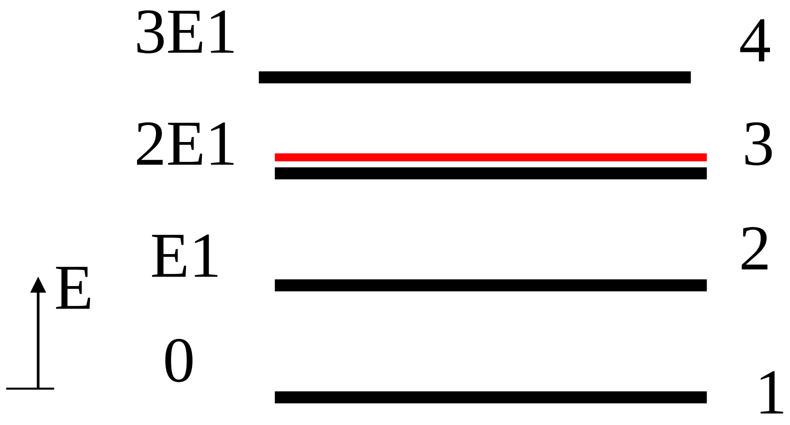
● has 4 energy levels.
Third energy level has a degeneracy of 2



Four different combinations



$$Z_a = \sum_{i=1}^{n_{ionization}} g_i \exp(\frac{-E_i}{kT})$$

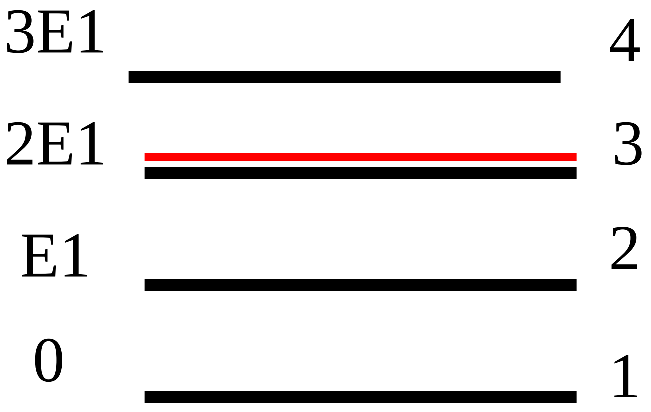


$$Z_a = 1 \times e^{\left(\frac{0}{kT}\right)} + 1 \times e^{\left(\frac{-E1}{kT}\right)} + 2 \times e^{\left(\frac{-2E1}{kT}\right)} + 1 \times e^{\left(\frac{-3E1}{kT}\right)}$$

$$e^{\left(\frac{-E1}{kT}\right)} = x$$

$$Z_a = 1 + x + 2x^2 + x^3$$

$$Z_a = 1 + x + 2x^2 + x^3$$



$$n_i = \frac{g_i}{Z_a}\overbrace{n_a}^{=3}\exp(\frac{-E_i}{kT})$$

Energy Conservation

$$3\times E1 = n_1\times 0 + n_2\times E1 + n_3\times 2\times E1 + n_4\times 3\times E1$$

$$\Downarrow$$

$$2x^3 + 2x^2 - 1 = 0$$

$$\Downarrow$$

$$x = 0.5652 \;\Rightarrow\; Z_a = 2.3847$$

When we look at one particle, this is the probability of being in that energy state

