Unit 3-11: The Ideal Bose Gas and Bose-Einstein Condensation

We now turn to the ideal (non-interacting particles) gas of bosons. The Bose occupation function for the average number of particles in a state with energy ϵ is,

$$n(\epsilon) = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon} - 1} \qquad \text{where } z \text{ is the fugacity, } z = \mathrm{e}^{\beta\mu} \geq 0 \tag{3.11.1}$$

Here we will consider spin-zero free bosons (particles in a box) with $\epsilon_{\mathbf{k}} = \hbar^2 k^2/2m$ and spin degeneracy $g_s = 1$.

Recall, for the occupation number $n(\epsilon_{\mathbf{k}})$ to remain positive at $\mathbf{k} = 0$, we need

$$n(\epsilon_{\mathbf{k}} = 0) = \frac{1}{z^{-1} - 1} = \frac{z}{1 - z} \geq 0 \qquad \Rightarrow \qquad z \leq 1 \qquad \Rightarrow \qquad \mu = k_B T \ln z \leq 0. \tag{3.11.2}$$

The density of particles is given by,

$$n = \frac{N}{V} = \frac{1}{V}\sum_{\mathbf{k}} n(\epsilon_{\mathbf{k}}) = \frac{1}{V(\Delta k)^3}\int_{-\infty}^{\infty} d^3k\, n(\epsilon_{\mathbf{k}}) = \frac{1}{(2\pi)^3}\int_0^{\infty} dk\, 4\pi k^2\, \frac{1}{z^{-1}\mathrm{e}^{\beta\hbar^2 k^2/2m} - 1} \tag{3.11.3}$$

Making a substitution of variables in the integration, $y = \beta\hbar^2 k^2/2m \;\Rightarrow\; k = \sqrt{2my/\beta\hbar^2}$ and $dk = \sqrt{2my/\beta\hbar^2}(dy/2y)$, we get

$$n = \frac{N}{V} = \left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \frac{4\pi}{(2\pi)^3}\,\frac{1}{2}\int_0^{\infty} dy\, \frac{y^{1/2}}{z^{-1}\mathrm{e}^{y} - 1} = \frac{1}{\lambda^3}\, g_{3/2}(z) \tag{3.11.4}$$

where $\lambda = (h^2/2\pi m k_B T)^{1/2}$ is the thermal wavelength, and

$$g_{3/2}(z) = \frac{2}{\sqrt{\pi}}\int_0^{\infty} dy\, \frac{y^{1/2}}{z^{-1}\mathrm{e}^{y} - 1} = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots \tag{3.11.5}$$

is one of the standard functions for bosons from Notes 3-8. Because the signs of all the terms in the series expansion of $g_{3/2}(z)$ are positive, and since $0 \leq z = \mathrm{e}^{\beta\mu} \leq 1$, we have that $g_{3/2}(z)$ is a monotonic increasing function of z for $0 \leq z \leq 1$.

As $z \to 1$, $g_{3/2}(z)$ approaches a *finite* constant,

$$g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots = \zeta(3/2) \simeq 2.612 \qquad \text{where } \zeta(x) \text{ is the Reimann zeta function.} \tag{3.11.6}$$

To see that $g_{3/2}(1)$ is finite, consider the following.

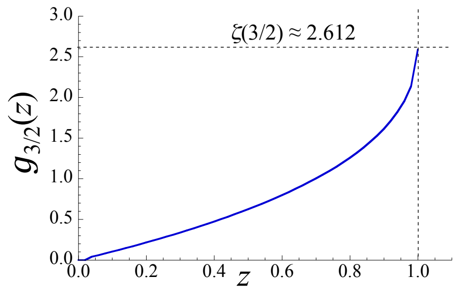
$$g_{3/2}(1) = \frac{2}{\sqrt{\pi}}\int_0^{\infty} dy\, \frac{y^{1/2}}{\mathrm{e}^{y} - 1} \qquad \text{as } y \to \infty, \text{ the integral converges since the integrand} \sim y^{1/2}e^{-y}. \tag{3.11.7}$$

