Chemical potential:

Helmholtz free energy

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T, V, N_{j \neq i}} \quad \text{and} \quad F = -k_B T \ln Z_N$$

$$\Rightarrow F = -k_B T \ln\left[\frac{(z_{sp_i})^{N_i}}{N_i!^{-1}}\right]$$

$$\Rightarrow \mu_i = -k_B T \frac{\partial}{\partial N_i}\left(N_i \ln z_{sp} - \ln N_i!\right)$$

apply Stirling's theorem: $\ln N! \simeq N \ln N - N$

$$\Rightarrow \mu_i = -k_B T \frac{\partial}{\partial N_i}\left(N_i \ln z_{sp_i} - N_i \ln N_i + N_i\right)$$

$$= -k_B T \left(\ln z_{sp_i} - \ln N_i\right)$$

since: $\frac{\partial}{\partial N_i}\left(-N_i \ln N_i + N_i\right) = \frac{\partial}{\partial N_i}\left(-N_i \ln N_i\right) + 1$

$$= -\ln N_i - \frac{N_i}{N_i} + 1 = -\ln N_i \cancel{-1} \cancel{+1}$$

apply product rule: $\frac{\partial}{\partial x}(u \cdot v) = \frac{\partial u}{\partial x} v + u \frac{\partial v}{\partial x}$

and $\frac{d(\ln x)}{dx} = \frac{1}{x}$

Ionisation processes in plasma:

→ in thermodynamic equilibrium:

- each ionisation process balanced by a corresponding reciprocal process:

  - photo ionization ⟺ 2-body recombination
  - impact ionization ⟺ 3-body recombination

→ impact ionization → high temperatures

→ photoionization requires short λ (high E) ⇒ UV

→ hot dilute plasma (corona)

- steady state reached 2-body recombination balances impact ionization i.e. collisional ionization very efficient but electrons are too few

⇒ "coronal equilibrium"
non-thermodynamic equilibrium

- Note: non-local processes, e.g. shocks, not governed by local equilibrium, electrons gained energy in a different place

Debye shielding:

→ perfectly neutral plasma : $Z n_i = n_e$

→ Boltzmann distribution (for electrons):

energy due to electrostatic potential

$$n_e = n_0 e^{-E/k_BT} = n_0 e^{e\phi/k_BT} \quad \text{as} \quad E = e\,\phi(r)$$

and $n_0 = Z n_i$

→ Gauss Law: $\nabla \cdot E = -\dfrac{\rho}{\varepsilon_0}$ where $\rho = n_i Z e - n_e e$

⇒ E field: $\underline{E} = \nabla \phi \Rightarrow \nabla \cdot E = \nabla \cdot \nabla \phi = \nabla^2 \phi$

⇒ Poisson's equation: $\boxed{\nabla^2 \phi = -\dfrac{\rho}{\varepsilon_0}}$

→ in spherical geometry:

$$\nabla^2 \phi = -\rho/\varepsilon_0 = \frac{1}{r^2} \cdot \frac{d}{dr}\left[r^2 \frac{d\phi}{dr}\right] = \frac{n_i Z e - n_e e}{\varepsilon_0}$$

$$= -\frac{e}{\varepsilon_0}\Big[\underset{\uparrow \atop Z n_i}{n_0} - \underbrace{n_0 e^{e\phi/k_BT}}_{n_e}\Big]$$

→ Taylor expand: $e^{e\phi/k_BT} \approx 1 + \dfrac{e\phi}{k_BT} + \dots$

for $e\phi \ll k_BT$

$$\Rightarrow \frac{1}{r^2} \cdot \frac{d}{dr}\left[r^2 \frac{d\phi}{dr}\right] = -\frac{e}{\varepsilon_0}\left[n_0 - n_0 - \frac{n_0 e \phi}{k_B T}\right]$$

$$= \boxed{\frac{n_0 e^2}{\varepsilon_0 k_B T} \phi}$$

→ boundary conditions : $\phi(r) \to 0$ as $r \to \infty$

and $\phi(r) \to \dfrac{q}{4\pi\varepsilon_0 r}$ as $r \to 0$

(unscreened potential)

→ general solution : $\boxed{\phi(r) = \dfrac{q}{4\pi\varepsilon_0 r} \cdot \underbrace{e^{-r/\lambda_D}}_{\text{screening effect}}}$

$$\Rightarrow \frac{d\phi}{dr} = \frac{q}{4\pi\varepsilon_0} \cdot \frac{d}{dr}\left(\frac{e^{-r/\lambda_D}}{r}\right) = \frac{q}{4\pi\varepsilon_0}\left(-\frac{e^{-r/\lambda_D}}{r\lambda_D} - \frac{e^{-r/\lambda_D}}{r^2}\right)$$

product rule

$$\boxed{\frac{d}{dx}(u \cdot v) = \frac{du}{dx} \cdot v + u\frac{dv}{dx}}$$

$$\Rightarrow r^2 \frac{d\phi}{dr} = -\frac{q}{4\pi\varepsilon_0}\left(\frac{r e^{-r/\lambda_D}}{\lambda_D} + e^{-r/\lambda_D}\right)$$