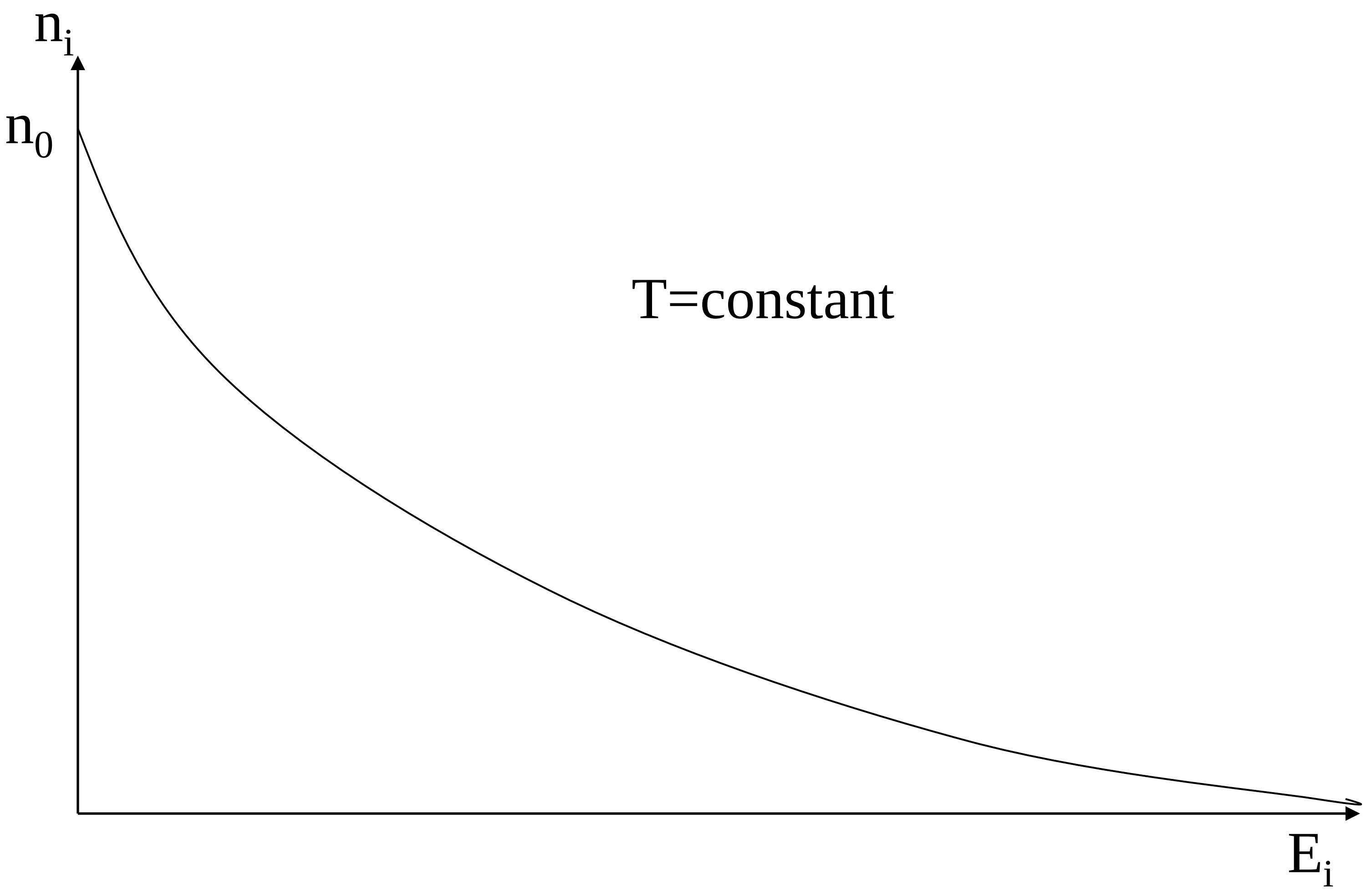
$n_1 = 1.2581$ %42

$n_2 = 0.7110$ %24

$n_3 = 0.8038$ %27

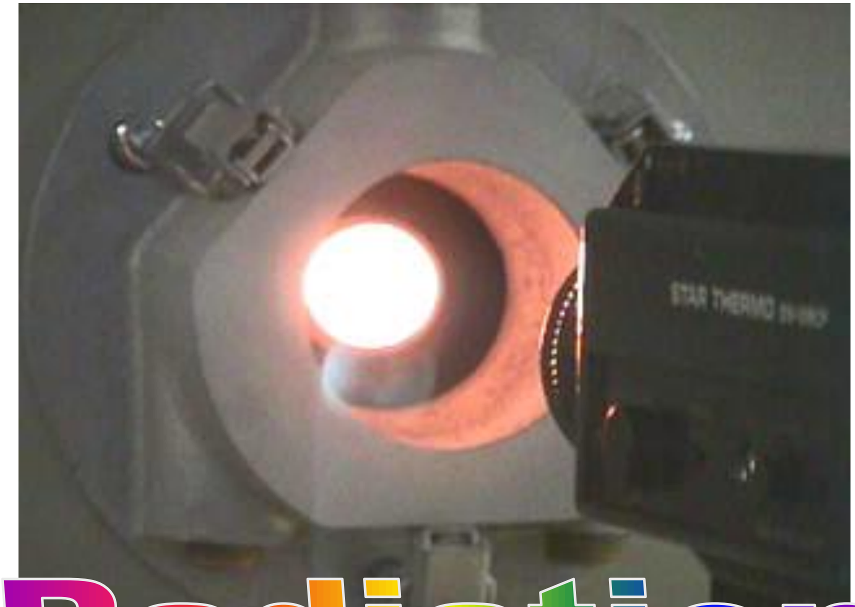
$n_4 = 0.2271$ %7

$$n_i = \frac{g_i}{Z_a} n_a \exp(\frac{-E_i}{kT})$$



EE 403/503

Introduction to Plasma Processing



Radiation

Dr. Kasra Etemadi
September 23, 2009

