The elementary processes and the plasma equilibrium

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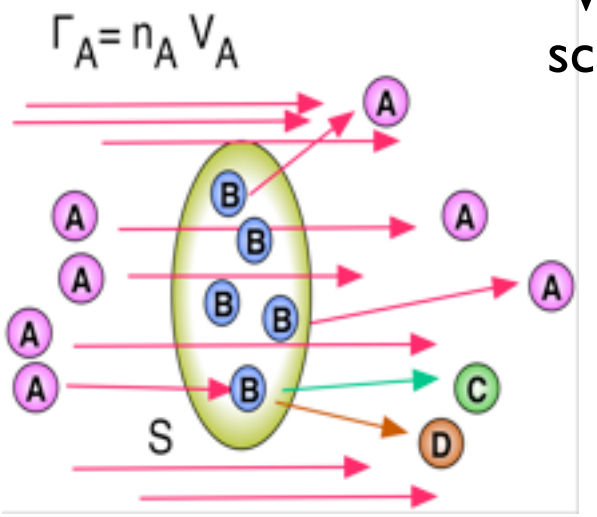
The collision cross section, ...



We calculate the number of collision events of *A* particles scattered by a single *B* target particle by time unit:

$$\frac{dQ_{AB}}{dt} = \dot{Q}_{AB} = \sigma_o \times \Gamma_A = \sigma_o \times (n_A\, v_A)$$

The effective surface of interaction between *A* and *B* particles.

The flux of A particles. The number of particles by time and surface unit.

we multiply by the density of targets,

$$\dot{q}_{AB} = n_B \times \frac{dQ_{AB}}{dt} = \sigma_o \times (n_A\, v_A) \times n_b$$

It gives the number of collisions (reactions) by time and volume unit. The *A* particles are removed by the reaction *A+B →C+D* and therefore, $\dot{q}_{AB} = -\dot{n}_A$

and then, $\dfrac{dn_A}{dt} = -n_B\,(\sigma_o\, n_A)\, v_A$ we obtain by integration

$$n_A(x) = n_{Ao}\, e^{-x/\lambda_c} \qquad \lambda_c = 1/(\sigma_o\, n_B)$$ The collision mean free path

$$n_A(t) = n_{Ao}\, e^{-t\,\nu_c} \qquad \nu_c = \sigma_o\, \nu_B\, v_A$$ The collision frequency

The atomic and molecular collisions in plasmas, ...

The interaction range

- ***Large:*** Involves charged particles; *fast process*, short time energy relaxation rates
- ***Short:*** Involves collisions with neutrals; *slow process*, large time energy relaxation rates.

Collisions are roughly classified as

- ***Elastic:*** The kinetic energy of colliding particles is conserved and retain their charges and initial internal states.
- ***Inelastic:*** A fraction of the kinetic energy is used to alter the internal states and/or to produce new particles.
- ***Superelastic:*** The potential energy is transformed in kinetic energy; the kinetic energy of the system after the collision event is greater.
- ***Radiative:*** A fraction of energy is emitted and/or absorbed as electromagnetic radiation.
- ***Charge exchange:*** The electric charge state of colliding particles is interchanged; a electric charge is transferred.

The differential collision cross section, ...

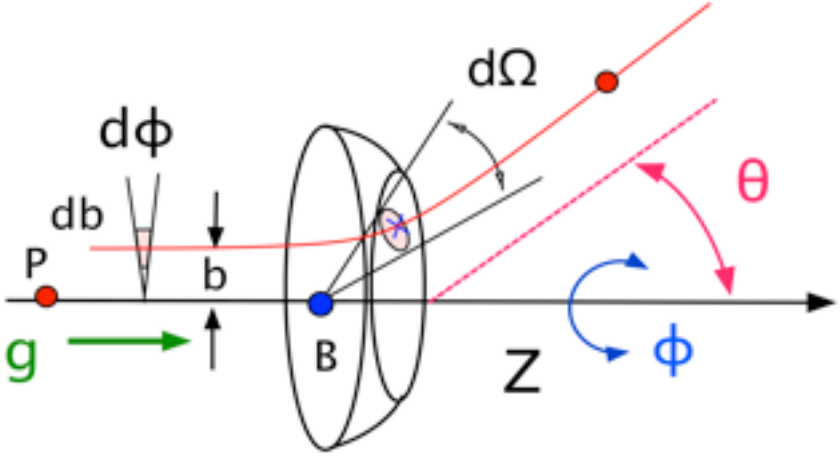
The number of collision events by time unit of *A* particles scattered by a single *B* target particle with velocity $d\mathbf{v}_A$ within the solid angle $d\Omega$.

