25 March

Recap:

Photon gas. massless $E = \hbar \omega$

Planck spectrum $P(\omega) \propto \dfrac{\omega^3}{e^{\beta \hbar \omega} - 1}$

solves "UV catastrophe"

✓ Solar radiation $T \sim 5800 \, K$

✓ CMB radiation $T \sim 2.725 \, K$

$\langle E \rangle_{ph} \propto V T^4 \qquad \rightarrow \qquad S, c_v \propto T^3$

Looking back to Eq. 94 for the grand-canonical potential, we see

$$\left(\frac{\Phi_{ph}}{T}\right) = \frac{V}{c^3\pi^2}\int_0^\infty d\omega\,\omega^2\log\left[1 - e^{-\beta\hbar\omega}\right] = \frac{VT^3}{\hbar^3c^3\pi^2}\int_0^\infty dx\,x^2\log\left[1 - e^{-x}\right],$$

[handwritten, red:] $x = \beta\hbar\omega$

changing variables to $x = \beta\hbar\omega = \hbar\omega/T$. The final factor in this expression is yet another delightful integral,

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$$\int_0^\infty dx\,x^2\log\left[1 - e^{-x}\right] = -2\zeta(4) = -\frac{\pi^4}{45}.$$

Since this gives us $S \propto VT^3$, we can conclude that the condition of constant entropy for a photon gas is $VT^3 = \text{constant}$, in contrast to the $VT^{3/2}$ dependence of Eq. 53 for classical non-relativistic particles.

At this point it is straightforward to take the derivative of the average internal energy if we express the constant-entropy condition as $T = bV^{-1/3}$, with b a constant:

$$P_{ph} = -\frac{\partial}{\partial V}\langle E\rangle_{ph}\bigg|_{S_{ph}} = -\frac{\partial}{\partial V}\frac{\pi^2}{15\hbar^3c^3}VT^4\bigg|_{S_{ph}} = \frac{-\pi^2}{15\hbar^3c}\frac{\partial}{\partial V}b^4V^{-1/3}$$

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$$= \frac{1}{3V}\left(\frac{\pi^2}{15\,b^3c^3}\right)b^4V^{-1/3}$$

$$= \frac{1}{3V}\langle E\rangle_{ph}$$

For the resulting equation of state for the photon gas, you should find

$$P_{ph}V = \frac{1}{3}\langle E\rangle_{ph} = \frac{\pi^4}{90\zeta(3)}\langle N\rangle_{ph}\,T. \tag{98}$$

The functional form is the same as the (classical, non-relativistic) ideal gas law, with just an additional numerical factor of

$$\frac{\pi^4}{90\zeta(3)} = \frac{\zeta(4)}{\zeta(3)}.$$

8.4 Non-relativistic ideal fermion gas

For the remainder of this unit we will turn our attention to applying the grand-canonical ensemble to investigate ideal gases of non-interacting fermions. We again take the approach of quantum statistics, defining micro-states by summing over the possible occupation numbers n_ℓ for each energy level $\mathcal{E}_\ell$ with (possibly not unique) energy E_ℓ. In contrast to the bosonic case considered above, the only possible occupation numbers are now $n_\ell = 0$ and 1, since the Pauli exclusion principle prevents multiple identical fermions from occupying the same energy level.

In Section 7.4 we derived the grand-canonical partition function (Eq. 88) that defines quantum Fermi–Dirac statistics for such systems of non-interacting fermions,

$$Z_g^{\mathsf{FD}}(\beta, \mu) = \prod_{\ell=0}^{\mathcal{L}} \left[1 + e^{-\beta(E_\ell - \mu)} \right],$$

in terms of the inverse temperature $\beta = 1/T$ and chemical potential μ. Recall that it is possible for systems of fermions to have any value for the chemical potential, either positive or negative, in contrast to the systems of bosons we considered above. From the corresponding grand-canonical potential,

$$\Phi_{\mathsf{FD}} = -T \log Z_g^{\mathsf{FD}} = -T \sum_{\ell=0}^{\mathcal{L}} \log \left[1 + e^{-\beta(E_\ell - \mu)} \right]$$

we can determine the large-scale properties of the system, including its average internal energy $\langle E \rangle$, average particle number $\langle N \rangle$, entropy S, and pressure P, along with the equation of state relating these quantities.

