## The Free Fermion Gas and Electrons in Metals

• *The system:* Formally, we will treat a gas of $N$ free fermions in thermal equilibrium at temperature $T$ in a box of volume $V$. Physically, however, this can be used as a model for the conducting electrons inside a metal (for which the mutual interactions can often be neglected if we consider them as cancelled by the presence of the nuclei); in this case, the energies below are all to be considered as just representing the kinetic energies above the bottom of the conduction band.

• *Goal:* We want to study properties of the occupation number distribution $\bar{N}(\epsilon_\alpha)$ as a function of energy, and use it to calculate the mean energy and heat capacity at low temperatures. If the gas is used to model conduction electrons in a metal, this $C_V$ will be their contribution to the total value for the solid.

• *Setup:* For convenience, we will model the system using a grand canonical ensemble. Thus, in principle, the total particle number is not fixed. However, in the thermodynamic limit $N$ is very strongly peaked around $\bar{N}$, so if we find $\bar{N}(\beta,\mu)$ we can substitute the fixed $N$ for $\bar{N}$ in this expression and invert it to find $\mu(\beta,N)$, which can then be used to calculate other thermodynamic quantities.

• *Starting Point:* For fermions the mean occupation number in a single-particle state of energy $\epsilon$ is given by the Fermi function $\bar{N}_\mathrm{F}(\epsilon)$ derived earlier, and for the density of states we use the same expression we used earlier for free massive bosons, using $g_s = 2$ for the number of spin states of an electron,

$$\bar{N}_\mathrm{F}(\epsilon) = \frac{1}{\mathrm{e}^{(\epsilon-\mu)\beta}+1} = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon}+1}\;, \qquad g(\epsilon) = g_s\,\frac{4\pi V}{(2\pi)^3}\,k^2\,\frac{\mathrm{d}k}{\mathrm{d}\epsilon} = \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon}\;.$$

Notice that in the $T\to\infty$ limit $F(\epsilon)$ approximates the Maxwell-Boltzmann distribution, and at any $T \neq 0$ the value of the Fermi function at $\epsilon = \mu$ is $\bar{N}_\mathrm{F}(\mu) = \frac{1}{2}$. Using these $\bar{N}_\mathrm{F}(\epsilon)$ and $g(\epsilon)$ the starting point for thermodynamical calculations is then

$$\bar{N} = \sum_\alpha \bar{N}_\alpha \approx \int_0^\infty \mathrm{d}\epsilon\, g(\epsilon)\,\bar{N}_\mathrm{F}(\epsilon)\;, \qquad \bar{E} = \sum_\alpha \bar{N}_\alpha\epsilon_\alpha \approx \int_0^\infty \mathrm{d}\epsilon\, g(\epsilon)\,\bar{N}_\mathrm{F}(\epsilon)\,\epsilon\;.$$

### Zero-Temperature Quantities

• *Occupation-number distribution:* At $T = 0$ the mean number of particles above in the single-particle state $\alpha$ becomes a step function whose value equals 1 for $\epsilon_\alpha < \mu$, and 0 for $\epsilon_\alpha > \mu$ (and by continuity we still set $\bar{N}(\mu) = \frac{1}{2}$). Thus, $\mu_0 = \mu(0)$ cannot be zero and we wish to find its value. Notice that, contrary to what happens in the case of bosons, in this case $0 \le \bar{N}_\alpha \le 1$ for any $\beta$ and $z$, so the value of $z$ is now unrestricted.

• *Fermi energy and temperature:* At $T = 0$ we can calculate exactly the sum for the mean number of particles as a function of $\mu_0$; setting then $\bar{N} = N$ gives an explicit expression for $\mu_0$ in terms of $N$. For electrons, since up to $\epsilon = \mu_0$ each state is occupied by exactly one electron,

$$\bar{N} = \int_0^{\mu_0}\mathrm{d}\epsilon\, g(\epsilon) = \frac{2}{3}\,\frac{Vm^{3/2}\mu_0^{3/2}}{\sqrt{2}\,\pi^2\hbar^3}\;, \qquad \text{or} \qquad \mu_0 = \left(3\pi^2\,\frac{N}{V}\right)^{2/3}\frac{\hbar^2}{2m} =: \epsilon_\mathrm{F} \qquad \text{(the Fermi energy)}\;.$$

From $\bar{N}(\epsilon)$ we see that at $T > T_\mathrm{F} = \epsilon_\mathrm{F}/k_\mathrm{B}$ thermal fluctuations start populating energy levels above $\epsilon_\mathrm{F} = \mu_0$.

• *Mean energy:* Using the Fermi energy, a similar calculation for the mean energy gives now

$$\bar{E} = \int_0^{\mu_0}\mathrm{d}\epsilon\,\epsilon\, g(\epsilon) = \frac{3}{5}\,\mu_0 N\;, \qquad \text{or} \qquad \frac{\bar{E}}{N} =: \bar{\epsilon} = \frac{3}{5}\,\epsilon_\mathrm{F} \qquad \left(\text{Notice that } \bar{\epsilon} > \tfrac{1}{2}\,\epsilon_\mathrm{F}\right)\;.$$

### Small-Temperature Quantities

• *Useful integrals:* When evaluating the finite-temperature corrections for quantities such as $\bar{N}$ and $\bar{E}$, we will need to calculate integrals of the following form, for some function $K(\epsilon)$ (in practice, $g(\epsilon)$ or $\epsilon\, g(\epsilon)$):

$$I(\mu,T) = \int_0^\infty \mathrm{d}\epsilon\, K(\epsilon)\,\bar{N}_\mathrm{F}(\epsilon) = \int_0^\infty \mathrm{d}\epsilon\,\frac{K(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)\beta}+1}\;.$$

