Statistical Physics

Matthew Wingate*

3 March 2010

*Comment & corrections to M.Wingate@damtp.cam.ac.uk . Notes and other information also available at http://www.damtp.cam.ac.uk/user/wingate/StatPhys

9 Fermi-Dirac distribution

Recall the Fermi-Dirac distribution arose from the partition function (7.2.12)

$$\begin{aligned} \mathcal{Z} &= \prod_r \sum_{n_r=0}^{1} \exp\left(-\beta n_r \left(\varepsilon_r - \mu\right)\right) \\ &= \prod_r \left(1 \,+\, e^{-\beta(\varepsilon_r-\mu)}\right) . \end{aligned}$$

We saw in §7.3 that the requirement that the volume per particle to be much larger than the thermal wavelength cubed, $V/N \gg \lambda^3$, is equivalent to the limit where $e^{\beta\mu} \ll 1$. This implies that we have negative chemical potential for both bosons and fermions in the classical limit. As T decreases, $\mu \to 0$ from below. In §8.3 we saw that the point $\mu = 0$ is a critical point in Bose gas, marking the onset of Bose-Einstein condensation. Mathematically, the geometric series in (7.2.8) diverges when $\mu > 0$. In contrast no such critical point occurs for a Fermi gas. In fact we will see that μ must change sign to become positive as $T \to 0$.

9.1 Degenerate Fermi gas

Let us look at the denominator of the Fermi-Dirac distribution

$$\bar{n}(\varepsilon) \;=\; \frac{g(\varepsilon)}{e^{\beta(\epsilon-\mu)} \,+\, 1} \tag{9.1.1}$$

in the limit $T \to 0$ (equivalently $\beta \to \infty$). For states with $\varepsilon < \mu$, the exponent in the denominator vanishes. For states with $\varepsilon > \mu$ the exponent tends to infinity. Therefore there zero temperature distribution is (see Figure 17)

$$\left.\frac{\bar{n}(\varepsilon)}{g(\varepsilon)}\right|_{T=0} \;=\; \begin{cases} 1\,, & \varepsilon < \mu \\ 0\,, & \varepsilon > \mu \end{cases} . \tag{9.1.2}$$

Above we have kept the temperature dependence of μ implicit, as we usually do. However, we should not forget that μ does vary as a function of T. The particular value at $T = 0$ is a special value, as indicated by the zero temperature distribution (9.1.2). It marks the energy below which all states are occupied and above which all states are unoccupied. It is called the **Fermi energy**: $\varepsilon_F \;\equiv\; \mu(T\!=\!0)$.

In what follows, we will again use the density of states for a nonrelativistic gas in 3 dimensions

$$g(\varepsilon) \;=\; \frac{g_s}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} V\sqrt{\varepsilon} \;\equiv\; KV\sqrt{\varepsilon}\,. \tag{9.1.3}$$

At zero temperature we can use (9.1.2) to calculate the average particle number as

$$N \;=\; KV\int_0^{\varepsilon_F} \mathrm{d}\varepsilon\,\sqrt{\varepsilon} \;=\; \frac{2}{3}\,KV\varepsilon_F^{3/2}\,. \tag{9.1.4}$$

