1D ELECTRON GAS : N e^- in $[0, L]$

a) PBC : $\psi(x+L) = \psi(x)$

b) Hard wall: $\psi(0) = \psi(L) = 0$

a) PBC

(1) EINGENVALUES & EIGENFUNCTIONS

- $\psi(x) = A e^{ikx}$

• periodicity $\Rightarrow$ $A e^{ik(x+L)} = A e^{ikx} \Rightarrow$

$$e^{i\cancel{k}\cdot\cancel{L}} = 1 \Rightarrow \boxed{k_n = \frac{2\pi}{L} n \quad n = 0, \pm 1, \pm 2 \dots}$$

• normalization $\Rightarrow \int_0^L |\psi(x)|^2 dx = 1 \Rightarrow \boxed{A = \frac{1}{\sqrt{L}}}$

- EINGENVALUES:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_k(x) = E_k \psi_k(x)$$

$\mathcal{E}_k = \frac{\hbar^2 k^2}{2m}$ with k discrete as above (k_n) $\Rightarrow$ $\boxed{E_n = \frac{2}{m}\left(\frac{\pi\hbar}{L}\right)^2 n^2}$

(2) one-body density $n(\cancel{x})$

$$n(x) = 2 \sum_{k_n \, occ.} |\psi_{k_n}(x)|^2 = 2 \sum_{|n|=0}^{n_{max}} |\psi_{k_n}(x)|^2$$

with:

$2n_{max} + 1 = N/2$ → for spin degeneracy $\Rightarrow \boxed{n_{max} = \frac{N-2}{4}}$

(for $n = 0$)

(since $n = \pm 1, \pm 2 \dots$ are ok)

$\boxed{n(x) = \frac{N}{L} = n_0}$ constant density

(the thermodynamic limit is the same)

(3) <u>energy of the highest occupied level.</u>

$$\mathcal{E}_{max} \equiv \mathcal{E}_F(N, L) = \frac{\hbar^2 k_F^2}{2m}\Bigg|_{k_F = \frac{2\pi}{L} n_{max}} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(\frac{N-2}{4}\right)^2$$

$$\Rightarrow \boxed{\mathcal{E}_F(N,L) = \frac{\hbar^2}{2m}\frac{\pi^2}{4}\left(\frac{N-2}{L}\right)^2 \xrightarrow[\substack{N,L\to\infty \\ \frac{N}{L}\to n_0}]{} \frac{\hbar^2\pi^2}{8m} n_0^2}$$

i.e. in the thermodyn. limit:

$$\mathcal{E}_F(N,L) = \mathcal{E}_F\left(\frac{N}{L}\right) \quad \text{and} \quad \boxed{\lim_{\substack{L,N\to\infty \\ \frac{N}{L}\to n_0}} k_F = \frac{\pi}{2} n_0}$$

(4) <u>Total energy</u>

$$\mathcal{E}_{tot}(N,L) = 2\sum_{k_n \text{ occ.}} \mathcal{E}_{k_n} = 2\sum_{n=-n_{max}}^{n_{max}} \frac{\hbar^2}{2m}\frac{4\pi^2}{L^2} n^2$$

$$= \frac{4\pi^2\hbar^2}{mL^2}\sum_{n=-n_{max}}^{n_{max}} n^2$$

$$= \frac{8\pi^2\hbar^2}{mL^2}\sum_{n=1}^{n_{max}} n^2 = \frac{8\pi^2\hbar^2}{mL^2}\frac{n_{max}(n_{max}+1)(2n_{max}+1)}{6}$$

$$= \ldots = N\frac{\hbar^2\pi^2}{24m}\left[\left(\frac{N}{L}\right)^2 - \frac{4}{L^2}\right] \quad (*)$$

in the thermodynamic limit:

$$\boxed{\lim_{N,L\to\infty} \mathcal{E}_{tot}(N,L) = N\frac{\hbar^2\pi^2}{24m}\left(\frac{N}{L}\right)^2 = \frac{1}{3}N\mathcal{E}_F\left(\frac{N}{L}\right)}$$

(compare with free e^- in 3D: $\mathcal{E}_{tot} = \frac{3}{5}N\mathcal{E}_F$)

Comment: in (*), only a "volume" term $\left(\propto N\mathcal{E}_V\left(\frac{N}{L}\right)\right)$ is present; no "surface" term $\left(\propto \mathcal{E}_S\left(\frac{N}{V}\right)\right)$ is present!

