# §2. Electron gas

## *) Second quantization formulation

Electron creation / annihilation operators:

$$c^{\dagger}_{\vec{k},\sigma}, \quad c_{\vec{k},\sigma}$$

$$\{c_{\vec{k},\sigma}, c_{\vec{k}',\sigma'}\} = \{c^{\dagger}_{\vec{k},\sigma}, c^{\dagger}_{\vec{k}',\sigma'}\} = 0$$

$$\{c_{\vec{k},\sigma}, c^{\dagger}_{\vec{k}',\sigma'}\} = \delta_{\vec{k},\vec{k}'}\delta_{\sigma\sigma'}$$

Fermi sphere $\quad |FS\rangle = \prod_{|\vec{k}|<k_F} \prod_{\sigma=\uparrow,\downarrow} c^{\dagger}_{\vec{k},\sigma}|0\rangle$

Energy $\quad E = \sum_{\substack{|\vec{k}|<k_F, \\ \sigma=\uparrow,\downarrow}} \varepsilon_{\vec{k}} = 2\sum_{|\vec{k}|<k_F} \varepsilon_{\vec{k}}$

— Second quantization vs. first quantization

Below we give justifications (not proof).

One electron state:

first-quantized form $\quad \Leftrightarrow \quad$ second-quantized form

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \quad \Leftrightarrow \quad c^{\dagger}_{\vec{k},\sigma}|0\rangle$$

$$c^\dagger_{\vec{k},\sigma} = \frac{1}{\sqrt{V}} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \psi^\dagger_\sigma(\vec{r})$$

$$= \int d\vec{r}\, \phi_{\vec{k}}(\vec{r})\, \psi^\dagger_\sigma(\vec{r})$$

First-quantized wave functions appear as expansion coefficients of the second-quantized creation operators.

Many-electron state:

first-quantized form — second-quantized form

"Slater determinant"

$$\psi(\{\vec{r}\}) = \det \begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_1) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e/2}) \\ \vdots & \ddots & \vdots \\ \cdots & \cdots & \cdots \end{pmatrix} \Leftrightarrow |FS\rangle = \prod_{\substack{|\vec{k}|<k_F \\ \sigma=\uparrow,\downarrow}} c^\dagger_{\vec{k},\sigma}|0\rangle$$

$\times$ (spin-$\downarrow$ part)

$$|FS\rangle = \left( c^\dagger_{\vec{k}_1,\uparrow} c^\dagger_{\vec{k}_2,\uparrow} \cdots c^\dagger_{\vec{k}_{N_e/2},\uparrow} \right) \left( c^\dagger_{\vec{k}_1,\downarrow} c^\dagger_{\vec{k}_2,\downarrow} \cdots c^\dagger_{\vec{k}_{N_e/2}} \right)|0\rangle$$

$\Big\|$ use inverse Fourier transformation

$$\int d\vec{r}_1 \cdots d\vec{r}_{N_e/2} \left[ \phi_{\vec{k}_1}(\vec{r}_1) \cdots \phi_{\vec{k}_{N_e/2}}(\vec{r}_{N_e/2}) \right] \psi^\dagger_\uparrow(\vec{r}_1) \cdots \psi^\dagger_\downarrow(\vec{r}_{N_e/2})$$

$\Big\|$ sum over all permutations of $\vec{r}_1, \ldots, \vec{r}_{N_e/2}$

$$\left(\frac{N_e}{2}\right)! \int d\vec{r}_1 \cdots d\vec{r}_{N_e/2} \sum_{\sigma \in S_{N_e/2}} \mathrm{sgn}(\sigma)\, \phi_{\vec{k}_1}(\vec{r}_{\sigma(1)}) \cdots \phi_{\vec{k}_{N_e/2}}(\vec{r}_{\sigma(N_e/2)})$$

$$\times \psi^\dagger_\uparrow(\vec{r}_1) \cdots \psi^\dagger_\uparrow(\vec{r}_{N_e/2})$$

$\Big\|$

$\det(\cdots)$ "Slater determinant"!