The integrand is largest at *small* y (recall, small y corresponds to low energy where $n(\epsilon)$ is largest). To see the behavior of the integral as $y \to 0$, we can expand the integrand for small y,

$$\frac{y^{1/2}}{\mathrm{e}^{y} - 1} \approx \frac{y^{1/2}}{1 + y - 1} = \frac{1}{y^{1/2}} \qquad \text{for small } y. \tag{3.11.8}$$

so for the small y part of the integral, say from $y = 0$ to some $y = y^* \ll 1$, we have,

$$\int_0^{y^*} dy\, \frac{y^{1/2}}{\mathrm{e}^{y} - 1} \approx \int_0^{y^*} dy\, \frac{1}{y^{1/2}} = 2y^{1/2}\Big|_0^{y^*} = 2{y^*}^{1/2} \quad \text{is finite.} \tag{3.11.9}$$



Therefore the integral for $g_{3/2}(1)$ converges at its lower limit $y \to 0$, and it converges at its upper limit $y \to \infty$, so $g_{3/2}(1)$ is finite. Since $g_{3/2}(z)$ is monotonic increasing in z, then $g_{3/2}(z)$ is finite for all $0 \le z \le 1$.

So we conclude,

$$n = \frac{N}{V} = \frac{g_{3/2}(z)}{\lambda^3} \le \frac{g_{3/2}(1)}{\lambda^3} = \frac{2.612}{\lambda^3} = 2.612\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{3.11.10}$$

The goal is then to find the value of z that gives the desired particle density n.

But we now have a contradiction! For a system with a fixed density of bosons n, as T decreases we will eventually get to a temperature below which the right most side of the above equation is less than n, and so the above equation must be violated! This happens at a critical temperature T_c where,

$$n = \frac{N}{V} = 2.612\left(\frac{2\pi m k_B T_c}{h^2}\right)^{3/2} \qquad \Rightarrow \qquad T_c = \left(\frac{n}{2.612}\right)^{2/3}\frac{h^2}{2\pi m k_B} \tag{3.11.11}$$

Thus, for $T = T_c$ we can satisfy Eq. (3.11.10) by the choice $z = 1$. For $T > T_c$ we can satisfy Eq. (3.11.10) by choosing an appropriate value of $z < 1$. But there is no value of z that can satisfy Eq. (3.11.10) when $T < T_c$.

<u>The solution to this paradox</u> is as follows.

When doing the sum over $\mathbf{k}$ to compute $n = N/V$ we made the approximation

$$\frac{1}{V}\sum_{\mathbf{k}} n(\epsilon_{\mathbf{k}}) \;\to\; \frac{1}{V(\Delta k)^3}\int_{-\infty}^{\infty} d^3k\, n(\epsilon_{\mathbf{k}}) = \frac{1}{(2\pi)^3}\int_0^{\infty} dk\, 4\pi k^2\, n(\epsilon_{\mathbf{k}}) \tag{3.11.12}$$

This approximation is usually exact when $V = L^3 \to \infty$ since then $\Delta k = 2\pi/L \to 0$ and the above is just the definition of an integral. But a problem can arise if $n(\epsilon_k)$ becomes singular. And in our case, $n(0) = n(\epsilon_{\mathbf{k}=0}) = z/(1-z)$ does become singular as $z \to 1$, which happens as T decreases to T_c.

When we make the above approximation to the sum, we are giving a weight $4\pi k^2/(2\pi^3)$ to the states with wavenumber $|\mathbf{k}|$. This gives *zero* weight to the state $\mathbf{k} = 0$, i.e. to the ground state. But as T decreases, more and more bosons will occupy the ground state, as it has the lowest energy. And as $T \to T_c$, and $z \to 1$, the number of bosons that can be in this ground state, $n(0) = z/(1-z)$, diverges. Replacing the sum by the integral therefore will not take into account this divergence of $n(0)$ as $z \to 1$, since it counts the state $\mathbf{k} = 0$ with zero weight. We therefore need to explicitly separate the ground state from the rest of the sum, and then we can write,

$$n = \frac{N}{V} = \frac{1}{V}\sum_{\mathbf{k}} n(\epsilon_{\mathbf{k}}) = \frac{n(0)}{V} + \frac{1}{(2\pi)^3}\int_0^{\infty} dk\, 4\pi k^2\, n(\epsilon_{\mathbf{k}}) = \frac{1}{V}\frac{z}{1-z} + \frac{1}{(2\pi)^3}\int_0^{\infty} dk\, 4\pi k^2\, n(\epsilon_{\mathbf{k}}) \tag{3.11.13}$$

