The Free Electron Gas Model

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SFI5769 - Chemical Physics and Thermodynamics of Gases and Solids

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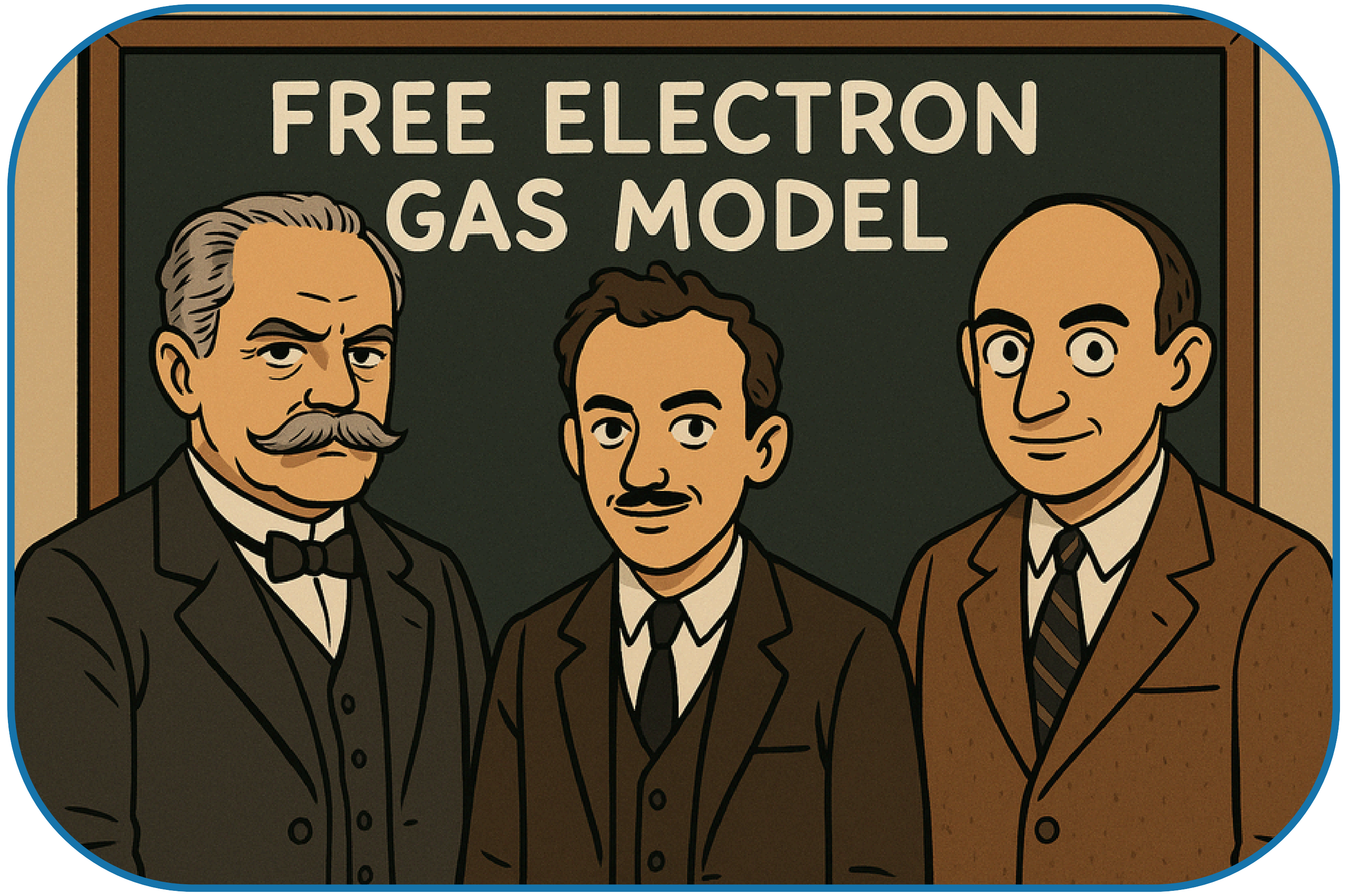

Cartoon image of Sommerfeld, Dirac and Fermi. Produced using ChatGPT.