$$d\dot{Q}_{AB} = n_A\, \sigma(g,\theta,\phi)\, |\mathbf{v}_A - \mathbf{v}_B|\, d\mathbf{v}_A\, d\Omega$$

$$d\Omega = \sin\theta\, d\theta\, d\phi$$

depends on the relative speed

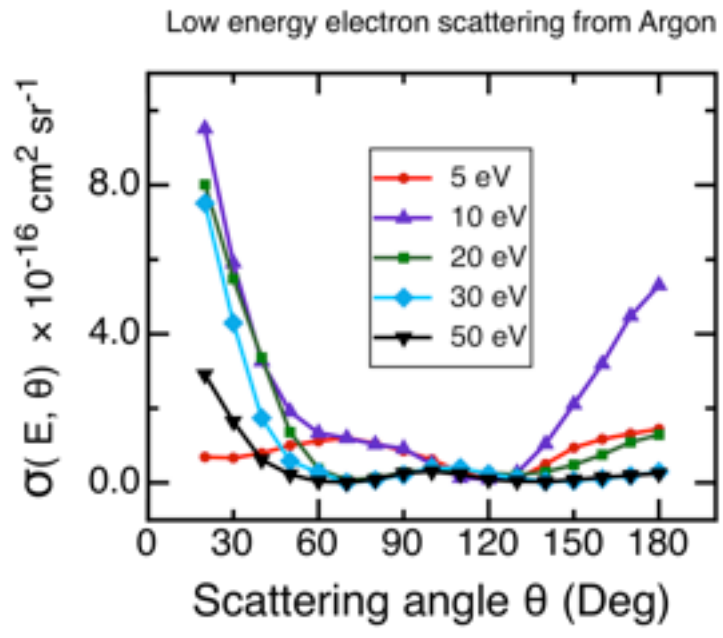
$$g = |\mathbf{v}_A - \mathbf{v}_B|$$



Outgoing number of *A* particles with velocity $d\mathbf{v}_A$ scattered within the solid angle $d\Omega$.

$$\sigma(g,\theta,\phi) = \frac{\left(d\dot{Q}_{AB}/d\mathbf{v}_A\, d\Omega\right)}{n_A\, |\mathbf{v}_A - \mathbf{v}_B|}$$

incoming incident flux of *A* particles



The total collision cross section, ...

Only depend on the relative speed *g* and is the number of collision events by time unit of *A* particles scattered by a single *B* particle with velocity $d\mathbf{v}_A$

$$d\dot{Q}_{AB} = n_A\, \sigma_T(g)\, |\mathbf{v}_A - \mathbf{v}_B|\, d\mathbf{v}_A$$

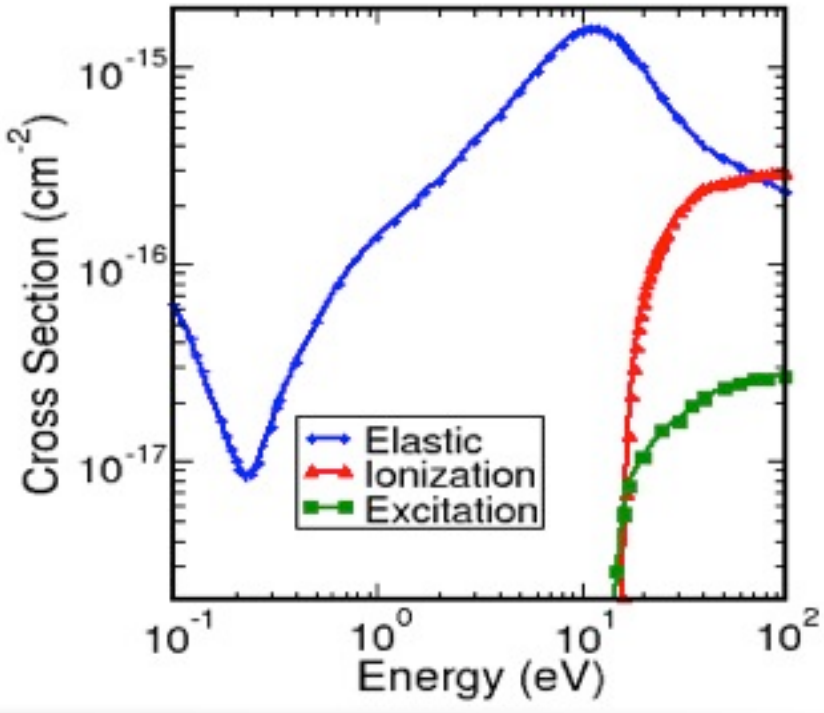
$$\sigma_T(|\mathbf{v}_A - \mathbf{v}_B|) = \int_0^{2\pi} \int_0^{\pi} \sigma(g, \theta, \phi)\, \sin\theta\, d\theta\, d\phi$$

