Chapter 19

Bose Condensation

We now turn to the low temperature limit of Bosons. In that case we have

$$N = \sum_j n_j, \quad n_j = \frac{1}{e^{\beta(e_j - \mu)} - 1}. \quad (19.1)$$

Because we require $0 \leq n_j < \infty$ we must have $\mu < \epsilon_0$, where $\epsilon_0$ is the lowest energy level. If, as before we write this as an integral, for a particle of zero spin, and mass $m$,

$$N = \frac{2\pi V}{(2\pi\hbar)^3} \frac{\epsilon^{1/2}}{e^{\beta(\epsilon - \mu)} - 1}. \quad (19.2)$$

But since $\epsilon_0 = 0$, we must have $\mu \leq 0$, and so $e^{-\beta\mu} \geq 0$, and we have the inequality

$$N \leq \frac{2\pi V}{(2\pi\hbar)^3} \frac{\epsilon^{1/2}}{e^{\beta\epsilon} - 1} = \frac{2\pi V}{(2\pi\hbar)^3} \beta^{-3/2} \int_0^{\infty} dx \frac{x^{1/2}}{e^x - 1}. \quad (19.3)$$

where the integral is [Eq. (7.16)]

$$\Gamma(3/2)\zeta(3/2) = \frac{\sqrt{\pi}}{2} (2.612 \ldots). \quad (19.4)$$

Thus, we obtain an inequality

$$\frac{N}{V} \leq 2.612 \left[\frac{2\pi mkT}{(2\pi\hbar)^3}\right]^{3/2}, \quad (19.5)$$

which cannot be true as $T \to 0$, since the density cannot go to zero if $N$ and $V$ are fixed.

How is this paradox resolved? The ground state, which is counted in the integral with zero weight, actually must have macroscopic occupation number.
Indeed, if $T_0$ is the temperature for which the equality in the above occurs, the number of particles in the excited states (other than the ground state) is for $T < T_0$,

$$\frac{N'}{N} = \left( \frac{T}{T_0} \right)^{3/2},$$

(19.6)

and the fraction of particles in the ground state is

$$\frac{N_0}{N} = \frac{N - N'}{N} = 1 - \left( \frac{T}{T_0} \right)^{3/2}.$$  

(19.7)

This says, at zero temperature, that all the particles are in the ground state. This, presumably, is the origin of superfluidity. Liquid He$^4$ becomes superfluid at the so-called lambda point, $T_\lambda = 2.19$K. [Numerically, we have

$$T_0 = \frac{\hbar^2}{2\pi mk} \left( \frac{N}{V} \right)^{2/3} \left( \frac{1}{2.612} \right)^{2/3},$$

(19.8)

which if the density and mass for He is inserted gives 3.13 K, not bad, considering interactions are not included.

Do the other states have macroscopic occupation? No. For example, with $\epsilon_0 = 0$, $\langle n_0 \rangle = -\frac{1}{\beta\mu}$, so $-1/\mu \sim \beta N$, and we recall, from Eq. (11.12), that the energy of the first excited state $\epsilon \sim V^{-2/3}$. Then the relative number of atoms in the first excited state is

$$\frac{\langle n_1 \rangle}{\langle n_0 \rangle} = \frac{e^{\beta(\epsilon_0 - \mu)} - 1}{e^{\beta(\epsilon_1 - \mu)} - 1} \approx -\frac{\mu}{\epsilon_1 - \mu}. $$

(19.9)

Thus

$$\frac{\langle n_1 \rangle}{\langle n_0 \rangle} \approx \frac{1}{1 + N/V^{2/3}kT} \sim \frac{\left( \frac{N}{V} \right)^{-2/3}}{N^{1/3}}.$$  

(19.10)

which goes to zero as $T \to 0$. For $N = 10^{22}$, and [Eq. (11.15)] $\epsilon_1 \sim 10^{-18}$ eV $\sim 10^{-14}$ K, the relative occupation number of the first excited state at $T = 1$ K is

$$\frac{\langle n_1 \rangle}{\langle n_0 \rangle} \sim \frac{1}{\beta N\epsilon_1} \sim 10^{-8}. $$

(19.11)