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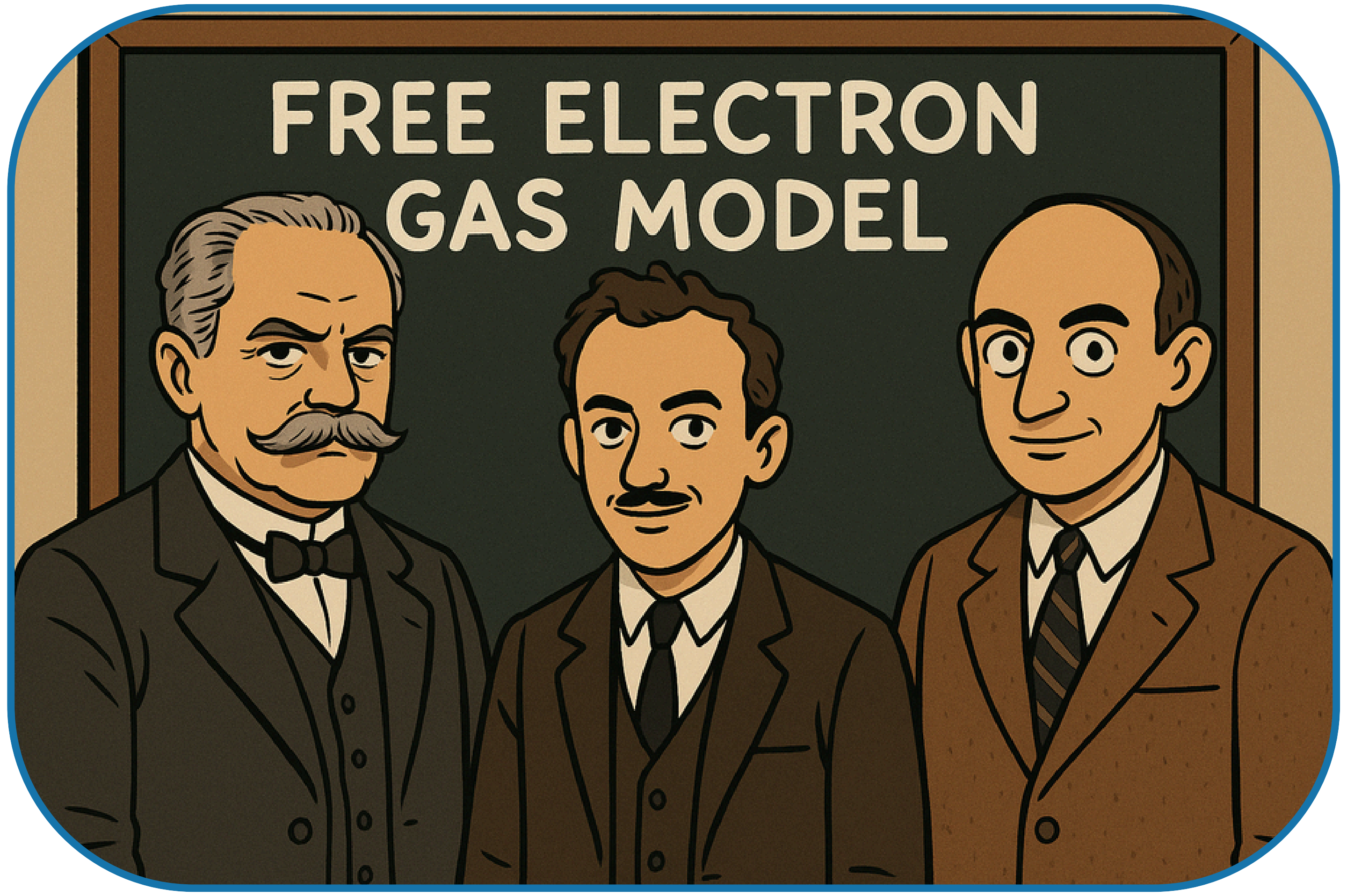

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A little bit of the history:

- Drude firstly proposed it, but in a classical and statistical physics view.
- Pauli principle and Fermi-Dirac statistics.
- Sommerfeld incorpored quantum effects.

Free Electron Gas Model!

Free Electron Gas Model

noninteracting

mathematical and physical modeling

Importance

- Understand properties of solids, mainly metals.
- Simple ideia that explains a lot of fundamental properties.
- Crucial to the development of the band theory.

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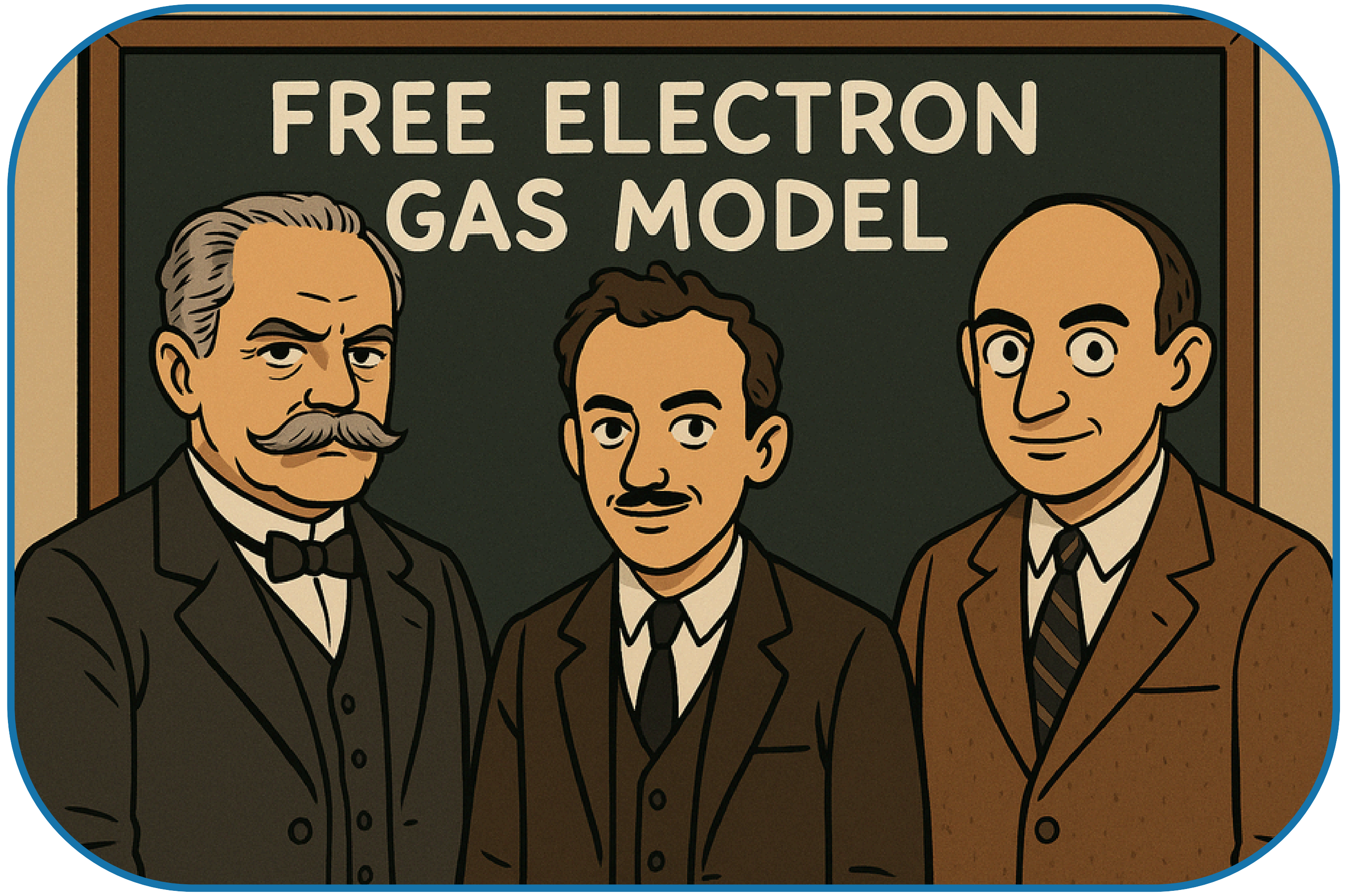

