

G25.2651: Statistical Mechanics

Notes for Lecture 19

I. THE FERMION QUANTUM IDEAL GAS: INTRODUCTION

For an ideal gas of fermions, we had shown that the problem of determining the equation of state was one of solving two equations

$$\frac{PV}{kT} = g \sum_{\mathbf{n}} \ln(1 + \zeta e^{-\beta \epsilon_{\mathbf{n}}})$$

$$\langle N \rangle = g \sum_{\mathbf{n}} \frac{\zeta e^{-\beta \epsilon_{\mathbf{n}}}}{1 + \zeta e^{-\beta \epsilon_{\mathbf{n}}}}$$

where the second of these must be solved for ζ in terms of ρ and substituted into the first to obtain P as a function of ρ .

As we did in the Boltzmann case, let us consider the thermodynamic limit $L \rightarrow \infty$ so that the spacing between energy levels becomes small. Then the sums can be replaced by integrals over the continuous variable \mathbf{n} . For the pressure, this replacement give rise to

$$\begin{aligned} \frac{PV}{kT} &= g \int d^3 \mathbf{n} \ln(1 + \zeta e^{-\beta \epsilon_{\mathbf{n}}}) \\ &= g \int d^3 \mathbf{n} \ln\left(1 + \zeta e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / mL^2}\right) \\ &= 4\pi g \int_0^\infty dn n^2 \ln\left(1 + \zeta e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / mL^2}\right) \end{aligned}$$

Change variables to

$$x = \sqrt{\frac{2\pi^2 \hbar^2}{mL^2}} n$$

Then,

$$\begin{aligned} \frac{PV}{kT} &= 4\pi g V \left(\frac{m}{2\pi^2 \beta \hbar^2}\right)^{3/2} \int_0^\infty dx x^2 \ln(1 + \zeta e^{-x^2}) \\ &= \frac{4Vg}{\sqrt{\pi} \lambda^3} \int_0^\infty dx x^2 \ln(1 + \zeta e^{-x^2}) \end{aligned}$$

The remaining integral can be evaluated by expanding the log in a power series and integrating the series term by term:

$$\ln(1 + \zeta e^{-\beta x^2}) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l} e^{-lx^2}$$

$$\begin{aligned} \frac{PV}{kT} &= \frac{4Vg}{\sqrt{\pi} \lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l} \int_0^\infty dx x^2 e^{-lx^2} \\ &= \frac{Vg}{\lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{5/2}} \end{aligned}$$

By the same technique, the average particle number $\langle N \rangle$ can be shown to be equal to

$$\langle N \rangle = \frac{Vg}{\lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{3/2}}$$

Multiplying both over these equations on both sides by λ^3/V gives

$$\begin{aligned} \frac{P\lambda^3}{gkT} &= \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{5/2}} \\ \frac{\rho\lambda^3}{g} &= \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{3/2}} \end{aligned}$$

Although exact solution of these equations analytically is intractable, we will consider their solutions in two interesting limits: The high temperature, low density limit and its counterpart, the low temperature, high density limit.

II. THE HIGH TEMPERATURE, LOW DENSITY LIMIT

Since $\zeta = \zeta(\rho)$, in the low density limit, the fugacity can be expanded in the form

$$\zeta = a_1\rho + a_2\rho^2 + a_3\rho^3 + \dots$$

Writing out the first few terms in the pressure and density equations, we have

$$\begin{aligned} \frac{P\lambda^3}{gkT} &= \zeta - \frac{\zeta^2}{2^{5/2}} + \frac{\zeta^3}{3^{5/2}} - \frac{\zeta^4}{4^{5/2}} + \dots \\ \frac{\rho\lambda^3}{g} &= \zeta - \frac{\zeta^2}{2^{3/2}} + \frac{\zeta^3}{3^{3/2}} - \frac{\zeta^4}{4^{3/2}} + \dots \end{aligned}$$