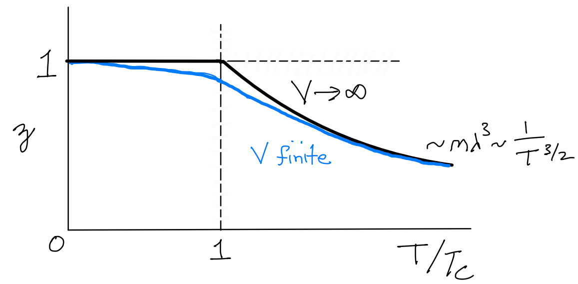
$$= \frac{1}{V}\frac{z}{1-z} + \frac{g_{3/2}(z)}{\lambda^3} \tag{3.11.14}$$

For $T > T_c$, where $z < 1$, the first term above from the ground state is finite, and will vanish in the thermodynamic limit $V \to \infty$. We then regain Eq. (3.11.10). However, for $T < T_c$ and finite V, we can avoid our paradox by choosing z as close to unity as needed, so that the first term in Eq. (3.11.14) becomes as large as needed to give the desired particle density n. This puts all the "missing" particles in the ground state. As $V \to \infty$, to keep the first term finite, we need to have $z \to 1$ (since $1/(\infty \times 0)$ is indeterminant). Thus we have the following in the thermodynamic limit $V \to \infty$: For $T > T_c$, $z < 1$ is chosen so that n is given by Eq. (3.11.10) and the first term in Eq. (3.11.14), $n(0)/V$, vanishes. For $T < T_c$, $z = 1$ and the density of particles in the ground state $n(0)/V$ is given by,

$$\frac{n(0)}{V} = n - \frac{g_{3/2}(1)}{\lambda^3} \tag{3.11.15}$$

Exactly at $T = T_c$, $z = 1$ and $n(0)/V = 0$.

Thus, above T_c the density of particles in the ground state $n(0)/V$ is zero. However, as T decreases below T_c, the density of particles in the ground state $n(0)/V$ increases from zero and becomes finite. As $T \to 0$, and $\lambda \to \infty$, all the particles go into the ground state and $n(0)/V \to n$ the total density of particles. T_c, given by Eq. (3.11.11), is the *Bose-Einstein condensation temperature*. For $T < T_c$, a finite fraction of the particles are in the ground state.



We can summarize the above by the sketch on the right. For finite V, it is always possible at any T to find a $z < 1$ so that the the density n is given by Eq. (3.11.14). But as $V \to \infty$, the only way to satisfy Eq. (3.11.14) is to have $z = 1$ for all $T \le T_c$. Thus, as $V \to \infty$, the fugacity $z(T)$ has a singular behavior at $T = T_c$. We will see in Unit 4 that this is a general property of phase transitions. A true singular behavior at a phase transition exists only in the thermodynamic limit $V \to \infty$. Note, at large T we approach the classical limit where, from the discussion in Notes 3-8 following Eq. (3.8.30), we have $z = n\lambda^3 \sim 1/T^{3/2}$.

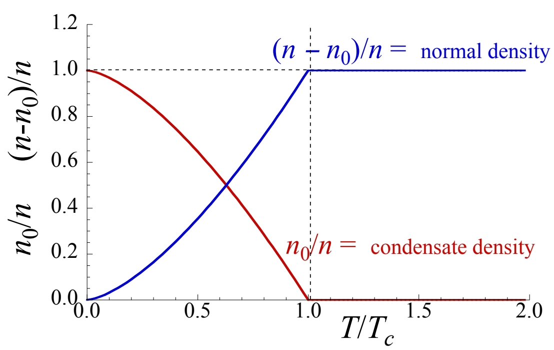
$$\text{For } V \to \infty \qquad \left.\begin{aligned} z(T) &\to 1 \\ \mu(T) &\to 0 \end{aligned}\right\} \quad \text{as } T \to T_c, \qquad \left.\begin{aligned} z(T) &= 1 \\ \mu(T) &= 0 \end{aligned}\right\} \quad \text{for } T \le T_c. \tag{3.11.16}$$