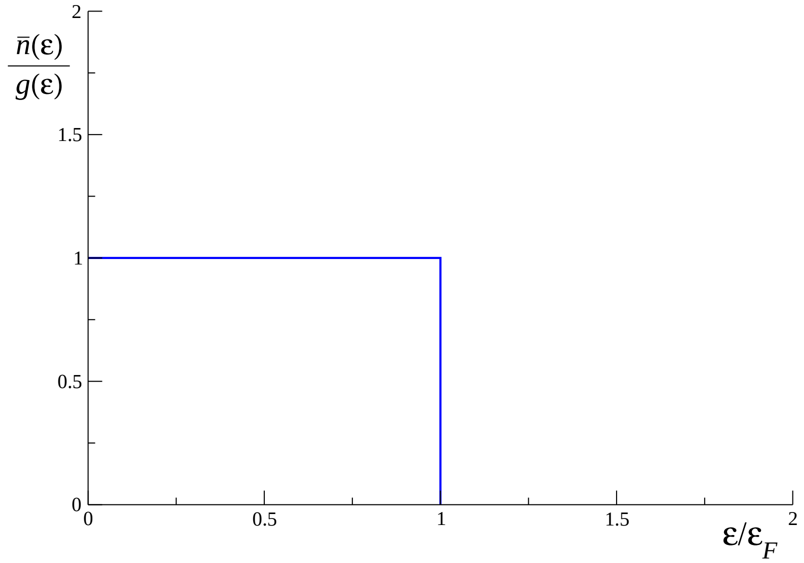

Figure 17: The Fermi-Dirac distribution at $T = 0$.

Particle number density, N/V, is something physically observable, so the Fermi energy can be determined by inverting (9.1.4)

$$\varepsilon_F \;=\; \left(\frac{1}{K}\,\frac{3}{2}\,\frac{N}{V}\right)^{2/3} . \tag{9.1.5}$$

Even in interacting systems (9.1.5) is used as a definition of Fermi energy, in terms of the density.

Turning back to the ideal Fermi gas, the energy at $T = 0$ is given by

$$E \;=\; \int_0^{\varepsilon_F} \mathrm{d}\varepsilon\, KV\varepsilon^{3/2} \;=\; \frac{2}{5}\,KV\varepsilon_F^{5/2} . \tag{9.1.6}$$

Dividing (9.1.6) by (9.1.4) we find the average energy per particle to be

$$\frac{E}{N} \;=\; \frac{3}{5}\,\varepsilon_F . \tag{9.1.7}$$

Note the contrast between this and the zero temperature energy of an ideal Bose gas: the zero temperature Fermi gas has *non-vanishing* energy.

Let us consider the grand potential

$$\begin{aligned}\Omega \;&=\; -kT\log\mathcal{Z}\\ &=\; -kT\int_0^\infty \mathrm{d}\varepsilon\, g(\varepsilon)\,\log\left(1 \,+\, e^{-\beta(\varepsilon-\mu)}\right) .\end{aligned} \tag{9.1.8}$$

In the $T \to 0$ limit

$$kT\log\left(1 \,+\, e^{-(\varepsilon-\mu)/kT}\right) \;=\; 0 \qquad \text{for states with } \varepsilon > \mu\,. \tag{9.1.9}$$

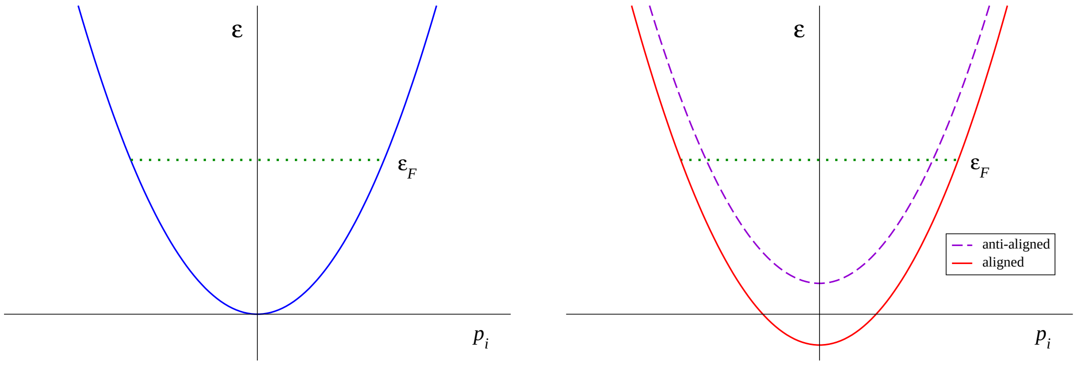

Figure 18: Single particle dispersion relations. Left: isolated gas of noninteracting fermions on the left. Right: gas of spin-$\frac{1}{2}$ fermions in the presence of a weak magnetic field, aligned spins have lower energy than anti-aligned spins. At $T = 0$, all allowed energy states below ε_F are occupied, while all energy states above ε_F are unoccupied. Note in the right plot, this means there are more aligned spins than anti-aligned spins.

