Apr. 22

Degenerate Quantum Gases

In the previous lecture, I introduced the Bose-Einstein and Fermi-Dirac quantum ideal gases. We worked out the basic formulae for the number density, energy, and entropy in these systems. We noted that, in the limit of low density, the quantum ideal gases have the classical ideal gas as a limit. In the limit of high density, there are interesting new behaviors, quite different from those of the classical idea gas. I will discuss the properties of the quantum idea gases at high density in this lecture.

Both high-density ideal gases have important physical applications. The dense Bose-Einstein gas exhibits *Bose condensation*, a phenomenon seen in low temperature He^4 and, more recently, in atomic gases at very low temperature. The dense Fermi-Dirac gas can be used to account *quantitatively* for the properties of electrons in metals. It is also applied to other dense collections of fermions, such as He^3 atoms in the liquid state and nucleons in atomic nuclei. The description is accurate despite the fact that the fermions have strong interactions. Landau explained this with the profound idea of *fermi liquid theory.*

I will begin with the fermion case. For definiteness, I will consider a dense gas of nonrelativistic fermions, for which

$$E(p) = \frac{p^2}{2m}$$

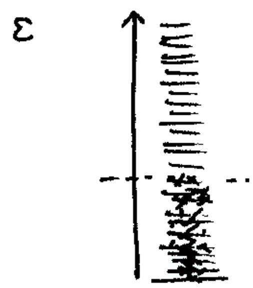
The average number of fermions in a quantum state is

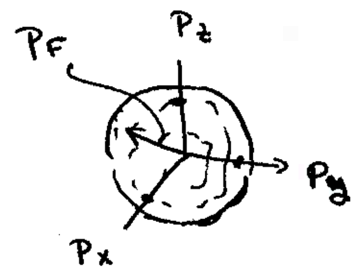
$$n(p) = \frac{1}{e^{\beta(E(p)-\mu)} + 1}$$

To begin our discussion, consider the implications of this formula at $T = 0$. The formula for the occupation number degenerates to

$$n(p) = \Theta(\mu - E(p)) = \begin{cases} 1 & E(p) < \mu \\ 0 & E(p) > \mu \end{cases}$$

This result actually accords with our intuition. At $T = 0$, the canonical ensemble becomes a projection onto the state of lowest energy. To find this state, for N fermions in a box of volume V, we must put the fermions into single-particle quantum states so that their total energy is as low as possible. Fermi-Dirac statistics dictate that there be at most one fermion per single-particle state. So we must fill the possible states from the bottom until we run out of particles.





The occupied states fill a sphere in momentum space. The radius of this sphere, p_F, is called the *Fermi momentum.* The corresponding energy

$$\varepsilon_F = \frac{p_F^2}{2m}$$

is called the *Fermi energy.* The surface of this sphere is also called the *Fermi surface.* Comparing to the expression above for the number density, we see that the chemical potential μ must be equal to the Fermi energy. The number density is then given in terms of μ by

$$N = gV \int \frac{d^3p}{(2\pi)^3} \; \theta(p_F - p)$$

$$\frac{p_F^2}{2m} = \varepsilon_F = \mu$$

Evaluating this expression, we find

$$N = \frac{gV}{2\pi^2} \int_0^{p_F} dp \, p^2 = \frac{gV}{2\pi^2} \frac{p_F^3}{3}$$

The fermions to which this analysis is typically applied—electrons, He^3 atoms, or nucleons—have spin $\frac{1}{2}$ and $g = 2$, so I will set $g = 2$ from here on. Then the Fermi momentum is given in terms of N by

$$p_F = \left(3\pi^2 N/V\right)^{1/3}$$

and the Fermi energy is

$$\epsilon_F = \frac{\left(3\pi^2 N/V\right)^{2/3}}{2m} = \frac{\left(3\pi^2 n\right)^{2/3}}{2m}$$

For conduction electrons in a metal,

$$n \sim 1/(1\,\text{Å})^3$$

giving

$$\epsilon_F \sim 10\,\text{eV}$$

So, at room temperature, $\epsilon_F \gg T$.