Outgoing number of *A* particles with velocity $d\mathbf{v}_A$

$$\sigma_T(|\mathbf{v}_A - \mathbf{v}_B|) = \frac{d\dot{Q}_{AB}/d\mathbf{v}_A}{n_A\, |\mathbf{v}_A - \mathbf{v}_B|}$$

incoming incident flux of *A* particles

The experimental data of the total cross sections are a function of the energy $E = mv_A^2/2$ (or $|\mathbf{v}_A|$)



The collisional processes, of ions, ...

The ion and neutral collisions			
	Scheme	Process	Macroscopic effect
1	$A + A \rightarrow A + A$	Elastic collision between neutral atoms	Transport of neutrals and energy thermalization
2	$A^+ + A \rightarrow A^+ + A$	Elastic collision between ions and neutral atoms	Transport of ions, diffusion and energy thermalization
3	$A + B^+ \rightarrow A^+ + B$	Resonant or non resonant charge exchange	Ion transport diffusion and energy thermalization
4	$A^* + A \rightarrow A^* + A$	Collisions between metastable and neutral atoms	Diffusion of metastable atoms
5	$A^* + B \rightarrow e + B^+ + A$	Penning ionization	Production of ions in gas mixtures
6	$A + B^* \rightarrow e + AB^+$	Associative ionization	Production of molecular ions in diatomic gas mixtures
7	$A + B^+ + C \rightarrow A + BC^+$	Ion association	Production of molecular ion in gas mixtures
8	$A^* + A^* \rightarrow e + A^+ + A$	Cross Penning reaction	Ion production from metastable atoms
9	$AB^- + AB^+ \rightarrow AB + AB$	Ion-ion recombination	Loss of negative ions in electronegative or diatomic gases

The collisions of ions, ...

Elastic collisions: $A + B \rightarrow B + A$

Charge exchange: $A + B^{+} \rightarrow B + A^{+}$

(resonant and non resonant)