For states with $\varepsilon < \mu$

$$\begin{aligned} kT \log\left(1 + e^{(\mu-\varepsilon)/kT}\right) &= kT\left[\frac{\mu-\varepsilon}{kT} + \log\left(e^{-(\mu-\varepsilon)/kT} + 1\right)\right] \\ &= \mu - \varepsilon \\ &= \varepsilon_F - \varepsilon\,. \end{aligned} \tag{9.1.10}$$

So the grand potential at $T = 0$ is

$$\begin{aligned} \Omega &= -KV\int_0^{\varepsilon_F} \mathrm{d}\varepsilon\,\sqrt{\varepsilon}(\varepsilon_F - \varepsilon) \\ &= -KV\left(\frac{2}{3}\varepsilon_F^{5/2} - \frac{2}{5}\varepsilon_F^{5/2}\right) \\ &= -\frac{2}{3}E\,. \end{aligned} \tag{9.1.11}$$

Since $\Omega = -PV$

$$PV = \frac{2}{3}E = \frac{2}{5}N\varepsilon_F > 0\,. \tag{9.1.12}$$

Even at zero temperature, the Fermi gas has nonzero pressure, called **Fermi pressure**. This is a physical consequence of Pauli's exclusion principle. The fact that 2 fermions cannot be in the same single-particle state results in a pressure. This effect is responsible for keeping old stars, which have spent most of their nuclear fuel, from completely collapsing. White dwarf stars and neutron stars are examples.

Sometimes it is useful to sketch the single particle dispersion relation. In the left plot of Figure 18 we show $\varepsilon(p)$ for a nonrelativistic gas. We can see by eye which momentum states are occupied (those with $\varepsilon < \varepsilon_F$) and which are empty at $T = 0$. Such a plot becomes more useful in more complicated examples. Consider a spin-$\frac{1}{2}$

gas of non-relativistic fermions, possessing magnetic moment μ_B, in the presence of a weak magnetic field B. The energy of a spin now has an additional term

$$\varepsilon_{\pm} \;=\; \frac{p^2}{2m} \;\pm\; \mu_B B \tag{9.1.13}$$

where the minus sign is for particles aligned with the magnetic field and the plus sign is for particles anti-aligned with the magnetic field. We see from the right side of Figure 18 that, as a consequence of the lower energy for aligned spins, we will first fill energy levels with spins aligned with B, and only afterwards fill levels with spins anti-aligned with B. We can calculate the number of particles in either state, say N_+ and N_-, from (9.1.4) after correctly adjusting the limits of integration. The magnetisation, the total magnetic moment of the gas, is just μ_B times the difference in particle number. We leave this as an exercise.

9.2 Fermi gas at low temperature, $T > 0$

Next we wish to calculate the leading correction to the zero temperature results of the previous section. In order to do so, we must consider the behaviour of integrals of the type

$$f_n(z) \;=\; \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}\,\mathrm{d}x}{z^{-1}e^x \,+\, 1}\,. \tag{9.2.1}$$

(See Pathria, Appendix E and Landau & Lifshitz, §58.) Before we proceed with approximations, note these integrals satisfy the recursion relation

$$z\,\frac{\partial}{\partial z}\,f_n(z) \;=\; f_{n-1}(z)\,. \tag{9.2.2}$$

(Differentiate and integrate by parts to verify this.)

At low temperatures (where $\mu > 0$ for Fermi gases) we have

$$\xi \;\equiv\; \frac{\mu}{kT} \;\gg\; 1\,. \tag{9.2.3}$$

We define ξ as a useful shorthand, since $z = e^{\xi}$. Now let us look at the denominator of the integrand in (9.2.1)

$$D \;=\; \frac{1}{e^{x-\xi} \,+\, 1}\,. \tag{9.2.4}$$

D is plotted in Figure 19. The length Δx over which D goes from 1 to 0 remains constant as $\xi \to \infty$, while the value of x at which this occurs is equal to ξ. Thus for large, but finite, ξ, the deviation from a step function is $\mathcal{O}\left(1/\xi\right)$.