The degenerate Fermi gas has nontrivial thermodynamic relations even at $T = 0$. The total energy of the gas is

$$E = 2V \int_0^{p_F} \frac{d^3p}{(2\pi)^3} \frac{p^2}{2m}$$

$$= \frac{V}{\pi^2} \frac{1}{2m} \int_0^{p_F} dp\, p^4 = \frac{1}{5\pi^2} \frac{p_F^5}{2m} \cdot V$$

so that

$$E = N \cdot \frac{3}{5} \varepsilon_F$$

Notice the scaling that

$$E \sim \frac{N^{5/3}}{V^{2/3}}$$

Then the pressure of the Fermi gas is

$$P = - \left.\frac{\partial F}{\partial V}\right|_{T,N} = - \left.\frac{\partial E}{\partial V}\right|_{T,N} \text{ at } T = 0$$

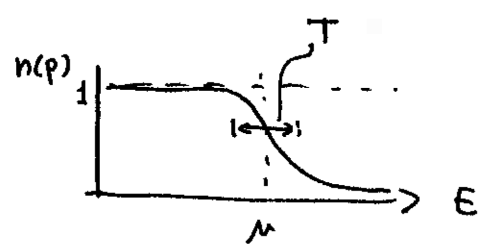
or

$$P = \frac{2}{3} \frac{E}{V}$$

The system has zero entropy, as required by the zeroth law since there is a unique ground state.

It is interesting, and important in the study of metals, to work out the properties of the fermion gas at a low but nonzero temperature:

$$0 < T \ll \varepsilon_F$$



In this case, $n(p)$ is not exactly a step function but rather makes a smooth transition from $n(p) \approx 1$ to $n(p) \approx 0$ in a small region near $E(p) = \mu$. The chemical potential remains close to the quantity ϵ_F computed above, but it might shift slightly as a function of T. To work out the properties of the gas as a function of T, we need to compute the thermodynamic functions for nonzero T and μ close to but not necessarily equal to ϵ_F and then eliminate μ in favor of N.

To compute thermodynamic functions, it would be useful to have an expansion for low temperature of the general integral

$$I = \int_0^\infty d\epsilon \; f(\epsilon) \; H(\epsilon)$$

where $f(\epsilon)$ is the Fermi function

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1}$$

and $H(\epsilon)$ is a smooth function, for example $H(\epsilon) = A\epsilon^n$. As $T \to 0$ or $\beta \to \infty$, this integral goes to

$$I \underset{T\to 0}{\longrightarrow} \int_0^\mu d\epsilon \; H(\epsilon)$$

We would like to compute the corrections to this limit for small T. I will now discuss a method for computing an expansion of these integrals in powers of T about the $T = 0$ result, called the *Sommerfeld expansion.*

Let

$$K(\epsilon) = \int_0^\epsilon d\epsilon' \; H(\epsilon')$$

Then we can make a first step toward evaluating the integral I by integrating by parts. This gives

$$I = f(\epsilon) K(\epsilon) \Big|_0^\infty - \int d\epsilon \, \frac{\partial f}{\partial \epsilon} K(\epsilon)$$

Since $f(\epsilon)$ falls off exponentially as $\epsilon \to 0$, the first term vanishes at the upper limit. It also vanishes at the lower limit if $H(\epsilon) \sim \epsilon^n$ with $n > 0$. To evaluate the second term, we need

$$\frac{\partial f}{\partial \epsilon} = -\frac{\beta e^{\beta(\epsilon-\mu)}}{\left(e^{\beta(\epsilon-\mu)}+1\right)^2} = -\frac{\beta}{\left(e^{\beta(\epsilon-\mu)}+1\right)\left(1+e^{-\beta(\epsilon-\mu)}\right)}$$

This very nice function falls off exponentially in both directions away from the Fermi energy! Then

$$I = \int_0^\infty d\epsilon \, \frac{\beta}{\left(e^{\beta(\epsilon-\mu)}+1\right)\left(1+e^{-\beta(\epsilon-\mu)}\right)} K(\epsilon)$$

and the result depends only on the behavior of $K(\epsilon)$ in the vicinity of $\epsilon = \mu$. To work out the integral further, expand $K(\epsilon)$ about this point,

$$K(\epsilon) = K(\mu) + (\epsilon-\mu) H(\mu) + \frac{(\epsilon-\mu)^2}{2} H'(\mu) + \cdots$$

Let

$$x = \beta(\epsilon-\mu) \qquad dx = \beta \, d\epsilon$$

Then

$$I = \int_{-\beta\mu}^{\infty} dx \, \frac{1}{(e^{x}+1)(1+e^{-x})} \left(K(\mu) + \frac{x}{\beta} H(\mu) + \frac{x^2}{2\beta^2} H'(\mu) + \cdots \right)$$