Dissociative ioniz.: $A^{*} + B \rightarrow B + A^{+} + e$

Attachment: $A + e^{-} \rightarrow A^{-}$

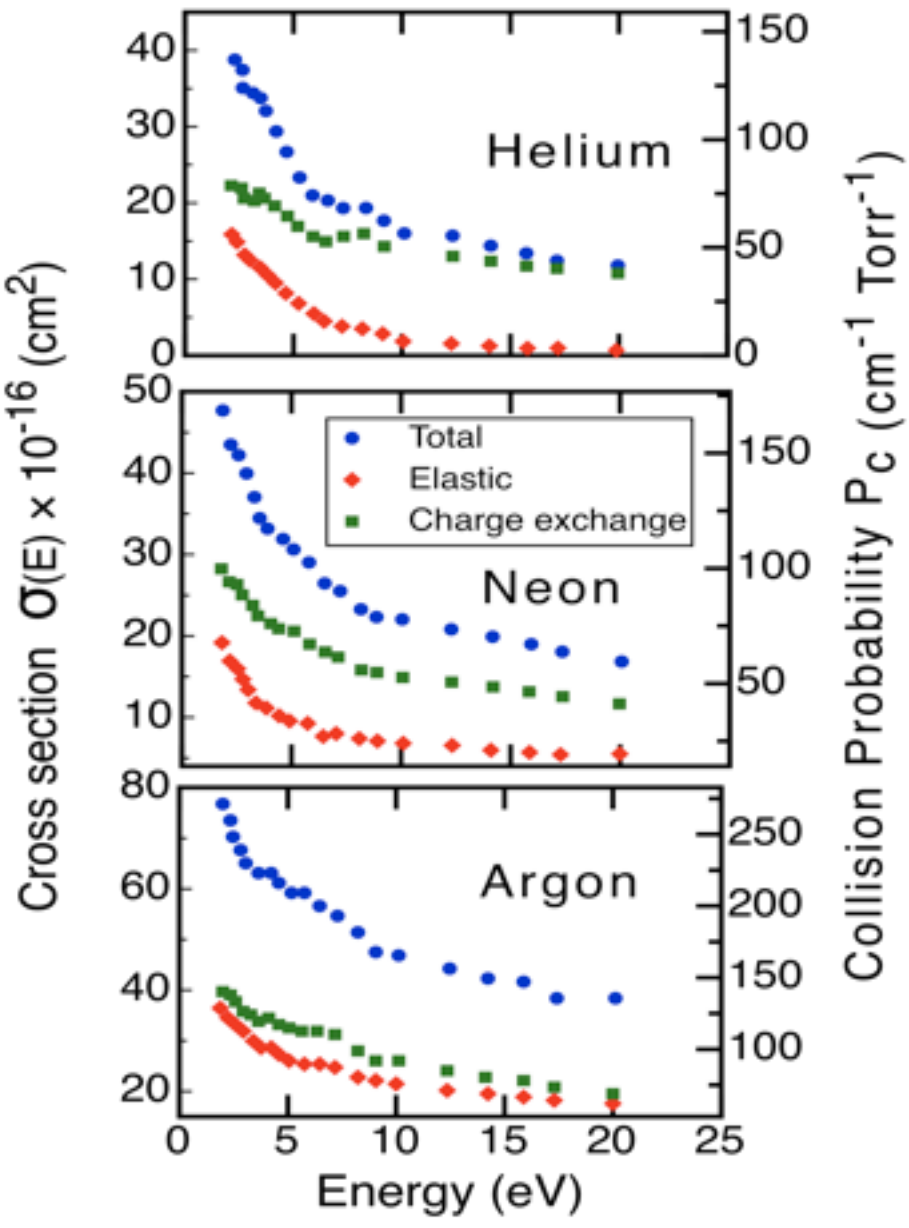
(Important for O_2, N_2, NO_2, ...)

... and photoprocesses ...

Photon energy: $E = h\nu$

Photoionization: $A + h\nu \rightarrow A^{+} + e$

Photoexcitation: $A + h\nu \rightarrow A^{*}$



The electron collisions with charge production, ...

Production of charges by electron collisions			
	Scheme	Process	Macroscopic effect
1	$e + A^+ \rightarrow e + A^+$	Elastic Coulomb collisions between electrons and ions	Transport and energy transfer in highly ionized plasmas.
2	$e + A \rightarrow e + A$	Elastic collision between electrons and neutrals	Electron transport and diffusion. Electron mobility.
3	$e + A \rightarrow e + A^*$	Excitation of neutrals by electron impact	Multiplication of metastable neutral atoms.
4	$e + AB \rightarrow e + AB^*$	Vibrational excitation	Energy transfer to vibrational levels of molecules.
5	$e + A \rightarrow 2e + A^+$	Electron impact ionization	Multiplication of ions and electrons from the ground state.
6	$e + A^* \rightarrow 2e + A^+$	Multistep ionization	Ionization of neutral atoms from an excited state.
7	$e + AB \rightarrow A + B^-$	Dissociative attachment	Production of negative ions in electronegative gases.
8	$e + A + B \rightarrow AB^-$	Three body attachment	
9	$e + AB \rightarrow 2e + A + B^+$	Dissociative ionization	Production of atomic ions in electronegative gases
10	$e + AB \rightarrow e + A + B$	Detachment by electron impact	Production of neutral atoms in molecular gases

The electron collisions with charge losses, ...

Recombination of charges by electron collisions			
	Scheme	Process	Macroscopic effect
10	$e + AB \rightarrow e + A + B$	Molecule dissociation by electron impact	Production of neutral atom in molecular gases
11	$e + A^{+} \rightarrow e + A$	De-excitation of neutrals (quenching)	Destruction of metastable neutral atoms
12	$2e + A^{+} \rightarrow e + A^{*}$	Three body recombination	Only relevant in dense highly ionized plasmas
13	$e + A^{+} \rightarrow h\nu + A$	Radiative recombination	
14	$e + AB^{+} \rightarrow A + B^{*}$	Dissociative recombination	Important in weakly ionized molecular plasmas
15	$e + A^{-} \rightarrow 2e + A$	Detachment by electron impact	Loss of negative ions in electronegative gases

The electron impact *elastic* collisions, ...