(Reasonable: NO "surfaces" present with PBC.!)

b) HARD WALLS $\psi(0) = \psi(L) = 0$

(1) General solution: linear combination of $e^{\pm ikx}$:

$$\psi(x) = A \sin kx$$

- boundary conditions: $\sin kL = 0 \Rightarrow$ $\boxed{k_n = \frac{\pi}{L} n \quad n = 1, 2, \dots \frac{N}{2}}$

Note: k and $-k_n$ are the same eigenstate $\Rightarrow$ consider only $n > 0$

$$\boxed{k_F = \frac{\pi}{L}\frac{N}{2}}$$

- normalization: $\int_0^L |\psi(x)|^2 dx = 1 \Rightarrow$

$$A^2 \int_0^L \sin^2 kx \, dx = \frac{A^2 L}{2} \Rightarrow \boxed{A = \sqrt{\frac{2}{L}}}$$

(2) density:

$$n(x) = 2 \sum_{k\,occ.} |\psi_k(x)|^2 = 2 \cdot \frac{2}{L} \sum_{n=1}^{N/2} \sin^2\left(\frac{\pi}{L} n x\right)$$

$$= \cancel{2} \cdot \frac{2}{L} \sum_{n=1}^{N/2} \frac{1}{\cancel{2}} \left[1 - \cos\left(\frac{2\pi}{L} n x\right)\right] \qquad \left(\frac{1-\cos\alpha}{2} = \sin^2\left(\frac{\alpha}{2}\right)\right)$$

$$= \frac{2}{L} \left[\sum_{n=1}^{N/2} 1 - \sum_{n=1}^{N/2} \frac{1}{2} \left(e^{i\frac{2\pi}{L}nx} + e^{-i\frac{2\pi}{L}nx}\right)\right]$$

$$= \frac{N}{L} - \frac{1}{L} \sum_{n=1}^{N/2} \left(\left(e^{i\alpha x}\right)^n + c.c.\right) \quad \text{with } \alpha = \frac{2\pi}{L}$$

Since: $\sum_{n=1}^{m} a^n = \frac{a - a^{m+1}}{1-a}$:

$$= \frac{N}{L} - \frac{1}{L} \left[\frac{e^{i\alpha x} - \left(e^{i\alpha x}\right)^{\left(\frac{N}{2}+1\right)}}{1 - e^{i\alpha x}} \cdot \frac{e^{-i\frac{\alpha x}{2}}}{e^{-i\frac{\alpha x}{2}}} + \frac{e^{-i\alpha x} - e^{-i\alpha x\left(\frac{N}{2}+1\right)}}{1 - e^{-i\alpha x}} \cdot \frac{e^{+i\frac{\alpha x}{2}}}{e^{+i\frac{\alpha}{2}}}\right]$$

$$= \frac{N}{L} - \frac{1}{L} \left[\frac{e^{i\frac{\alpha}{2}x} - e^{i\alpha x\frac{N+1}{2}}}{e^{-i\frac{\alpha}{2}x} - e^{i\frac{\alpha}{2}x}} + \frac{e^{-i\frac{\alpha}{2}x} - e^{-i\alpha x\frac{N+1}{2}}}{e^{i\frac{\alpha}{2}x} - e^{-i\frac{\alpha}{2}x}}\right]$$

$$n(x) = \frac{N}{L} - \frac{1}{L} \frac{1}{e^{i\frac{\alpha}{2}x} - e^{-i\frac{\alpha}{2}x}} \cdot$$

$$\cdot \left[e^{-i\frac{\alpha}{2}x} - e^{i\frac{\alpha}{2}x} + e^{i\alpha\frac{N+1}{2}x} - e^{-i\alpha\frac{N+1}{2}x} \right]$$

$$= \frac{N}{L} + \frac{1}{L} - \frac{1}{L} \frac{\operatorname{sen} \alpha\left(\frac{N+1}{2}\right)x}{\operatorname{sen}\frac{\alpha x}{2}}, \left(\text{remember } \alpha = \frac{2\pi}{L}\right) \Rightarrow$$

