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 $A+B \rightarrow C+D$ and therefore, $\dot{q}_{AB} = -\dot{n}_A$

and then,

$$\frac{dn_A}{dt} = -n_B (\sigma_o n_A) v_A$$

we obtain by integration

$$n_A(x) = n_{Ao} e^{-x/\lambda_c} \quad \lambda_c = 1/(\sigma_o n_B)$$

$$n_A(t) = n_{Ao} e^{-t \nu_c} \quad \nu_c = \sigma_o \nu_B \nu_A$$

The collision mean free path

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

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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 $d\mathbf{v}_A$

$$dQ_{AB} = n_A \sigma_T(g) |\mathbf{v}_A - \mathbf{v}_B| d\mathbf{v}_A$$

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

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

$$\sigma_T(|\mathbf{v}_A - \mathbf{v}_B|) = \frac{dQ_{AB}/d\mathbf{v}_A}{n_A |\mathbf{v}_A - \mathbf{v}_B|}$$

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

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Process</th>
<th>Macroscopic effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A + A → A + A</td>
<td>Elastic collision between neutral atoms</td>
</tr>
<tr>
<td>2</td>
<td>A⁺ + A → A⁺ + A</td>
<td>Elastic collision between ions and neutral atoms</td>
</tr>
<tr>
<td>3</td>
<td>A + B⁺ → A⁺ + B</td>
<td>Resonant or non resonant charge exchange</td>
</tr>
<tr>
<td>4</td>
<td>A* + A → A* + A</td>
<td>Collisions between metastable and neutral atoms</td>
</tr>
<tr>
<td>5</td>
<td>A* + B → e + B⁺ + A</td>
<td>Penning ionization</td>
</tr>
<tr>
<td>6</td>
<td>A + B* → e + AB⁺</td>
<td>Associative ionization</td>
</tr>
<tr>
<td>7</td>
<td>A + B⁺ + C → A + BC⁺</td>
<td>Ion association</td>
</tr>
<tr>
<td>8</td>
<td>A* + A* → e + A⁺ + A</td>
<td>Cross Penning reaction</td>
</tr>
<tr>
<td>9</td>
<td>AB⁻ + AB⁺ → AB + AB</td>
<td>Ion-ion recombination</td>
</tr>
</tbody>
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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: \[ A + h \nu \rightarrow A^* \]
### Production of charges by electron collisions

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<tr>
<td>1</td>
<td>$e + A^+ \rightarrow e + A^+$</td>
<td>Elastic Coulomb collisions between electrons and ions</td>
</tr>
<tr>
<td>3</td>
<td>$e + A \rightarrow e + A^*$</td>
<td>Excitation of neutrals by electron impact</td>
</tr>
<tr>
<td>4</td>
<td>$e + AB \rightarrow e + AB^*$</td>
<td>Vibrational excitation</td>
</tr>
<tr>
<td>5</td>
<td>$e + A \rightarrow 2e + A^+$</td>
<td>Electron impact ionization</td>
</tr>
<tr>
<td>6</td>
<td>$e + A^* \rightarrow 2e + A^+$</td>
<td>Multistep ionization</td>
</tr>
<tr>
<td>7</td>
<td>$e + AB \rightarrow A + B^-$</td>
<td>Dissociative attachment</td>
</tr>
<tr>
<td>8</td>
<td>$e + A + B \rightarrow AB^-$</td>
<td>Three body attachment</td>
</tr>
<tr>
<td>9</td>
<td>$e + AB \rightarrow 2e + A + B^+$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>10</td>
<td>$e + AB \rightarrow e + A + B$</td>
<td>Detachment by electron impact</td>
</tr>
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</table>
Recombination of charges by electron collisions

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<tr>
<td>10</td>
<td>$e + AB \rightarrow e + A + B$</td>
<td>Molecule dissociation by electron impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Production of neutral atom in molecular gases</td>
</tr>
<tr>
<td>11</td>
<td>$e + A^+ \rightarrow e + A$</td>
<td>De-excitation of neutrals (quenching)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Destruction of metastable neutral atoms</td>
</tr>
<tr>
<td>12</td>
<td>$2e + A^+ \rightarrow e + A^*$</td>
<td>Three body recombination</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Only relevant in dense highly ionized plasmas</td>
</tr>
<tr>
<td>13</td>
<td>$e + A^+ \rightarrow h\nu + A$</td>
<td>Radiative recombination</td>
</tr>
<tr>
<td>14</td>
<td>$e + AB^+ \rightarrow A + B^*$</td>
<td>Dissociative recombination</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Important in weakly ionized molecular plasmas</td>
</tr>
<tr>
<td>15</td>
<td>$e + A^- \rightarrow 2e + A$</td>
<td>Detachment by electron impact</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Loss of negative ions in electronegative gases</td>
</tr>
</tbody>
</table>
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,

\[ \delta = \frac{2m_e}{m_i} \]

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

Usually, the electron energy losses are negligible. The energy transfer between electron and neutrals is low … except when the collision frequency becomes \( \nu \sim 1/\delta \) or equivalently, high neutral pressures.

**Ramssauer effect**

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The electron impact *inelastic* collisions, ...

**Electron impact ionization:** \[ A + e \rightarrow A^+ + 2e \]

**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, ...
The electron impact ionization frequency, ...

\[ \frac{dn_e}{dt} = \nu_I n_e = k_I n_a n_e = n_e Q_I \]

reaction rate

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

\[ Q_I = n_a \int_{v_I}^{\infty} \sigma_I(|v_e|) |v_e| f(v_e) \, dv_e \]

piecewise approximation 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 is the reverse reaction of ion production and its reaction rate depends on the particular collisional processes.

\[
\begin{align*}
A^* + B & \leftrightarrow B + A^* + e^- \\
A + e^- & \leftrightarrow A^+ + e^- \\
A + e^- & \leftrightarrow A^- \\
\ldots, & \leftrightarrow \ldots
\end{align*}
\]

All possible processes, ...

On average

Recombination rate

\[
\frac{dn_e}{dt} = -k_R n_i n_e
\]

Local equilibrium

\[
n_e \simeq n_i
\]

On average, the plasma decreases with time as,

\[
n(t) = \frac{n_o}{1 + n_o k_R t} \simeq \frac{1}{k_R t}
\]

\[k_R \sim 10^{-7} \text{ cm}^3/\text{s}\]

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

\[
\begin{align*}
A^+ + e^- & \rightarrow A^+ + e^- \\
e^- + e^- & \rightarrow e^- + e^- \\
A^+ + A^+ & \rightarrow A^+ + A^+
\end{align*}
\]

- 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,

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

for $\theta = \pi/2$ we might estimate, $\Delta p = m v_o$

$$r_0 \sim \frac{e^2}{4\pi\varepsilon_o m_e v_o^2} \quad \sigma_o(v_o) = \pi r_o^2$$

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

and using the thermal speed,

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

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

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

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 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; $k_B T_e \gg k_B T_i \approx k_B T_a$