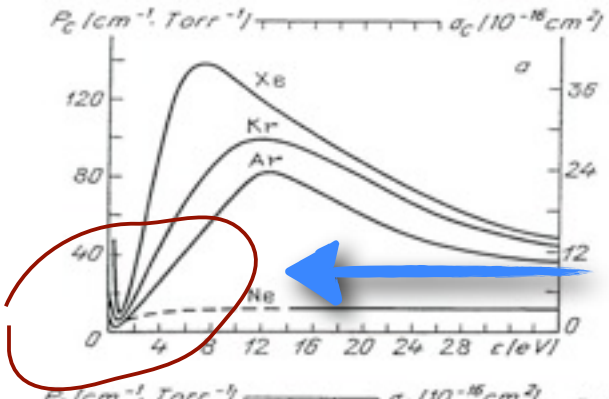
Elastic collisions:

$$A + e \rightarrow A + e$$

The amount of the electron energy lost by collision is of the order, $\delta = 2m_e/m_i$

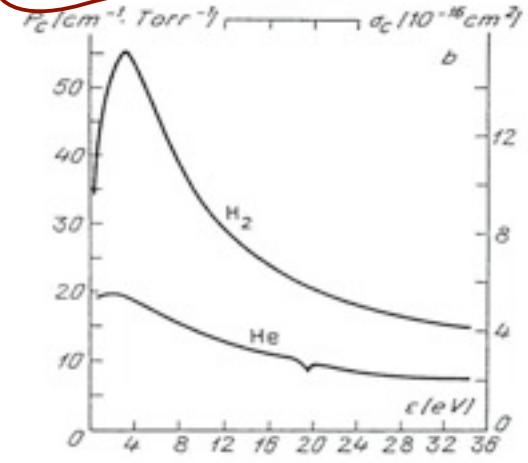
$$\Delta E = \delta \times \nu_c = \left(\frac{2m_e}{m_i}\right) n_a \, \sigma_c \, V_t$$

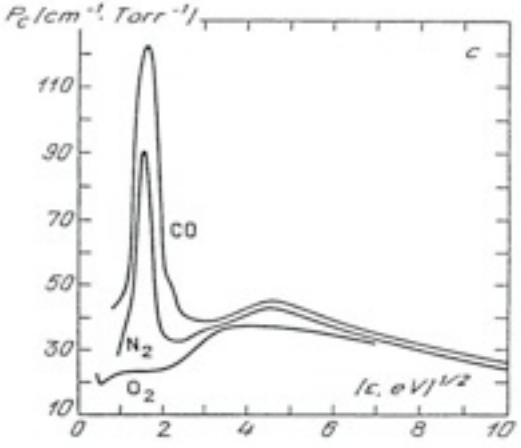
Usually, the electron energy losses are negligible. The energy transfer between electron and neutrals is low … except when the collision frequency becomes ν ~ 1/δ or equivalently, high neutral pressures.

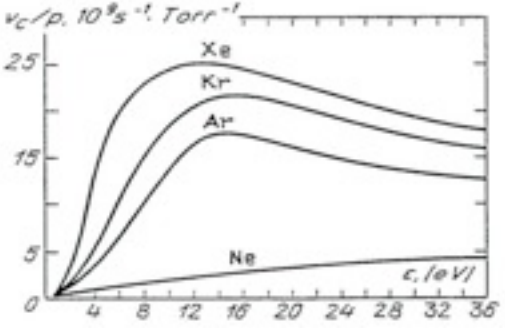


Experimental cross sections and probabilities of elastic collisions of electrons for different gases. The probability P_c is the number of collisions per cm or inverse free path length, at $p = 1$ Torr and $t = 0°$ C. From [2.3]

