EE 403/503
Introduction to Plasma Processing

The kinetic Theory of Gases

&

Plasma Properties

Dr. Kasra Etemadi
October 5, 2011

Outline

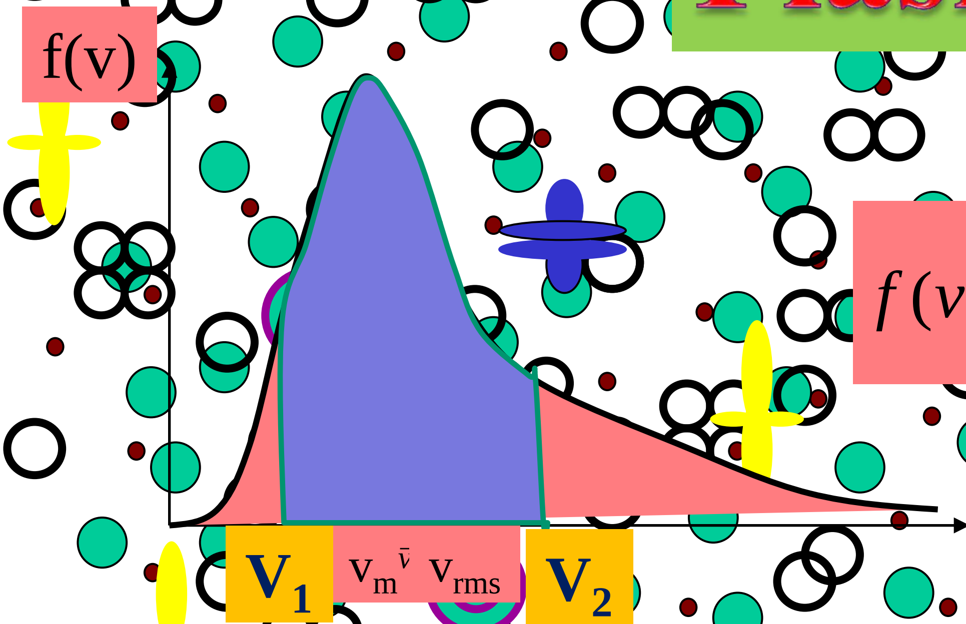
1- Summary of Kinetic Theory of Gases

2- Radiation

3- E4

4- Plasma Properties

Plasma



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

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

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

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

E3: Percentage of particles having speed between V_1 and V_2

$$\frac{N_{V_1 \to V_2}}{N} = 1 + \frac{2}{\sqrt{\pi}} U e^{-U^2} - erf(U)$$

The Saha Equation

$e + A^+ \rightarrow A$

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

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	$E_i - \Delta E_i$ **$\Delta E_{ionization} = 6.96 \cdot 10^{-13} n_e^{1/3}$ [eV]**		
$E_{ionization}$	Ionization potential of neutral atoms		
$\Delta E_{ionization}$	Lowering of ionization potential		

Pressure

$$p_{total} = p_{molecules} + p_{atoms} + p_{ions} + p_{etectons}$$

$$p = n\,k\,T$$

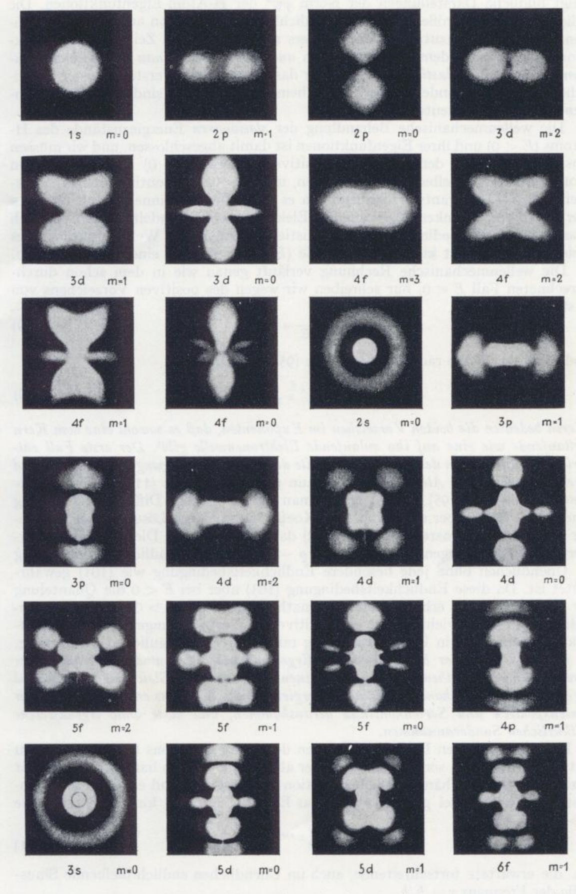
For multi-temperature Plasmas:

$$p = n_e k T_e + n_{ion} k T_i + n_a k T_a$$

For equilibrium plasmas:

$$p = (n_a + n_{ion} + n_a) k T$$

Hydrogen



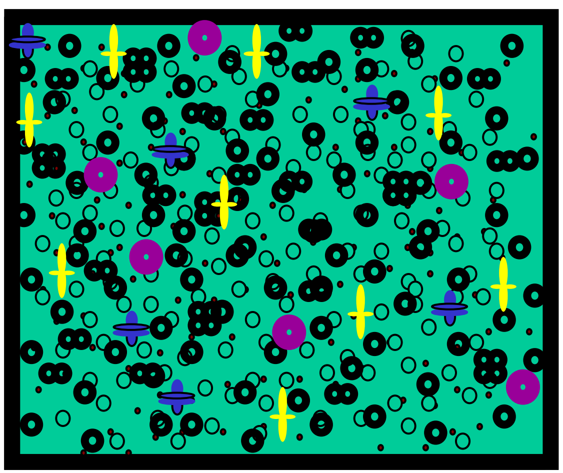
$$n_i = \frac{g_i}{Z_a} n_a \exp\left(\frac{-E_i}{kT}\right)$$

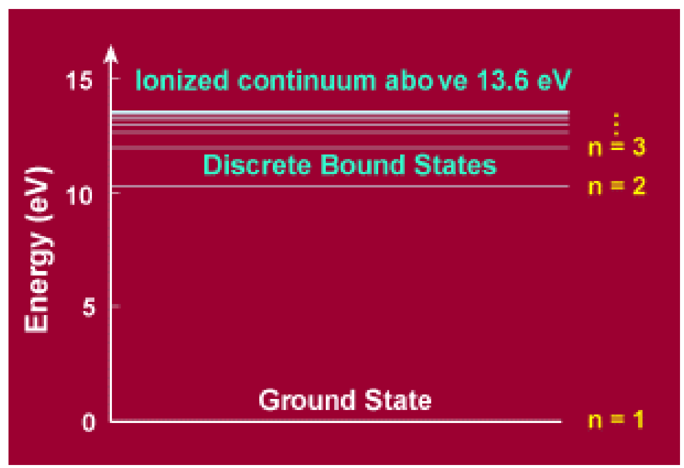
n_i	Number densityof atom in ith energy state
E_i	Energy state of the ith energy level
g_i	Degeneracy
Z_a	Partition function
n_a	Total number of atoms
T	Temperature
k	Boltzmann Constant