$$n(x) = \frac{N}{L} + \frac{1}{L} - \frac{1}{L} \frac{\operatorname{sen}\frac{\pi}{L}(N+1)x}{\operatorname{sen}\frac{\pi}{L}x} \cdot \frac{\frac{\pi}{L}x}{\frac{\pi}{L}(N+1)x} \cdot \frac{\frac{\pi}{L}(N+1)x}{\frac{\pi}{L}x}$$

since $j_0(x) \equiv \frac{\sin x}{x}$:

$$n(x) = \frac{N}{L} + \frac{1}{L} - \frac{1}{L} \frac{j_0\left(\frac{\pi}{L}(N+1)x\right)}{j_0\left(\frac{\pi}{L}x\right)} \cdot (N+1)$$

$$= \frac{N+1}{L} \cdot \left\{ 1 - \frac{j_0\left(\frac{\pi}{L}(N+1)x\right)}{j_0\left(\frac{\pi}{L}x\right)} \right\}$$

$$\Rightarrow \boxed{n(x) = \frac{N}{L}\left(1+\frac{1}{N}\right)\left\{1 - \frac{j_0\left(\frac{\pi}{L}(N+1)x\right)}{j_0\left(\frac{\pi}{L}x\right)}\right\}}$$

Before studying the thermodynamic limit, review the properties of $j_0(x)$:

$\lim_{x\to 0} j_0(x) = 1$

$j_0(x_i) = 0$ for $x_i = \pm n\pi$

$j_0\left(\frac{\pi}{2}\right) = \frac{2}{\pi}$

$j_0(-x) = j_0(x)$; $j(\pi - x) = \frac{x}{\pi - x}$

$n(x)$ can be rewritten in terms of $n_0 = \frac{N}{L}$:

$$n(x) = n_0 \left[\left(1 + \frac{1}{N}\right) \left(1 - \frac{j_0(\pi n_0 x (1+1/N))}{j_0(\pi x n_0 / N)} \right) \right.$$

In the thermodynamic limit $(N \to \infty, \frac{N}{L} \to n_0)$:

$$\boxed{n_\infty(x) = \lim_{\substack{N \to \infty \\ L}} n(x) = n_0 \left(1 - j_0(\pi n_0 x) \right)}$$

Since $n(L-x) = n(x)$, we limit our study to $x \to 0$ and finite values of x, up to $\frac{L}{2}$.

$$\lim_{x \to 0} n_\infty(x) = 0$$

$$\lim_{x \to \frac{L}{2}} n_\infty(x) = n_0 \left(1 - \underbrace{j_0\left(\frac{\pi}{2} L n_0\right)}_{?} \right)$$

(here $L \to \infty$)

Remember : $j_0(x) = \frac{\sin x}{x}$
therefore $\lim_{x \to \infty} j_0(x) = 0$

$$= n_0$$

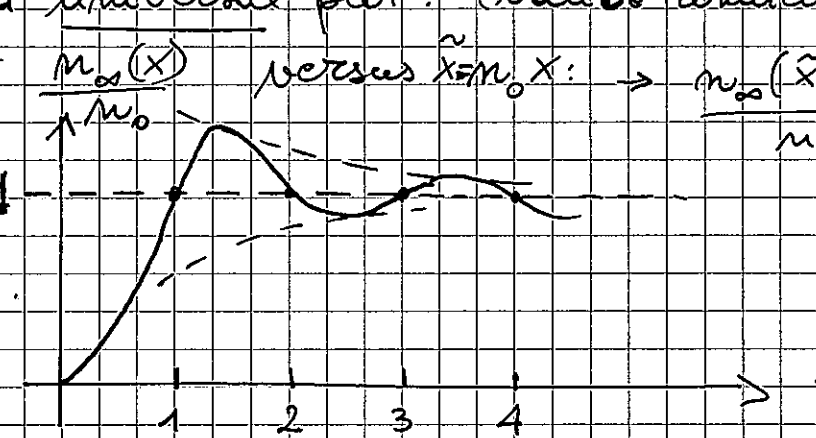
Other relevant values:

$$n_\infty(x) = n_0 \quad \text{for} \quad j_0(\pi n_0 x) = 0 \Rightarrow \sin(\pi n_0 x) = 0$$

$$\Rightarrow \cancel{\pi} n_0 x = \pm n \cancel{\pi}$$

$$\Rightarrow x = \pm n \frac{1}{n_0}$$

For a universal plot: (valid whatever is n_0):
plot $\frac{n_\infty(x)}{n_0}$ versus $\tilde{x} = n_0 x$: $\to \frac{n_\infty(\tilde{x}/n_0)}{n_0} = 1 - j_0(\pi \tilde{x})$