Ramssauer effect







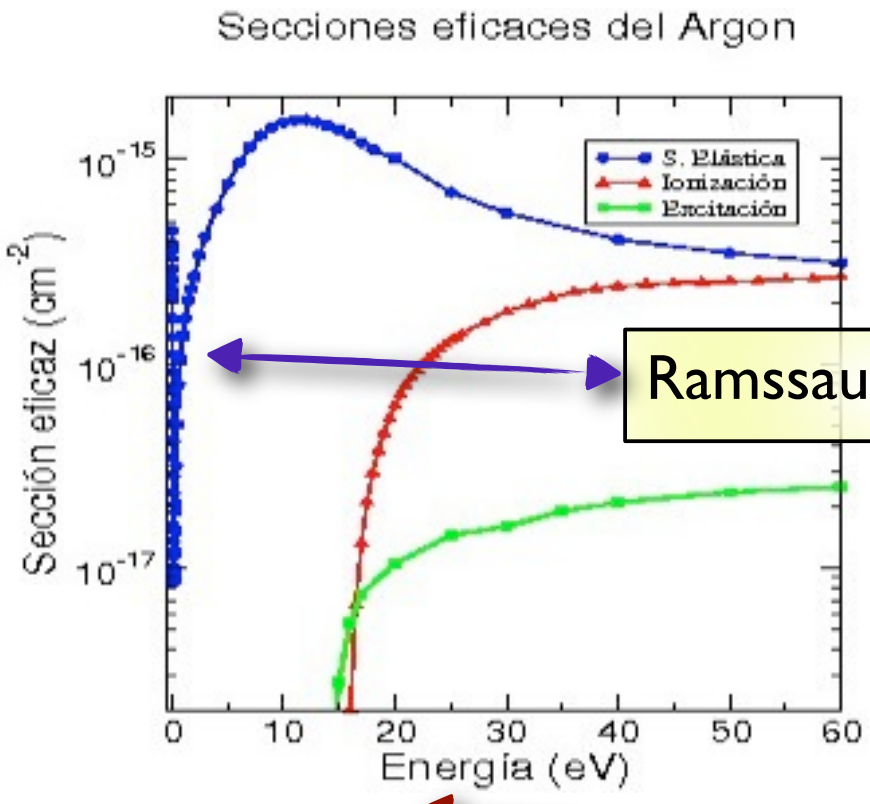
Frequencies of elastic collisions of electrons for different gases

The electron impact *inelastic* collisions, ...

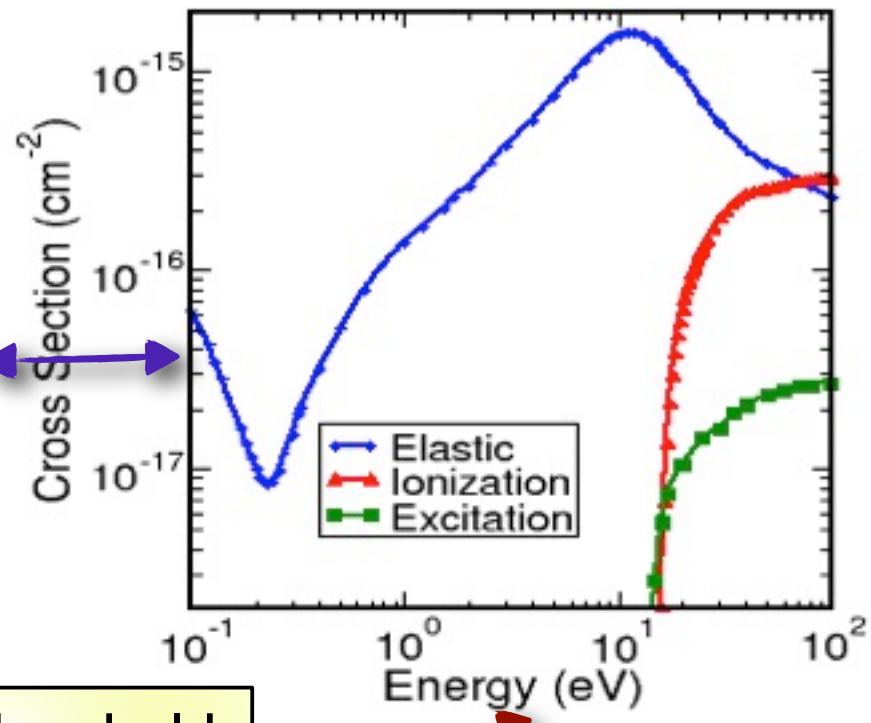
Electron impact ionization: $A + e \rightarrow A^{+} + 2\,e$

Electron impact excitation: $A + e \rightarrow A^{*} + e$

Ionization and excitation collisions have a threshold energy for the colliding electron. Note when the axis are in log or linear scales, ...