$$\Rightarrow \frac{d}{dr}\left(r^2 \frac{d\phi}{dr}\right) = -\frac{q}{4\pi\varepsilon_0}\left(-\frac{r e^{-r/\lambda_D}}{\lambda_D^2} + \cancel{\frac{e^{-r/\lambda_D}}{\lambda_D}} - \cancel{\frac{e^{-r/\lambda_D}}{\lambda_D}}\right)$$

$$\Rightarrow \frac{1}{r^2} \cdot \frac{d}{dr}\left[r^2 \frac{d\phi}{dr}\right] = \frac{q}{4\pi\varepsilon_0} \cdot \left(\frac{e^{-r/\lambda_D}}{r \lambda_D^2}\right)$$

$$= \frac{n_0 e^2}{\varepsilon_0 k_B T} \phi$$

$$\Rightarrow \frac{n_e e^2}{\varepsilon_0 k_B T} \cdot \underbrace{\frac{\cancel{q}}{\cancel{4\pi \varepsilon_0 r}} \cdot e^{\cancel{-r/\lambda_D}}}_{\phi(r) \text{ general solution}} = \frac{\cancel{q}}{\cancel{4\pi\varepsilon_0 r}} \cdot \frac{e^{\cancel{-r/\lambda_D}}}{\lambda_D^2}$$

$$\Rightarrow \frac{1}{\lambda_D^2} = \frac{n_e e^2}{\varepsilon_0 k_B T}$$

$T = T_e \rightarrow$ electron temperature

$\therefore$ Debye length: $\boxed{\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{n_e e^2}}}$

$$\approx 7430 \sqrt{\frac{k_B T_e}{n_0}}$$

where $n_0 = n_e = Z n_i$

Plasma parameter:

⇒ volume of a sphere: $V = \frac{4}{3}\pi r^3$
$\quad\quad\quad\quad\hookrightarrow \lambda_D$

⇒ no. of particles inside "Debye sphere"

$$N_D = n_e \frac{4}{3}\pi \lambda_D^2 \quad \text{as number density } n_e = \frac{N}{V}$$
$$\Rightarrow N = n_e \cdot V$$

and $\phi = \frac{Q}{4\pi\varepsilon_0 r}$ where $Q = Ze$ and $r = n_e^{-1/3}$

⇒ ionisation threshold: $k_B T > e\phi$

$$k_B T > \frac{Ze^2 n_e^{\frac{1}{3}}}{4\pi\varepsilon_0} \Rightarrow N_D^{2/3} \cong \frac{4\pi\varepsilon_0 k_B T}{Ze^2 n_e^{1/3}} > 1$$

$$\text{as } N_D = n_e \frac{4}{3}\pi\lambda_D^3 = \frac{4}{3}\pi\, n_e \underbrace{\left(\frac{\varepsilon_0 k_B T}{n_0 e^2}\right)^{3/2}}_{\lambda_D^3} = \frac{4}{3}\pi\left(\frac{\varepsilon_0 k_B T}{n_e^{1/3} e^2}\right)^{3/2}$$

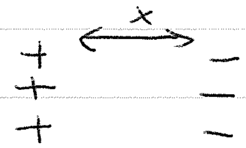
$$\frac{n_e^{2/2}}{n_e^{3/2}} = \frac{1}{n_e^{1/2}} = \left(\frac{1}{n_e^{1/3}}\right)^{3/2} = \frac{1}{n_e^{\frac{3}{3\cdot 2}}}$$

⇒ proportional to $N_D^{2/3}$!

⇒ condition for ionisation: $\boxed{N_D > 1}$

Plasma frequency

- Langmuir / electron plasma oscillation
  → departure from quasi neutrality



⇒ electric field displacing e^-

Gauss law: $$|\underline{E}| = \frac{n \cdot e}{4\pi r^2 \varepsilon_0} \cdot x$$

↑ Gauss surface

as $n_e = \frac{n}{4\pi r^2}$ $\qquad E = \frac{n_e e x}{\varepsilon_0}$

→ equation of motion: $\mathbf{F} = m_e \frac{d^2x}{dt} = -eE = -\frac{n_e e^2 x}{\varepsilon_0}$

→ trial solution (2nd order differential equation): $\boxed{x = e^{i\omega_p t}}$

$$\Rightarrow \frac{d^2x}{dt^2} = -\omega_p^2 e^{i\omega_p t} = -\omega_p^2 \cdot \cancel{x} = \frac{n_e e^2 \cancel{x}}{\varepsilon_0 m_e}$$

$$\therefore \boxed{\omega_p = \left(\frac{n_e e^2}{\varepsilon_0 m_e}\right)^{1/2}}$$ plasma frequency (for electrons)

→ natural resonant frequency of plasmas

$y = e^x$ and $x = i\omega_p t$ $\qquad \frac{d^2y}{dt} = \frac{d^2y}{dx^2} \cdot \frac{d^2x}{dt^2} = \frac{d^2(e^x)}{dx^2} \cdot \frac{d^2(i\omega_p t)}{dt^2}$

$$= e^x \cdot \underbrace{i^2}_{=-1} \omega_p^2$$