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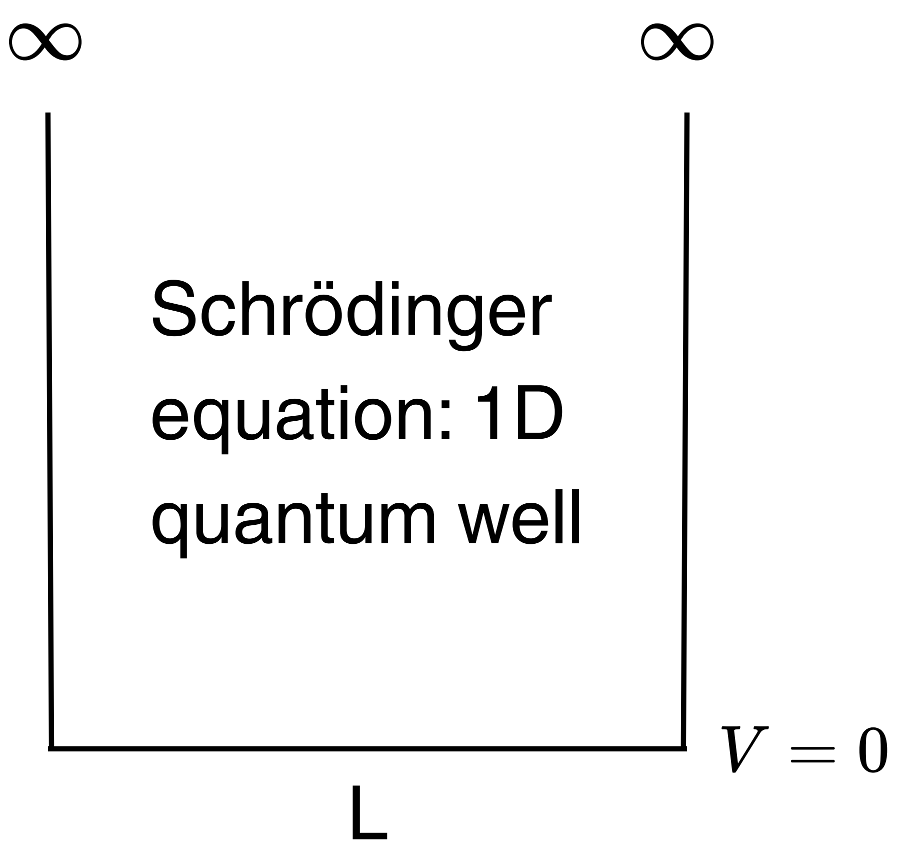
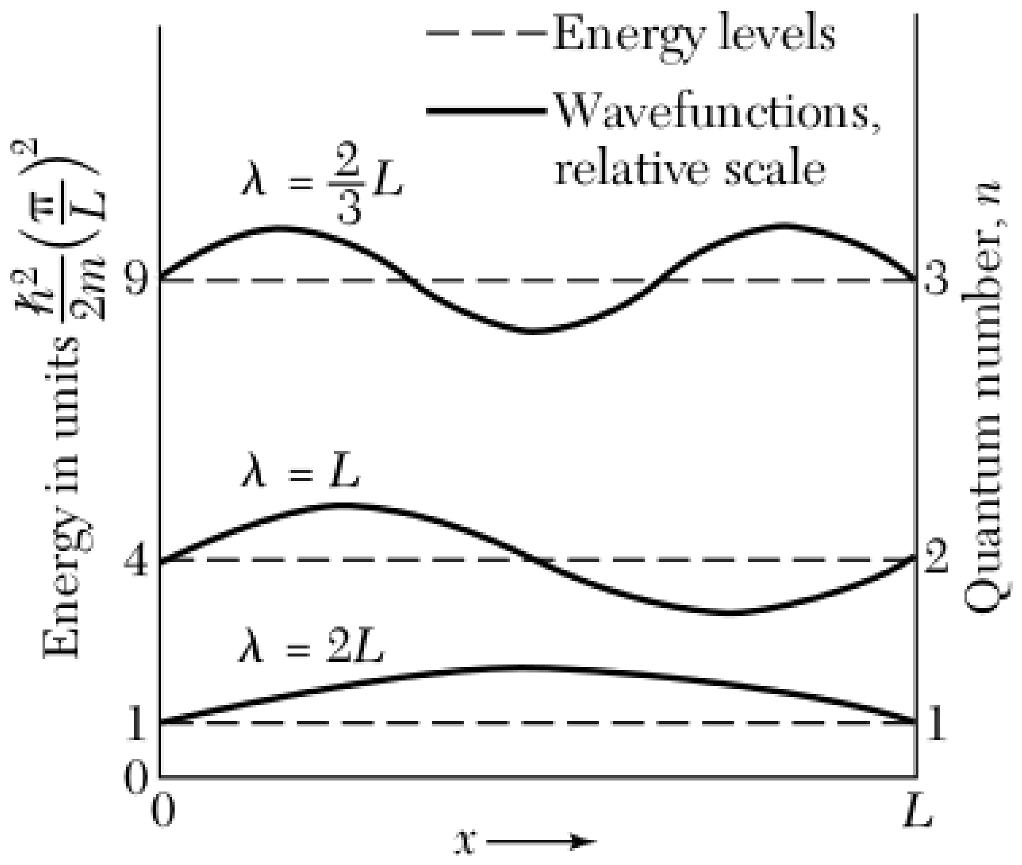
Quantum Well