Since the first factor falls off exponentially away from $\epsilon = \mu$, we make negligible error in extending the range of the integral to $(-\infty, \infty)$. Since this factor is symmetric under $x \leftrightarrow -x$, the terms odd in x vanish. The even terms involve the integral

$$\int_{-\infty}^{\infty} dx \, \frac{x^{2n}}{(2n)!} \frac{1}{(e^{x}+1)(e^{-x}+1)} = 2 \int_{0}^{\infty} dx \, \frac{x^{2n}}{(2n)!} \frac{e^{-x}}{(1+e^{-x})^2}$$

$$= \frac{2}{(2n)!} \int_0^{\infty} dx \, x^{2n} \left(e^{-x} - 2e^{-2x} + 3e^{-3x} - \cdots \right)$$

$$= 2 \frac{1}{(2n)!} \left(\int_0^{\infty} dx \, x^{2n} e^{-x} \right) \left(1 - \frac{2}{2^{2n+1}} + \frac{3}{3^{2n+1}} - \cdots \right)$$

We saw this series in the previous lecture, and we evaluated it there in terms of the Riemann zeta function. Thus

$$= 2 \frac{1}{(2n)!} \Gamma(2n+1) \zeta(2n) \left(1 - \frac{1}{2^{2n-1}} \right) = 2\zeta(2n) \left(1 - \frac{1}{2^{2n-1}} \right)$$

Then, finally, the integral I takes the form

$$I = \int_0^{\infty} d\epsilon \, f(\epsilon) H(\epsilon) = \int_0^{\mu} d\epsilon \, H(\epsilon) + \sum_{n=1}^{\infty} 2\left(1 - \frac{1}{2^{2n-1}}\right) \zeta(2n) T^{2n} \left. \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon) \right|_{\epsilon=\mu}$$

or, more explicitly

$$\int_0^{\infty} d\epsilon \, f(\epsilon) H(\epsilon) = \int_0^{\mu} d\epsilon \, H(\epsilon) + \frac{\pi^2}{6} T^2 H'(\mu) + \cdots$$

We can use this expansion to analyze the number density and energy density in a fermion gas. For N,

$$N = 2V \int \frac{d^3p}{(2\pi)^3}\, n(p)$$

$$= \frac{1}{\pi^2} V \int dp\, p^2\, n(p)$$

so that

$$\frac{N}{V} = \frac{\sqrt{2}\, m^{3/2}}{\pi^2} \int d\varepsilon\, \sqrt{\varepsilon}\, f(\varepsilon)$$

Thus, for this case,

$$H = \frac{\sqrt{2}\, m^{3/2}}{\pi^2} \sqrt{\varepsilon}$$

Plugging into the master formula, we find

$$\frac{N}{V} = \frac{2}{3} \frac{\sqrt{2} m^{3/2}}{\pi^2} \mu^{3/2} + \frac{\pi^2}{6} T^2 \cdot \frac{1}{2} \frac{\sqrt{2} m^{3/2}}{\pi^2} \frac{1}{\sqrt{\mu}} + \cdots$$

I will take the zero-temperature value of the chemical potential to define the Fermi energy ϵ_F at all temperatures. Then we can write N/V in terms of ϵ_F,

$$N/V = \frac{2}{3} \frac{\sqrt{2} m^{3/2}}{\pi^2} \varepsilon_F^{3/2}$$

This gives μ at a nonzero temperature in terms of ϵ_F,

$$\varepsilon_F^{3/2} = \mu^{3/2} + \frac{\pi^2}{8} T^2 \frac{1}{\mu^{1/2}} + \cdots$$

The solution of this equation for μ is

$$\mu^{3/2} = \varepsilon_F^{3/2} - \frac{\pi^2}{8} T^2 \frac{1}{\varepsilon_F^{1/2}} + \cdots$$

or

$$\mu = \varepsilon_F - \frac{\pi^2}{12} \frac{T^2}{\varepsilon_F} + \cdots$$

We can evaluate the energy of the fermion gas in a similar way. Since

$$E = 2V \int \frac{d^3p}{(2\pi)^3} \frac{p^2}{2m} n(p)$$

the energy integral is given by

$$\mathcal{H} = \frac{\sqrt{2}\, m^{3/2}}{\pi^2} \cdot \varepsilon^{3/2}$$

Then

$$\frac{E}{V} = \frac{2}{5} \frac{\sqrt{2}\, m^{3/2}}{\pi^2} \mu^{5/2} + \frac{\pi^2}{6} T^2 \frac{3}{2} \frac{\sqrt{2}\, m^{3/2}}{\pi^2} \mu^{1/2} + \cdots$$