Blackbody Radiation

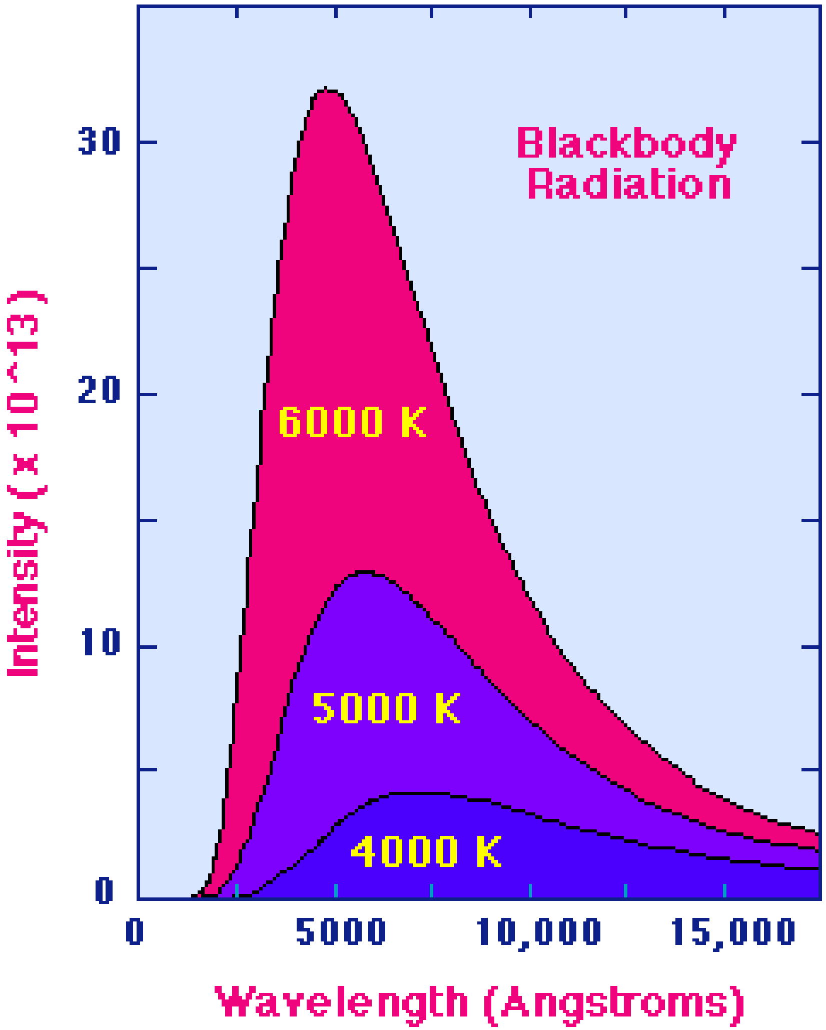
$$E(\lambda,T)=\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}}-1}$$

Steffan-Boltzmann Law:

$$E=\sigma T^4$$

Wien Displacement Law:

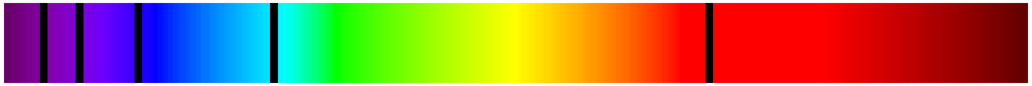
$$\lambda_{Max}=\frac{3\times10^7}{T}$$ (λ is in Å)