Concrete calculations require specifying the energy levels of the particles that compose the gas, including the degeneracies of any distinct energy levels $\{\mathcal{E}_m, \mathcal{E}_n\}$, $m \neq n$, with the same energy $E_m = E_n$. In this section we'll begin by considering non-relativistic particles, expanding on our review of such systems in Section 8.1. In a volume $V = L^3$, the energy levels are defined by the non-zero quantized energies

$$E(k) = \varepsilon \left(k_x^2 + k_y^2 + k_z^2 \right) \qquad \varepsilon \equiv \frac{\hbar^2 \pi^2}{2mL^2} \qquad k_{x,y,z} = 1, 2, \cdots.$$

In addition to the usual degeneracies coming from permutations of (k_x, k_y, k_z) that we have already analyzed, for each distinct $\vec{k}$ typical fermions such as electrons have two degenerate energy levels with the same energy $E(k)$. This arises from a quantum property called *spin*, rather than the two polarizations for photons discussed in Section 8.1: 'spin-up' and 'spin-down' electrons with the same momenta and energies occupy distinct, degenerate energy levels. This property of spin is related to the spin–statistics theorem mentioned in Section 7.2, and is another topic we can discuss further in a tutorial if there is interest. For our statistical physics purposes it will suffice simply to incorporate this information into our ansatz as input.

The grand-canonical potential for an ideal gas of non-relativistic fermions is therefore

$$\Phi_f = -T \sum_{\ell=0}^{\mathcal{L}} \log\left[1 + e^{-\beta(E_\ell - \mu)}\right] = -2T \sum_{\vec{k}} \log\left[1 + \exp\left(-\frac{\hbar^2 \pi^2 k^2}{2mL^2 T} + \frac{\mu}{T}\right)\right].$$

We can again proceed by considering the gas in a large volume and approximating the sum over discrete integer $k_{x,y,z}$ by integrals over continuous real $\widehat{k}_{x,y,z}$:

$$\Phi_f \approx -2T \int d\widehat{k}_x \, d\widehat{k}_y \, d\widehat{k}_z \, \log\left[1 + \exp\left(-\frac{\hbar^2 \pi^2 \widehat{k}^2}{2mL^2 T} + \frac{\mu}{T}\right)\right].$$

Converting to spherical coordinates and carrying out the angular integrations over the $\frac{\pi}{2}$ solid angle of the octant of the sphere with $k_{x,y,z} > 0$, we have

$$\Phi_f \approx -\pi T \int_0^\infty d\widehat{k} \, \widehat{k}^2 \log\left[1 + \exp\left(-\frac{\hbar^2 \pi^2 \widehat{k}^2}{2mL^2 T} + \frac{\mu}{T}\right)\right].$$

In the same spirit as the change of variables we carried out to integrate over photon frequencies $\omega = E_{\text{ph}}/\hbar$, we will now change variables to integrate over the fermion energy $E = \dfrac{\hbar^2 \pi^2}{2mL^2} \widehat{k}^2$:

$$\widehat{k} = \frac{L\sqrt{m}}{\pi\hbar}\sqrt{2E} \qquad d\widehat{k} = \frac{L\sqrt{m}}{\pi\hbar}\frac{dE}{\sqrt{2E}}$$

$$\Phi_f = -\pi T \left(\frac{L^3 m^{3/2}}{\pi^3 \hbar^3}\right) \int_0^\infty \frac{dE}{\sqrt{2E}} (2E) \log\left(1 + e^{-\beta(E-\mu)}\right)$$

$$= -\frac{\sqrt{2}m^3}{\pi^{3/2}\hbar^3} V\sqrt{T} \int_0^\infty \log\left(1 + e^{-\beta(E-\mu)}\right)\sqrt{E}\, dE$$

As for the case of a photon gas, Eq. 94, you should find $\Phi_f \propto VT$. It will be convenient to keep this grand-canonical potential in the form of an integral over the energy E, which we will evaluate after taking appropriate derivatives to determine the thermodynamics and equation of state for non-relativistic fermions.