After plugging in the value of μ found above, the energy becomes

$$E/V = \frac{2}{5}\frac{\sqrt{2}\,m^{3/2}}{\pi^2}\left(\varepsilon_F^{5/2} - \frac{5\pi^2}{24}T^2\varepsilon_F^{1/2} + \cdots\right)$$

$$+ \frac{\pi^2}{6}T^2 \cdot \frac{3}{2}\cdot\frac{\sqrt{2}\,m^{3/2}}{\pi^2}\varepsilon_F^{1/2} + \cdots$$

$$= \frac{3}{5}\frac{N}{V}\varepsilon_F + \frac{N}{V}\frac{T^2}{\varepsilon_F}\pi^2\,\frac{3}{2}\left(-\frac{1}{12}+\frac{1}{4}\right) + \cdots$$

Then, finally,

$$E = \frac{3}{5}N\varepsilon_F + \frac{\pi^2}{4}N\frac{T^2}{\varepsilon_F} + \cdots$$

The derivative of this is the specific heat,

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \frac{\pi^2}{2}N\frac{T}{\varepsilon_F} + \mathcal{O}(T^3)$$

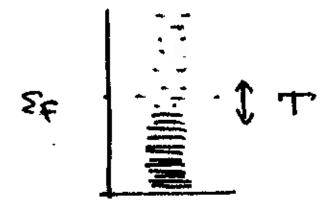
which we see is *linear* in T.

This formula contains quite a bit of physics. First, it is instructive to compare these formulae for the energy and specific heat to those for a classical ideal gas,

$$E = \frac{3}{2}NT \qquad C_V = \frac{3}{2}N$$

In a classical gas, all of the atoms can rearrange their positions in phase space in response to heating of the system. But in a degenerate fermion gas, most of the fermions are locked into place well below the Fermi energy. Only the fermions near the Fermi surface can absorb energy and change their state. At temperature T, only the fraction

$$T/\varepsilon_F$$



of the fermions are free to react to heating. This explains the general magnitude of the specific heat.

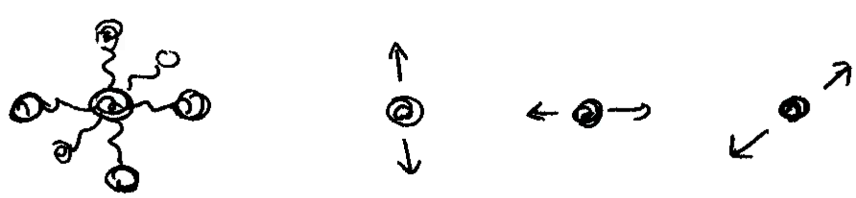
Next, we can apply the specific heat formula to build a theory of the specific heat of a metal. There are two major components. The electrons in the metal contribution a term in the specific heat proportional to T. If N_e is the number of conduction electrons, then

$$C_V\Big|_e = \frac{\pi^2}{2} N_e \frac{T}{\varepsilon_F}$$

The specific heat of a metal also receives a contribution from *phonons*, the quantized sound waves or atomic lattice vibrations. Phonons of small momentum have energy

$$E = c_s p$$

where c_s is the speed of sound. This relation is valid up to some momentum of the order of $\hbar/a$, where a is the spacing of the atoms in the metal. The corresponding phonon energy is typically greater than room temperature, so we can estimate the specific heat from phonons by assuming at this formula is valid for all p. For phonons, $g = 3$, corresponding to three possible directions of atomic vibrations