$$\hat{H}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = E_n\psi_n(x)$$

solution: $$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

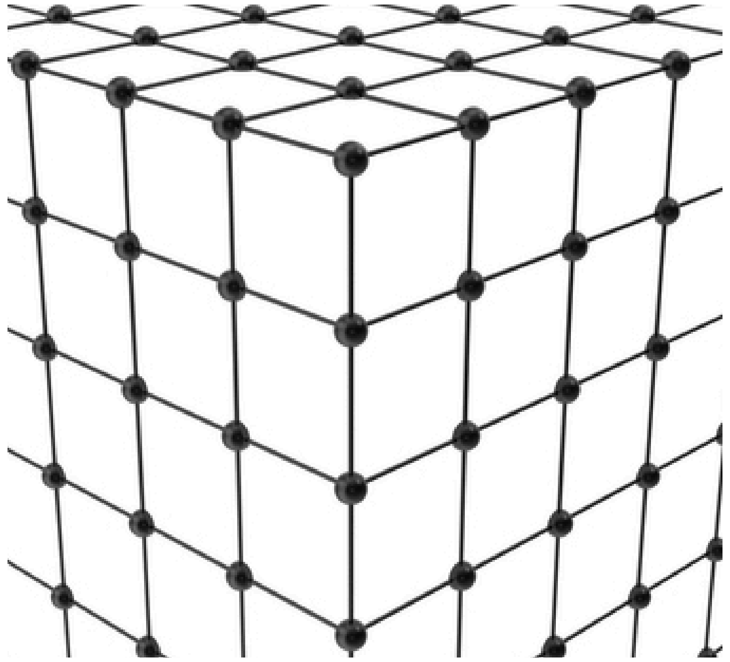
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}n^2$$



Source: C. Kittel, Introduction to solid state physics, 8th ed. Hoboken, NY: Wiley (2005)

Expandind to 3 dimensions...

Born-von Karman periodic boundary conditions
(cube of L side inifinity lattice)



https://www.pixelsquid.com/png/cube-grid-patterned-black-3078631786566128952?image=G03

plane wave solution

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

where

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}$$

and the energy

$$E_{\vec{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

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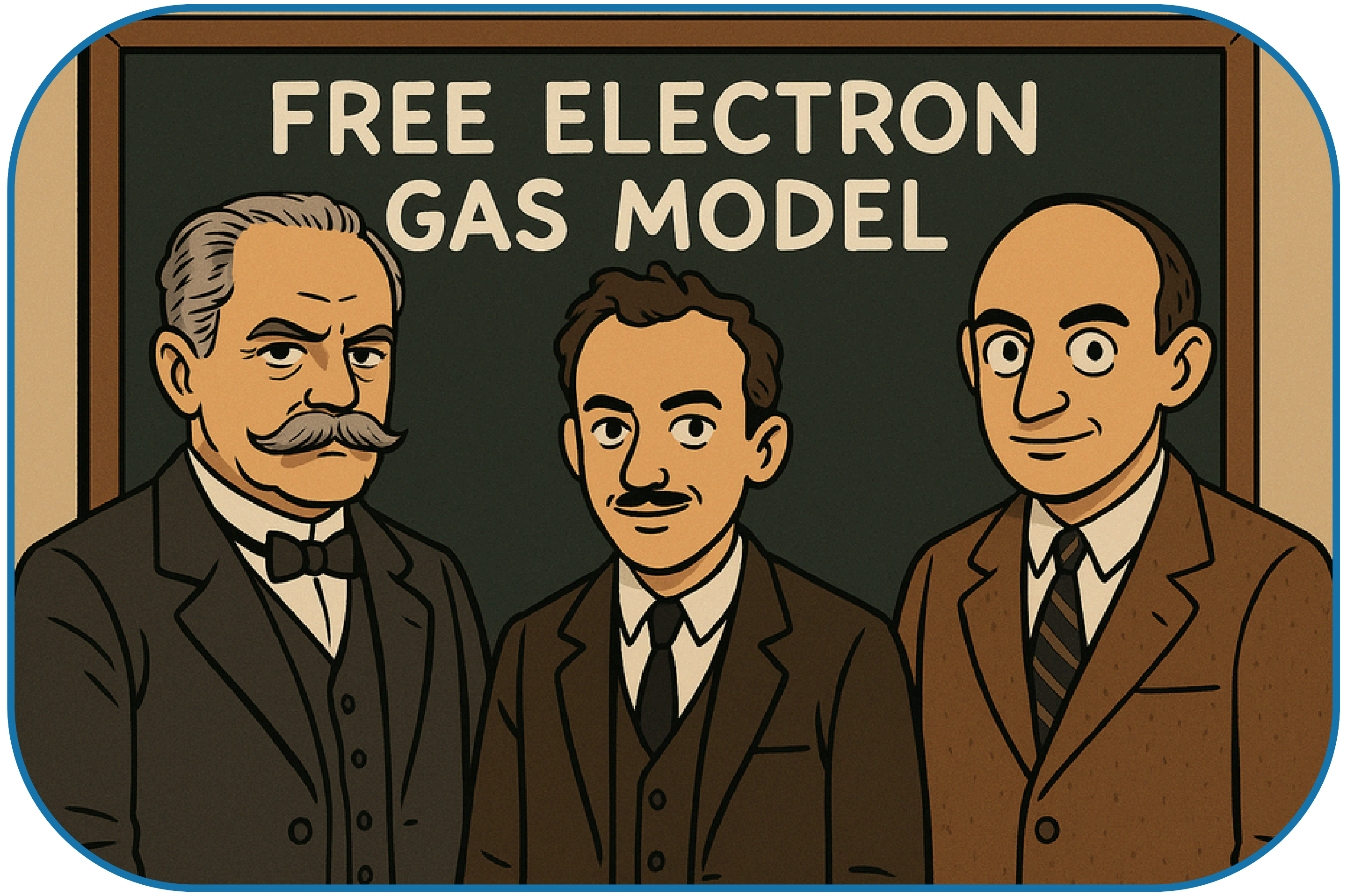