$$|FS\rangle \propto \int d\vec{r}_1 \cdots d\vec{r}_{N_e} \det\begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_1) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e/2}) \\ \vdots & & \vdots \\ \phi_{\vec{k}_{N_e/2}}(\vec{r}_1) & \cdots & \phi_{\vec{k}_{N_e/2}}(\vec{r}_{N_e/2}) \end{pmatrix}$$

$$\times \det\begin{pmatrix} \phi_{\vec{k}_1}(\vec{r}_{N_e/2+1}) & \cdots & \phi_{\vec{k}_1}(\vec{r}_{N_e}) \\ \vdots & & \vdots \\ \phi_{\vec{k}_{N_e/2}}(\vec{r}_{N_e/2+1}) & \cdots & \phi_{\vec{k}_{N_e/2}}(\vec{r}_{N_e}) \end{pmatrix}$$

$$\times \psi_\uparrow^\dagger(\vec{r}_1) \cdots \psi_\uparrow^\dagger(\vec{r}_{N_e/2}) \psi_\downarrow^\dagger(\vec{r}_{N_e/2+1}) \cdots \psi_\downarrow^\dagger(\vec{r}_{N_e}) |0\rangle$$

$$= \int d\vec{r}_1 \cdots d\vec{r}_{N_e} \; \Psi(\vec{r}_1, \ldots, \vec{r}_{N_e}) \psi_\uparrow^\dagger(\vec{r}_1) \cdots \psi_\uparrow^\dagger(\vec{r}_{N_e/2})$$

$$\times \psi_\downarrow^\dagger(\vec{r}_{N_e/2+1}) \cdots \psi_\downarrow^\dagger(\vec{r}_{N_e}) |0\rangle$$

$\Psi(\vec{r}_1, \ldots, \vec{r}_{N_e})$: first-quantized Slater determinant wave functions

Hamiltonian:

| first-quantized form | second-quantized form |
|---|---|
| $H = -\sum_{j=1}^{N_e} \frac{\hbar^2}{2m} (\vec{\nabla}_j)^2$ | $H = \sum_{\vec{k},\sigma} \varepsilon_{\vec{k}} c_{\vec{k},\sigma}^\dagger c_{\vec{k},\sigma}$ |
| $\Leftrightarrow$ | $= \int d\vec{r} \sum_{\sigma=\uparrow,\downarrow} \psi_\sigma^\dagger(\vec{r}) \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2\right) \psi_\sigma(\vec{r})$ |

use $\psi_\sigma(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} c_{\vec{k},\sigma} e^{i\vec{k}\cdot\vec{r}}$

(See justification below)

Particle-number operator for an electron with wave-vector $\vec{k}$ and spin $\sigma$:

$$n_{\vec{k},\sigma} = c^{\dagger}_{\vec{k},\sigma} c_{\vec{k},\sigma}$$

$$\begin{cases} n_{\vec{k},\sigma}|0\rangle = 0 \\ n_{\vec{k},\sigma} c^{\dagger}_{\vec{k},\sigma}|0\rangle = c^{\dagger}_{\vec{k},\sigma}|0\rangle \end{cases} \Rightarrow$$

$n_{\vec{k},\sigma}$ has eigenvalue 0 and 1.

Pauli's exclusion principle!

$$\left(c^{\dagger}_{\vec{k},\sigma}\right)^2 = 0$$

$$\Rightarrow H|FS\rangle = \sum_{\vec{k}} \sum_{\sigma=\uparrow,\downarrow} \varepsilon_{\vec{k}}\, n_{\vec{k},\sigma} \prod_{\substack{|\vec{k}'|<k_F, \\ \sigma'=\uparrow,\downarrow}} c^{\dagger}_{\vec{k}',\sigma'}|0\rangle$$

$$= \sum_{|\vec{k}|<k_F} \sum_{\sigma=\uparrow,\downarrow} \varepsilon_{\vec{k}} \prod_{\substack{|\vec{k}'|<k_F \\ \sigma'=\uparrow,\downarrow}} c^{\dagger}_{\vec{k}',\sigma'}|0\rangle$$

$$= 2 \sum_{|\vec{k}|<k_F} \varepsilon_{\vec{k}}\, |FS\rangle$$

$$= E$$

✓

This shows that the second-quantized Hamiltonian has the second-quantized state as its eigenstate with the expected eigenvalue.

General idea on the derivation of second-quantized operators from first-quantized forms :

"match matrix elements"

Matrix elements of second-quantized operators in second-quantized partide occupation basis

||

Matrix elements of first-quantized operators in first-quantized wave functions

Example : Coloumb interactions

$$\sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \Longleftrightarrow \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \sum_{\sigma_1,\sigma_2} \psi^+_{\sigma_1}(\vec{r}_1) \psi^+_{\sigma_2}(\vec{r}_2)$$

$$\times \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \psi_{\sigma_2}(\vec{r}_2) \psi_{\sigma_1}(\vec{r}_1)$$

Check matrix elements in real space !