The leading result is obtained by treating D as a step function. Then the integral (9.2.1) becomes

$$\Gamma(n) f_n(e^{\xi}) \;=\; \int_0^{\xi} x^{n-1}\,\mathrm{d}x \;=\; \frac{\xi^n}{n}\,. \tag{9.2.5}$$

At next-to-leading order, we break the integration interval into 2 intervals, and conveniently rewrite the integrand in the first term:

$$\Gamma(n) f_n(e^{\xi}) \;=\; \int_0^{\xi} x^{n-1}\left[1 \,-\, \frac{1}{e^{\xi-x} \,+\, 1}\right]\mathrm{d}x \;+\; \int_{\xi}^{\infty} x^{n-1}\left[\frac{1}{e^{x-\xi} \,+\, 1}\right]\mathrm{d}x \tag{9.2.6}$$

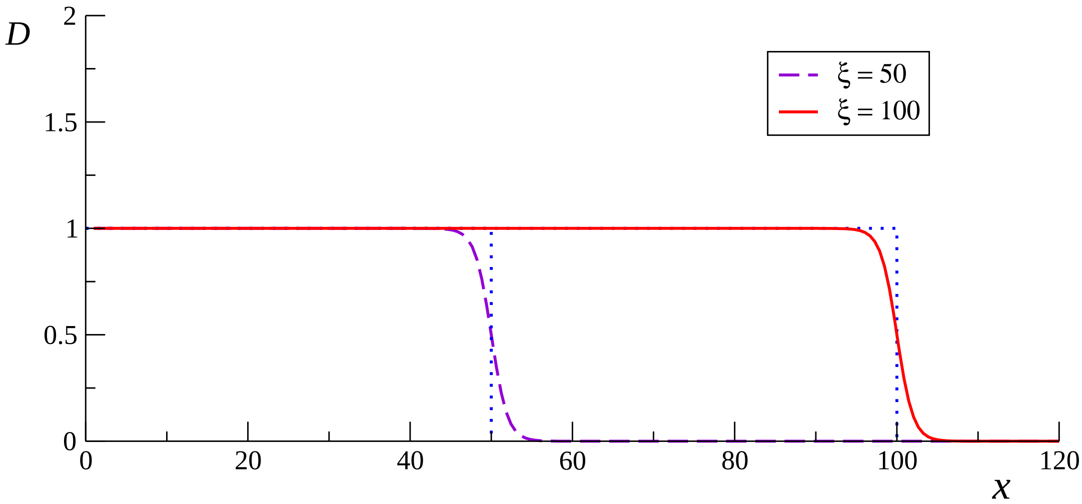

Figure 19: The quantity $D = 1/(e^{x-\xi} + 1)$.

and letting $\eta_1 = \xi - x$ and $\eta_2 = x - \xi$

$$= \frac{\xi^n}{n} + \int_{\xi}^{0} \frac{(\xi - \eta_1)^{n-1}\,\mathrm{d}\eta_1}{e^{\eta_1} + 1} + \int_{0}^{\infty} \frac{(\xi + \eta_2)^{n-1}\,\mathrm{d}\eta_2}{e^{\eta_2} + 1}\,. \tag{9.2.7}$$

Note that the first term is the leading order result (9.2.5).

Next are the following steps

1. The integrands are only non-negligible when $\eta_1 \approx 0$ and $\eta_2 \approx 0$. Therefore we can change the upper limit of integration in the first integral of (9.2.7) to ∞.

2. We can combine the integrals using a common integration variable $\eta_1 = \eta_2 \equiv \eta$

$$\Gamma(n) f_n(e^{\xi}) = \frac{\xi^n}{n} + \int_0^{\infty} \mathrm{d}\eta\, \frac{[(\xi + \eta)^{n-1} - (\xi - \eta)^{n-1}]}{e^{\eta} + 1}\,. \tag{9.2.8}$$

3. A binomial series expansion of $(1 \pm \frac{\eta}{\xi})^{n-1}$ yields[8]

$$\Gamma(n) f_n(e^{\xi}) = \frac{\xi^n}{n} + 2 \sum_{\text{odd } j} \binom{n-1}{j} \left[\xi^{n-1-j} \int_0^{\infty} \frac{\eta^j\,\mathrm{d}\eta}{e^{\eta} + 1} \right]. \tag{9.2.9}$$

The integrals are also related to the Riemann zeta function

$$\int_0^{\infty} \frac{\eta^j\,\mathrm{d}\eta}{e^{\eta} + 1} = \left(1 - \frac{1}{2^j}\right) \Gamma(j+1)\,\zeta(j+1)\,. \tag{9.2.10}$$

(This can be seen, in part, by expanding the denominator as was done in (8.3.5).)