Then, using the formulae from the discussion of the photon gas in the previous lecture, we find for phonons

$$\frac{E}{V} = 3 \cdot \frac{\pi^2}{30} \frac{T^4}{c_s^3}$$

and thus

$$C_V \Big|_{ph} = \frac{6}{15} \pi^2 \frac{T^3}{c_s^3}$$

It is convenient to define the *Deybe momentum* p_D by the relation

$$N_{at}/V = \int_0^{p_D} \frac{d^3p}{(2\pi)^3}$$

where N_{at} is the number of atoms in the metal. Then

$$p_D = \left(6\pi^2 N_{at}/V\right)^{1/3}$$

and the corresponding phonon energy is

$$\omega_D = c_s p_D$$

This is called the *Debye energy* or the *Debye temperature*; it estimates the temperature at which the phonon dispersion relation ceases to be linear. In terms of ω_D, we can write the specific heat of phonons as

$$C_V \Big|_{ph} = \frac{12\pi^4}{5} N_{at} \left(\frac{T}{\omega_D}\right)^3$$

The phonon contribution depends on temperature as T^3, so one might think that the electron contribution would always dominate. However, in a typical metal, the characteristic temperatures for electrons and phonons are

$$\text{Fermi temperature} \qquad \frac{\varepsilon_F}{k_B} \sim \text{few} \times 10^4 \; {}^\circ K$$

$$\text{Debye temperature} \qquad \frac{\omega_D}{k_B} \sim \text{few} \times 10^2 \; {}^\circ K$$

But the numerical coefficients are quite different,

$$\frac{12\pi^4}{5} \Big/ \pi^2/2 \qquad = \quad 48.$$

Thus, if $N_{at} \sim N_e$, the two contributions are in the relation

$$\frac{c_V|_{ph}}{c_V|_e} \approx 50 \frac{(T/\omega_D)^3}{(T/\varepsilon_F)}$$

Then

$$\frac{c_V|_{ph}}{c_V|_e} \sim 10^6 \quad \text{at} \quad T = 300^\circ K$$
$$\text{(room temperature)}$$

but

$$\frac{c_V|_{ph}}{c_V|_e} \sim 1 \quad \text{at} \quad T = 1^\circ K$$

We can now turn to the analysis of the high-density behavior of the ideal Bose-Einstein gas. The mean occupation number in a Bose-Einstein gas is

$$n(p) = \frac{1}{e^{\beta(p^2/2m - \mu)} - 1}$$

This expression can become arbitrarily large, and it can even have a singularity if $\mu > 0$. Worse, if $\mu > 0$, then, for small p, $n(p)$ is negative,

$$n(p) = \frac{1}{e^{-\beta\mu} - 1} < 0 \quad \text{at} \quad |\vec{p}| = 0$$

which is nonsense from a physical point of view. Thus, for the Bose-Einstein gas, we must have

$$\mu < 0$$

For $\mu < 0$, $n(p, \beta, \mu)$ *decreases* as $|\mu|$ is increased. The value of μ is determined by the equation

$$N = gV \int \frac{d^3p}{(2\pi)^3} \frac{1}{[e^{\beta(p^2/2m - \mu)} - 1]}$$

If N/V is small, we can choose a large negative value of μ that satisfies this equation. If we then increase N/V, we can continue to find a solution by making μ less negative. However, it is possible that taking $\mu \to 0^-$ in the equation corresponds to a finite value of N, which I will call $\overline{N}$. For $N > \overline{N}$, we have a problem, because we apparently can no longer adjust μ to produce such a large value of N.

To make this problem more concrete, I will compute $\overline{N}$. From here on, I will set $g = 1$, the value of g for He^4. The condition for $\overline{N}$ is

$$\overline{N} = V \int \frac{d^3p}{(2\pi)^3} \frac{1}{e^{\beta p^2/2m} - 1}$$

We can readily evaluate the integral.

$$\bar{N}/V = \frac{1}{2\pi^2} \int_0^\infty dp \; p^2 \; \frac{1}{e^{\beta p^2/2m} - 1}$$

Let $x = \beta p^2/2m$, $dx = \beta p dp/m$. Then

$$\bar{N}/V = \frac{1}{\sqrt{2}\,\pi^2} \left(\frac{m}{\beta}\right)^{3/2} \int_0^\infty dx \; x^{1/2} \frac{1}{e^x - 1}$$

$$= \frac{1}{\sqrt{2}\,\pi^2} \left(\frac{m}{\beta}\right)^{3/2} \int_0^\infty dx \; x^{1/2} \left(e^{-x} + e^{-2x} + e^{-3x} + \cdots\right)$$

so that

$$\bar{N}/V = \frac{1}{\sqrt{2}\,\pi^2} \left(\frac{m}{\beta}\right)^{3/2} \Gamma(3/2)\, \zeta(3/2)$$

Since $\Gamma(\frac{3}{2}) = \sqrt{\pi}/2$, this is

$$\frac{\bar{N}}{V} = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \cdot \zeta(3/2)$$

with $\zeta(\frac{3}{2}) = 2.612...$ The limit $\mu \to 0$ from below then gives the limiting density of bosons,

$$N \underset{\mu \to 0^-}{\longrightarrow} \bar{N}(T) = 2.61 \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

The quantity in parentheses is the thermal de Broglie wavelength of a boson.