Link1

Continuous ↔ Line

Continuous Spectrum

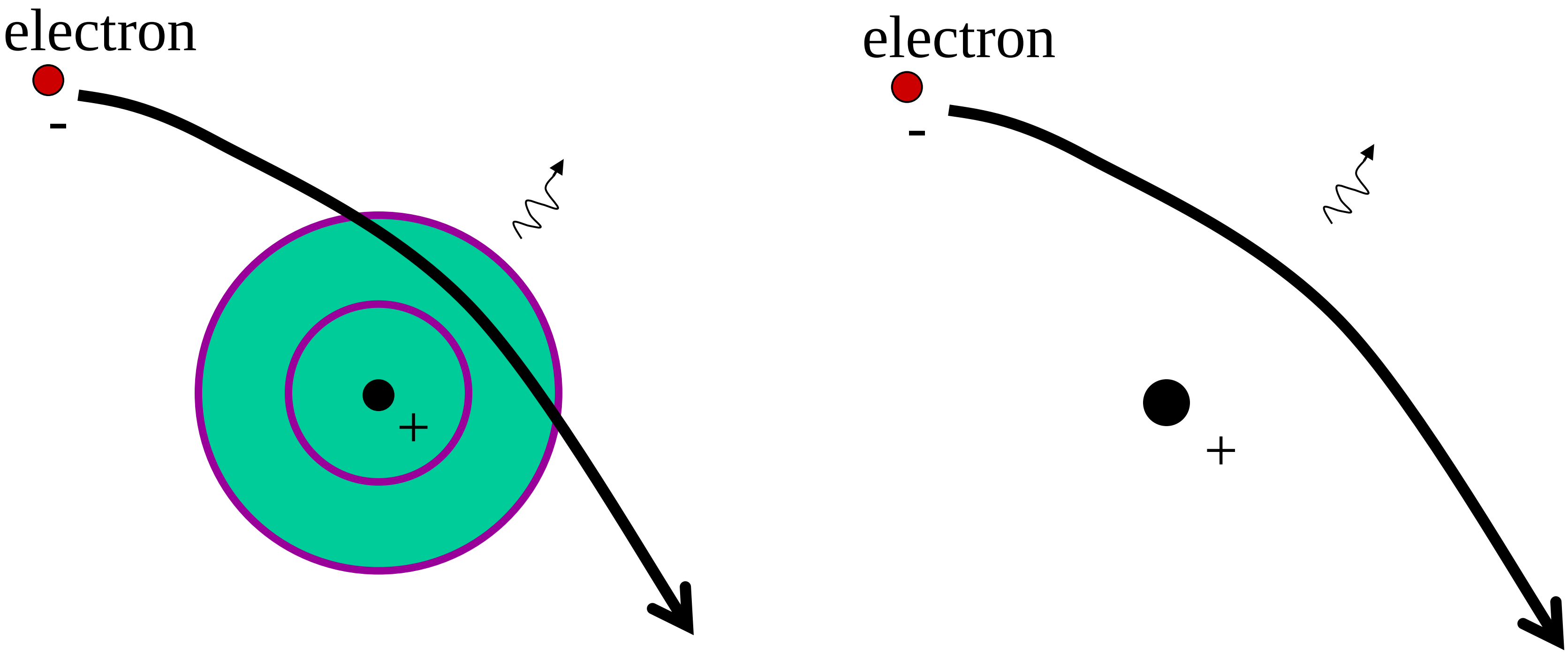


Absorption Spectrum of Hydrogen

Emission Spectrum of Hydrogen

Colors

Continuous Spectrum

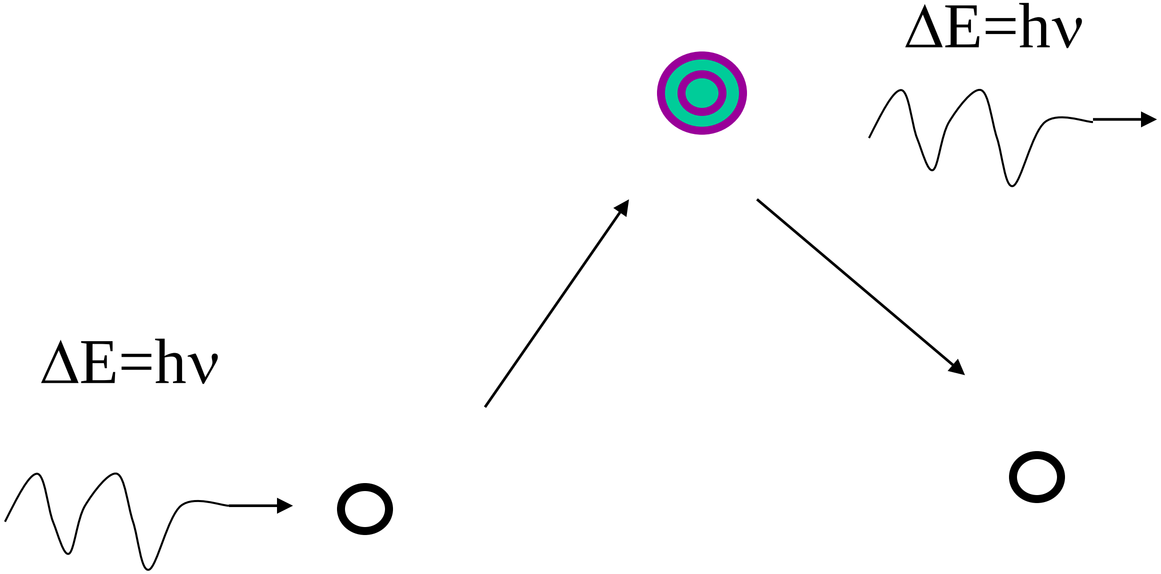


$$\varepsilon_{\lambda}(T) = 1.63075\times 10^{-28}\frac{N_e^2}{\lambda^2 T^{1/2}}\xi(\lambda,T)$$

$$\xi(\lambda,T) = \frac{g_i}{Z_i}\xi^{fb}(\lambda,T)(1-e^{-\frac{C}{\lambda T}}) + \xi^{ff}(\lambda,T)e^{-\frac{c}{\lambda T}}$$