[8]For noninteger n, the binomial coefficients are defined in terms of the Γ function, and the series is infinite.

4. Writing out the first 2 terms we find

$$f_n(e^\xi) = \frac{\xi^n}{\Gamma(n+1)}\left[1 + n(n-1)\frac{\pi^2}{6}\frac{1}{\xi^2} + \mathcal{O}\left(\tfrac{1}{\xi^4}\right)\right] \tag{9.2.11}$$

We should point out that the expansion about $1/\xi$ is an asymptotic, rather than a convergent, series. It neglects a non-expansible term proportional to $e^{-\xi}$. The neglected term vanishes identically for half-integer values of n, exactly those values we need for fermion physics. (See footnote in Pathria, Appendix E.)

This was a lot of work, but now we can read off thermodynamic results.

$$N = \frac{KV}{\beta^{3/2}}\Gamma(\tfrac{3}{2})\, f_{\frac{3}{2}}(z) = \frac{g_s V}{\lambda^3}\, f_{\frac{3}{2}}(z) \tag{9.2.12}$$

$$= \frac{KV}{\beta^{3/2}}\frac{\sqrt{\pi}}{2}\frac{4}{3\sqrt{\pi}}(\log z)^{3/2}\left[1 + \frac{\pi^2}{8}\frac{1}{(\log z)^2} + \ldots\right]$$

$$= KV\frac{2}{3}\mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 + \ldots\right]. \tag{9.2.13}$$

Recall the definition of the Fermi energy (9.1.5). We can substitute ε_F in (9.2.13) for the ratio N/V and solve for the μ in the prefactor as

$$\mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2 + \ldots\right]. \tag{9.2.14}$$

In the last term, we can make the leading order substitution $\mu = \varepsilon_F$ since corrections will be of the same, higher order as the presently truncated terms

$$\mu = \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + \ldots\right]. \tag{9.2.15}$$

Similarly, we can calculate the mean energy

$$E = KV\frac{2}{5}\mu^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{kT}{\mu}\right)^2 + \ldots\right]. \tag{9.2.16}$$

Dividing (9.2.16) by (9.2.13) we find

$$\frac{E}{N} = \frac{3}{5}\mu\left[1 + \frac{\pi^2}{2}\left(\frac{kT}{\mu}\right)^2 + \ldots\right] \tag{9.2.17}$$

$$= \frac{3}{5}\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + \ldots\right]. \tag{9.2.18}$$

The heat capacity at low temperatures is

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = Nk\frac{\pi^2}{2}\frac{T}{T_F}, \tag{9.2.19}$$

where we introduce the **Fermi temperature** $T_F = \varepsilon_F/k$ (recall Boltzmann's constant does nothing but change temperature units into energy units).

From $PV = \frac{2}{3}E$ we can find the pressure. From $F = -PV + \mu N$ we can find the free energy. From this we can calculate the entropy at low temperatures as

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\,\frac{\pi^2}{2}\,\frac{T}{T_F}\,. \tag{9.2.20}$$

Note that $S \to 0$ as $T \to 0$.

$$S = 0 = k\log W \quad \Rightarrow \quad W = 1 \tag{9.2.21}$$

At absolute zero temperature, there is a single accessible state. The fact that the entropy should vanish at zero temperature is called **Nernst's theorem**, or the **third law of thermodynamics**. Like all important theorems in physics, it is only proved for trivial systems, and taken as a first principle for others.

Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapter 9, 10, §11.5.

2. R K Pathria, *Statistical Mechanics*, (Pergamon Press, 1985), §8.1, Appendix E.

3. L D Landau and E M Lifshitz, *Statistical Physics*, (Pergamon Press, 1980), §§57-58.