

VII.D Non-relativistic Gas

Quantum particles are further characterized by a *spin* s . In the absence of a magnetic field different spin states have the same energy, and a *spin degeneracy* factor, $g = 2s + 1$, multiplies eqs.(VII.28)–(VII.31). In particular, for a non-relativistic gas in three dimensions ($\mathcal{E}(\vec{k}) = \hbar^2 k^2 / 2m$, and $\sum_{\vec{k}} \rightarrow V \int d^3 \vec{k} / (2\pi)^3$) these equations reduce to

$$\left\{ \begin{array}{l} \beta P_\eta = \frac{\ln \mathcal{Q}_\eta}{V} = \eta g \int \frac{d^3 \vec{k}}{(2\pi)^3} \ln \left[1 - \eta z \exp \left(-\frac{\beta \hbar^2 k^2}{2m} \right) \right], \\ n_\eta \equiv \frac{N_\eta}{V} = g \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{1}{z^{-1} \exp \left(\frac{\beta \hbar^2 k^2}{2m} \right) - \eta}, \\ \varepsilon_\eta \equiv \frac{E_\eta}{V} = g \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \frac{1}{z^{-1} \exp \left(\frac{\beta \hbar^2 k^2}{2m} \right) - \eta}. \end{array} \right. \quad (\text{VII.32})$$

To simplify these equations, we change variables to $x = \beta \hbar^2 k^2 / (2m)$, so that

$$k = \frac{\sqrt{2mk_B T}}{\hbar} x^{1/2} = \frac{2\pi^{1/2}}{\lambda} x^{1/2}, \quad \implies \quad dk = \frac{\pi^{1/2}}{\lambda} x^{-1/2} dx.$$

Substituting into eqs.(VII.32) gives

$$\left\{ \begin{array}{l} \beta P_\eta = -\eta \frac{g}{2\pi^2} \frac{4\pi^{3/2}}{\lambda^3} \int_0^\infty dx x^{1/2} \ln(1 - \eta z e^{-x}) \\ \quad = \frac{g}{\lambda^3} \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{dx x^{3/2}}{z^{-1} e^x - \eta}, \quad (\text{integration by parts}) \\ n_\eta = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx x^{1/2}}{z^{-1} e^x - \eta}, \\ \beta \varepsilon_\eta = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx x^{3/2}}{z^{-1} e^x - \eta}. \end{array} \right. \quad (\text{VII.33})$$

We now define two sets of functions by

$$f_m^\eta(z) = \frac{1}{(m-1)!} \int_0^\infty \frac{dx x^{m-1}}{z^{-1} e^x - \eta}. \quad (\text{VII.34})$$

For non-integer arguments, the function $m! \equiv \Gamma(m+1)$ is defined by the integral $\int_0^\infty dx x^m e^{-x}$. In particular, from this definition it follows that $(1/2)! = \sqrt{\pi}/2$, and $(3/2)! = (3/2)\sqrt{\pi}/2$. Eqs.(VII.33) now take the simple form

$$\left\{ \begin{array}{l} \beta P_\eta = \frac{g}{\lambda^3} f_{5/2}^\eta(z), \\ n_\eta = \frac{g}{\lambda^3} f_{3/2}^\eta(z), \\ \varepsilon_\eta = \frac{3}{2} P_\eta \quad . \end{array} \right. \quad (\text{VII.35})$$

These results completely describe the thermodynamics of ideal quantum gases as a function of z . To find the equation of state $P_\eta(n_\eta, T)$, we need to solve for z in terms of density. This requires knowledge of the behavior of the functions $f_m^\eta(z)$.