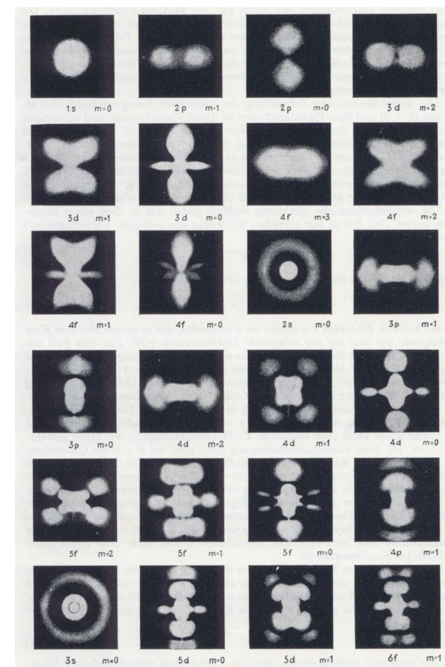
$$n_i = \frac{g_i}{Z_a} n_a \exp\left(\frac{-E_i}{kT}\right)$$

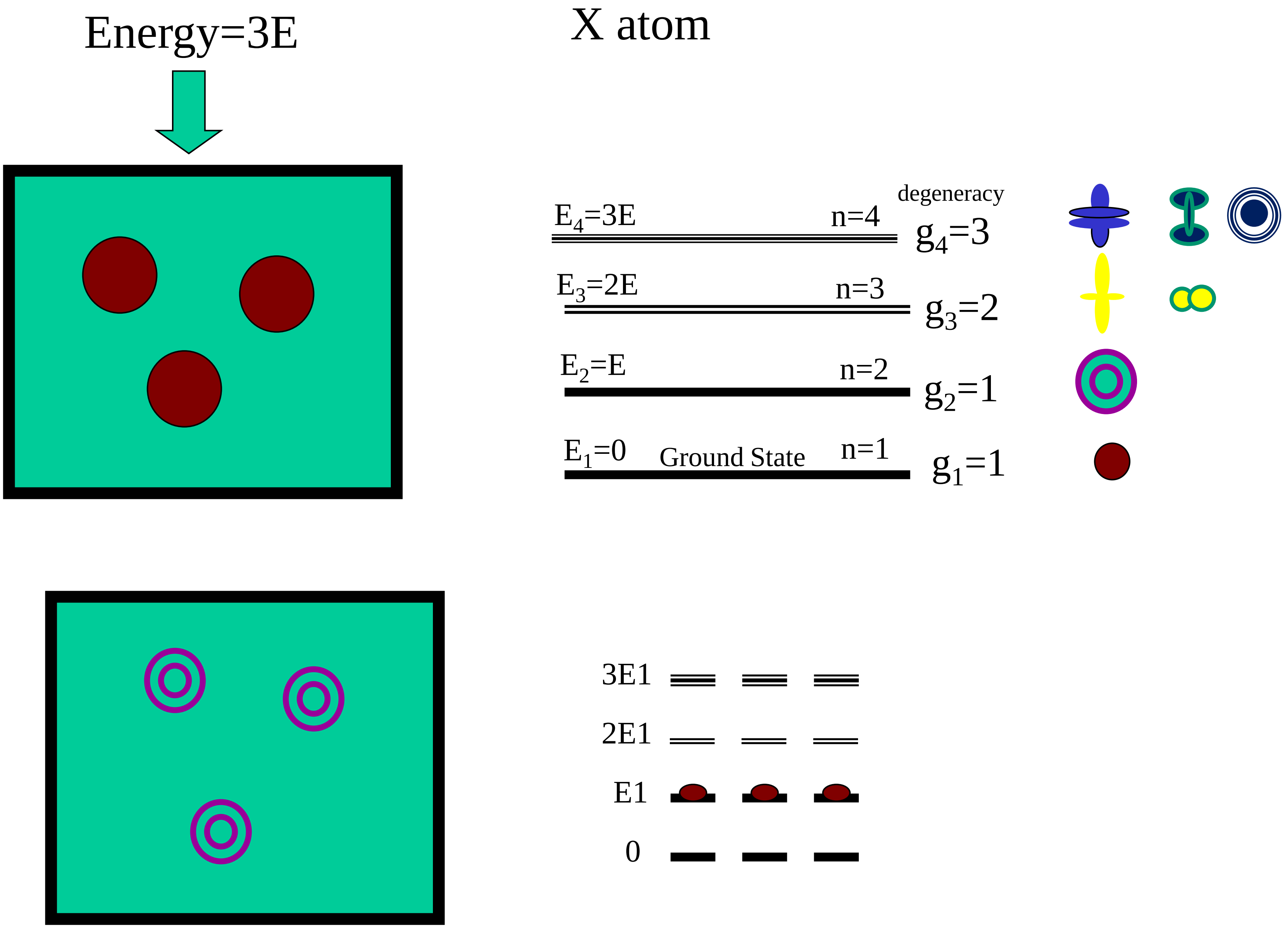
n_i	Number densityof atom in i^{th} energy state
E_i	Energy state of the i^{th} energy level
g_i	Degeneracy
Z_a	Partition function $Z_a = \sum_{i=1}^{n_{ionization}} g_i \exp\left(\frac{-E_i}{kT}\right)$
n_a	Total number of atoms
T	Temperature
k	Boltzmann Constant