Ramssauer effect



Energy thresholds

The electron impact ionization frequency, ...

Ionization frequency

$$\frac{dn_e}{dt} = \nu_I\, n_e = k_I\, n_a\, n_e = n_e\, Q_I$$

Reaction rate

$$Q_I = n_a \int_{E_I}^{\infty} \sigma_I(E)\, \sqrt{E}\, g(E)\, dE$$

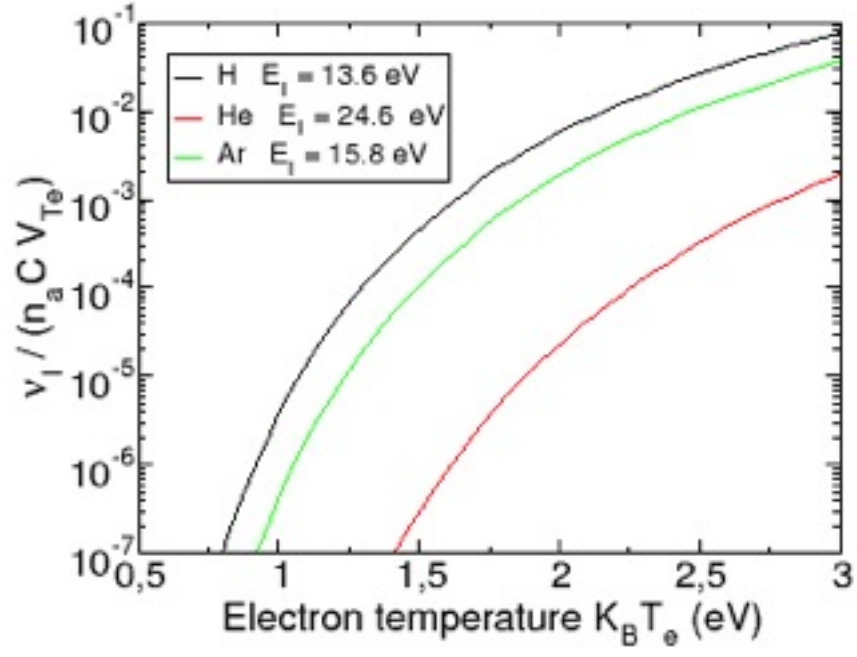
$$Q_I = n_a \int_{v_I}^{\infty} \sigma_I(|\mathbf{v}_e|)\, |\mathbf{v}_e|\, f(\mathbf{v}_e)\, d\mathbf{v}_e$$

Piecewise aproximation for the ionization cross section:

$$\sigma_I(E) = \begin{cases} C\,(E - E_I) & E \geq E_I \\ 0 & E < E_I \end{cases}$$

and for a Maxwell Boltzmann distribution

$$Q_I = n_a\, C\, v_{th}\, (1 + 2k_B T_e)\, e^{-E_I/k_B T_e}$$



The recombination ...

The recombination is the *reverse reaction of ion production* and its reaction rate depends on the particular collisional processes.

$A^* + B \leftarrow B + A^+ + e^-$

$A + e^- \leftarrow A^+ + e^-$

$A + e^- \leftarrow A^-$

..., ← ...

All possible processes, ...

On average

Recombination rate

$$\frac{dn_e}{dt} = -k_R\, n_i\, n_e$$

$$\frac{dn_e}{dt} = -k_R\, n^2$$

Local equilibrium

$$n_e \simeq n_i$$

$$\frac{1}{n} = \frac{1}{n_o} + k_R\, t$$

On average, the plasma decreases with time as,

$$n(t) = \frac{n_o}{1 + n_o\, k_R\, t} \simeq \frac{1}{k_R\, t} \qquad k_R \sim 10^{-7}\ \mathrm{cm}^3/s$$

and the typical time scale is in the order of 0,1 microseconds

The charged particle collisions, …

The relevance of charged particle collisions rely on the ionization degree of the neutral gas. In dense plasmas these *Coulomb collisions* may involve more than two particles.