8.5 Low-temperature equation of state

In contrast to the photon gas, we need to retain the chemical potential in our analyses of non-relativistic fermions, which makes these calculations more complicated. To achieve a different simplification, we can focus on the low-temperature regime where we expect quantum Fermi–Dirac statistics to differ significantly from the classical case we considered back in Section 4.1. As we saw in Section 7.5, it is only at high temperatures, with large negative chemical

potential, that the classical approach provides a good approximation to the true quantum physics.

To see how low temperatures simplify the analysis of the non-relativistic fermion gas, it will prove profitable to first analyze the average particle number

$$\langle N \rangle_{\mathrm{f}} = -\frac{\partial}{\partial \mu} \Phi_{\mathrm{f}},$$

using the grand-canonical potential we computed above. In analogy to the Planck spectrum we derived for the photon gas in Section 8.2, we first express the average particle number density as an integral over energies,

$$\frac{\langle N \rangle_{\mathrm{f}}}{V} = \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \int_0^\infty F(E)\sqrt{E}\, dE, \tag{99}$$

where the function $F(E)$ is known as the Fermi function. In contrast to the Planck spectrum, some constant factors are kept separate from $F(E)$, so that it more closely resembles the average occupation numbers $\langle n_\ell \rangle$ we computed in Section 7.5:

$$\frac{\langle N \rangle_{\mathrm{f}}}{V} = -\frac{\partial}{\partial \mu}\frac{\Phi_{\mathrm{f}}}{V} = \frac{\sqrt{2m^3}\, T}{\pi^2 \hbar^3} \int_0^\infty \frac{\partial}{\partial \mu} \log\left(1 + e^{-\beta(E-\mu)} \right) \sqrt{E}\, dE$$

$$= \frac{\sqrt{2m^3}\, T}{\pi^2 \hbar^3} \int_0^\infty \frac{e^{-\beta(E-\mu)}\, \beta}{1 + e^{-\beta(E-\mu)}} \sqrt{E}\, dE$$

$$= \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \int_0^\infty \frac{1}{e^{\beta(E-\mu)} + 1} \sqrt{E}\, dE \implies F(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

As usual in the grand-canonical approach, the average particle number density and Fermi function depend on both the inverse temperature β and the chemical potential μ. Expressing $F(E)$ in terms of the dimensionless ratios E/μ and T/μ,

$$F(E) = \frac{1}{\exp\left[\frac{E-\mu}{T}\right] + 1} = \frac{1}{\exp\left[\frac{\mu}{T}\left(\frac{E}{\mu} - 1\right)\right] + 1} = \frac{1}{\left(\exp\left[\frac{E}{\mu} - 1\right]\right)^{\mu/T} + 1},$$

we can highlight the two main features of the figure below, which plots the Fermi function against E/μ for various temperatures T/μ. Here we assume a positive chemical potential, $\mu > 0$, which we will soon show is required for low-temperature non-relativistic fermion gases.