The high temperature, low density (non-degenerate) limit will be examined first. In this limit, z is small, and

$$\begin{aligned}
f_m^\eta(z) &= \frac{1}{(m-1)!} \int_0^\infty \frac{dx x^{m-1}}{z^{-1}e^x - \eta} = \frac{1}{(m-1)!} \int_0^\infty dx x^{m-1} (ze^{-x}) (1 - \eta ze^{-x})^{-1} \\
&= \frac{1}{(m-1)!} \int_0^\infty dx x^{m-1} \sum_{\alpha=1}^\infty (ze^{-x})^\alpha \eta^{\alpha+1} \\
&= \sum_{\alpha=1}^\infty \eta^{\alpha+1} z^\alpha \frac{1}{(m-1)!} \int_0^\infty dx x^{m-1} e^{-\alpha x} \\
&= \sum_{\alpha=1}^\infty \eta^{\alpha+1} \frac{z^\alpha}{\alpha^m} = z + \eta \frac{z^2}{2^m} + \frac{z^3}{3^m} + \eta \frac{z^4}{4^m} + \dots.
\end{aligned} \tag{VII.36}$$

We thus find (self-consistently) that $f_m^\eta(z)$, and hence $n_\eta(z)$ and $P_\eta(z)$, are indeed small as $z \rightarrow 0$. Eqs.(VII.35) in this limit give,

$$\begin{cases} \frac{n_\eta \lambda^3}{g} = f_{3/2}^\eta(z) = z + \eta \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \eta \frac{z^4}{4^{3/2}} + \dots, \\ \frac{\beta P_\eta \lambda^3}{g} = f_{5/2}^\eta(z) = z + \eta \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \eta \frac{z^4}{4^{5/2}} + \dots. \end{cases} \tag{VII.37}$$

The first of the above equations can be solved perturbatively, by the recursive procedure of substituting the solution up to a lower order, as

$$\begin{aligned}
z &= \frac{n_\eta \lambda^3}{g} - \eta \frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} - \dots \\
&= \left(\frac{n_\eta \lambda^3}{g} \right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g} \right)^2 - \dots \\
&= \left(\frac{n_\eta \lambda^3}{g} \right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g} \right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) \left(\frac{n_\eta \lambda^3}{g} \right)^3 - \dots.
\end{aligned} \tag{VII.38}$$

Substituting this solution into the second leads to

$$\begin{aligned}
\frac{\beta P_\eta \lambda^3}{g} &= \left(\frac{n_\eta \lambda^3}{g} \right) - \frac{\eta}{2^{3/2}} \left(\frac{n_\eta \lambda^3}{g} \right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) \left(\frac{n_\eta \lambda^3}{g} \right)^3 \\
&\quad + \frac{\eta}{2^{5/2}} \left(\frac{n_\eta \lambda^3}{g} \right)^2 - \frac{1}{8} \left(\frac{n_\eta \lambda^3}{g} \right)^3 + \frac{1}{3^{5/2}} \left(\frac{n_\eta \lambda^3}{g} \right)^3 + \dots.
\end{aligned}$$

The pressure of the quantum gas can thus be obtained from the virial expansion,

$$P_\eta = n_\eta k_B T \left[1 - \frac{\eta}{2^{5/2}} \left(\frac{n_\eta \lambda^3}{g} \right) + \left(\frac{1}{8} - \frac{2}{3^{5/2}} \right) \left(\frac{n_\eta \lambda^3}{g} \right)^2 + \dots \right]. \quad (\text{VII.39})$$

The second virial coefficient $B_2 = -\eta \lambda^3 / (2^{5/2} g)$, agrees with eq.(VII.22) computed in the canonical ensemble for $g = 1$. The natural (dimensionless) expansion parameter is $n_\eta \lambda^3 / g$, and quantum mechanical effects become important when $n_\eta \lambda^3 \geq g$; the *quantum degenerate* limit. The behavior of fermi and bose gases is very different in this degenerate limit of low temperatures and high densities, and the two cases will be discussed separately in the following sections.