Substituting the expansion for $\zeta(\rho)$ into the density equation gives

$$\frac{\rho\lambda^3}{g} = (a_1\rho + a_2\rho^2 + a_3\rho^3 + \dots) - \frac{1}{2^{3/2}}(a_1\rho + a_2\rho^2 + a_3\rho^3 + \dots)^2 + \frac{1}{3^{3/2}}(a_1\rho + a_2\rho^2 + a_3\rho^3 + \dots)^3 + \dots$$

This equation can now be solved perturbatively, equating like powers of ρ on both sides. For example, working only to first order in ρ , yields:

$$\frac{\rho\lambda^3}{g} = a_1\rho \quad \Rightarrow \quad a_1 = \frac{\lambda^3}{g} \quad \Rightarrow \quad \zeta \approx \frac{\lambda^3\rho}{g}$$

When this is substituted into the pressure equation, and only first order terms in the density are kept, we find

$$\frac{P\lambda^3}{gkT} = \frac{\rho\lambda^3}{g} \quad \Rightarrow \quad \frac{P}{kT} = \rho = \frac{\langle N \rangle}{V}$$

which is just the classical ideal gas equation. Working, now, to second order in ρ , we have, from the density equation

$$\frac{\lambda^3\rho}{g} = \frac{\lambda^3\rho}{g} + a_2\rho^2 - \frac{1}{2^{3/2}} \frac{\lambda^6\rho^2}{g^2}$$

or

$$a_2 = \frac{\lambda^6}{2^{3/2}g^2}$$

Thus,

$$\zeta \approx \frac{\lambda^3\rho}{g} + \frac{\lambda^6}{2^{3/2}g^2}\rho^2$$

and the equation of state becomes

$$\frac{P}{kT} = \rho + \frac{\lambda^3}{2^{5/2}g}\rho^2$$

From this, we can read off the second virial coefficient

$$B_2(T) = \frac{\lambda^3}{2^{5/2}g} \approx 0.1768 \frac{\lambda^3}{g} > 0$$

It is particularly interesting to note that there is a nonzero second virial coefficient in spite of the fact that there are no interactions among the particles. The implication is that there is an “effective” interaction among the particles as a result of the fermionic spin statistics. Moreover, this effective interaction is such that it tends to increase the pressure above the classical ideal gas result ($B_2(T) > 0$). Thus, the effective interaction is repulsive in nature. This is a consequence of the Pauli exclusion principle: The particle energies must be distributed among the available levels in such a way that no two particles can occupy the same quantum state, thus giving rise to an “effective” repulsion between them.

If we look at the third order correction to the pressure, we find that

$$\begin{aligned} a_3 &= \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \frac{\lambda^9}{g^3} \\ \zeta &= \frac{\lambda^3 \rho}{g} + \frac{\lambda^6}{2^{3/2}g^2} \rho^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) \frac{\lambda^9}{g^3} \rho^3 \\ \frac{P}{kT} &= \rho + \frac{\lambda^3}{2^{5/2}g} \rho^2 + \frac{\lambda^6}{g^2} \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right) \rho^3 \end{aligned}$$

so that $B_3(T) < 0$. Thus, one must go out to third order in the density expansion to find a contribution that tends to decrease the pressure.

III. THE HIGH DENSITY, LOW TEMPERATURE LIMIT

Recall that the density equation could be expressed as an integral

$$\rho\lambda^3 = \frac{4g}{\sqrt{\pi}} \int_0^\infty \frac{x^2 dx}{\zeta^{-1}e^{-x^2} + 1}$$

which lead to an expansion in powers of ζ . It is also possible to develop an expansion in powers of $\ln \zeta \equiv mu/kT$. This is accomplished by letting

$$\nu = \ln \zeta = \frac{\mu}{kT}$$

and developing an expansion in powers of ν . In order to see how this is done, consider making a change of variables in the integral $y = x^2$, $x = \sqrt{y}$, $dx = dy/(2\sqrt{y})$. Then

$$\rho\lambda^3 = \frac{2g}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y} dy}{e^{y-\nu} + 1}$$