First, we can see that the point $E = \mu$, where $F(E) = 1/2$ for any non-zero temperature, is a threshold at which the behaviour of the Fermi function changes. For larger energies $E > \mu$, the exponential factor $\exp\left[\frac{E}{\mu} - 1\right] > 1$ and drives

$F(E) \to 0$ as the energy increases. For smaller energies $E < \mu$, the exponential factor $\exp\left[\frac{E}{\mu} - 1\right] < 1$ and vanishes as the energy decreases, leaving $F(E) \to 1$. These two asymptotic limits reflect the possible energy level occupation numbers for fermions, $n_\ell = 0$ and 1. Second, smaller temperatures cause much more rapid approach to these two limits, with the exponential factor either enhanced (if $E > \mu$) or suppressed (if $E < \mu$) by a power $\mu/T \gg 1$.
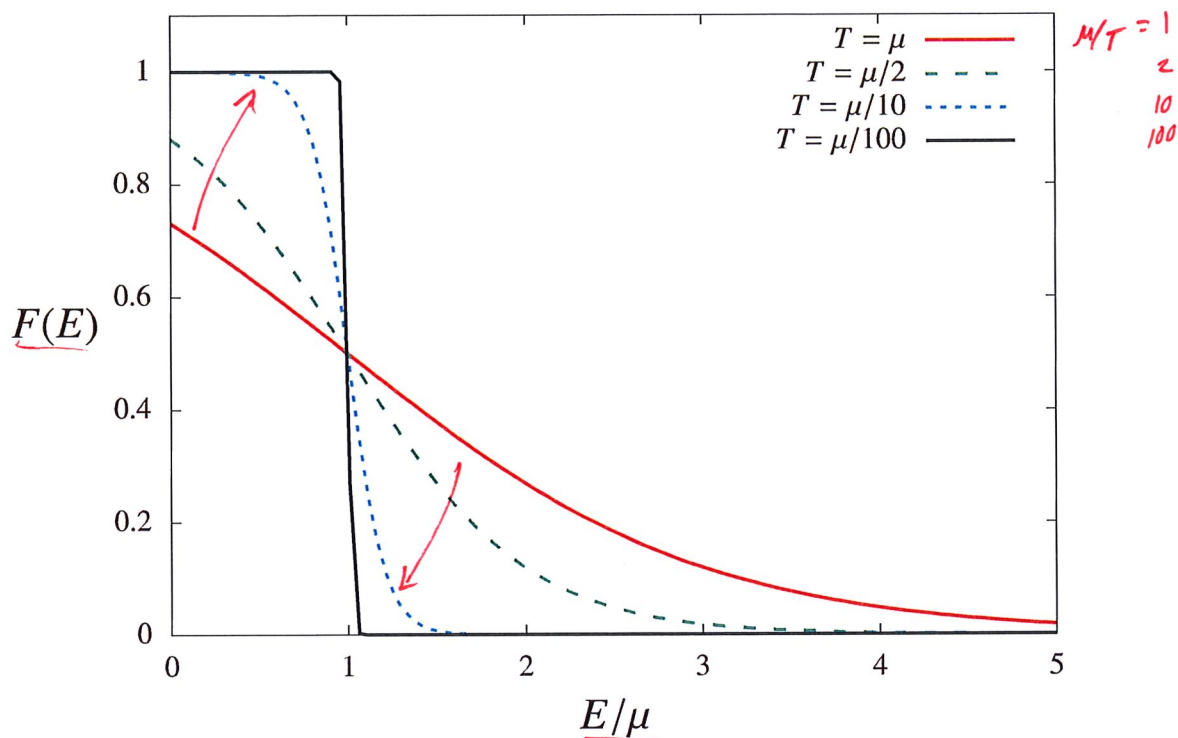
Therefore, for small temperatures $T \ll \mu$, we can simplify our calculations by approximating the Fermi function as a step function,

$$F(E) \approx \begin{cases} 1 & \text{for } E < \mu \\ 0 & \text{otherwise} \end{cases}. \tag{100}$$

Using this approximation, what is the resulting average particle number density?

$$\frac{\langle N \rangle_f}{V} = \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \int_0^\infty F(E)\sqrt{E}\, dE = \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \int_0^\mu \sqrt{E}\, dE$$

$$= \frac{\sqrt{2m^3}}{\pi^2 \hbar^3} \left(\frac{2}{3} E^{3/2} \right)_0^\mu$$

$$= \frac{(2m\mu)^{3/2}}{3\pi^2 \hbar^3}$$