Hydrogen

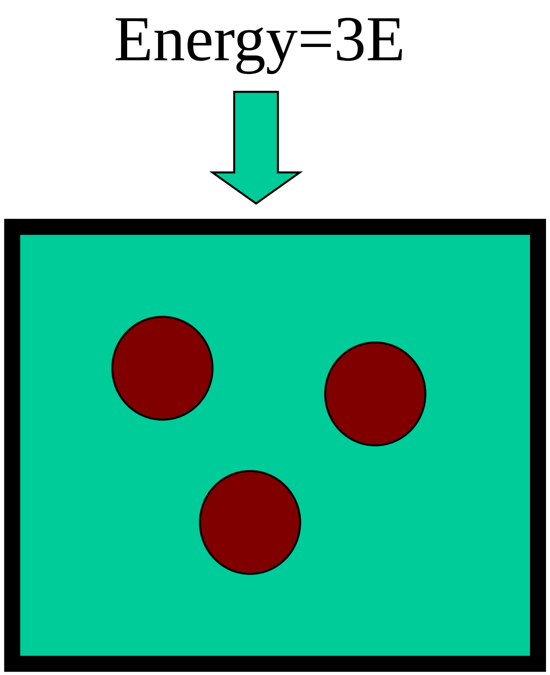


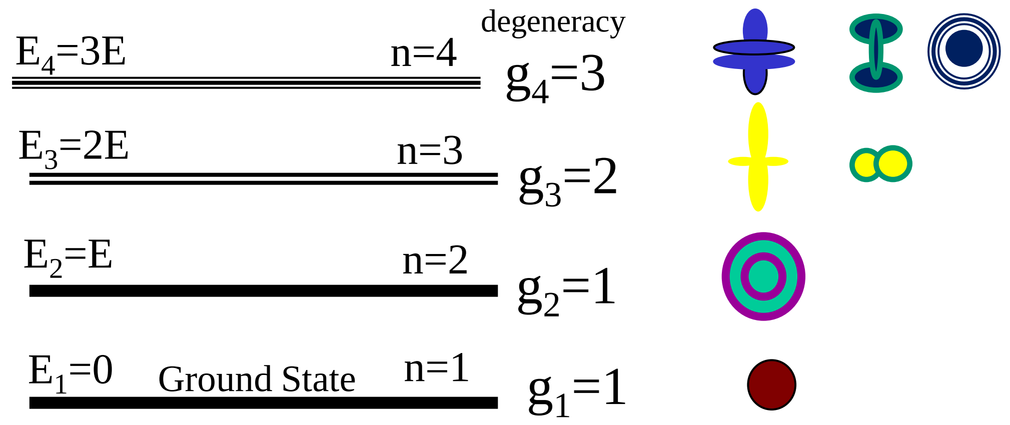


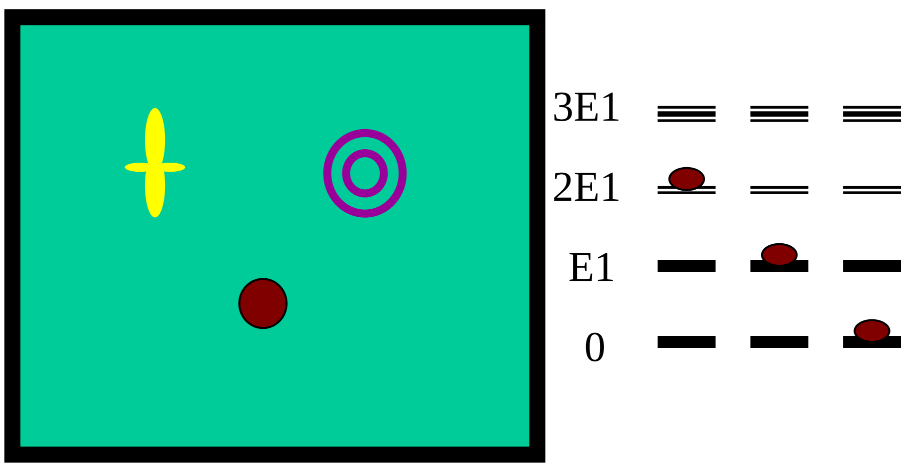


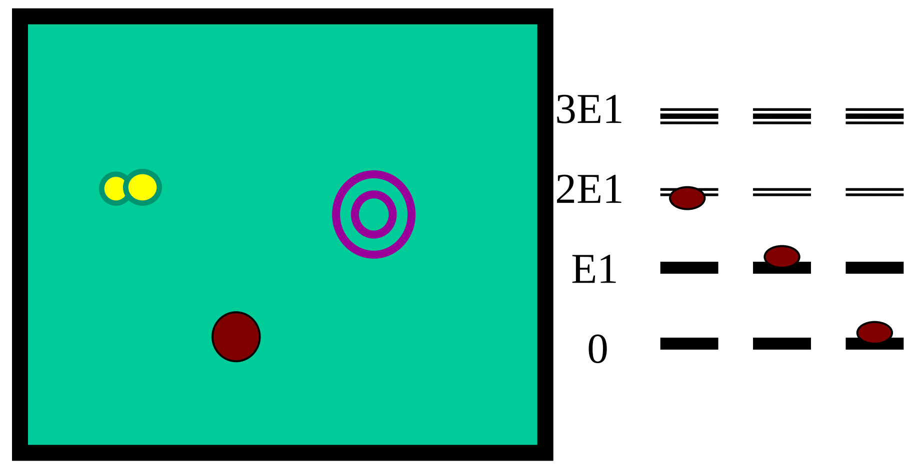

Energy=3E
X atom
degeneracy
E4=3E
n=4
g4=3
E3=2E
n=3
g3=2
E2=E
n=2
g2=1
E1=0
Ground State
n=1
g1=1
3E1
2E1
E1
0