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The Fermi Sphere and Fermi Energy

Pauli exclusion principle

electrons are fermions

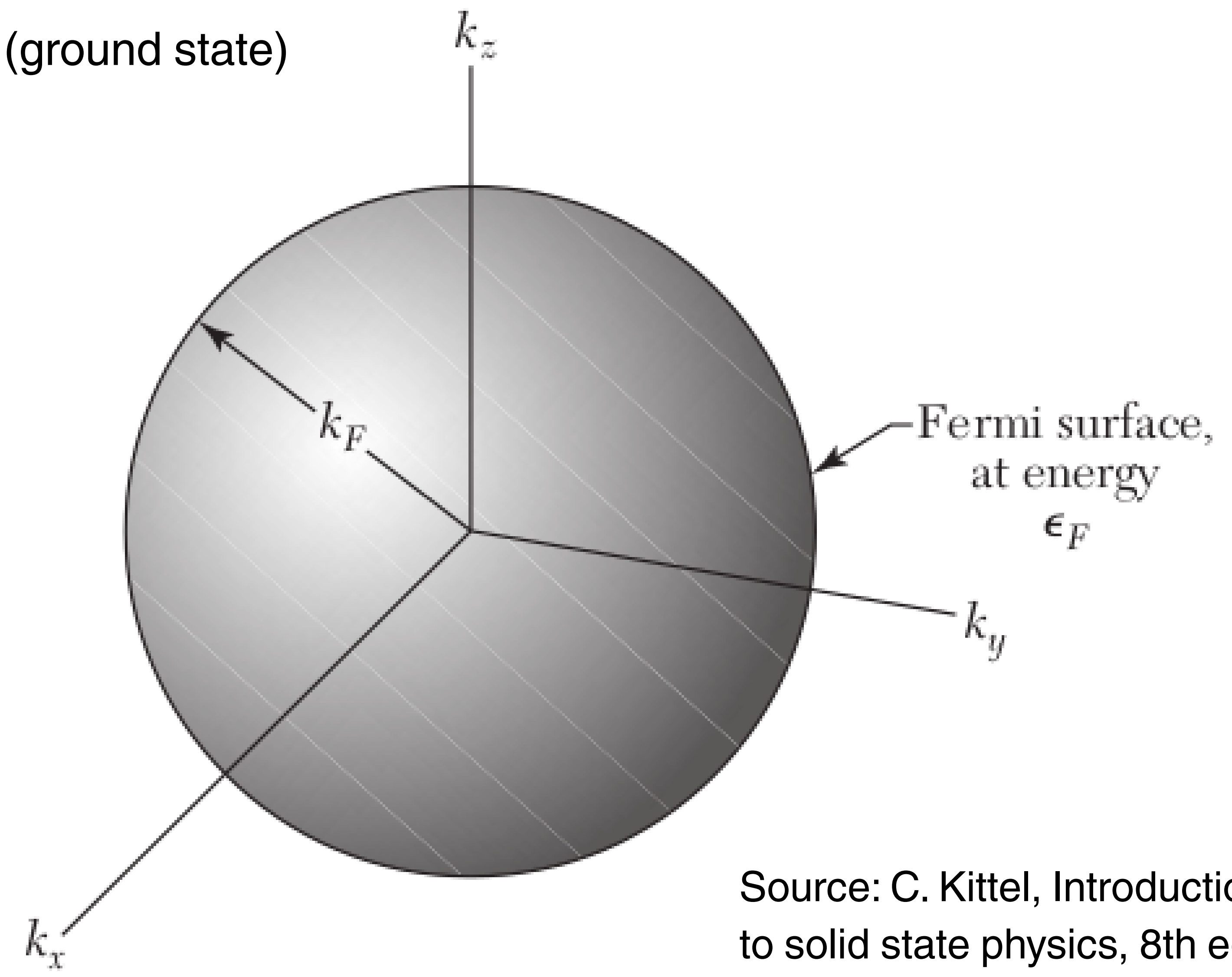
Fermi sphere

spin up and down

quantized energy levels

Fermi energy: the last occupied level energy

T = 0 (ground state)