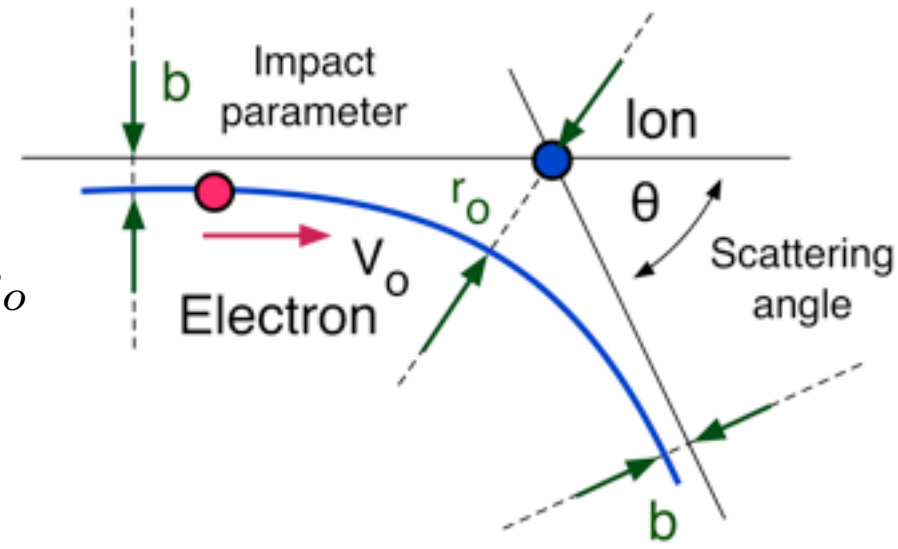
$$\left.\begin{array}{l} A^+ + e^- \rightarrow A^+ + e^- \\ e^- + e^- \rightarrow e^- + e^- \\ A^+ + A^+ \rightarrow A^+ + A^+ \end{array}\right\}$$

- Colliding particles are deflected at distances much larger than the atomic radius
- Small angle scattering dominates.
- Dense plasma; Coulomb potential is screened $\sim\lambda_D$ but energetic particles penetrate the Debye sphere.

A rough estimation, …

The electron momentum exchange,

$$\Delta p \simeq |F_e| \times T_{int} \sim \frac{e^2}{4\pi\epsilon_o\, r_o^2} \times \frac{r_o}{v_o}$$



for θ = π/2 we might *estimate*, $\Delta p = m\, v_o$

$$r_0 \sim \frac{e^2}{4\pi\epsilon_o m_e\, v_o^2} \qquad \sigma_o(v_o) = \pi\, r_o^2$$

$$\nu_{ei} = n_e\, \sigma_o(v_o)\, v_o \qquad \nu_{ei} = \frac{\pi\, n_e\, e^4}{(4\pi\epsilon_o)^2\, m_e^2\, v_o^3}$$

and using the thermal speed,

$$v_o = \sqrt{k_B T_e / m_e}$$

we obtain,

$$\nu_{ei} = \frac{\pi\, n_e\, e^4}{(4\pi\epsilon_o)^2 \sqrt{m_e}\, (k_B T_e)^{3/2}}$$

This is an order of magnitude estimation, but similar to the result of the thorough analysis by Spitzer involving the Coulomb logarithm Λ (between 0.1 - 20.0)

$$\nu_{ei} = \frac{\pi\, n_e\, e^4}{(4\pi\epsilon_o)^2 \sqrt{m_e}\, (k_B T_e)^{3/2}} \ln \Lambda \qquad \Lambda = \langle \lambda_D / r_o \rangle$$

F.F. Chen. *Introduction to Plasma Physics and Control. Fusion*. Chap. 5, sec. 5.6.2. Plenum Press (1984) and A. Piel. *Plasma Physics.* Chap. 4, sec. 4.2.5, Springer (2010)-

The hierarchy of equilibrium states, …

A plasma (or any other statistical population of particles) is in *thermodynamic equilibrium* when the rates of collisional and radiative processes are balanced by their reverse reactions.

- *Optically thick*, a photon cannot leave the plasma region
- The system has a blackbody radiation spectrum.
- The physical properties are constant in time and uniform in space.

The plasma is in *local equilibrium* when all collisional processes for charge production are balanced by of particle recombination, but not the radiative processes.

- Electromagnetic radiation is emitted, photons leave the plasma region
- All particles are in equilibrium at the same temperature.

The plasma is in *partial equilibrium* when only a small number of elementary processes are balanced.

- Multithermal equilibrium states; $k_B T_e >> k_B T_i \approx k_B T_a$