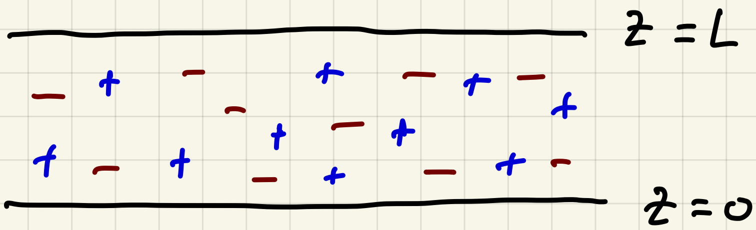
Electrolyte between conducting plates



$V(0) = 0$, $V(L) = V$

$$\nabla^2 \phi = \kappa_D^2 \phi \Rightarrow \phi = A e^{\kappa_D z} + B e^{-\kappa_D z}$$

$$\phi(0) = 0 = A + B \Rightarrow B = -A$$

$$\phi(L) = V = A e^{\kappa_D L} + B e^{-\kappa_D L} = 2A \sinh(\kappa_D L)$$

So we have $A = -B = \dfrac{V}{2\sinh(\kappa_D L)}$ and

$$\phi(z) = \frac{V \sinh(\kappa_D z)}{\sinh(\kappa_D L)}$$

DH theory is valid provided $n \lambda_D^3 \gg 1$, i.e. there are many screening charges within a volume λ_D^3.

Electron gas : Thomas-Fermi screening $(T=0)$

Assume $\phi(\vec{r})$ smoothly varying. Define a local Fermi wavevector $k_F(\vec{r})$ by

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2(\vec{r})}{2m} - e\phi(\vec{r})$$

$$\Rightarrow \quad k_F(\vec{r}) = \left[\frac{2m}{\hbar^2}\left(\mathcal{E}_F + e\phi(\vec{r})\right)\right]^{1/2}$$

The local electron density is then

$$n(\vec{r}) = \frac{k_F^3(\vec{r})}{3\pi^2} = n_\infty\left(1 + \frac{e\phi(\vec{r})}{\mathcal{E}_F}\right)^{3/2}$$

where $\phi(\infty) = 0$. Poisson's eqn :

$$\nabla^2\phi = 4\pi e n_\infty\left[\left(1 + \frac{e\phi}{\mathcal{E}_F}\right)^{3/2} - 1\right] - 4\pi\rho_{ext}$$

uniform neutralizing background

external charges

If $|e\phi| << \mathcal{E}_F$ then

$$\nabla^2\phi = \underbrace{\frac{6\pi n_\infty e^2}{\mathcal{E}_F}}_{K_{TF}^2}\phi - 4\pi\rho_{ext}$$

with $\kappa_{TF} = \left(\frac{6\pi n_\infty e^2}{\varepsilon_F}\right)^{1/2}$. TF valid provided $n_\infty \lambda_{TF}^3 \gg 1$ where $\lambda_{TF} = \kappa_{TF}^{-1}$ = TF screening length.

For general dispersions, we may write

$$\delta n(\vec{r}) = e\phi(\vec{r})\, g(\varepsilon_F)$$

$$\nabla^2\phi = -4\pi(-e\,\delta n) = 4\pi e^2 g(\varepsilon_F)\,\phi$$

and thus $\kappa_{TF} = \left(4\pi e^2 g(\varepsilon_F)\right)^{1/2}$. A point charge Q gets screened, so $\phi(\vec{r}) = \frac{Q}{r} e^{-\kappa_{TF} r}$.

The TF atom

Ion = nucleus of charge $+Ze$ and electron cloud of charge $-Ne$. Assume isotropy. Define

$$\varepsilon_F + e\phi(\vec{r}) \equiv \frac{Ze^2}{r}\,\chi(r/r_0)$$

with $\chi(u)$ and r_0 as yet undetermined.

We expect an unscreened nuclear charge at short distances, hence $\chi(0) = 1$. The net ionic charge is $Q = (Z-N)e$.

Again, $k_F(\vec{r}) = \left(\frac{2m}{\hbar^2}\right)^{1/2}\left(\varepsilon_F + e\phi(\vec{r})\right)^{1/2}$ so

$$\nabla^2\phi = 4\pi e \cdot \frac{k_F^3(\vec{r})}{3\pi^2} - 4\pi Z e\,\delta(\vec{r})$$

and with $\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2} r$ for isotropic, so

$$\nabla^2\phi = e^{-1}\cdot\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(r\cdot\frac{Ze^2}{r}\chi(r/r_0)\right)$$

$$= \frac{Ze}{r}\cdot\frac{1}{r_0^2}\cdot\chi''(r/r_0)$$

$$= \frac{4\pi e}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{Ze^2}{r}\chi(r/r_0)\right)^{3/2}$$

$$\Rightarrow \frac{Ze}{r_0^3}\frac{\chi''(u)}{u} = \frac{4e}{3\pi}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{Ze^2}{r_0}\right)^{3/2}\left(\frac{\chi(u)}{u}\right)^{3/2}$$

$$\chi''(u) = \frac{4}{3\pi}Z^{1/2}e^3\left(\frac{2m}{\hbar^2}\right)^{3/2} r_0^{3/2}\cdot\frac{\chi^{3/2}(u)}{u^{1/2}}$$