Integrate by parts using

$$\begin{aligned} u &= \frac{1}{e^{y-\nu} + 1} & du &= -\frac{1}{(e^{y-\nu} + 1)^2} e^{y-\nu} dy \\ dv &= y^{1/2} dy & v &= \frac{2}{3} y^{3/2} \end{aligned}$$

so that

$$\rho\lambda^3 = \frac{4g}{3\sqrt{\pi}} \int_0^\infty \frac{y^{3/2} e^{y-\nu} dy}{(e^{y-\nu} + 1)^2}$$

If we now expand $y^{3/2}$ about $y = \nu$:

$$y^{3/2} = \nu^{3/2} + \frac{3}{2}\nu^{1/2}(y - \nu) + \frac{3}{8}\nu^{-1/2}(y - \nu)^2 + \dots$$

substitute this expansion into the integral and perform the resulting integrals over y , we find

$$\rho\lambda^3 = \frac{4g}{3\sqrt{\pi}} \left[(\ln \zeta)^{3/2} + \frac{\pi^2}{8}(\ln \zeta)^{-1/2} + \dots \right] + \mathcal{O}(1/\zeta)$$

where the fact that $\mu/kT \gg 1$ has been used owing to the low temperature. Since we are in the high density limit, $\zeta(\rho)$ is expected to be large as well so that the series, whose error goes as powers of $1/\zeta$ will converge. As $T \rightarrow 0$, $\zeta \rightarrow \infty$ and only one term in the above expansion survives:

$$\rho\lambda^3 = \rho \left(\frac{2\pi\hbar^2}{mkT} \right) \approx \frac{4g}{3\sqrt{\pi}} (\ln \zeta)^{3/2} = \frac{4g}{3\sqrt{\pi}} \left(\frac{\mu}{kT} \right)^{3/2}$$

Solving for μ gives

$$\mu = \frac{\hbar^2}{2m} \left(\frac{6\pi^2\rho}{g} \right)^{2/3} \equiv \mu_0 = \varepsilon_F$$

which is independent of T . The special value of the chemical potential $\mu_0 = \mu(T = 0)$ is known as the *Fermi energy*. To see what its physical meaning is, consider the expression for the average number of particles:

$$\langle N \rangle = \sum_m \sum_{\mathbf{n}} \frac{\zeta e^{-\beta\varepsilon_{\mathbf{n}}}}{1 + \zeta e^{-\beta\varepsilon_{\mathbf{n}}}}$$

However, recall that

$$\sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m} = N$$

for a specific number of particles. Averaging both sides gives

$$\langle N \rangle = \sum_m \sum_{\mathbf{n}} \langle f_{\mathbf{n}m} \rangle$$

Comparing these two expressions, we see that the average occupation number of a given state with quantum number \mathbf{n} and m is

$$\langle f_{\mathbf{n}m} \rangle = \frac{e^{-\beta(\varepsilon_{\mathbf{n}} - \mu)}}{1 + e^{-\beta(\varepsilon_{\mathbf{n}} - \mu)}} = \frac{1}{1 + e^{\beta(\varepsilon_{\mathbf{n}} - \mu)}}$$

As $T \rightarrow 0$, $\beta \rightarrow \infty$, and $e^{\beta(\varepsilon_{\mathbf{n}} - \mu_0)} \rightarrow \infty$ if $\varepsilon_{\mathbf{n}} > \mu_0$, and $e^{\beta(\varepsilon_{\mathbf{n}} - \mu_0)} \rightarrow 0$ if $\varepsilon_{\mathbf{n}} < \mu_0$. Thus, at $T = 0$, we have the result

$$\langle f_{\mathbf{n}m} \rangle = \begin{cases} 0 & \varepsilon_{\mathbf{n}} > \varepsilon_F \\ 1 & \varepsilon_{\mathbf{n}} < \varepsilon_F \end{cases} = \theta(\varepsilon_F - \varepsilon_{\mathbf{n}})$$

A plot of the occupation average occupation number vs. $\varepsilon_{\mathbf{n}}$ at $T = 0$ is shown in the plot below:

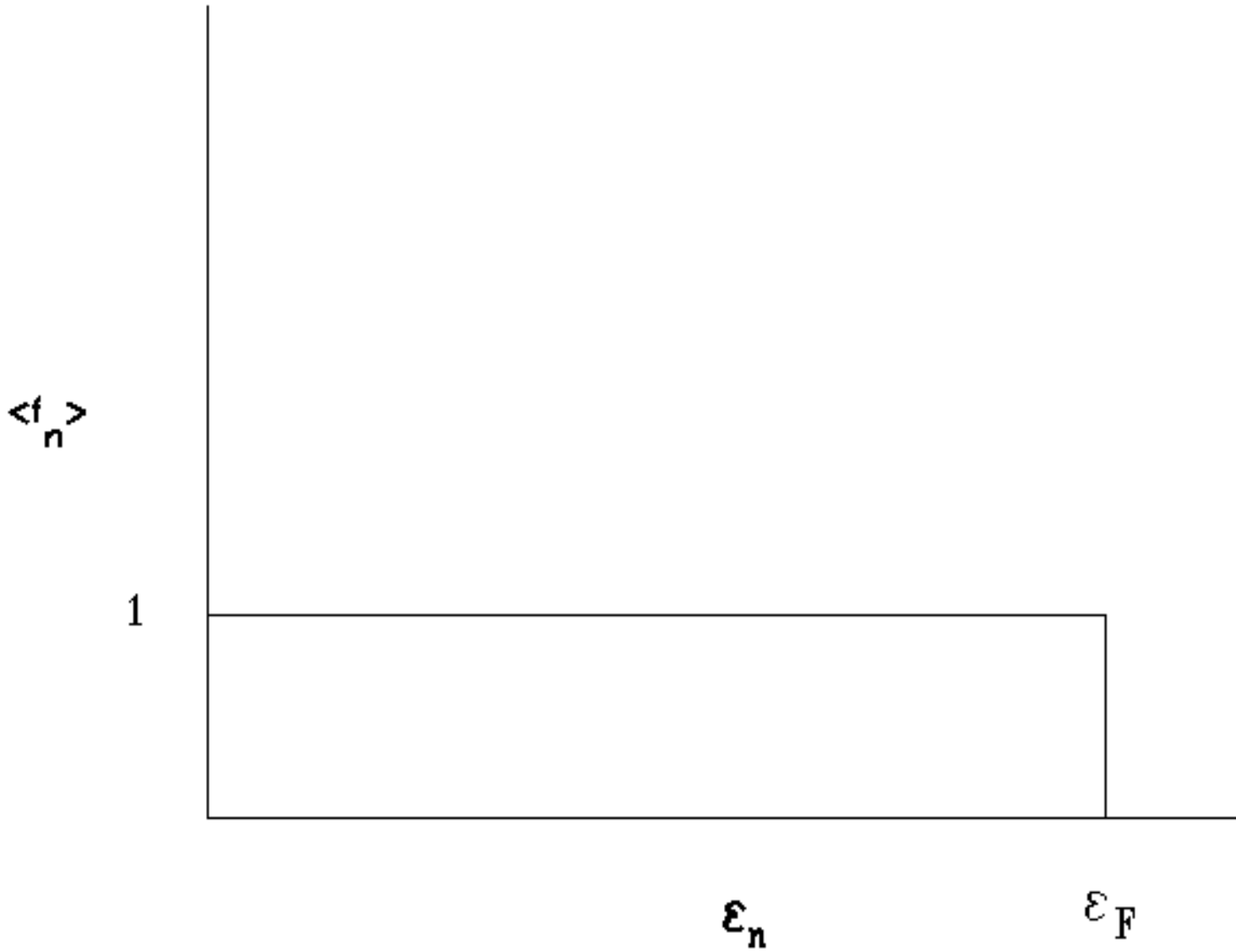


FIG. 1.