Let’s calculate the number of particles in excited states:

$$N' = \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \int_0^\infty \frac{d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}\epsilon^{1/2},$$

$$= \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{1/2} \zeta e^{-\beta \epsilon}}{1 - \zeta e^{-\beta \epsilon}},$$

$$= \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \sum_{n=1}^\infty \int_0^\infty d\epsilon \epsilon^{1/2} (\zeta e^{-\beta \epsilon})^n,$$

$$= \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \sum_{n=1}^\infty \zeta^n (\beta n)^{-3/2} \Gamma(3/2) = \frac{V (2\pi mkT)^{3/2}}{(2\pi \hbar)^3} \sum_{n=1}^\infty \frac{\zeta^n}{n^{3/2}},$$

(19.12)
where $\zeta = e^{\beta \mu}$. Similarly, since the ground is taken to have zero energy, the total energy has contributions only from excited states,

$$U = \frac{2\pi V}{(2\pi \hbar)^3} (2m)^{3/2} \sum_{n=1}^{\infty} \int_0^\infty d\varepsilon \varepsilon^{3/2} (\zeta e^{-\beta \varepsilon})^n$$

$$= \frac{3}{2} V \frac{(2\pi mkT)^{3/2}}{(2\pi \hbar)^3} kT \sum_{n=1}^{\infty} \zeta^n n^{3/2}.$$  \hspace{1cm} (19.13)

For $T < T_0$, $\mu = 0$ or $\zeta = 1$, so

$$\frac{U}{N'} = \frac{3}{2} kT \zeta^{(5/2)}  = 0.513 \frac{3}{2} kT,$$ \hspace{1cm} (19.14)

$$\frac{U}{N} = \frac{U}{N'} N = 0.513 \frac{3}{2} kT \left( \frac{T}{T_0} \right)^{3/2}, \hspace{1cm} (19.15)$$

and the specific heat is

$$c_v = \frac{dU}{dT} = 0.513 \frac{3}{2} k N \left( \frac{T}{T_0} \right)^{3/2} = 1.28 \frac{3}{2} k \left( \frac{T}{T_0} \right)^{3/2}.$$ \hspace{1cm} (19.16)

Note that this exceeds the equipartition value for $T = T_0$.

For $T \gg T_0$, $\mu < 0$ and $\zeta < 1$, and $N' = N$. Then

$$N = V \frac{(2\pi mkT)^{3/2}}{(2\pi \hbar)^3} \zeta \left( 1 + \frac{\zeta}{2^{3/2}} + \ldots \right)$$

$$= N(T = T_0) = V \frac{(2\pi mkT_0)^{3/2}}{(2\pi \hbar)^3} 2.612,$$ \hspace{1cm} (19.17)

so if $\zeta \ll 1$,

$$\zeta = 2.612 \left( \frac{T_0}{T} \right)^{3/2}.$$ \hspace{1cm} (19.18)

Then, perturbatively,

$$\frac{U}{N} = \frac{3}{2} kT \left( \frac{\zeta + \zeta^{2} + \ldots}{\zeta + \frac{\zeta}{2^{3/2}} + \ldots} \right) = \frac{3}{2} kT \left( 1 - \frac{\zeta}{4\sqrt{2}} \right)$$

$$= \frac{3}{2} kT \left( 1 - \frac{2.612}{4\sqrt{2}} \left( \frac{T_0}{T} \right)^{3/2} \right),$$ \hspace{1cm} (19.19)

and then the specific heat is

$$c_v = \frac{3}{2} Nk \left( 1 + 0.23 \left( \frac{T_0}{T} \right)^{3/2} \right).$$ \hspace{1cm} (19.20)

Note that as $T \rightarrow T_0$ from above, we get close to the same number as in Eq. (19.16), from below.
Finally, let us discuss thermodynamic quantities for $T < T_0$: The entropy is

$$S = \int_0^T dT \frac{C_V}{T} = N k (1.28) \left( \frac{T}{T_0} \right)^{3/2}.$$  \hspace{1cm} (19.21)

The Helmholtz free energy is

$$F = U - T S = 0.513 N k T \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{3}{2} - \frac{5}{2} \right) = -0.513 N k T \left( \frac{T}{T_0} \right)^{3/2} = -\frac{2}{3} U.$$  \hspace{1cm} (19.22)

which last relation is already known—see Eq. (17.26) (recall $\mu = 0$ here). From this it follows that the pressure is

$$p = \frac{2}{3} \frac{U}{V} = 0.513 \frac{N k T_0}{V} \left( \frac{T}{T_0} \right)^{5/2}.$$  \hspace{1cm} (19.23)