1 715 Lecture Notes: Gases, Part II

1.1 Non-ideal Gases

We consider again a classical gas with \( \frac{1}{2m} \hbar^2 N^{2/3} \ll kT \). (I emphasize once more that this case includes essentially all gases.) But now the particles \( i \) and \( j \) are taken to have an interaction energy \( V(\vec{r}_i - \vec{r}_j) \).

The partition function is

\[
Q = \frac{1}{N!h^{3N}} \int d^3p_1 d^3p_2 \ldots d^3p_N
\times \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\{-\beta \sum_i \frac{p_i^2}{2m} - \beta \sum_{i < j} V(\vec{r}_i - \vec{r}_j)\}
\]

\[
= \frac{1}{N!h^{3N}} \int d^3p_1 d^3p_2 \ldots d^3p_N \exp\{-\beta \sum_i \frac{p_i^2}{2m}\}
\times \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\{-\beta \sum_{i < j} V(\vec{r}_i - \vec{r}_j)\}
\]

\[
= \frac{1}{V_N} Q_{id} Q_V,
\]

where \( Q_{id} \) is the ideal gas partition function and

\[
Q_V = \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\{-\beta \sum_{i < j} V(\vec{r}_i - \vec{r}_j)\}.
\]

Only in classical mechanics does \( Q \) factorize so neatly. To save writing, let us define \( V_{ij} = V(\vec{r}_i - \vec{r}_j) \). Now \( \beta V_{ij} \) will generally be small if the gas is classical, so \( \exp\{-\beta V_{ij} - 1\} \) is also small. This leads us to rewrite \( Q_V \) as

\[
Q_V = \int d^3r_1 d^3r_2 \ldots d^3r_N \prod_{i < j} \{e^{-\beta V_{ij}}\}
\]

\[
= \int d^3r_1 d^3r_2 \ldots d^3r_N \prod_{i < j} \{1 + (e^{-\beta V_{ij}} - 1)\}
\]

\[
\approx \int d^3r_1 d^3r_2 \ldots d^3r_N \{1 + \sum_{i < j} (e^{-\beta V_{ij}} - 1)\}
\]

\[
= V^N + \frac{1}{2} N(N-1)V^{N-2} \int dr_1 dr_2 \{\exp[-\beta V(\vec{r}_1 - \vec{r}_2)] - 1\}.
\]

Here again we have used \( \prod_{i < j} (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} \) if \( f_{ij} \ll 1 \). (Actually this argument is overly glib, but the actual derivation of this approximation is too intricate to enter into here.) Now

\[
\ln(V^{-N} Q_V) = \ln \left[ 1 + \frac{N(N-1)}{2V^2} \int dr_1 dr_2 \{\exp[-\beta V(\vec{r}_1 - \vec{r}_2)] - 1\} \right],
\]
since every term in the sum over \( i \) and \( j \) is the same. We change variables to relative and center-of-mass coordinates: \( \vec{r}' = \vec{r}'_1 - \vec{r}'_2 \) and \( \vec{u}' = (\vec{r}'_1 + \vec{r}'_2)/2 \). The integral over \( \vec{u}' \) is trivial and equals the total volume. Now use the fact that \( \ln(1 + x) \sim x \) if \( x \ll 1 \), simplify and use \( N - 1 \approx N \) to find

\[
\ln(V^{-N} Q_V) = \frac{N^2}{V^2} \int d^3r \{e^{-\beta V(r)} - 1\}. \quad (12)
\]

Let us define

\[
B(T) = \frac{1}{2} \int [1 - e^{-\beta V(r)}] d^3r. \quad (13)
\]

This quantity will depend on the particular gas in question through \( V(\vec{r}') \), but does not depend on volume. The free energy is

\[
A = -kT \log Q = -kT \log Q_{id} - kT \log [V^{-N} Q_V] = A_{id} + N^2 kTB(T)/V \quad (15)
\]

The pressure is given by

\[
P = -(\partial A/\partial V)_T = \frac{NkT}{V} + \frac{N^2}{V^2} kTB(T). \quad (17)
\]

If the other terms in the expansion of the logarithm were included, then we would have

\[
P = \frac{NkT}{V} \left( 1 + \frac{N}{V} B(T) + \left( \frac{N}{V} \right)^2 C(T) \ldots \right). \quad (18)
\]

This is called the virial expansion for the equation of state. It is obviously an expansion around low density. \( B(T) \) is called the second virial coefficient, \( C(T) \) is the third, etc. They measure the deviation from nonideality.