Thus, at $T = 0$, the particles will exactly fill up all of the energy levels up to an energy value ϵ_F above which no energy levels will be occupied. As T is increased, the probability of an excitation above the Fermi energy becomes nonzero, and the average occupation (shown for several different values of β) appears as follows:

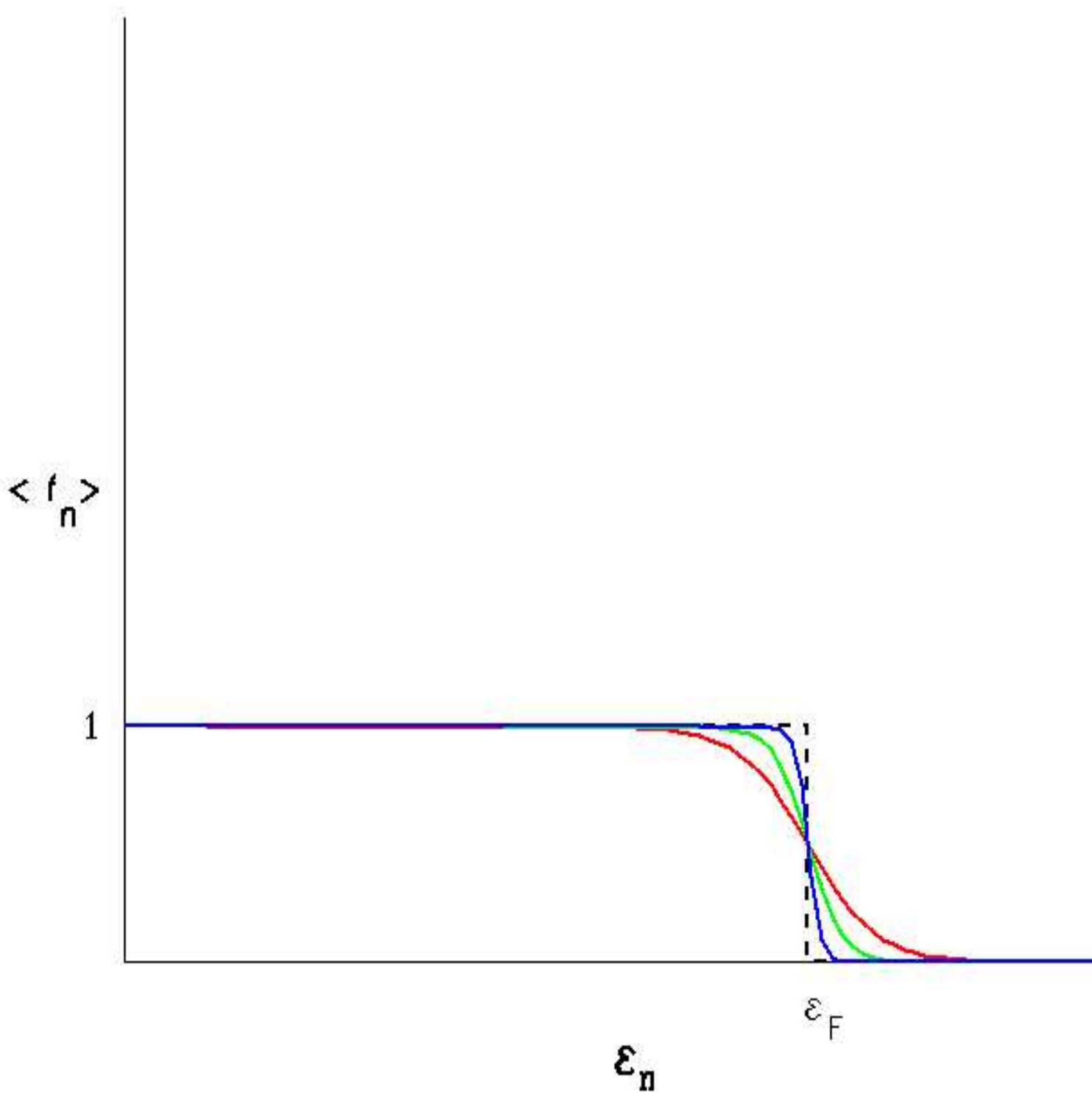


FIG. 2.