For $T \le T_c$, we have from Eq. (3.11.15), that the density of particles in the ground state is,

$$\frac{n(0)}{V} = n - \frac{g_{3/2}(1)}{\lambda^3} = n - 2.612\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \tag{3.11.17}$$

Using T_c from Eq. (3.11.11) we then get,

$$\boxed{n_0 \equiv \frac{n(0)}{V} = n\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]} \tag{3.11.18}$$



For $T < T_c$, the particles in the ground state are called the *condensate*. The density of particles in the ground state $n(0)/V$ is called the *condensate density*. The remaining particles in excited states, $n - n_0$, is called the *normal density*.

Close to T_c, with $T = T_c - \delta T$ and $\delta T \ll T_c$, we have $1 - (T/T_c)^{3/2} \approx (3/2)(\delta T/T_c)$. So the condensate density n_0 vanishes linearly as $T \to T_c$ from below.

The state at $T > T_c$ is often called the *normal state*, since here the normal density is equal to total particle density. The state at $T = 0$ is when the condensate density equals the total particle density. The state at $0 < T < T_c$ is often called the *mixed state*, since here we have both condensate *and* normal particles.

<u>Pressure</u>

We now consider what effect Bose-Einstein condensation might have on the pressure of the ideal Bose gas.

For the pressure we have,

$$\frac{p}{k_B T} = \frac{1}{V}\ln\mathcal{L} = -\frac{1}{V}\sum_{\mathbf{k}}\ln\left[1 - z\mathrm{e}^{-\beta\epsilon_{\mathbf{k}}}\right] \tag{3.11.19}$$

So like we did with the density N/V, we will first split off the ground state contribution, and then approximate the remaining terms in the sum with an integral,

$$\frac{p}{k_BT} = -\frac{1}{V}\ln(1-z) - \frac{1}{(2\pi)^3}\int_0^\infty dk\, 4\pi k^2\, \ln\left[1 - z\mathrm{e}^{-\beta\hbar^2k^2/2m}\right] \tag{3.11.20}$$

$$= \frac{1}{V}\ln\left(\frac{1}{1-z}\right) + \frac{g_{5/2}(z)}{\lambda^3} \tag{3.11.21}$$

where $g_{5/2}(z) = \dfrac{1}{\Gamma(5/2)}\displaystyle\int_0^\infty dy\, \frac{y^{3/2}}{z^{-1}\mathrm{e}^y - 1}$ is one of the Bose standard functions, as we discussed in Notes 3-8.

Now, as we discussed above, the number of bosons that occupy the ground state is,

$$n(0) = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon_{\mathbf{k}=0}} - 1} = \frac{1}{z^{-1}-1} = \frac{z}{1-z} \qquad \Rightarrow \qquad n(0)+1 = \frac{z}{1-z} + 1 = \frac{1}{1-z} \tag{3.11.22}$$

So,

$$\frac{p}{k_BT} = \frac{1}{V}\ln\Big(n(0)+1\Big) + \frac{g_{5/2}(z)}{\lambda^3} \tag{3.11.23}$$

In the thermodynamic limit $V \to \infty$, the first term vanishes, since $n(0) \le N = nV$ and $\lim_{V\to\infty}\left[\frac{1}{V}\ln(nV+1)\right] = 0$, since $\ln V$ grows less rapidly than does V.

So the condensate does *not* contribute anything to the pressure!

We have,

$$\frac{p}{k_BT} = \frac{g_{5/2}(z)}{\lambda^3} = g_{5/2}(z)\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} \qquad \Rightarrow \qquad p = g_{5/2}(z(T))\left(\frac{2\pi m}{h^2}\right)^{3/2}(k_BT)^{5/2} \tag{3.11.24}$$

Recall, for a system of fixed density n, $z(T)$ must be chosen to be a function of T that gives the desired density n.