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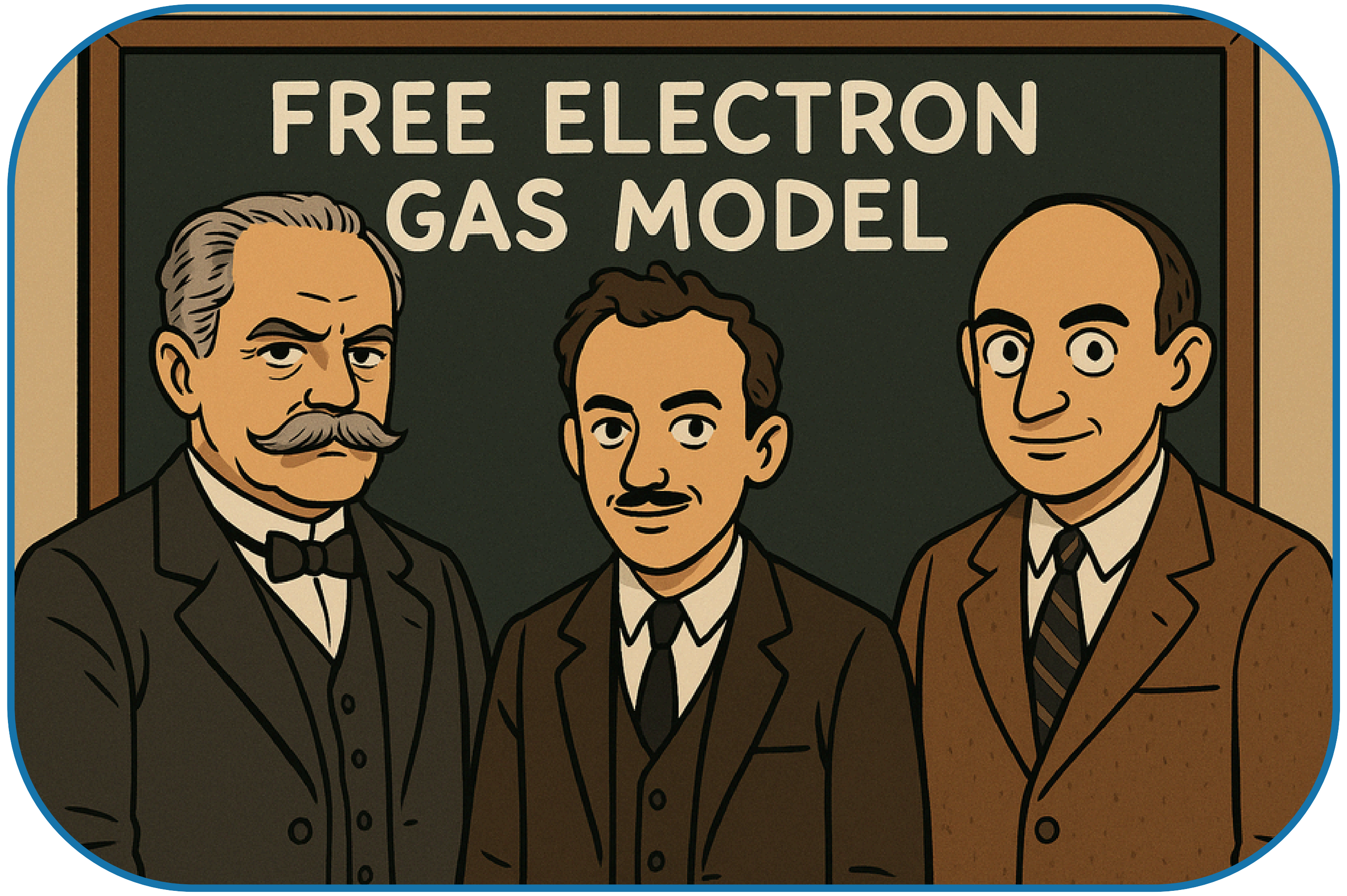

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Density of States and the Fermi-Dirac Distribution

The density of states, g(E), is defined as the number of available electronic states per unit volume,per unit energy range.

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2} = \frac{V}{3\pi^2}\frac{(2m)^{3/2}}{\hbar^3}E^{3/2}$$

$$g(E) = \frac{1}{V}\frac{dN(E)}{dE} = \frac{d}{dE}\left[\frac{1}{3\pi^2}(2m)^{3/2}\frac{1}{\hbar^3}E^{3/2}\right]$$

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

density of states $\propto$ square root of the energy

Fermi-dirac distribution function:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

where k_B is the Boltzmann constant and μ is the chemical potential.

$T = 0$, all energy states completely filled $f(E) = 1$ for $E < E_F$.

$T > 0$, some electrons gain energy and smeares out of the Fermi sphere.

$\approx k_b T$

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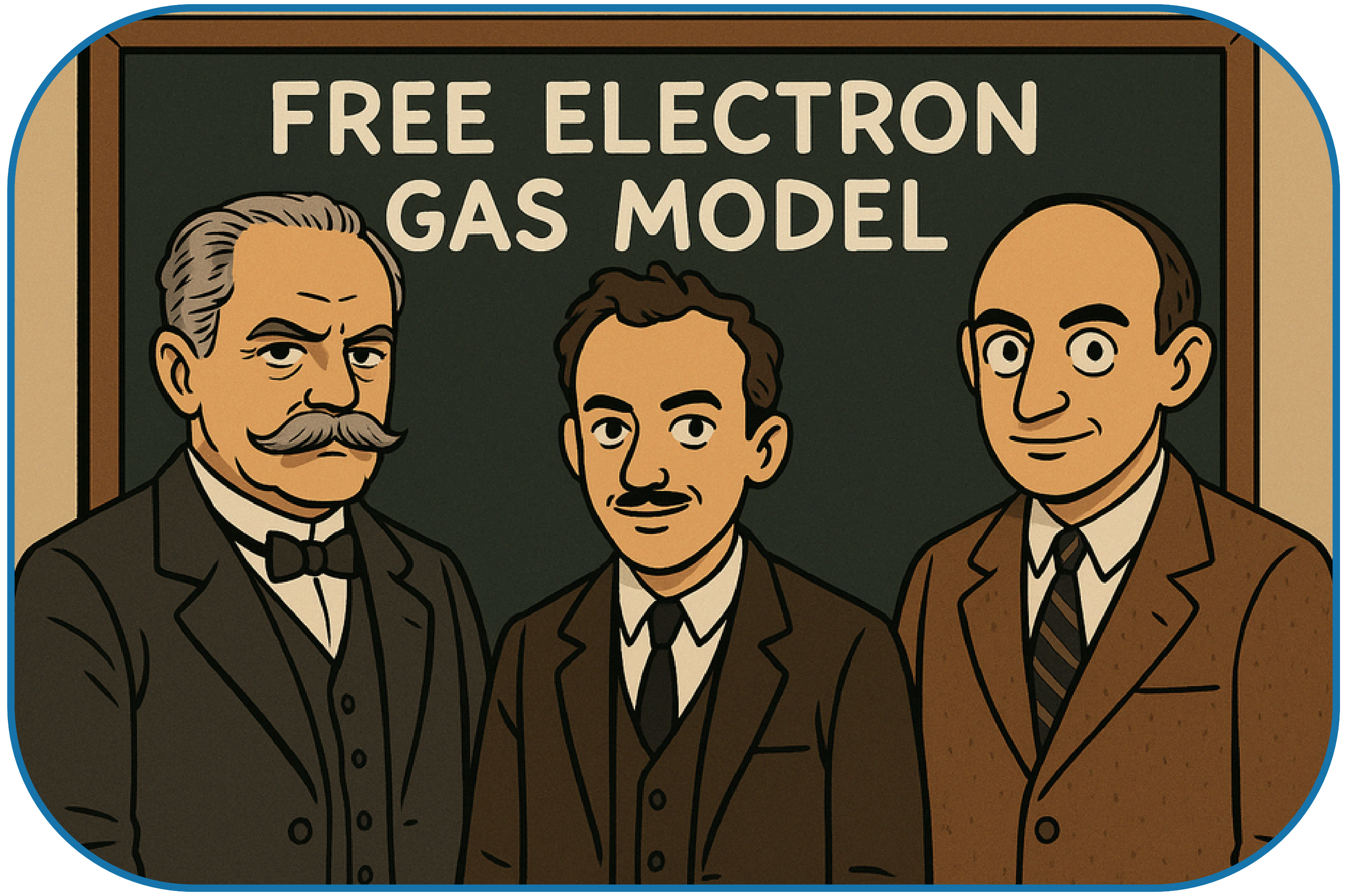