Let us calculate \( B(T) \) in a simple model for \( V(\vec{r}') \).

\[
V(\vec{r}') = \infty, \quad 0 < r < 2r_0, \quad (19)
\]

and

\[
V(\vec{r}') = -\frac{C}{r_0^6} \quad r > 2r_0. \quad (20)
\]

This is a model for the van der Waals interaction. We assume \( kT >> C/(2r_0)^6 \). Now

\[
B(T) = \frac{1}{2} 4\pi \int_0^{2r_0} (1 - e^{-\beta V}) r^2 dr + \frac{1}{2} 4\pi \int_{2r_0}^{\infty} (1 - e^{-\beta V}) r^2 dr \quad (21)
\]

\[
\approx \frac{1}{2} 4\pi \int_0^{2r_0} r^2 dr - \frac{1}{2} 4\pi \beta \int_{2r_0}^{\infty} \frac{C}{r_0^6} r^2 dr. \quad (22)
\]

Hence

\[
B(T) = \frac{16\pi r_0^3}{3} - \frac{\pi C}{12kT r_0^3} = b - a/kT, \quad (23)
\]

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where \( b = 16\pi r_0^3/3 \) and \( a = \pi C/12r_0^3 \). So the virial expansion becomes

\[
P = \frac{NkT}{V} + \frac{N^2\hbar kT}{V^2} - a\frac{N^2}{V^2}.
\]

For low densities \( b << V/N \), this is approximately

\[
P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2},
\]

which is just van der Waals equation. Note that \( b \) is just the excluded volume and \( a \) is a measure of the strength of the attraction, just as in our earlier intuitive derivation.

### 1.2 Ideal Fermi Gas

We now return to the ideal gas, but consider the quantum case of spin 1/2 fermions at low temperature, \( kT << \hbar^2 n^{2/3}/2m \). Quantum effects dominate and classical intuition is almost useless for this case, which applies approximately to electrons in metals (including white dwarf stars), neutrons in neutron stars, and liquid \(^3\)He. We have derived the two basic equations already:

\[
N = 2 \sum_k \{\exp[\beta(\epsilon_k - \mu)] + 1\}^{-1},
\]

and

\[
PV/kT = 2 \sum_k \ln\{1 + \exp[\beta(\mu - \epsilon_k)]\}.
\]

Let's look first at the number equation first, which more simply is

\[
N = 2 \sum_k n_k.
\]

(I will drop the bar indicating thermal averaging on the \( n_k \).)

At zero temperature:

\[
n_k = 0, \quad \epsilon_k > \mu
\]

and

\[
n_k = 1, \quad \epsilon_k < \mu.
\]

Let us define \( k_F \) and \( \epsilon_F \) by \( \epsilon_F = \hbar^2 k_F^2/2m = \mu(T = 0) \). Explicitly, we have

\[
N = 2 \sum_k n_k(T = 0) = 2 \sum_k \left[1 - \frac{1}{2} \int d^3k \frac{V}{(2\pi)^3} = V k_F^3/3\pi^2
\]

Hence \( k_F = (3\pi^2 n)^{1/3} \). This is called the Fermi wavevector. \( \epsilon_F = \mu(T = 0) \) is called the Fermi energy. In the ground state, all states with energy less than
the Fermi energy are occupied, and all states with energy above the Fermi energy are empty. The ground state energy is

$$U(T = 0) = \sum_k \sum_{|k| < k_F} \epsilon_k n_k(T = 0) = 2V(2\pi)^3 \int_{|k| < k_F} \frac{h^2 k^2}{2m} d^3 k$$

$$= \frac{V \hbar^2}{8\pi^3 m} \int_0^{k_F} k^4 dk = \frac{V \hbar^2}{10\pi^2 m} k_F^5,$$  \hspace{1cm} (33)

which may also be written as

$$U(T = 0) = \frac{3}{5} N \epsilon_F. \hspace{1cm} (34)$$

The average energy per particle is \( \frac{3}{5} \) of the maximum energy. \( \epsilon_F \sim 1eV \) for a typical metal \((n \sim 10^{24}/cm^3, m \) is the mass of the electron) and \( \epsilon_F \sim 10^{-4}eV \) for \( ^3He \) \((n \sim 10^{22}/cm^3 \) and \( m \) is three times the mass of the proton). For white dwarfs, the density depends on the total mass of the star, but can be very high, much higher than for ordinary metals. The degeneracy condition can be formulated as \( kT << \epsilon_F \). For metals, this is \( T << 10^4 K \). For \( ^3He, T << 1K \).