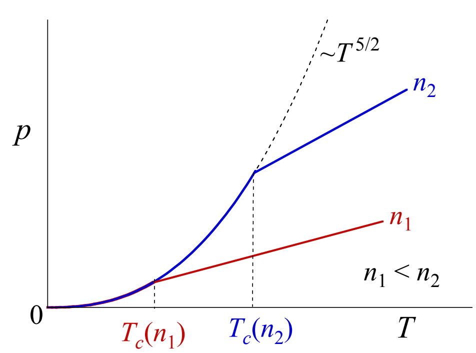
In the thermodynamic limit of $V \to \infty$, we have $z = 1$ for all $T \le T_c(n)$, and $g_{5/2}(z=1) = \zeta(5/2) = 1.342$ is finite.

Therefore, for $T \le T_c(n)$ (the critical temperature depends on the system's fixed density), we have,

$$p = g_{5/2}(1)\left(\frac{2\pi m}{h^2}\right)^{3/2}(k_BT)^{5/2} = 1.342\left(\frac{2\pi m}{h^2}\right)^{3/2}(k_BT)^{5/2} \tag{3.11.25}$$

For $T \le T_c$, the pressure $p \propto T^{5/2}$ is *independent of the system density!*

On the right we sketch curves of p vs T at constant density n (isochores). The isochores for different n are the same $\sim T^{5/2}$ curve provided $T < T_c(n)$, since in the mixed state p is independent of n. From Eq. (3.11.11) we have $T_c(n) \sim n^{2/3}$. As T increases above $T_c(n)$ the isochores depart from the common $\sim T^{5/2}$ curve, and at large T approaching the classical limit, $p = nk_BT$.

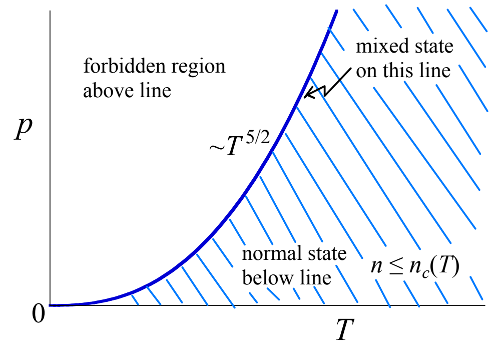


We can define $n_c(T)$ as the inverse of $T_c(n)$. From Eq. (3.11.11) we have,

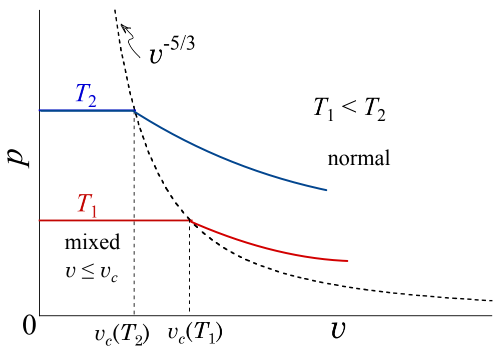
$$n_c(T) = 2.612\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2} \tag{3.11.26}$$

$n_c(T)$ is the critical density at a given T. At fixed T, a system with density $n > n_c(T)$ will be in a Bose condensed mixed. A system with $n < n_c(T)$ will be in the normal state.

We can now draw the phase diagram in the $p-T$ plane. The mixed state for $n > n_c(T)$ is represented by the single line $\propto T^{5/2}$, no matter what the density n of the system. This is because, at fixed T, p is independent of n in the mixed state. The normal state is represented by the region below this line; at fixed T, this is when $n < n_c(T)$. The region above the line is the "forbidden region." No value of T and n will result in a pressure p that lies in this region.



One can also consider the Bose-Einstein condensation transition in terms of the variables p and $v = V/N = 1/n$, the specific volume. At the transition we have $p \propto [T_c(n)]^{5/2}$ and $T_c(n) \propto n^{2/3}$. Therefore, at the transition, $p \propto (n^{2/3})^{5/2} = n^{5/3} = v^{-5/3}$. Curves of p vs v at different constant T (isotherms) therefore look as in the sketch on the right. For $v < v_c(T)$, one is in the mixed state where p is independent of the density n, and hence independent of $v = 1/n$; the isotherms in this region are therefore straight horizontal lines. As v increases above $v_c(T)$, the isotherms of p vs v decrease. At high T, where one approaches the classical limit, one has $p \sim 1/v$ (from $p = nk_BT = k_BT/v$).