- Note that $k_F = \frac{\pi}{2} n_0$; therefore, it is reasonable that x is measured in terms of $\frac{1}{n_0} \left(= \frac{\pi}{2 k_F} \right)$ in the universal plot

Comments:

- good model (simple) for metallic surface
- "Friedel oscillations" determined by free e^- wavelength at $\mathcal{E}_F$: $\lambda_F = \frac{2\pi}{k_F}$
- low $n_0 \Rightarrow$ low $k_F \Rightarrow$ towards the classical limit $n(x) \to n_0$ for $|x| \leq L$
- Symmetry property of $n(x)$:

$$n(\cancel{L-x}) = n(x)$$

- 3D case:

$$n(z) = n_0\left(1 + 3\,\frac{\cos(2k_F z)}{(2k_F z)^2} - \frac{\sin(2k_F z)}{(2k_F z)^3}\right)$$

1D case:

$$\boxed{n(z) = n_0\left(1 - \frac{\sin(2k_F x)}{2k_F x}\right)}$$

The density $n(x)$ first reaches its bulk value n_0 after a distance given by $2k_F x = \pi$, so we can say that the "thickness" of the surface "spill-out" of the e^- density distribution in a simple metal is $\sim 1/k_F$, i.e. $\sim 1\,\text{Å}$.

(3) $$\boxed{\mathcal{E}_F(N,L) = ?} = \frac{\hbar^2}{2m} k_{max}^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2\left(\frac{N}{2}\right)^2 = \boxed{\frac{\hbar^2\pi^2}{8m} n_0^2}$$

remains this also in the thermodynamic limit.

(4) $\mathcal{E}_{TOT}(N,L) = ?$

$$\mathcal{E}_{TOT} = 2\sum_{n=1}^{N/2} \frac{\hbar^2}{2m}\frac{\pi^2}{L^2} n^2 = \frac{\cancel{2}\hbar^2}{\cancel{2}m}\frac{\pi^2}{L^2}\sum_{n=1}^{N/2} n^2$$

$$= \frac{\hbar^2\pi^2}{mL^2}\cdot\underbrace{\frac{1}{6}\frac{N}{2}\left(\frac{N}{2}+1\right)(N+1)}$$

$$= \frac{1}{24} N(N+2)(N+1)$$

$$= \frac{1}{24} N(N^2+3N+2)$$

$$= N\frac{\hbar^2\pi^2}{24m}\left[\left(\frac{N}{L}\right)^2 + 3\frac{N}{L^2} + \frac{2}{L^2}\right]$$

$$\boxed{\mathcal{E}_{TOT}(N,L) = N\mathcal{E}_V\left(\frac{N}{L}\right) + \mathcal{E}_S\left(\frac{N}{L}\right) + \frac{1}{L}\Delta\mathcal{E}\left(\frac{N}{L}\right)}$$

where:

$$\mathcal{E}_V\left(\frac{N}{L}\right) = \frac{\hbar^2\pi^2}{24m}\left(\frac{N}{L}\right)^2 \quad \text{"volume term"}$$

$$\mathcal{E}_S\left(\frac{N}{L}\right) = \frac{\hbar^2\pi^2}{8m}\left(\frac{N}{L}\right)^2 \quad \text{"surface term"}$$

$$\Delta\mathcal{E}\left(\frac{N}{L}\right) = \frac{\hbar^2\pi^2}{12m}\frac{N}{L}$$

so that:
$$\lim_{\substack{N,L\to\infty \\ N/L = n_0}} \mathcal{E}_{TOT}(N,L) = N\mathcal{E}_V\left(\frac{N}{L}\right) + \mathcal{E}_S\left(\frac{N}{L}\right)$$

Also in this case, as in **(a)** PBC: $\mathcal{E}_{TOT} = \frac{1}{3}N\mathcal{E}_F$ in the thermod. limit