( only diagonal ones are non-vanishing . )

## *) Free electron gas at $T > 0$

$$Z = \mathrm{Tr}\, e^{-\beta(H-\mu n)} \qquad \beta = \frac{1}{k_B T}$$

$$n = \sum_{\vec{k},\sigma} n_{\vec{k},\sigma} = \sum_{\vec{k},\sigma} c^+_{\vec{k},\sigma} c_{\vec{k},\sigma}$$

It's more convenient to control the particle number $N_e$ with a chemical potential $\mu$.

has to be determined!

$$Z = \mathrm{Tr}\, e^{-\beta \sum_{\vec{k},\sigma} (\varepsilon_{\vec{k}} - \mu) c^+_{\vec{k},\sigma} c_{\vec{k},\sigma}}$$

$$= \mathrm{Tr} \prod_{\vec{k},\sigma} e^{-\beta(\varepsilon_{\vec{k}} - \mu) n_{\vec{k},\sigma}}$$

$$\to \sum_{\{n_{\vec{k},\sigma}\}} \langle \{n_{\vec{k},\sigma}\} | \cdots | \{n_{\vec{k},\sigma}\} \rangle$$

$$\{n_{\vec{k},\sigma}\} \;\|\; 0,1$$

$$= \prod_{\vec{k},\sigma} \sum_{n_{\vec{k},\sigma}=0,1} e^{-\beta(\varepsilon_{\vec{k}} - \mu) n_{\vec{k},\sigma}}$$

$$= \prod_{\vec{k},\sigma} \left[ 1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)} \right]$$

$$= \prod_{\vec{k}} \left[ 1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)} \right]^2$$

$$\langle n_{\vec{k},\sigma} \rangle_T = \frac{1}{Z} \mathrm{Tr}\left[ n_{\vec{k},\sigma} e^{-\beta(H-\mu N)} \right]$$

$= \dots$ (mostly repeat the steps for $Z$, except for one mode: $n_{\vec{k},\sigma}$.)

All factors cancel except for this one!

$$= \frac{\sum_{n_{\vec{k},\sigma}=0,1} n_{\vec{k},\sigma} e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}{\sum_{n_{\vec{k},\sigma}=0,1} e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}$$

$$= \frac{e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}{1+e^{-\beta(\varepsilon_{\vec{k}}-\mu)}}$$

$$= \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)}+1}$$

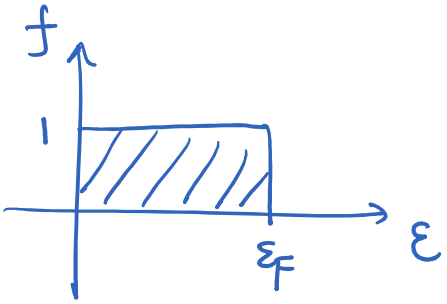
Fermi-Dirac distribution!

(as expected ...)

$$f(\varepsilon,\mu,T) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

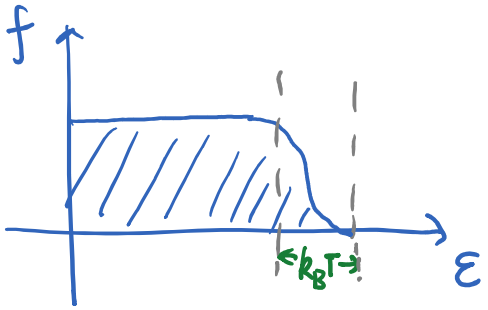
$\mu$ has to be determined by the # of electrons.