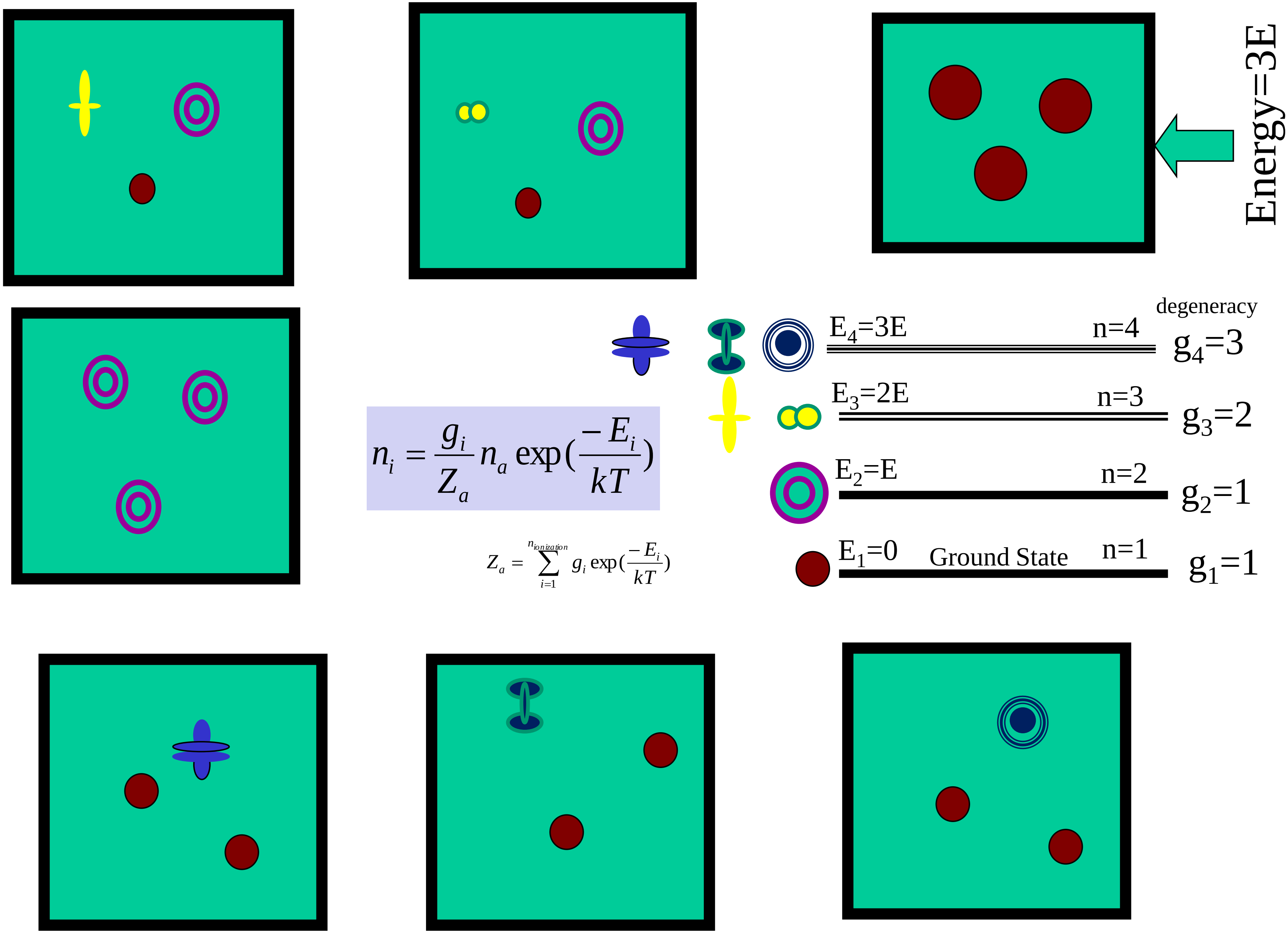
X atom


Energy=3E


degeneracy
$E_4=3E$
n=4
$g_4=3$
$E_3=2E$
n=3
$g_3=2$
$E_2=E$
n=2
$g_2=1$
$E_1=0$
Ground State
n=1
$g_1=1$


3E1
2E1
E1
0


3E1
2E1
E1
0


Energy=3E
degeneracy
$E_4=3E$ n=4 $g_4=3$
$E_3=2E$ n=3 $g_3=2$
$E_2=E$ n=2 $g_2=1$
$E_1=0$ Ground State n=1 $g_1=1$
$n_i = \frac{g_i}{Z_a} n_a \exp(\frac{-E_i}{kT})$
$Z_a = \sum_{i=1}^{n_{ionization}} g_i \exp(\frac{-E_i}{kT})$

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Radiation

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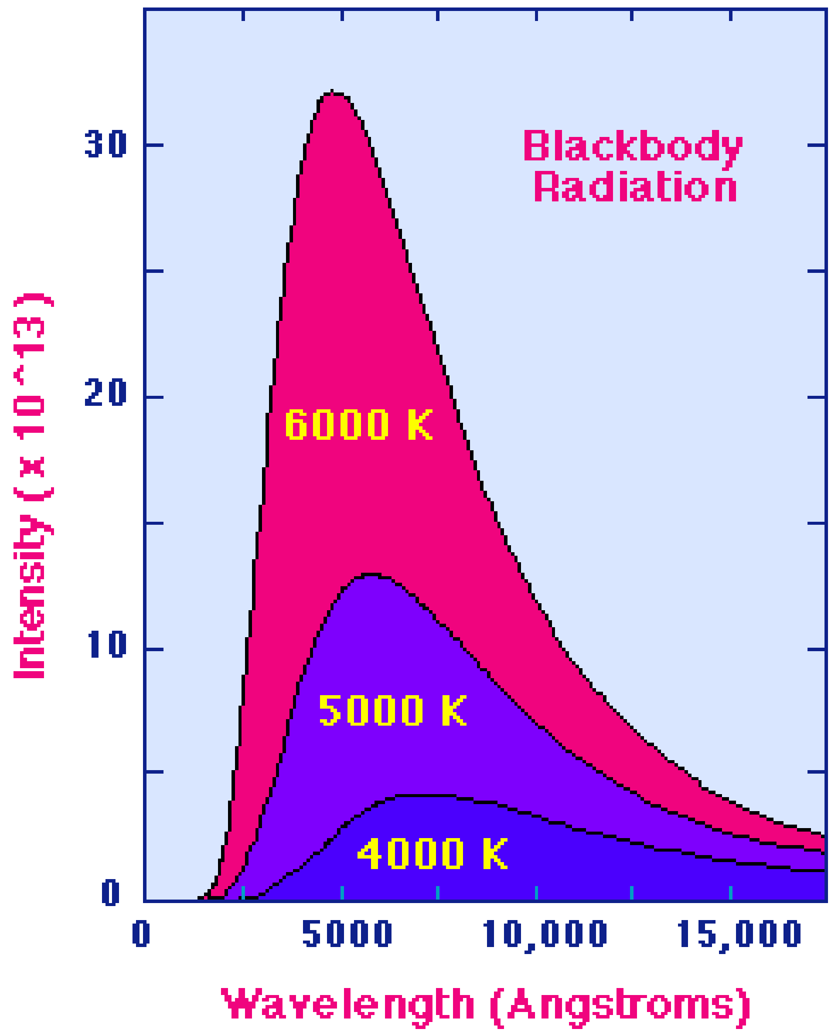
Blackbody Radiation

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



Stefan-Boltzmann Law:

$$E=\sigma T^4$$

$$\sigma = 5.67\times10^{-8} \quad \left[Jm^{-2}s^{-1}K^{-4}\right]$$

Wien Displacement Law:

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

Link1

Continuous ⟷ Line

4000 Å 7500 Å

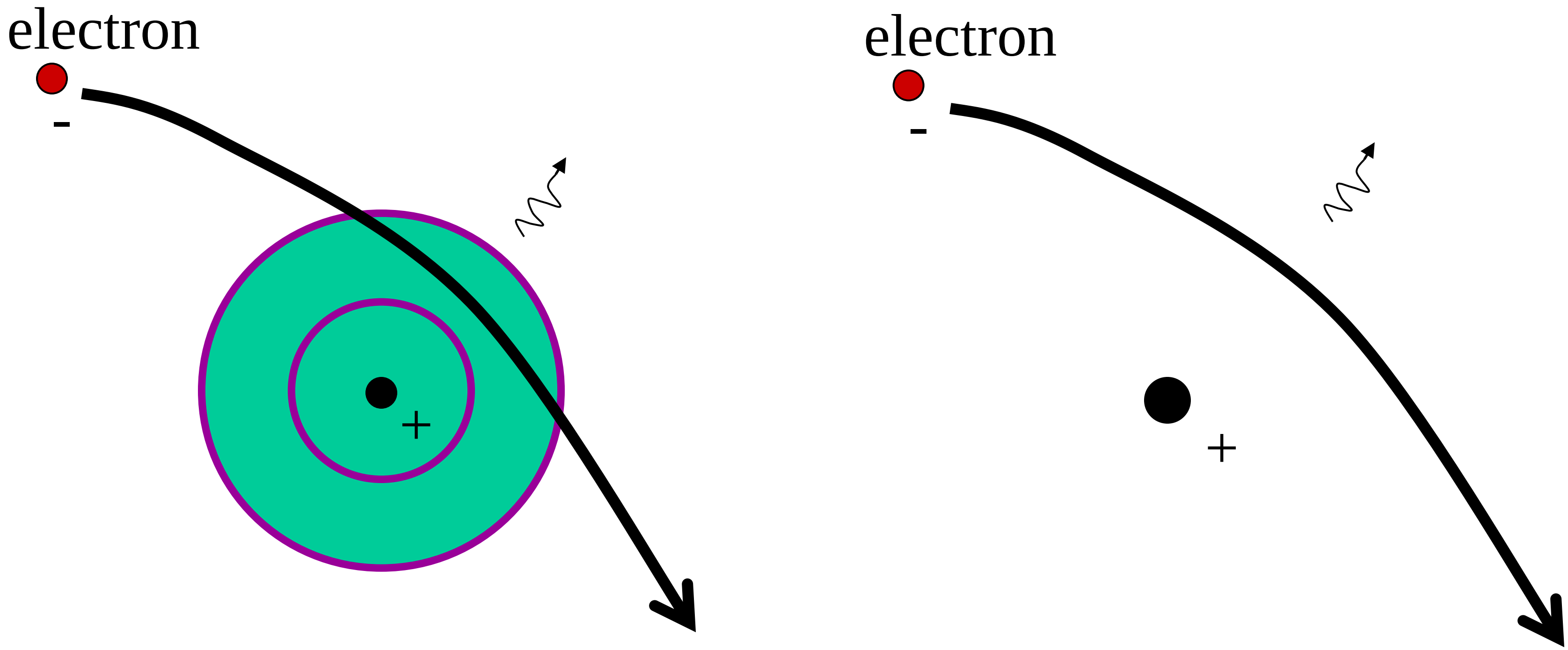
Continuous Spectrum

Absorption Spectrum of Hydrogen

Emission Spectrum of Hydrogen

Colors

Continuous Spectrum



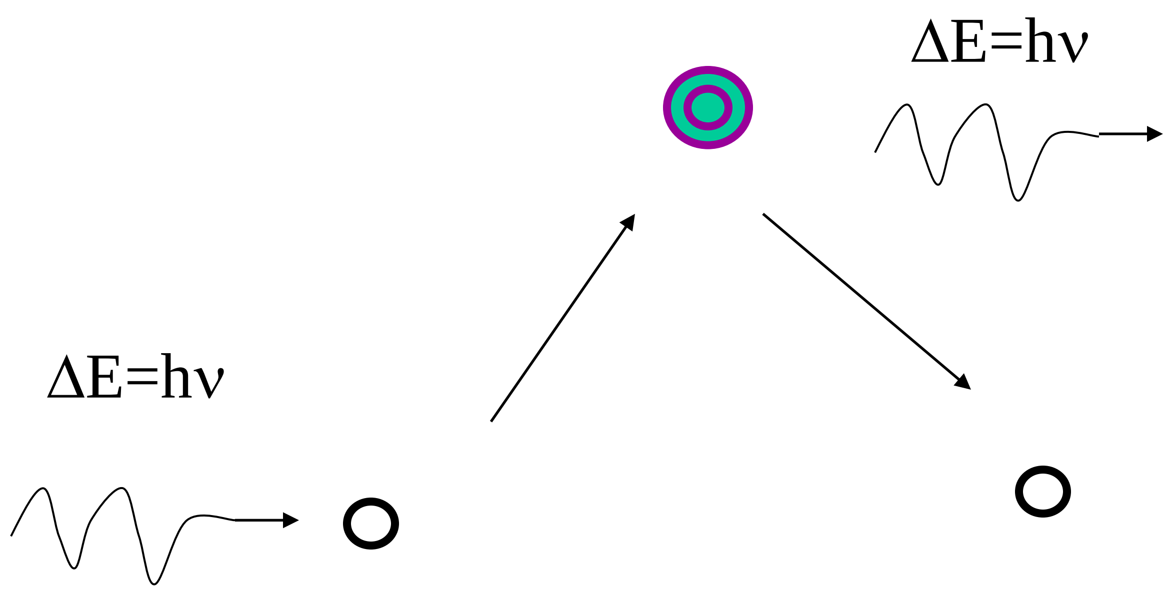
$$\varepsilon_{\lambda}(T) = 1.63075\times10^{-28}\frac{N_e^2}{\lambda^2 T^{1/2}}\xi(\lambda,T)$$

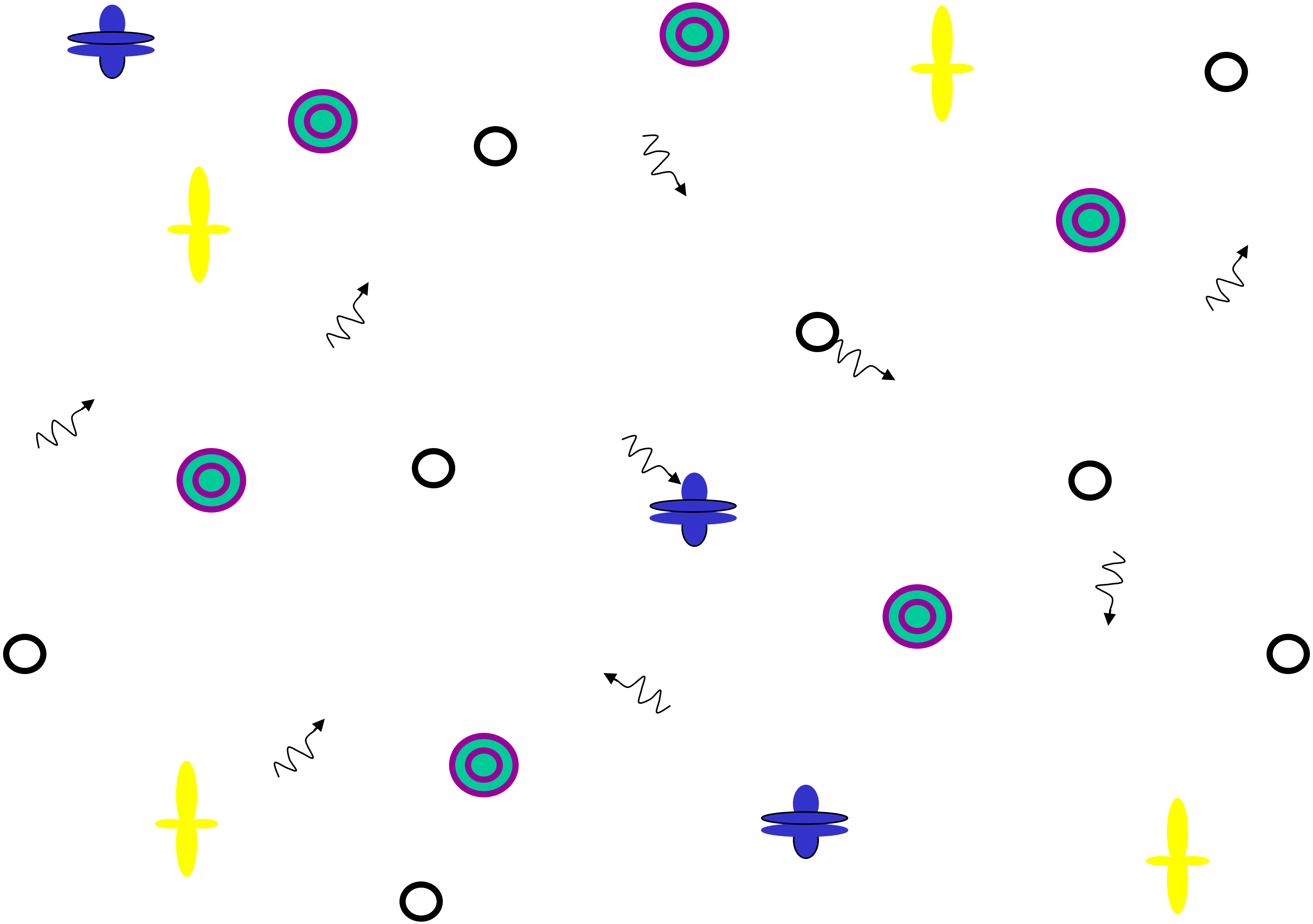
$$\xi(\lambda,T) = \frac{g_i}{Z_i}\xi^{fb}(\lambda,T)(1-e^{-\frac{C}{\lambda T}}) + \xi^{ff}(\lambda,T)e^{-\frac{c}{\lambda T}}$$