Thus, setting $r_0 \equiv \frac{\hbar^2}{2me^2}\left(\frac{3\pi}{4\sqrt{2}}\right)^{2/3} = 0.885\,Z^{-1/3}a_B$

we obtain the TF eqn,

$$\chi''(u) = \frac{1}{\sqrt{u}}\chi^{3/2}(u)$$

Boundary conditions:

- $\chi(0) = 1$

- For positive ions, with $Z > N$, there is perfect screening at the ionic boundary $R = u^* r_0$ with $\chi(u^*) = 0$ and

$$\vec{E}(R\hat{r}) = \frac{(Z-N)e}{R}\hat{r} = -\vec{\nabla}\phi$$
$$= -\frac{Ze^2}{R^2}\left\{\chi(u^*) - u^*\chi'(u^*)\right\}$$

$$\Rightarrow \quad -u^*\chi'(u^*) = 1 - \frac{N}{Z}$$

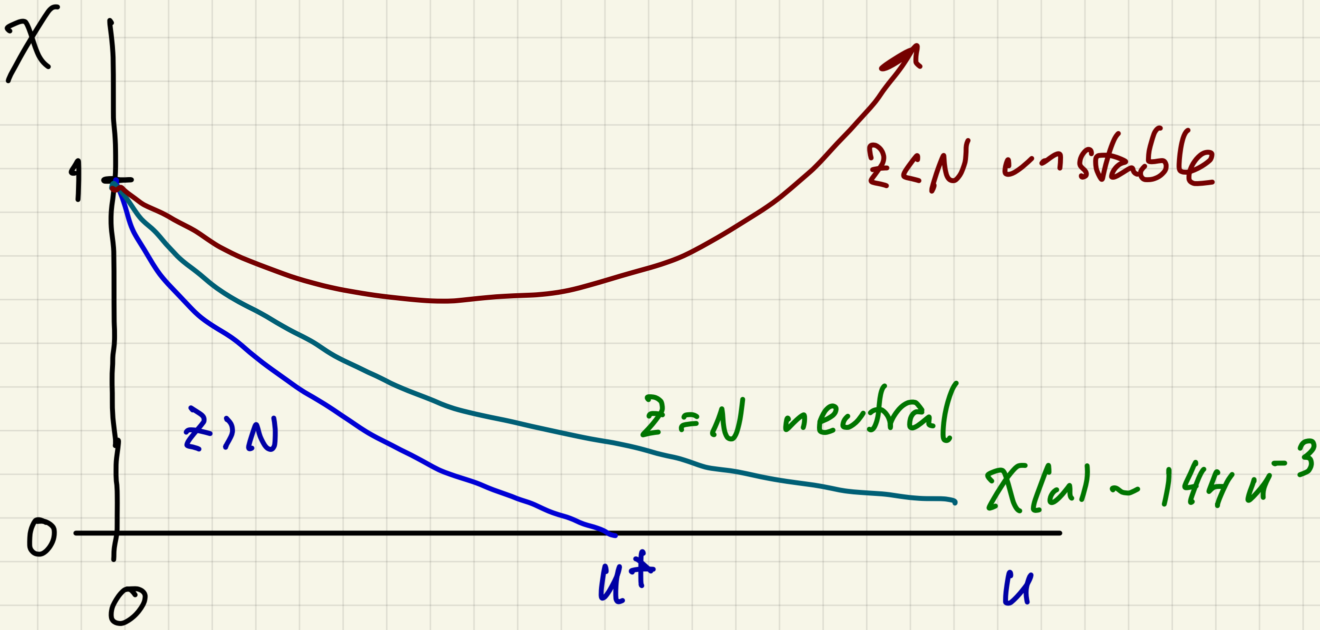
For an atom, $N = Z$, and there is no finite atomic boundary where $\chi(u^*)$ vanishes.

Try a power law: $\chi(u \to \infty) = C u^{-p}$

$$\chi'' = p(p+1)\,C\,u^{-(p+2)} = \frac{\chi^{3/2}}{\sqrt{u}} = C^{3/2}u^{-(3p+1)/2}$$

Thus $\frac{1}{2}(3p+1) = p+2 \Rightarrow p = 3$

$$C^{1/2} = p(p+1) = 12 \Rightarrow C = 144$$



X
1
0
0
z<N unstable
z>N
z=N neutral
X(u) ~ 144 u^-3
u*
u