For low temperatures $T \ll T_\text{F} = \epsilon_\text{F}/k_\text{B}$ we can evaluate $I(\mu,T)$ as a Sommerfeld series expansion around $T = 0$, where $I(\mu,0) = \int_0^\mu \mathrm{d}\epsilon\, K(\epsilon)$. To proceed, introduce the variable $x := \beta(\mu-\epsilon) \in (-\infty, \beta\mu)$ and write

$$I(\mu,T) = -k_\text{B}T \left[\int_{\beta\mu}^0 \mathrm{d}x\, \frac{K(\mu - k_\text{B}T\,x)}{\mathrm{e}^{-x}+1} + \int_0^{-\infty} \mathrm{d}x\, \frac{K(\mu - k_\text{B}T\,x)}{\mathrm{e}^{-x}+1}\right]$$
$$= \int_0^\mu \mathrm{d}\epsilon\, K(\epsilon) - k_\text{B}T \int_0^{\beta\mu} \mathrm{d}x\, \frac{K(\mu - k_\text{B}T\,x)}{\mathrm{e}^{x}+1} + k_\text{B}T \int_0^{\infty} \mathrm{d}x\, \frac{K(\mu + k_\text{B}T\,x)}{\mathrm{e}^{x}+1}\ ,$$

where we have separated the parts with $x > 0$ and $x < 0$, used the identity $1/(\mathrm{e}^{-x}+1) = 1 - 1/(\mathrm{e}^x+1)$ in the first term and replaced $x \mapsto -x$ in the second one, and restored $\epsilon$ in the first resulting integral. The second integral can be extended to $+\infty$ with an excellent approximation as $T \to 0$. The second and third integrals then become similar, and expanding terms in powers of $T$ (notice that $\mathrm{d}\mu/\mathrm{d}T \neq 0$) we get

$$I(\mu,T) = \int_0^{\mu_0} \mathrm{d}\epsilon\, K(\epsilon) + (\mu-\mu_0)\, K(\mu_0) + \mathcal{O}(\mu-\mu_0)^2 +$$
$$+\ 2\,K'(\mu_0)\,(k_\text{B}T)^2 \int_0^\infty \frac{x\,\mathrm{d}x}{\mathrm{e}^x+1} + \frac{2}{3!}\,K'''(\mu_0)\,(k_\text{B}T)^4 \int_0^\infty \frac{x^3\,\mathrm{d}x}{\mathrm{e}^x+1} + \dots\ .$$

• *Finite-temperature corrections:* The leading-order corrections to quantities such as $\mu$ and $\bar{E}$ for $T$ close to 0 can be obtained from the first term after the $T = 0$ one in the low-temperature expansion of the corresponding $I(\mu,T)$. The expressions to use for $\bar{N}$ and $\bar{E}$ are $I(\mu,T)$ with $K(\epsilon) = g(\epsilon)$ and $\epsilon\, g(\epsilon)$, respectively, or

$$\bar{N} = \int_0^\infty \mathrm{d}\epsilon\, \frac{g(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)\beta}+1}\ , \qquad \bar{E} = \int_0^\infty \mathrm{d}\epsilon\, \frac{\epsilon\, g(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)\beta}+1}\ .$$

**Thermodynamics**

• *Chemical potential:* We expand $\bar{N}(T,\mu)$ and defining $T_\text{F} := \epsilon_\text{F}/k_\text{B}$ equate the expression to $N$ to find

$$\mu = \epsilon_\text{F} \left[1 - \frac{\pi^2}{12}\,\frac{T^2}{T_\text{F}^2} + \dots\right]\ .$$

• *Heat capacity:* The mean energy is given by $I(\mu,T)$ with $K(\epsilon) = \epsilon\, g(\epsilon)$, or

$$\bar{E} = \int_0^\infty \mathrm{d}\epsilon\, \frac{\epsilon\, g(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)\beta}+1} = \bar{E}(0) + (k_\text{B}T)^2\, g(\mu_0)\, \frac{\pi^2}{12} = \frac{3}{5}\, N\epsilon_\text{F} + \frac{\pi^2}{4}\, \frac{T^2}{T_\text{F}^2}\, N\epsilon_\text{F} + \dots\ ,$$

from which

$$C_{V,N} = \frac{\pi^2}{6}\, k_\text{B}^2 T\, g(\mu_0) = \frac{\pi^2}{2}\, Nk_\text{B}\, \frac{T}{T_\text{F}} + \dots\ .$$

We see therefore that $C_{V,N} \to 0$ as $T \to 0$, consistently with the third law of thermodynamics.

• *Pressure equation of state:* [See the lecture notes on the effects of quantum statistics. It leads to a fermion degeneracy pressure which has applications, e.g., to the structure of white dwarf stars and neutron stars.]

**Reading**

• *Course textbook:* Kennett, Ch 8, §§ 8.1-8.2.
• *Other books:* Chandler, § 4.5; Halley, end of Ch 5; Huang, Ch 16; Mattis & Swendsen, Ch 6 (first half); Pathria & Beale, Ch 8 (esp. § 8.1); Plischke & Bergersen, §§ 12.2.4–12.2.5; Reif, § 9.16; Schwabl, § 4.3.