Thermodynamic functions

The above are the main things you should know. But one can continue and ask about the thermodynamic properties of the ideal Bose gas.

Specific heat at constant volume

In particular we now want to compute the specific heat at constant volume, C_V, of the ideal Bose gas, and see how it behaves at the Bose-Einstein transition T_c. The calculation is a bit tedious.

Earlier in Eq. (3.8.19) we had found $\dfrac{E}{V} = \dfrac{3}{2}p$. Therefore,

$$\frac{E}{N} = \frac{3}{2}\frac{pV}{N} = \frac{3}{2}pv = \frac{3}{2}\frac{k_BTv}{\lambda^3}\,g_{5/2}(z) \tag{3.11.27}$$

Recall, $z = 1$ in the mixed state $T < T_c$, while $z < 1$ in the normal state $T > T_c$.

In the above equation we should regard E/N as a function of either v *or* z. That is, we either determine v for a given z and T, or we determine z for a given v and T (recall, $z = \mathrm{e}^{\beta\mu}$, $v = V/N$, and N and μ are conjugate variables).

The specific heat per particle, at constant volume, is then,

$$\frac{C_V}{Nk_B} = \frac{1}{Nk_B}\left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{1}{k_B}\left(\frac{\partial (E/N)}{\partial T}\right)_{V,N} = \frac{3}{2}v\left[\frac{d}{dT}\left(\frac{T}{\lambda^3}\right)g_{5/2}(z) + \frac{T}{\lambda^3}\left(\frac{\partial g_{5/2}(z)}{\partial z}\right)\frac{dz}{dT}\right] \tag{3.11.28}$$

For $T < T_c$, $z = 1$ is constant, so $\dfrac{dz}{dT} = 0$ and only the first term in Eq. (3.11.28) remains. We have,

$$\frac{T}{\lambda^3} \propto T^{5/2}, \quad \text{so} \quad \frac{d}{dT}\left(\frac{T}{\lambda^3}\right) = \frac{5}{2}\left(\frac{T}{\lambda^3}\right)\frac{1}{T} = \frac{5}{2}\frac{1}{\lambda^3} \tag{3.11.29}$$

and so,

$$\frac{C_V}{Nk_B} = \frac{3}{2}v\left(\frac{5}{2}\frac{1}{\lambda^3}\right)g_{5/2}(1) = \frac{15}{4}g_{5/2}(1)\frac{v}{\lambda^3} = \frac{15}{4}\,g_{5/2}(1)v\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} \tag{3.11.30}$$

At $T = T_c$, $n = \dfrac{g_{3/2}(1)}{\lambda_c^3}$ and $v = \dfrac{1}{n}$, so,

$$\frac{C_V(T_c^-)}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)} = \frac{15}{4}\frac{1.341}{2.612} = 1.925 \qquad (3.11.31)$$

Note, this value of $C_V = 1.925Nk_B$ is *larger* than the classical ideal gas value of $C_V = 1.5Nk_B$.

So for $T < T_c$ we have,

$$\boxed{\frac{C_V}{Nk_B} = 1.925\left(\frac{T}{T_c}\right)^{3/2} \qquad \text{for } T < T_c} \qquad (3.11.32)$$

For $T > T_c$, z varies with T and so we need to also evaluate the second term in Eq. (3.11.28).

The first term in Eq. (3.11.28) gives: $\dfrac{15}{4} g_{5/2}(z(T))\dfrac{v}{\lambda^3}$ where now $z < 1$ depends on T.

To get the second term: from Pathria and Beale Appendix D Eq. (10), $z\dfrac{d}{dz}\left[g_\nu(z)\right] = g_{\nu-1}(z)$

$$\Rightarrow \qquad \frac{dg_{5/2}}{dz}\frac{dz}{dT} = \frac{g_{3/2}}{z}\frac{dz}{dT} \qquad (3.11.33)$$

To find $\dfrac{1}{z}\dfrac{dz}{dT}$ consider our earlier result of Eq. (**??**) for the density when $T > T_c$,

$$n = \frac{g_{3/2}(z)}{\lambda^3} \qquad \text{determines } z(T) \text{ for fixed } n \qquad (3.11.34)$$