Thus, there is a finite probability that some of the levels just above the Fermi energy will become occupied as T is raised slightly above $T = 0$. At $T = 0$, the highest occupied energy eigenvalue must satisfy

$$\epsilon_n = \epsilon_F$$

$$\frac{2\pi^2 \hbar^2}{mL^2} |\mathbf{n}|^2 = \varepsilon_F$$

$$\frac{2\pi^2 \hbar^2}{mL^2} (n_x^2 + n_y^2 + n_z^2) = \varepsilon_F$$

This defines a spherical surface in \mathbf{n} space, which is known as the *Fermi Surface*. Note that the Fermi surface is only a sphere for the ideal gas. For systems in which interactions are included, the Fermi surface can be a much more complicated surface, and studying the properties of this surface is a task that occupies the time of many a solid-state physicist.

A. Zero-temperature thermodynamics

In order to derive an expression for the average particle number, recall that

$$\langle N \rangle = \sum_m \sum_{\mathbf{n}} \langle f_{\mathbf{n}m} \rangle = \sum_m \sum_{\mathbf{n}} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) = g \sum_{\mathbf{n}} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}})$$

In the thermodynamic limit, we may take the sum over to an integration:

$$\langle N \rangle = 4\pi g \int_0^\infty dn n^2 \theta(\varepsilon_F - \varepsilon_{\mathbf{n}})$$

But

$$\varepsilon_{\mathbf{n}} = \frac{2\pi^2 \hbar^2}{mL^2} n^2$$

Therefore, it proves useful to change variables of integration from n to $\varepsilon_{\mathbf{n}}$, using the above relation:

$$n = \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^{1/2} \varepsilon_{\mathbf{n}}^{1/2}$$

$$dn = \frac{1}{2} \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^{1/2} \varepsilon_{\mathbf{n}}^{-1/2}$$

Thus,

$$\begin{aligned} \langle N \rangle &= 4\pi g \int_0^\infty dn n^2 \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) \\ &= 2\pi \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon_{\mathbf{n}} \varepsilon_{\mathbf{n}}^{1/2} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) \\ &= 2\pi g \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} \\ \langle N \rangle &= \frac{4\pi g}{3} \left(\frac{m}{2\pi \hbar^2} \right)^{3/2} V \varepsilon_F^{3/2} \end{aligned}$$

In order to derive an expression for the average energy, recall that the energy eigenvalues were given by

$$E_{\{f_{\mathbf{n}}\}} = \sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m} \varepsilon_{\mathbf{n}}$$

Therefore, the average energy is given by

$$\langle H \rangle = E = \sum_m \sum_{\mathbf{n}} \langle f_{\mathbf{n}m} \rangle \varepsilon_{\mathbf{n}}$$

At $T = 0$, this becomes

$$\begin{aligned}
E &= g \sum_{\mathbf{n}} \theta(\varepsilon_{\text{F}} - \varepsilon_{\mathbf{n}}) \varepsilon_{\mathbf{n}} \\
&\rightarrow g \int d^3\mathbf{n} \theta(\varepsilon_{\text{F}} - \varepsilon_{\mathbf{n}}) \varepsilon_{\mathbf{n}} \\
&= 4\pi g \int_0^{\infty} dn n^2 \theta(\varepsilon_{\text{F}} - \varepsilon_{\mathbf{n}}) \varepsilon_{\mathbf{n}}
\end{aligned}$$

If the same change of variables is made, one finds that

$$\begin{aligned}
E &= 4\pi g \int_0^{\infty} d\varepsilon_{\mathbf{n}} \frac{1}{2} \left(\frac{mL^2}{2\pi^2\hbar^2} \right)^{3/2} \varepsilon_{\mathbf{n}}^{3/2} \theta(\varepsilon_{\text{F}} - \varepsilon_{\mathbf{n}}) \\
&= 2\pi g \left(\frac{m}{2\pi^2\hbar^2} \right)^{3/2} V \int_0^{\varepsilon_{\text{F}}} d\varepsilon_{\mathbf{n}} \varepsilon_{\mathbf{n}}^{3/2} \\
&= \frac{4\pi g}{5} \left(\frac{m}{2\pi^2\hbar^2} \right)^{3/2} \varepsilon_{\text{F}}^{5/2}
\end{aligned}$$

Thus, the average energy can be seen to be related to the average particle number by

$$E = \frac{3}{5} \langle N \rangle \varepsilon_{\text{F}}$$

which is clearly not 0 (as it would be classically).