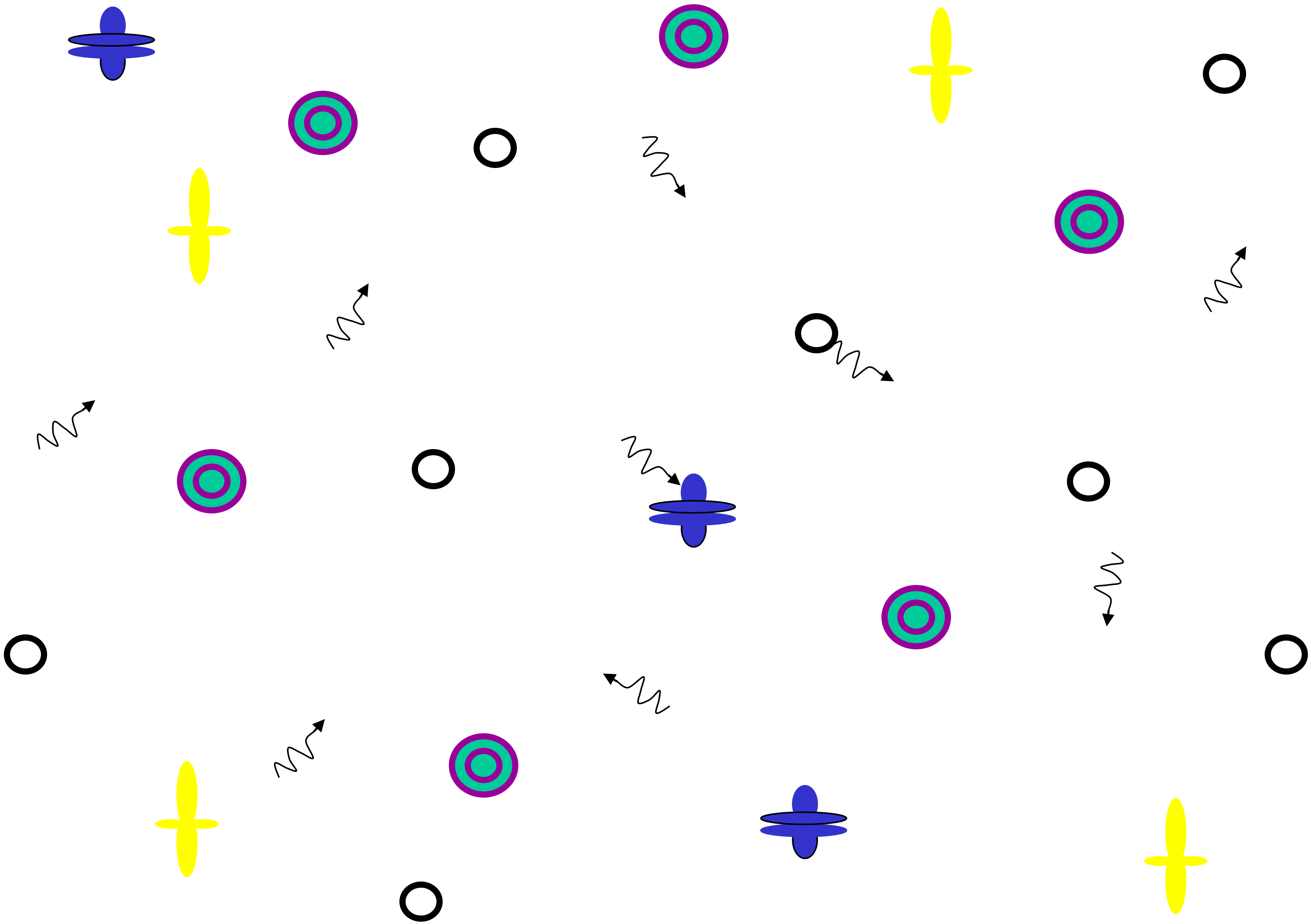
Spectral Lines

Absorption **Emission**

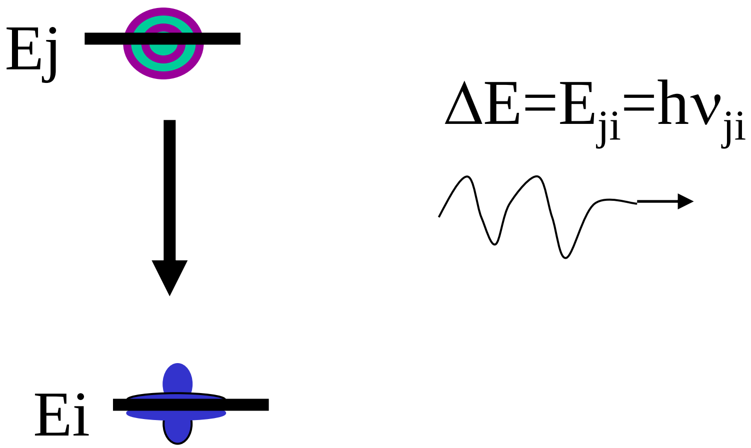


$\Delta E=h\nu$

$\Delta E=h\nu$



Radiation Energy



$\Delta E = E_{ji} = h\nu_{ji}$

$$E_\lambda = \frac{1}{4\pi} n_j A_{ji} E_{ji} = \frac{1}{4\pi} n_j A_{ji} h \nu_{ji}$$

$$E_\lambda = \frac{1}{4\pi} n_a \frac{g_j}{Z_a} \exp\left(\frac{-E_j}{kT}\right) A_{ij} h \nu_{ji}$$

$$E_{total} = \sum_\lambda E_\lambda + E_{continum}$$

Plasmas

Optically Thin ⟷ Optically Thick

Maxwellian Distribution

$$f(v) = 4\pi(\frac{m}{2\pi kT})^{3/2} v^2 \exp(-\frac{mv^2}{2kT})$$

T_{Maxwellian}

Boltzmann Distribution

$$n_i = \frac{g_i}{Z_a} n_a \exp(\frac{-E_i}{kT})$$

$\mathbf{T}_{\mathbf{Boltzmann}}$

Saha Equation

$$\frac{n_e n_i}{n_a} = \frac{(2\pi m_e kT)^{3/2}}{h^3} \frac{2Z_i}{Za} \exp(\frac{-e\chi_a}{kT})$$

$\mathbf{T}_{\mathbf{Saha}}$

Planck’s Function

$$E(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

$\mathbf{T}_{\mathbf{Planck}}$

Complete Thermodynamic Equilibrium

$$T_{\text{Maxwellian}} = T_{\text{Boltzmann}} = T_{\text{Saha}} = T_{\text{Planck}}$$

Local Thermodynamic Equilibrium

$$T_{\text{Maxwellian}} = T_{\text{Boltzmann}} = T_{\text{Saha}}$$

Partial Local Thermodynamic Equilibrium

$$T_{\text{Maxwellian}} = T_{\text{Saha}}$$

Example

For an atmospheric pressure hydrogen plasmas having a temperature of 10,000 K determine the following:

- number density of atoms, ions and electrons
- Maximum number densities of atoms, ions and electrons that can contribute to excitation of hydrogen atoms from ground state.
- Density distribution of energy states of hydrogen atomes
- Intensity [J/cm-3] of hydrogen spectral line at 1215.72 Å (first excited to ground state, g_u=8, Z_H =2, A_{ul}=4.699e8 s-1)

Project (Deadline October 5, 2011)

Prepare a Powerpoint presentation (PPP) with the format similar to final presentation (see the Presentation Format as described in the EE403/503 website).

Transfer this file to the your memory space assigned for your project.

Put a link on top of your index.html file to access the PPP file.

You still need to continue on your project with new research materials.