Therefore, for fixed n we have,

$$0 = \frac{dn}{dT} = \frac{d}{dT}\left(\frac{1}{\lambda^3}\right) g_{3/2} + \frac{1}{\lambda^3}\frac{dg_{3/2}}{dz}\frac{dz}{dT} = \frac{3}{2}\frac{g_{3/2}}{\lambda^3 T} + \frac{g_{1/2}}{\lambda^3}\frac{1}{z}\frac{dz}{dT} \qquad (3.11.35)$$

$$\Rightarrow \qquad \frac{1}{z}\frac{dz}{dT} = -\frac{3}{2}\frac{g_{3/2}}{g_{1/2}}\frac{1}{T} \qquad (3.11.36)$$

Putting that into the second term in Eq. (3.11.28) then gives,

$$\boxed{\frac{C_V}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} \qquad \text{for } T > T_c} \qquad (3.11.37)$$

where we used, $v/\lambda^3 = 1/n\lambda^3 = 1/g_{3/2}(z)$ from Eq. (3.11.34).

Now note that $g_{1/2}(1) = \sum_{\ell=1}^{\infty}\dfrac{1}{\ell^{1/2}} \to \infty$, so as $T \to T_c^+$ from above, and so $z \to 1$, we have,

$$\frac{C_V(T_c^+)}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)} - \frac{9}{4}\frac{g_{3/2}(1)}{\infty} = \frac{15}{4}\frac{1.341}{2.612} = 1.925 \qquad (3.11.38)$$

Comparing to Eq. (3.11.31) we therefore see that C_V is *continuous* at T_c.

Finally we want to show that, although C_V is continuous at T_c, its derivative $\dfrac{dC_V}{dT}$ is *discontinuous*.

<u>For $T < T_c$</u>, we have from Eq. (3.11.32) that $\dfrac{C_V}{Nk_B} = 1.925\left(\dfrac{T}{T_c}\right)^{3/2}$. So,

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{3}{2}(1.925)\left(\frac{T}{T_c}\right)^{1/2}\frac{1}{T_c} = 2.89\left(\frac{T}{T_c}\right)^{1/2}\frac{1}{T_c} \qquad (3.11.39)$$

So the slope at $T = T_c^-$ (just below T_c) is,

$$\boxed{\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{2.89}{T_c} \qquad \text{for } T = T_c^-} \qquad (3.11.40)$$

<u>For $T > T_c$</u>, we have from Eq. (3.11.37), $\dfrac{C_V}{Nk_B} = \dfrac{15}{4}\dfrac{g_{5/2}(z)}{g_{3/2}(z)} - \dfrac{9}{4}\dfrac{g_{3/2}(z)}{g_{1/2}(z)}$. So,

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = \frac{15}{4}\left[\frac{g_{3/2}\frac{dg_{5/2}}{dz}\frac{dz}{dT} - g_{5/2}\frac{dg_{3/2}}{dz}\frac{dz}{dT}}{[g_{3/2}(z)]^2}\right] - \frac{9}{4}\left[\frac{g_{1/2}\frac{dg_{3/2}}{dz}\frac{dz}{dT} - g_{3/2}\frac{dg_{1/2}}{dz}\frac{dz}{dT}}{[g_{1/2}(z)]^2}\right] \qquad (3.11.41)$$

$$= \frac{1}{z}\frac{dz}{dT}\left(\frac{15}{4}\left[\frac{g_{3/2}^2 - g_{5/2}\,g_{1/2}}{g_{3/2}^2}\right] - \frac{9}{4}\left[\frac{g_{1/2}^2 - g_{3/2}\,g_{-1/2}}{g_{1/2}^2}\right]\right) \qquad (3.11.42)$$

where we used $z\dfrac{d}{dz}\left[g_\nu(z)\right] = g_{\nu-1}(z)$ from Pathria and Beale Appendix D.

