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.

• *Density of states:* If we assume that f and the one-particle energies $\epsilon(k)$ depend only on the magnitude k of $\mathbf{k}$, and not on γ, the calculation of the density of states for free electrons proceeds in the same way as for massive bosons and we find, using $g_s = 2$ for the number of spin states of an electron,

$$g(\epsilon) = g_s \frac{4\pi V}{(2\pi)^3}\, k^2\, \frac{\mathrm{d}k}{\mathrm{d}\epsilon} = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}\ .$$

• *Occupation-number distribution:* The mean number of particles in a single-particle state of energy ϵ for fermions is given by the Fermi function, derived earlier,

$$\bar{N}(\epsilon) = F(\epsilon) = \frac{1}{\mathrm{e}^{(\epsilon-\mu)\beta}+1} = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon}+1}\ .$$

Notice that at any (non-zero) temperature, the value of the Fermi function at $\epsilon = \mu$ is $F(\mu) = \frac{1}{2}$; in the $T \to \infty$ limit, instead, $F(\epsilon)$ approximates the Maxwell-Boltzmann distribution.

Using $g(\epsilon)$ and $\bar{N}(\epsilon)$ we can now write down, as the starting point for thermodynamical calculations,

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

Zero-Temperature Quantities

• *Occupation-number distribution:* At $T = 0$ the mean number of particles above in the single-particle state α 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 β 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 μ_0; setting then $\bar{N} = N$ gives an explicit expression for μ_0 in terms of N. For electrons, since up to $\epsilon = \mu_0$ each state is occupied by exactly one electron,

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

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

$$\bar{E} = \int_0^{\mu_0} \mathrm{d}\epsilon\, \epsilon\, g(\epsilon) = \frac{3}{5}\, \mu_0 N\ , \qquad \text{or} \qquad \bar{\epsilon} = \frac{3}{5}\, \epsilon_\mathrm{F}\ .$$

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 $K(\epsilon)$:

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

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

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

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 ϵ 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 integral then become similar, and expanding terms in powers of T we get

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

• *Finite-temperature corrections:* The leading-order correction to each quantity such as μ and $\bar{E}$ for $T>0$ 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 equate the expression to N to find μ.

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

$$\bar{E} = \int_0^\infty \mathrm{d}\epsilon\, \frac{\epsilon\, g(\epsilon)}{\mathrm{e}^{(\epsilon-\mu)\beta}+1} = \bar{E}(0) + (k_\mathrm{B}T)^2\, g(\mu_0)\, \frac{\pi^2}{12} \ ,$$

from which

$$C_{V,N} = \frac{\pi^2}{6}\, k_\mathrm{B}^2 T\, g(\mu_0) \ .$$

• *Remark:* From the principle of equipartition we might have expected a constant $C_{V,N}$. But, since in general

$$C_{V,N} = T\, \frac{\partial S}{\partial T}\Big|_{V,N} \ ,$$

this would have implied a $S \to -\infty$ at low T, which is inconsistent 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, Sections 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, in particular §8.1; Plischke & Bergersen, §§12.2.4–12.2.5; Reif, §9.16; Schwabl, §4.3.