The next step is to get an expansion for low temperature. This is a little bit tricky for the following reason. The number equation can be written as

$$n = \frac{N}{V} = \frac{1}{(2\pi)^3} \int_0^\infty k^2 dk \frac{1}{e^{\epsilon_k - \beta \mu} + 1}. \hspace{1cm} (35)$$

At low \( T \), this looks like

$$n = \frac{N}{V} = k_F^3 / 3\pi^2 + \mathcal{O}(T^2) + \mathcal{O}(e^{-\epsilon_F / kT}) + \ldots \hspace{1cm} (36)$$

In other words the expression is not analytic at \( T = 0 \) and possesses no power series. The nonanalytic part is exponentially small for \( kT << \epsilon_F \), however, so if we can subtract it out, then we can obtain very accurate results. We do this as follows. Let \( y = \beta k \). Then

$$n = \frac{\sqrt{2}}{\pi^2} \frac{m}{\beta \hbar^2 \mu} \int_0^\infty y(\cosh(y \beta \mu) + 1)^{-1} dy \hspace{1cm} (37)$$

for \( \beta \mu >> 1 \), so the sloping part of the curve is very short.

The derivative of this function would be very sharply peaked, and it is easy to make approximations on such functions. So we integrate by parts

$$n = \frac{\sqrt{2}}{\pi^2} \frac{m}{\beta \hbar^2 \mu} \int_0^\infty \frac{y^{3/2} e^{-\beta \mu}}{3/2 (e^{y \beta \mu} + 1)^2} dy \hspace{1cm} (38)$$
The surface term is of order $e^{-\beta\mu}$ and is therefore dropped. We now expand $y^{3/2}$ in a Taylor series around $\beta\mu$ to get

$$n = \frac{2\sqrt{2}}{3\pi^2} \left( \frac{m}{\beta h^2} \right)^{3/2} \times$$

$$\int_0^\infty \left\{ \frac{1}{3} (\beta\mu)^{3/2} + \frac{3}{2} (y - \beta\mu)(\beta\mu)^{1/2} + \frac{3}{8} (y - \beta\mu)(\beta\mu)^{-1/2} + \ldots \right\} \frac{e^{y - \beta\mu}}{(e^{y - \beta\mu} + 1)^2} \, dy$$

$$\approx \frac{1}{3\pi^2} \left( \frac{2m}{\beta h^2} \right)^{3/2} \int_{-\beta\mu}^{\infty} \left[ (\beta\mu)^{3/2} + \frac{3}{2} x(\beta\mu)^{1/2} + \frac{3}{8} x^2(\beta\mu)^{-1/2} \right] \frac{e^x}{(e^x + 1)^2} \, dx.$$  

(40)

Now note that $e^x/(e^x + 1)^2 < e^x$. Hence

$$\int_{-\infty}^{-\beta\mu} \frac{e^x}{(e^x + 1)^2} \, dx < \int_{-\infty}^{-\beta\mu} e^x \, dx = e^{-\beta\mu},$$

(42)

which is very small. So now we can extend the integral over $x$ to $x = -\infty$:

$$n \approx \frac{1}{3\pi^2} \left( \frac{2m}{\beta h^2} \right)^{3/2} \left[ (\beta\mu)^{3/2} + \frac{3}{8} (\beta\mu)^{-1/2} \right] = \frac{1}{3\pi^2} \left( \frac{2m\mu}{h^2} \right)^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT}{\mu} \right)^2 \right]$$

(43)

That gets rid of the last $e^{-\beta\mu}$ terms and now we have a real power series expansion in $\beta = 1/kT$. Performing the integrals (exercise!) gives

$$n \approx \frac{1}{3\pi^2} \left( \frac{2m}{\beta h^2} \right)^{3/2} \left[ (\beta\mu)^{3/2} + \frac{\pi^2}{8} (\beta\mu)^{-1/2} \right] = \frac{1}{3\pi^2} \left( \frac{2m\mu}{h^2} \right)^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT}{\mu} \right)^2 \right]$$

(44)

Other useful relations can be obtained by taking

$$(3\pi^2 n)^{2/3} = \frac{2m\mu}{h^3} \left[ 1 + \frac{\pi^2}{8} \left( \frac{kT/\mu}{\mu} \right)^2 \right]^{2/3},$$