$T=0$: $\quad f(\varepsilon,\mu,T) = \begin{cases} 1, & 0<\varepsilon<\mu \\ 0, & \varepsilon>\mu \ \& \ \varepsilon<0 \end{cases}$




$\Rightarrow \quad \mu(T=0) = \varepsilon_F$

$T > 0$ and $T \ll T_F = \frac{\varepsilon_F}{k_B}$ ($10^4 \sim 10^5$ K in metals)




$\mu$ has a weak dependence on $T$.
(close to $\varepsilon_F$)

$$N_e = \sum_{\vec{k},\sigma} \langle n_{\vec{k},\sigma} \rangle_T = \sum_{\vec{k},\sigma} \frac{1}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$$= \sum_{\vec{k},\sigma} \int_{-\infty}^{\infty} d\varepsilon \; \delta(\varepsilon - \varepsilon_{\vec{k}}) \frac{1}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$\delta(\varepsilon - \varepsilon_{\vec{k}}) \rightarrow D(\varepsilon)$

$$= \int_{-\infty}^{\infty} d\varepsilon \; D(\varepsilon) f(\varepsilon, \mu, T)$$

Sommerfeld expansion (low $T$):

$$\int_{-\infty}^{\infty} d\varepsilon \; f(\varepsilon, \mu, T) \, g(\varepsilon)$$

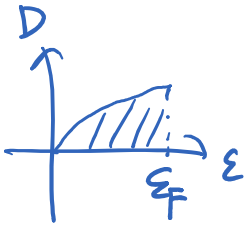
$$= \int_{-\infty}^{\mu} d\varepsilon \; g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + O(T^4)$$

$$\Rightarrow \quad N_e \simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu)$$

Differentiate with respect to $T$:

$$D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3} k_B^2 T\, D'(\mu) = 0$$

$$\Rightarrow \quad \frac{d\mu}{dT} = -\frac{\pi^2}{3} k_B^2 T \frac{D'(\mu)}{D(\mu)}$$




If $D(\varepsilon)$ increases with $\varepsilon$ for $\varepsilon \simeq \varepsilon_F$ (i.e. $D'(\varepsilon_F) > 0$)

$\mu$ decreases when $T$ increases !

3D electron gas:

$$D(\varepsilon) \propto \sqrt{\varepsilon} \Rightarrow \frac{D'(\mu)}{D(\mu)} = \frac{1}{2\mu}$$

$$\mu(T) = \varepsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right]$$

$$= \varepsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right] \quad T \ll T_F \sim 10^4\,K$$

## — Specific heat of 3D electron gas

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Internal energy:

$$U(T) = \int_{-\infty}^{\infty} d\varepsilon\, D(\varepsilon)\, f(\varepsilon,\mu,T)\,\varepsilon$$

$$\simeq \int_{-\infty}^{\mu} d\varepsilon\, D(\varepsilon)\,\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \left[D(\mu) + \mu D'(\mu)\right]$$

$$\Rightarrow \quad C_V = \left(\frac{dU}{dT}\right)_V$$

$$= \mu D(\mu)\frac{d\mu}{dT} + \frac{\pi^2}{3} k_B^2 T \left[D(\mu) + \mu D'(\mu)\right]$$

$$\frac{\pi^2}{3} k_B^2 T D'(\mu) + D(T)\frac{d\mu}{dT} = 0$$

(See page ⑨)

$$= \frac{\pi^2}{3} k_B T^2 D(\mu)$$

$$\simeq \frac{\pi^2}{3} k_B T\, D(\varepsilon_F)$$

Last lecture:

$$D(\varepsilon) = \frac{3}{2}\frac{N_e}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}$$

$$\Downarrow$$

$$D(\varepsilon_F) = \frac{3}{2}\frac{N_e}{\varepsilon_F}$$

$$= \frac{\pi^2}{2} N_e \frac{k_B T}{\varepsilon_F}$$

Specifit heat per unit volume:

$$c_V = \frac{C_V}{V} = \frac{\pi^2}{2} k_B\, n \cdot \frac{T}{T_F}$$

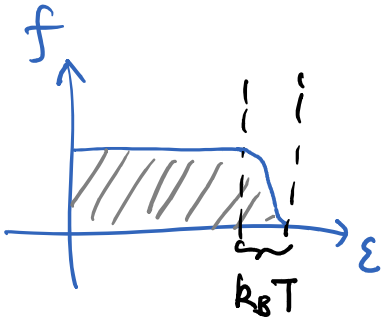
$n$: electron density $n = \frac{N_e}{V}$

$\Rightarrow C_V = \gamma T$ linear in $T$ !

$\gamma = \frac{\pi^2}{2} \frac{k_B}{T_F} n$

Compare to 3D classical non-interacting particles:

$C_{V,\text{classical}} = \frac{3}{2} k_B n$




very small fraction: $\frac{k_B T}{\varepsilon_F} \ll 1$

Quantum effect !

Only electrons close to the Fermi energy $\varepsilon_F$ have substantial contributions to the specific heat.