Spectral Lines

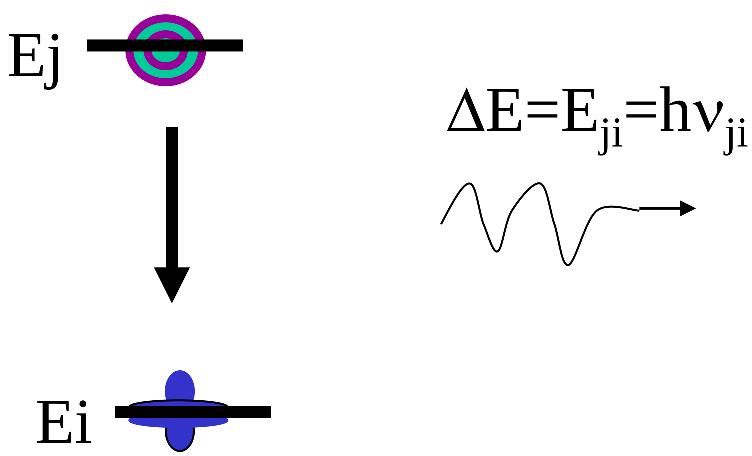
Absorption

Emission





Radiation Energy



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

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

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

Plasmas

Optically Thin $\longleftrightarrow$ Optically Thick

Maxwellian Distribution

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

$T_{Maxwellian}$

Boltzmann Distribution

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

$T_{Boltzmann}$

Saha Equation

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

T_{Saha}

Planck's Function

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

T_{Planck}

Complete Thermodynamic Equilibrium

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

Local Thermodynamic Equilibrium

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

Partial Local Thermodynamic Equilibrium

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

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)

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Plasma Properties

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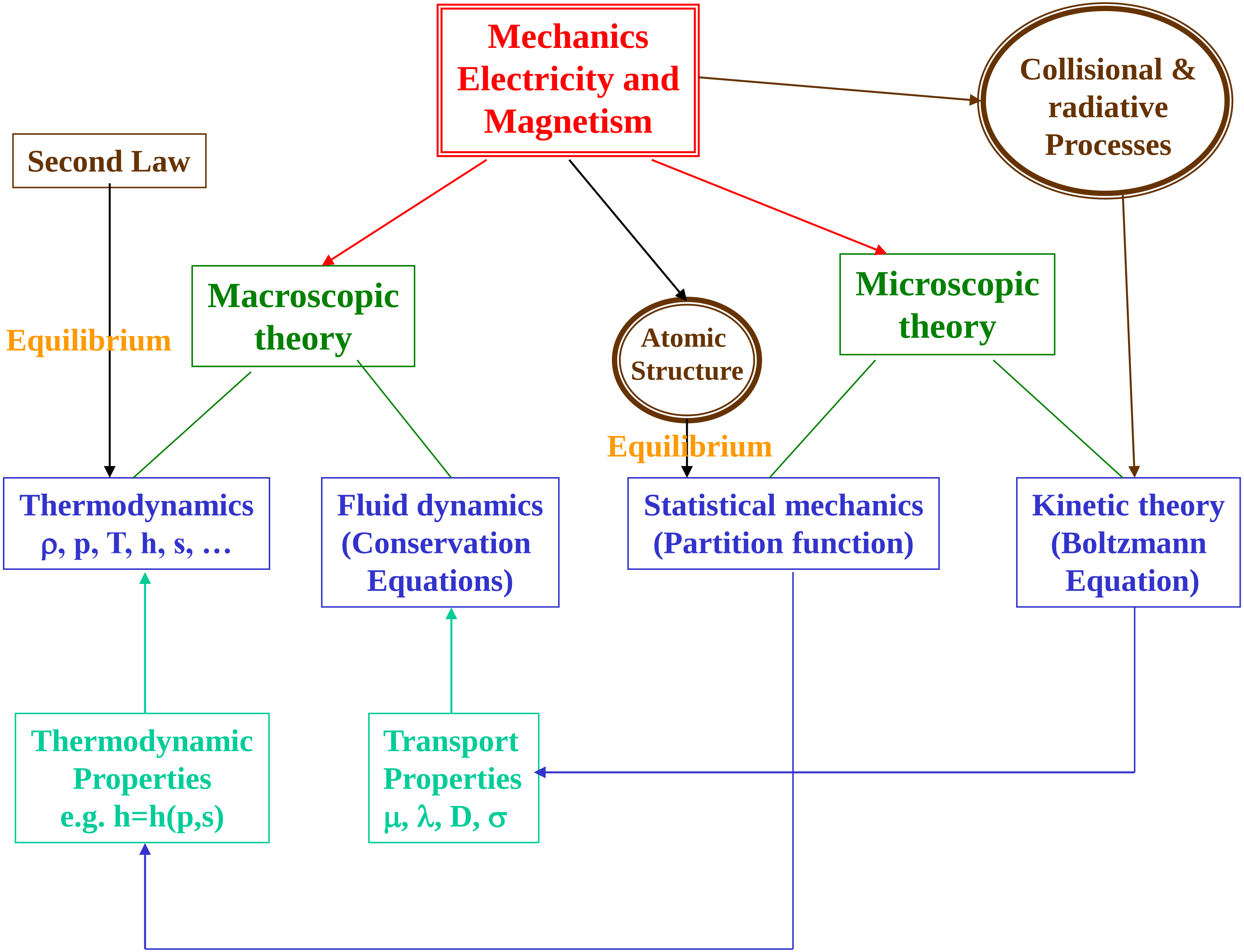

Mechanics
Electricity and
Magnetism
Collisional &
radiative
Processes
Second Law
Macroscopic
theory
Equilibrium
Atomic
Structure
Microscopic
theory
Equilibrium
Thermodynamics
ρ, p, T, h, s, …
Fluid dynamics
(Conservation
Equations)
Statistical mechanics
(Partition function)
Kinetic theory
(Boltzmann
Equation)
Thermodynamic
Properties
e.g. h=h(p,s)
Transport
Properties
μ, λ, D, σ

Boltzmann Equation

Net rate of increase of species s, as a result of collisions between particles of species s with those of species r