It must be possible to arrange for an N larger than $\overline{N}$, but how? Notice that, if μ is very close to zero, the value of $n(p)$ for the very lowest discrete one-particle state at $\vec{p} = 0$ is

$$n(\vec{p}=0) = \frac{1}{e^{-\beta\mu} - 1} \cong \frac{1}{\beta|\mu|}$$

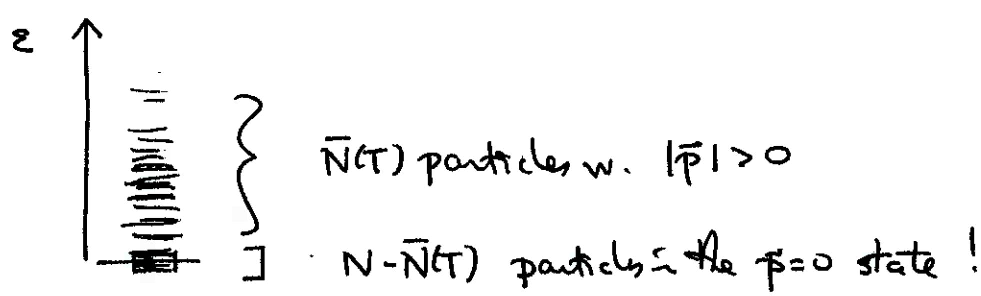
This can itself become arbitrarily large as $\mu \to 0^-$. We can then satisfy the equation for μ by setting

$$n(\vec{p}=0) = N - \overline{N}$$

which requires

$$\mu = -\frac{1}{\beta\,(N - \overline{N})}$$

This leads to the following curious situation:



We have $\overline{N}$ particles in quantum states with finite $\vec{p}$, but also a macroscopic number of particles $(N - \overline{N})$ in the single quantum state with $\vec{p} = 0$. This is called *Bose-Einstein condensation.*

To observe Bose-Einstein condensation, we would start with N particles in a volume V at a high temperature, such that $N < \overline{N}(T)$. We would then lower the temperature. Since $\overline{N} \sim T^{3/2}$, we would eventually find a temperature T_c where

$\overline{N}(T_c) = N$. Below this temperature, the Bose-Einstein condensate would form. The expression for T_c is

$$T_c = \left(\frac{2\pi\hbar^2}{m}\right)\left(\frac{N}{V}\frac{1}{\eta(3/2)}\right)^{2/3}$$

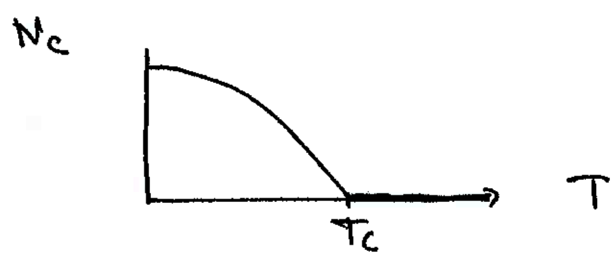
If we now decreased the temperature further, the number of particles in condensate would increase according to

$$N_c = N - \overline{N}(T) = \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \eta(3/2)\left(T_c^{3/2} - T^{3/2}\right)$$

or, more simply

$$N_c = N\left(1 - \frac{T}{T_c}\right)^{3/2}$$

Notice that this behavior is non-analytic in T at $T = T_c$,



Similarly, though the specific heat of an ideal Bose-Einstein gas is continuous at T_c, the slope of the quantity

$$\left.\frac{\partial c_V}{\partial T}\right|_{V,N}$$

is discontinuous at T_c. This is our first example of non-analytic behavior of thermodynamic quantities at a specific transition temperature. Such non-analytic behavior occurs in many thermodynamic systems. It is associated with changes of thermodynamic phase. We will study such singularities in detail in the rest of this course.