VII.E The Degenerate Fermi Gas

At zero temperature, the fermi occupation number,

$$\langle n_{\vec{k}} \rangle_- = \frac{1}{e^{\beta(\mathcal{E}(\vec{k}) - \mu)} + 1}, \quad (\text{VII.40})$$

is one for $\mathcal{E}(\vec{k}) < \mu$, and zero otherwise. The limiting value of μ at zero temperature is called the *fermi energy*, \mathcal{E}_F , and all one-particle states of energy less than \mathcal{E}_F are occupied, forming a *fermi sea*. For the ideal gas with $\mathcal{E}(\vec{k}) = \hbar^2 k^2 / (2m)$, there is a corresponding *fermi wavenumber* k_F , calculated from

$$N = \sum_{|\vec{k}| \leq k_F} (2s + 1) = gV \int^{k < k_F} \frac{d^3 \vec{k}}{(2\pi)^3} = g \frac{V}{6\pi^2} k_F^3. \quad (\text{VII.41})$$

In terms of the density $n = N/V$,

$$k_F = \left(\frac{6\pi^2 n}{g} \right)^{1/3}, \quad \implies \quad \mathcal{E}_F(n) = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 n}{g} \right)^{2/3}. \quad (\text{VII.42})$$

Note that while in a classical treatment the ideal gas has a large density of states at $T = 0$ (from $\Omega_{\text{Classical}} = V^N / N!$), the quantum fermi gas has a unique ground state with $\Omega = 1$. Once the one-particle momenta are specified (all \vec{k} for $|\vec{k}| < k_F$), there is only one anti-symmetrized state, as constructed in eq.(VII.7).

To see how the fermi sea is modified at small temperatures, we need the behavior of $f_m^-(z)$ for large z which, after integration by parts, is

$$f_m^-(z) = \frac{1}{m!} \int_0^\infty dx x^m \frac{d}{dx} \left(\frac{-1}{z^{-1} e^x + 1} \right).$$

Since the fermi occupation number changes abruptly from one to zero, its derivative in the above equation is sharply peaked. We can expand around this peak by setting $x = \ln z + t$, and extending the range of integration to $-\infty < t < +\infty$, as

$$\begin{aligned}
f_m^-(z) &\approx \frac{1}{m!} \int_{-\infty}^{\infty} dt (\ln z + t)^m \frac{d}{dt} \left(\frac{-1}{e^t + 1} \right) \\
&= \frac{1}{m!} \int_{-\infty}^{\infty} dt \sum_{\alpha=0}^{\infty} \binom{m}{\alpha} t^\alpha (\ln z)^{m-\alpha} \frac{d}{dt} \left(\frac{-1}{e^t + 1} \right) \\
&= \frac{(\ln z)^m}{m!} \sum_{\alpha=0}^{\infty} \frac{m!}{\alpha!(m-\alpha)!} (\ln z)^{-\alpha} \int_{-\infty}^{\infty} dt t^\alpha \frac{d}{dt} \left(\frac{-1}{e^t + 1} \right).
\end{aligned} \tag{VII.43}$$

Using the (anti-) symmetry of the integrand under $t \rightarrow -t$, and un-doing the integration by parts yields,

$$\frac{1}{\alpha!} \int_{-\infty}^{\infty} dt t^\alpha \frac{d}{dt} \left(\frac{-1}{e^t + 1} \right) = \begin{cases} 0 & \text{for } \alpha \text{ odd,} \\ \frac{2}{(\alpha-1)!} \int_0^{\infty} dt \frac{t^{\alpha-1}}{e^t + 1} = 2f_\alpha^-(1) & \text{for } \alpha \text{ even.} \end{cases}$$

Inserting the above into eq.(VII.43), and using tabulated values for the integrals $f_\alpha^-(1)$, leads to the *Sommerfeld expansion*,

$$\begin{aligned}
\lim_{z \rightarrow \infty} f_m^-(z) &= \frac{(\ln z)^m}{m!} \sum_{\alpha=0}^{\text{even}} 2f_\alpha^-(1) \frac{m!}{(m-\alpha)!} (\ln z)^{-\alpha} \\
&= \frac{(\ln z)^m}{m!} \left[1 + \frac{\pi^2}{6} \frac{m(m-1)}{(\ln z)^2} + \frac{7\pi^4}{360} \frac{m(m-1)(m-2)(m-3)}{(\ln z)^4} + \dots \right].
\end{aligned} \tag{VII.44}$$