(45)

or

$$\epsilon_F = \mu \left[ 1 + \frac{\pi^2}{12} \left( kT/\epsilon_F \right)^2 \right],$$

(46)

and

$$\mu = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( kT/\epsilon_F \right)^2 \right].$$

(47)

This is all in the approximation that $kT << \epsilon_F$. Thus $\mu$ is a decreasing function of temperature. By the same method,

$$U(T) = 2 \sum_{k} \frac{nk^2 h^2}{2m}$$

$$= \frac{Vk^2}{2\pi^2 m} \int_0^{\infty} k^4 [e^{k(h/\mu)} + 1]^{-1} \, dk$$

(48)

$$= \frac{3}{5} N\epsilon_F [1 + \frac{5\pi^2}{12} \left( kT/\epsilon_F \right)^2].$$

(49)

(50)
and

$$C_V = (\partial U / \partial T)_V = \frac{N \pi^2 k^2}{2 \epsilon_F} T. \tag{51}$$

This gives the equation of state as well, because of the relation $PV = \frac{2}{3} U$, which we now derive:

$$\frac{PV}{kT} = 2 \sum_k \ln[1 + e^{-\beta(\epsilon - \mu)}], \tag{52}$$

Changing the sum to an integral and changing to the variable $\epsilon = h^2 k^2 / 2m$ gives:

$$\frac{PV}{kT} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \epsilon^{1/2} \ln \left[1 + e^{-\beta(\epsilon - \mu)}\right] d\epsilon \tag{53}$$

$$= \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \epsilon^{1/2} \frac{\beta e^{\beta(\epsilon - \mu)} d\epsilon}{1 + e^{\beta(\epsilon - \mu)}}. \tag{54}$$

$U(T)$, on the other hand, may be written as

$$U(T) = 2 \sum_k \frac{n_k}{(\hbar^2 k^2 / 2m)} \tag{55}$$

$$= \frac{V}{\pi^2} \int_0^\infty k^2 e^{\beta(\epsilon - \mu)} + 1^{-1} dk \tag{56}$$

$$= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \epsilon^{3/2} [e^{\beta(\epsilon - \mu)} + 1]^{-1} d\epsilon. \tag{57}$$

Comparison of these two formulas yields $PV = \frac{2}{3} U$. So

$$PV = \frac{2}{5} N \epsilon_F [1 + \frac{5\pi^2}{12} (kT/\epsilon_F)^2]. \tag{58}$$

Now we have all the formulas we need. Let’s think about the physics. At low temperatures $PV = \frac{2}{5} N \epsilon_F$ - the pressure is not zero, as it would be for the classical equation of state. This is purely due to the Pauli principle. Instead of particles losing all their kinetic energy, they are constrained to occupy higher states. They continue to bounce off the walls. This pressure begins to increase when $kT \sim \epsilon_F$, eventually going over to the classical $PV = N kT$. Because of
the relation \( U = \frac{3}{2} p V \), we can make similar statements about \( U \). Quantum effects give it a finite value at \( T = 0 \). At \( T \sim \epsilon_F/k \), we find a crossover to \( U = \frac{3}{2} NkT \). This also allows us to plot

\[
C_V = (\partial U / \partial T)_V
\]

and

\[
S = \int_0^T \frac{C_V(T')}{T'} dT'.
\]

A final quantity of interest is \( \mu \), the chemical potential. \( \mu(T = 0) = \epsilon_F \) and initially decreases with temperature.

At high temperatures \( T > \epsilon_F/k \) we have \( e^{\beta \mu} << 1 \). This might be reached in classical plasmas in fusion experiments or in astrophysics. The Fermi statistics go over to Boltzmann statistics, that is, the classical case. For example, the high temperature limit of the number equation is

\[
n = \frac{1}{4\pi^2} e^{\beta \mu} \left( \frac{2m}{\beta \hbar^2} \right)^{3/2}.
\]

Rearranging, we find

\[
\frac{\mu}{kT} = -\frac{3}{2} \ln(kT) + \ln \left[ \frac{4\pi^2 n \hbar^3}{(2m)^{3/2}} \right]
\]

The occupation function

\[
n_F = \frac{1}{e^{\beta (\epsilon_f - \mu)} + 1}
\]

crosses over from a step function at \( T = 0 \) to a Boltzmann function

\[
n_F = e^{-\beta (\epsilon_f - \mu)} + 1
\]

since the \(+1\) becomes negligible once \(-\mu/kT \gg 1\). This occurs, once again, at approximately \( T = \epsilon_F/k \).