Species distribution function $f_s(x,v,t)$

External forces

$$\frac{\partial}{\partial t}(n_s f_s) + \vec{v}.\nabla n_s f_s + \frac{F_s}{m_s}\cdot n_s \nabla_v f_s = \sum_r C_{sr}$$

Number of particles n_s

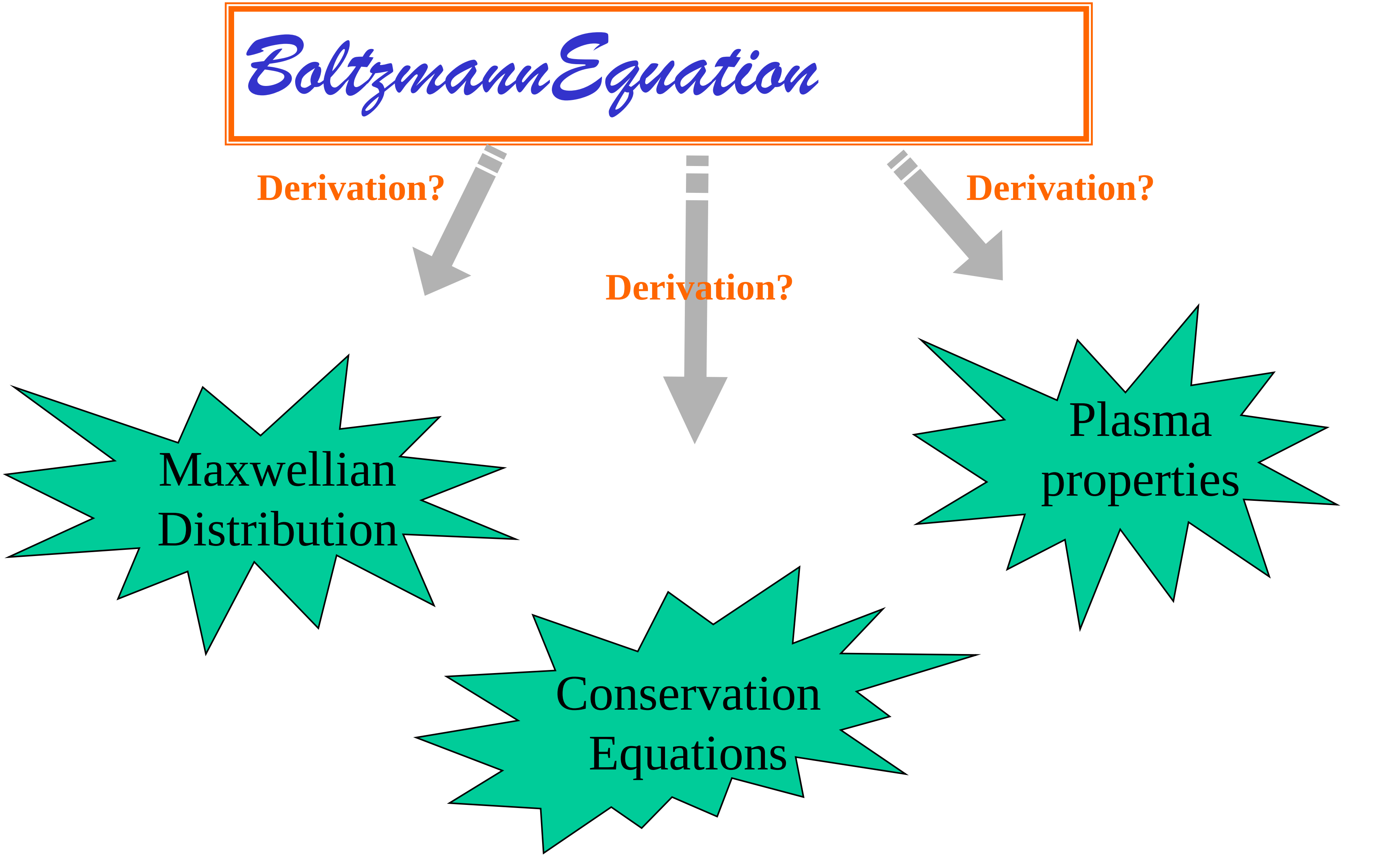
Velocity

Mass of species s

Impact parameter

after the collision

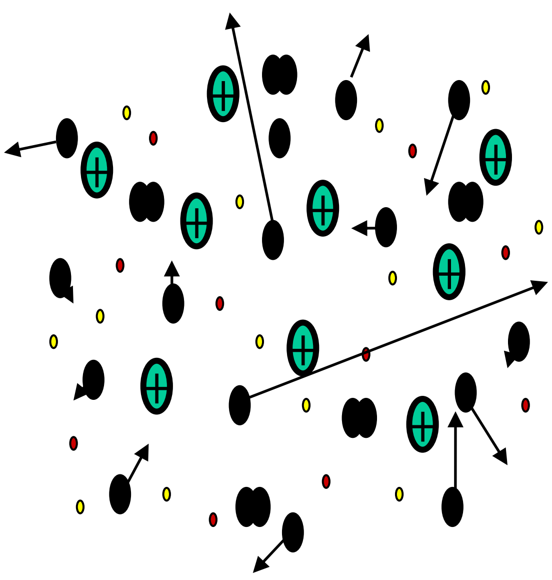
$$C_{sr} = n_r n_s \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[f_s(v_s')\, f_r(v_r') - f_s(v_s)\, f_r(v_r)\right] v_{rs}\, b\, db\, dv_r$$

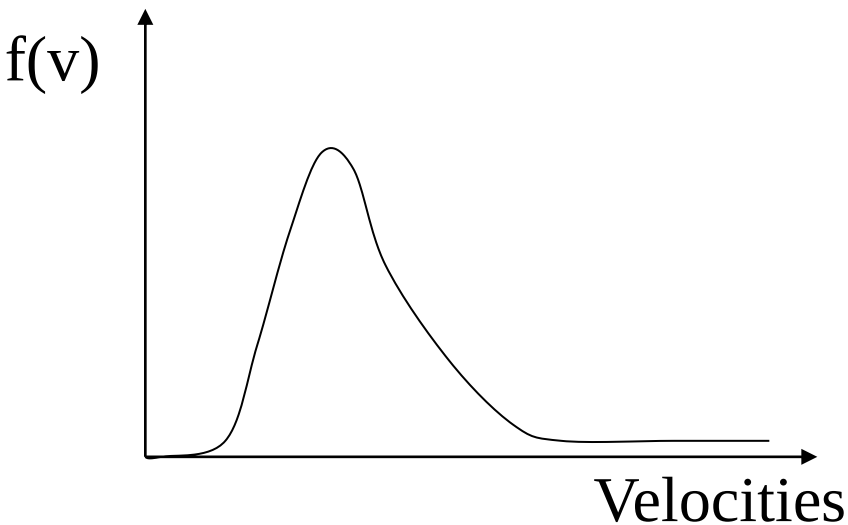

BoltzmannEquation
Derivation?
Derivation?
Derivation?
Maxwellian Distribution
Conservation Equations
Plasma properties