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Consequences and Applications

Electrical Condutivity and Ohm's Law

Drude model: $$m\frac{d\vec{v}_d}{dt} = -e\vec{E} - \frac{m\vec{v}_d}{\tau}$$

solving $$\vec{v}_d = -\frac{e\tau}{m}\vec{E}$$

Relating $\vec{v}_d$ and $\vec{j}$ we get the Ohm's Law:

$$\sigma = \frac{ne^2\tau}{m}$$

Electronic Heat Capacity

Classically each e- $\longrightarrow$ $\frac{3}{2}k_BT$

The number of "active thermal electrons" are the out of the Fermi sphere

$$\Delta U \approx N_{\text{eff}} \cdot (k_BT) \approx g(E_F)(k_BT)^2$$

using $C_{el} = dU/dT$

$$C_{\text{el}} = \frac{\pi^2}{3}g(E_F)k_B^2T = \frac{\pi^2}{2}Nk_B\left(\frac{T}{T_F}\right)$$

dependence on T (!)

Thermal Conductivity and the Wiedemann-Franz Law

In metals, heat is primarily transported by the same free electrons that conduct electricity.

The thermal conductivity κ can be estimated from kinetic theory.

The Wiedemann-Franz law is an empirical observation that the ratio of thermal to electrical conductivity for metals is directly proportional to temperature.

Computing for metals, we got

$$L = \frac{\kappa}{\sigma T}$$

$$L = 2.44 \times 10^{-8} W\Omega K^{-2}$$

what is a great result for the model, because agrees with the experimental values.

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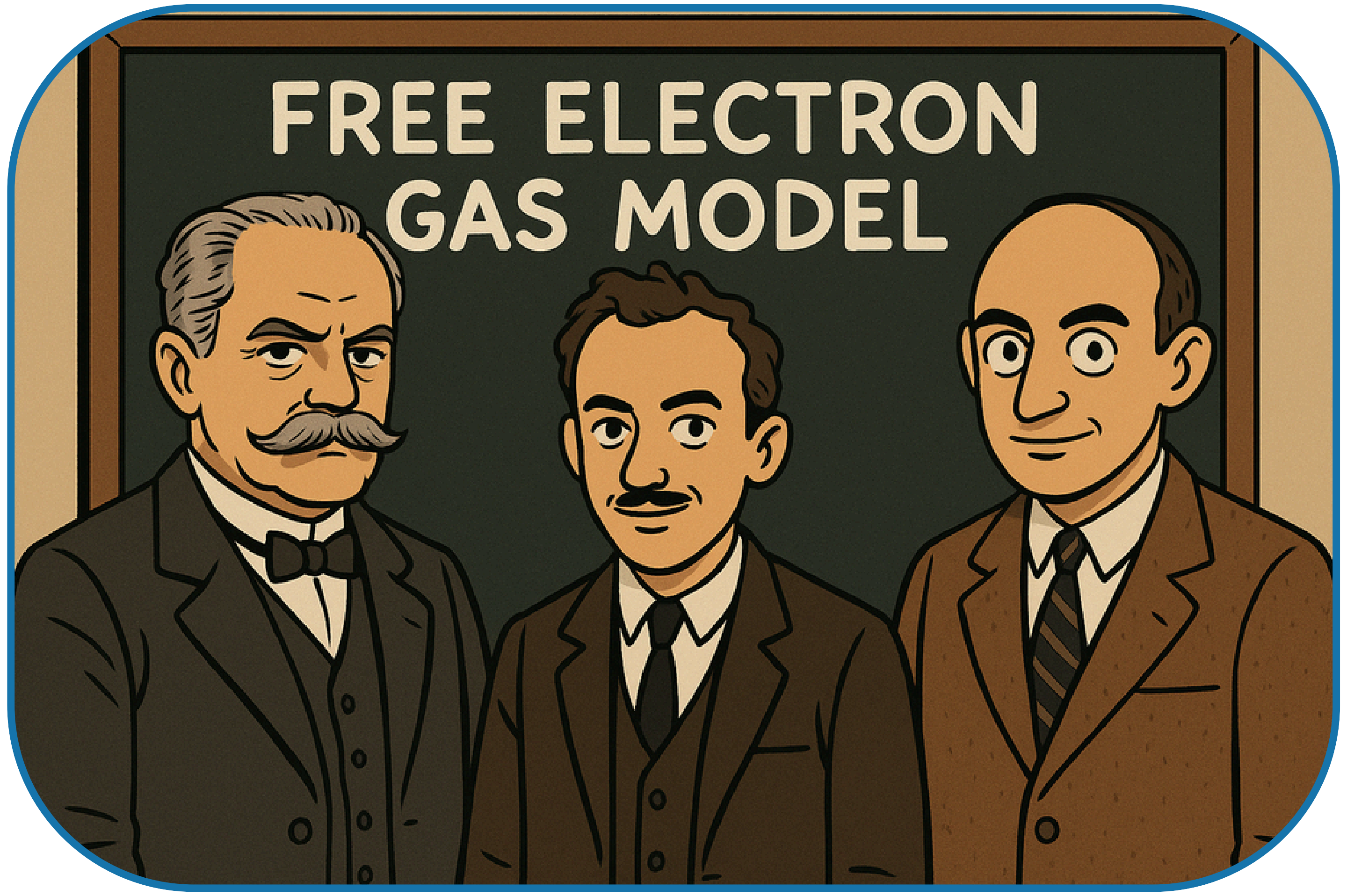