Note that the pressure can be obtained simply in the following way: Recognize that

$$\frac{PV}{kT} = \frac{Vg}{\lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{5/2}} = \ln \mathcal{Z}(\zeta, V, T)$$

The energy is given by

$$E = - \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z}(\zeta, V, T) \right)_{\zeta, V}$$

Thus,

$$E = \frac{3}{2\beta} \frac{Vg}{\lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \zeta^l}{l^{5/2}}$$

Comparing these two equations for the energy and pressure shows that

$$E = \frac{3}{2} PV \quad \Rightarrow \quad P = \frac{2}{3} \frac{E}{V}$$

Note, that just like the energy, the pressure at $T = 0$ is not zero. The $T = 0$ values of both the energy and pressure are:

$$\begin{aligned}
E &= \frac{3}{5} \langle N \rangle \varepsilon_{\text{F}} \\
P &= \frac{2}{5} \frac{\langle N \rangle}{V} \varepsilon_{\text{F}}
\end{aligned}$$

These are referred to as the *zero-point* energy and pressure and are purely quantum mechanical in nature. The fact that the pressure does not vanish at $T = 0$ is again a consequence of the Pauli exclusion principle and the effective repulsive interaction that also showed up in the low density, high temperature limit. Using the expansion for $\rho\lambda^3$, we can derive the thermodynamics in this limit.

B. Thermodynamics at low temperature

Finite temperature thermal corrections can be obtained by starting with the expansion derived earlier: Note that

$$\begin{aligned}\rho\lambda^3 &= \frac{4g}{3\sqrt{\pi}} \left[(\ln \zeta)^{3/2} + \frac{\pi^2}{8} (\ln \zeta)^{-1/2} + \dots \right] \\ &= \frac{4g}{3\sqrt{\pi}} \left[\left(\frac{\mu}{kT} \right)^{3/2} + \frac{\pi^2}{8} \left(\frac{\mu}{kT} \right)^{-1/2} + \dots \right] \\ &= \frac{4g}{3\sqrt{\pi}} \left[\left(\frac{\mu}{kT} \right)^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 + \dots \right) \right]\end{aligned}$$

The term proportional to T^2 is a small thermal correction to the $T = 0$ limit. As such, it is small and we can replace the μ appearing there with $\mu_0 = \varepsilon_F$ to the same order in T :

$$\rho\lambda^3 = \frac{4g}{3\sqrt{\pi}} \left[\left(\frac{\mu}{kT} \right)^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{kT}{\varepsilon_F} \right)^2 + \dots \right) \right]$$

Solving this, now, for μ (which is equivalent to solving for ζ) gives

$$\begin{aligned}\mu &\approx kT \left[\frac{3\rho\lambda^3\sqrt{\pi}}{4g} \right]^{2/3} \frac{1}{\left[1 + \frac{\pi^2}{8} \left(\frac{kT}{\varepsilon_F} \right)^2 \right]^{2/3}} \\ &\approx \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 + \dots \right]\end{aligned}$$

where the second line is obtained by expanding $1/(1+x)^{2/3}$ about $x = 0$.

In order to obtain the thermal corrections, one must expand the average occupation number formula about the $\mu_0 = \varepsilon_F$ value using the expansion obtained above for μ and then do the integrals. The result is simply

$$E = \frac{3}{5} N \varepsilon_F \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\varepsilon_F} \right)^2 + \dots \right]$$

The thermal correction is necessary in order to obtain the heat capacity at constant volume, which is given by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Using the above expression for the energy, one finds

$$\frac{C_V}{\langle N \rangle k} = \frac{\pi^2 kT}{2\varepsilon_F}$$

From the thermally-corrected expression for the energy, the pressure can be obtained immediately:

$$P = \frac{2}{5} \rho \varepsilon_F \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\varepsilon_F} \right)^2 + \dots \right]$$