Maxwellian distribution

Neglecting all external forces in Boltzmann equation gives the Maxwell distribution function:

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





Conservation Equatios

General Form

Dependent variable

Specific to a particular Meaning of Φ

$$\frac{\partial}{\partial t}(\rho\Phi) + \nabla\cdot(\rho\vec{u}\Phi) = \nabla\cdot(\Gamma\nabla\Phi) + S$$

Unsteady term

Convection term

Diffusion term

Source term

Examples:

General:

$$\boxed{\frac{\partial}{\partial t}(\rho\Phi) + \nabla\cdot(\rho\vec{u}\Phi) = \nabla\cdot(\Gamma\nabla\Phi) + S}$$

$\Phi = 1$

$$\frac{\partial}{\partial t}(\rho) + \nabla\cdot(\rho\vec{u}) = 0$$

$\Phi = \vec{u}$

$$\frac{\partial}{\partial t}(\rho\vec{u}) + \nabla\cdot(\rho\vec{u}\vec{u}) = \nabla\cdot(\Gamma\nabla\vec{u}) + \nabla p + S_m$$

$\Phi = m_l$

$$\frac{\partial}{\partial t}(\rho m_l) + \nabla\cdot(\rho\vec{u}m_l) = \nabla\cdot(\Gamma\nabla m_l) + R_l$$

$\Phi = h$

$$\frac{\partial}{\partial t}(\rho h) + \nabla\cdot(\rho\vec{u}h) = \nabla\cdot(\frac{k}{c_p}\nabla\Phi) + S_h$$

To utilize the conservation equations in your application, you need:

-a set of conservation equations that are required to describes your applications

-Set up your initial condition and boundary conditions

-Provide the required thermodynamic and transport properties

Solve the conservation equations analytically or numerically

Transport Properties

1- Diffusivity (Page 49)

Movement of gas particles from high density to low density gas by random walk

Particle Flux

Diffusion Coefficient

$$\Gamma = n v_d = -D \nabla n$$

Fick's Law

Density

Drift Velocity

Average Velocity

$$D \approx \frac{1}{3} v_c \lambda^2 = \frac{1}{3} \bar{v} \lambda = \frac{1}{3} \bar{v}^2 \tau \quad \text{if} \quad \frac{\lambda}{n}\frac{\partial n}{\partial x} = \frac{\lambda}{L} << 1$$

Collision Frequency

Mean Free Path

For a monolithic gas:

$$D = 2.06 \times 10^{-12} \frac{\sqrt{mT}}{\sigma}$$

Cross section for binary hard-sphere collisions

2- Electrical Conductivity

Current Density $\longrightarrow$ $$J = \sigma E$$ [A/m^2]

Electrical Conductivity $\rightarrow$ $$\sigma = \frac{e^2 n_e}{m_e \nu_e}$$

3- Thermal Conductivity

Heat Flux $\longrightarrow$ $$q = -\kappa \nabla T$$

Thermal Conductivity $\rightarrow$ $$\kappa \approx f \bar{v} \lambda$$

Degree of Freedom

Heat Capacity

For a monolithic gas: $$\kappa = \frac{25}{64} \frac{fk}{\sigma} \left(\frac{\pi k T}{m} \right)^{1/2} = \frac{C_v \bar{v}}{3 N_{Avag} \sigma_{cross}}$$

4- Viscosity

Force resulting from the net transport of momentum from one region to another

$$F = \eta \frac{du}{dz} \qquad [N/m^2]$$

Coefficient of Viscosity

$$\eta = \frac{1}{3} \frac{m\bar{v}}{\sigma_{cross}} \qquad [Ns/m^2]$$

Cross section for the binary hard-sphere collision

5- Mobility

Mobility

Drift Velocity

$$U_{e_d} = -\mu_e E$$

Electric Field

$$\mu_e = \frac{3}{4} \frac{e}{n\sigma} \left(\frac{2\pi}{m_e kT} \right)^{1/2}$$

Thermodynamic Properties

Link1

1- Internal Energy

2- Enthalpy

3- Entropy

4- Gibbs Free Energy

Partition Function

$$Z = \sum_{s} g_s e^{-\frac{E_s}{kT}}$$

$$E_s = E_{transitional} + E_{electronic} + E_{vibrational} + E_{rotational} + E_{ionization}$$

$$Z = Z_{transitional} \times Z_{electronic} \times Z_{vibrational} \times Z_{rotational} \times Z_{ionization}$$

$$Z = \sum_s g_s e^{-\frac{E_s}{kT}}$$

$$Z = Z_{transitional} + Z_{electronic} + Z_{vibrational} + Z_{rotational} + Z_{ionization}$$

$$Z_{transitional} = \int\int_{-\infty}^{+\infty}\int \frac{V}{h^3} e^{-\frac{m\vec{v}^2}{2kT}} d\vec{v} = \frac{V}{h^3}(2\pi mkT)^{3/2}$$

$$Z_{electronics} = \sum_i (2j+1) e^{-\frac{E_i}{kT}} = \sum_i 2n^2 e^{-\frac{E_i}{kT}}$$

For Hydrogen

$$Z_{ionization} = e^{-\frac{\chi_i}{kT}}$$

For molecule made of two identical atoms (rigid rotator):

$$Z_{rotational} = \frac{1}{2}\sum_{j=0}^{\infty}(2j+1)e^{-\left[\frac{h^2}{8\pi^2\Theta}j(j+1)\right]/kT} = \frac{8\pi^2\Theta}{2h^2}kT$$

Approximate Solution

For harmonic oscillation

$$Z_{oscillation} = \sum_{\nu=0}^{\infty} e^{-\frac{h\nu(\nu+1/2)}{kT}} = \frac{1}{2\sinh(h\nu/2kT)}$$

$$Z = \sum_{s} g_s e^{-\frac{E_s}{kT}}$$

Total partition function for a system composed of N identical, Indistinguishable particles:

$$Z_{total} = \frac{Z^N}{N!}$$

$$U = \frac{kT^2}{N} \frac{\partial}{\partial t} (\ln Z_{total})$$

Internal Energy

Sum of energies of individual atoms or molecules

$$S = \frac{k}{N} \ln Z_{total} + \frac{U}{T}$$

Entropy

Definition: $dS = \frac{dQ}{T}$

$S = k \ln W$

Probability of system

$$H = U + P\frac{V}{N}$$

Enthalpy

Definition: H=U+pV

$$G = H - TS$$

Gibbs Free Energy

Definition: G=U-TS+pV

Equilibrium Concept

In a Complete Thermal Equilibrium (CTE) system the following conditions are met.

1- Radiation emitted by the system follow Black Body Radiation

2-All species have Maxwellian distribution

3- Kinetic equilibrium must exist, ie., $T_e=T_h$ (E/P is small, T is high)

4- Collision process establish excitation and ionization equilibrium

5- Spatial variations are small

Local Thermodynamic Equilibrium (LTE) means that conditions 2-5 are met.

Partial Local Thermodynamic Equilibrium (PLTE) means that one condition is only partially validated (e.g. excitation may not exactly follow the Boltzmann distribution).