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Limitations and Failures

Existence of insulators

- Accoding to the model → every element with valence electrons should be a metal.
- It cannot answer why Sodium is a metal while Diamond is an insulator.
- The concept of an energy band gap, which is the defining characteristic of semiconductors and insulators, is completely absent.

Hall Effect

For all metal the hall coeficient must be negative (all carriers are electrons)

$$R_H = -\frac{1}{ne}$$

some experiments shows that some metals has a positive Hall coeficient.

carriers → holes!

Limitations and Failures

Free Path Paradox

Model → angstroms of distance of the ions, free path in this order.

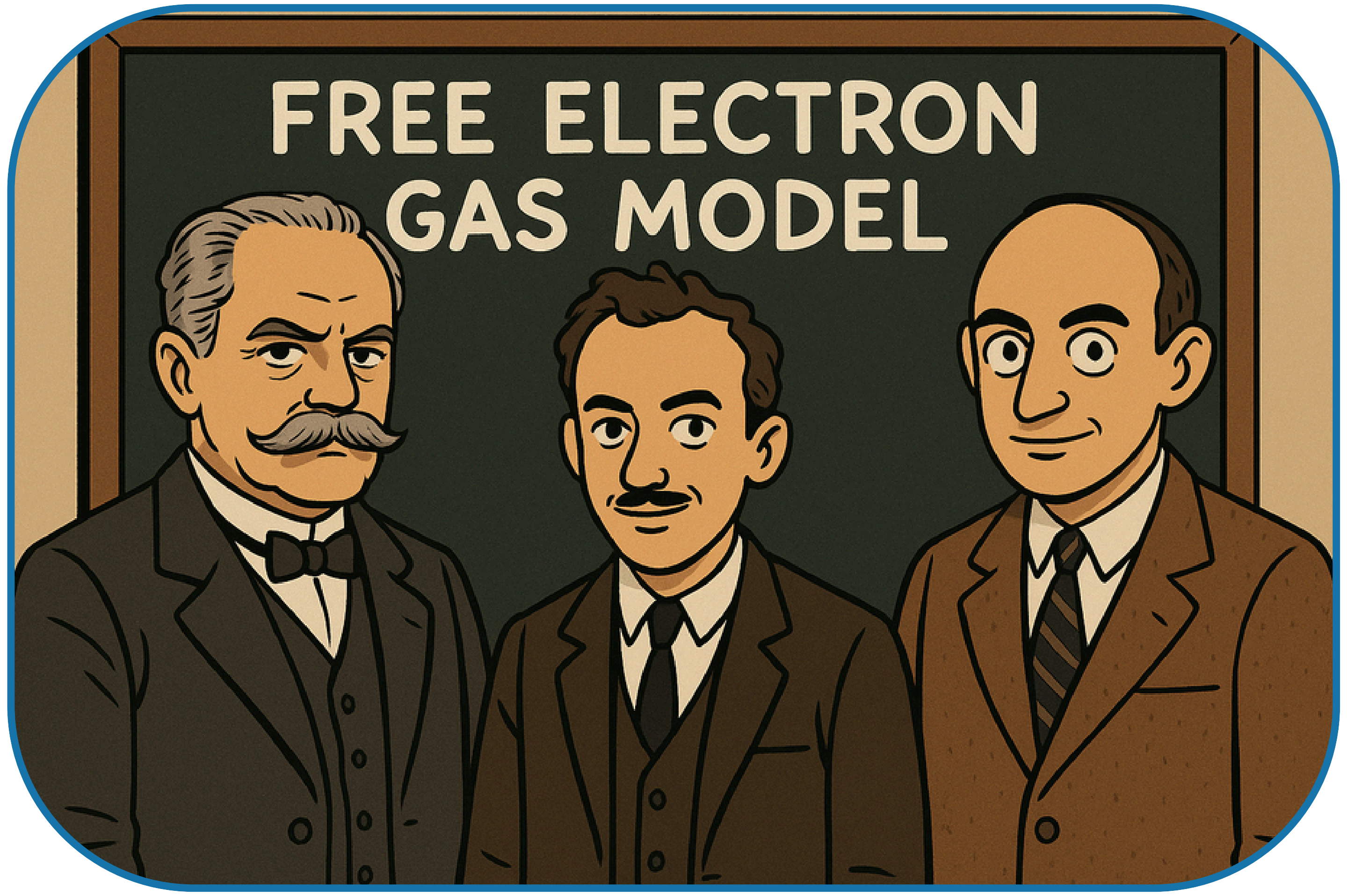
Experimental → tens to hundreds of angstroms (!)

The model fails to explain why electrons appear to ignore the vast majority of the ions in the lattice. This paradox is solve using the band theory.

Cohesion and Crystal Structure

The arrangement of atoms in a crystal is a direct result of the complex interplay between the electron wavefunctions and the discrete ion potentials.

This phenomenon the free electron model cannot capture.



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Thanks for your attention!

Any questions?