In the degenerate limit, the density and chemical potential are related by

$$\frac{n\lambda^3}{g} = f_{3/2}^-(z) = \frac{(\ln z)^{3/2}}{(3/2)!} \left[1 + \frac{\pi^2}{6} \frac{3}{2} \frac{1}{2} (\ln z)^{-2} + \dots \right] \gg 1. \tag{VII.45}$$

The lowest order result reproduces the expression in eq.(VII.41) for the fermi energy,

$$\lim_{T \rightarrow 0} \ln z = \left[\frac{3}{4\sqrt{\pi}} \frac{n\lambda^3}{g} \right]^{2/3} = \frac{\beta\hbar^2}{2m} \left(\frac{6\pi^2 n}{g} \right)^{2/3} = \beta\mathcal{E}_F.$$

Inserting the zero temperature limit into eq.(VII.45) gives the first order correction,

$$\ln z = \beta\mathcal{E}_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + \dots \right]^{-2/3} = \beta\mathcal{E}_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + \dots \right]. \tag{VII.46}$$

The appropriate dimensionless expansion parameter is $(k_B T/\mathcal{E}_F)$. Note that the fermion chemical potential $\mu = k_B T \ln z$, is positive at low temperatures, and negative at high temperatures (from eq.(VII.38)). It changes sign at a temperature proportional to \mathcal{E}_F/k_B .

The low temperature expansion for the pressure is

$$\begin{aligned}\beta P &= \frac{g}{\lambda^3} f_{5/2}^-(z) = \frac{g}{\lambda^3} \frac{(\ln z)^{5/2}}{(5/2)!} \left[1 + \frac{\pi^2}{6} \frac{5}{2} \frac{3}{2} (\ln z)^{-2} + \dots \right] \\ &= \frac{g}{\lambda^3} \frac{8(\beta \mathcal{E}_F)^{5/2}}{15\sqrt{\pi}} \left[1 - \frac{5}{2} \frac{\pi^2}{12} \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + \dots \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + \dots \right] \\ &= P_F \left[1 + \frac{5}{12} \pi^2 \left(\frac{k_B T}{\mathcal{E}_F} \right)^2 + \dots \right],\end{aligned}\tag{VII.47}$$

where $P_F = (2/5)n\mathcal{E}_F$ is the *fermi pressure*. Unlike its classical counterpart, the fermi gas at zero temperature has finite pressure and internal energy.

The low temperature expansion for the internal energy is obtained easily from eq.(VII.47) using

$$\frac{E}{V} = \frac{3}{2}P = \frac{3}{5}nk_B T_F \left[1 + \frac{5}{12}\pi^2 \left(\frac{T}{T_F} \right)^2 + \dots \right],\tag{VII.48}$$

where we have introduced the *fermi temperature* $T_F = \mathcal{E}_F/k_B$. Eq.(VII.48) leads to a low temperature heat capacity,

$$C_V = \frac{dE}{dT} = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right) + \mathcal{O} \left(\frac{T}{T_F} \right)^2.\tag{VII.49}$$

The linear vanishing of the heat capacity as $T \rightarrow 0$ is a general feature of a fermi gas, valid in all dimensions. It has the following simple physical interpretation: The probability of occupying single-particle states, eq.(VII.40), is very close to a step function at small temperatures. Only particles within a distance of approximately $k_B T$ of the fermi energy can be thermally excited. This represents only a small fraction T/T_F , of the total number of electrons. Each excited particle gains an energy of the order of $k_B T$, leading to a change in the internal energy of approximately $k_B T N (T/T_F)$. Hence the heat capacity is given by $C_V = dE/dT \sim N k_B T/T_F$. This conclusion is also valid for an interacting fermi gas. The fact that only a small number, $N(T/T_F)$, of fermions are excited at small temperatures accounts for many interesting properties of fermi gases. For example, the magnetic susceptibility of a classical gas of N non-interacting particles of magnetic moment μ_B follows the Curie law, $\chi \propto N\mu_B^2/(k_B T)$. Since quantum mechanically, only a fraction of spins contributes at low temperatures, the low temperature susceptibility saturates to a (Pauli) value of $\chi \propto N\mu_B^2/(k_B T_F)$ (see the problems for the details of this calculation.)