Finally, use $\dfrac{1}{z}\dfrac{dz}{dT} = -\dfrac{3}{2}\dfrac{g_{3/2}}{g_{1/2}}\dfrac{1}{T}$ as found earlier in Eq. (3.11.36), and we get,

$$\frac{d}{dT}\left(\frac{C_V}{Nk_B}\right) = -\frac{3}{8T}\frac{g_{3/2}}{g_{1/2}}\left(15\left[1 - \frac{g_{5/2}\,g_{1/2}}{g_{3/2}^2}\right] - 9\left[1 - \frac{g_{3/2}\,g_{-1/2}}{g_{1/2}^2}\right]\right) \qquad (3.11.43)$$

Now as $T \to T_c^+$ from above, and so $z \to 1$, we have that $g_{5/2}(1)$ and $g_{3/2}(1)$ are finite, but $g_{1/2}(1)$ and $g_{-1/2}(1) \to \infty$. So at $T = T_c^+$ we have

$$\frac{d}{dT}\left(\frac{C_V(T_c^+)}{Nk_B}\right) = \frac{45}{8T_c}\frac{g_{5/2}(1)}{g_{3/2}(1)} - \frac{27}{8T_c}g_{3/2}^2(1)\,\frac{g_{-1/2}(1)}{g_{1/2}^3(1)} \qquad (3.11.44)$$

Now from Pathria and Beale Appendix D Eq. (8) we have, $g_\nu(1) = \lim_{a\to 0}\dfrac{\Gamma(1-\nu)}{a^{1-\nu}}$. So,

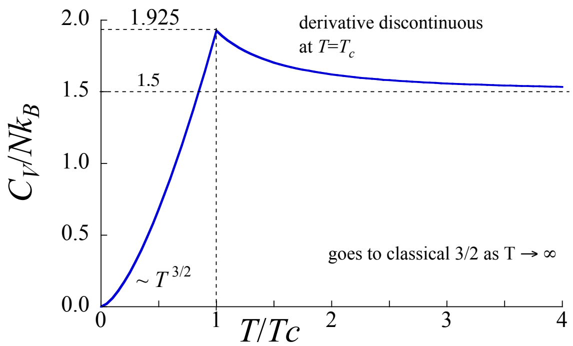
$$\frac{g_{-1/2}(1)}{g_{1/2}^3(1)} = \lim_{a\to 0}\frac{\Gamma(3/2)}{a^{3/2}}\left(\frac{a^{1/2}}{\Gamma(1/2)}\right)^3 = \frac{\Gamma(3/2)}{[\Gamma(1/2)]^3} = \frac{\frac{1}{2}\pi^{1/2}}{\pi^{3/2}} = \frac{1}{2\pi} \qquad (3.11.45)$$

since $\Gamma(1/2) = \sqrt{\pi}$ and $\Gamma(3/2) = \sqrt{\pi}/2$. So,

$$\frac{d}{dT}\left(\frac{C_V(T_c^+)}{Nk_B}\right) = \frac{45}{8}\frac{1.341}{2.612}\frac{1}{T_c} - \frac{27}{8}\frac{(2.612)^2}{2\pi}\frac{1}{T_c} = \frac{2.89}{T_c} - \frac{3.66}{T_c} \qquad (3.11.46)$$

$$\boxed{\frac{d}{dT}\left(\frac{C_V(T_c^+)}{Nk_B}\right) = \frac{-0.77}{T_c} \qquad \text{for } T = T_c^+} \qquad (3.11.47)$$

So comparing to Eq. (3.11.40), we see that the slope of C_V at T_c is discontinuous, and that C_V has a *cusp* at T_c.



Entropy

For a gas with a single species of particles, we had for the Gibbs free energy, $G = N\mu$. Also, $G = E - TS + pV$, so we have,

$$N\mu = E - TS + pV \qquad \Rightarrow \qquad S = \frac{E + pV - N\mu}{T} \qquad \Rightarrow \qquad \frac{S}{Nk_B} = \frac{E + pV}{Nk_BT} - \frac{\mu}{k_BT} \tag{3.11.48}$$

Earlier we had $E = (3/2)pV \;\Rightarrow\; pV = (2/3)E$, so,

$$\frac{S}{Nk_BT} = \frac{5}{3}\frac{E}{N}\frac{1}{k_BT} - \frac{\mu}{k_BT} \tag{3.11.49}$$

Earlier we had in Eq. (3.11.27) $\dfrac{E}{N} = \dfrac{3}{2}\dfrac{k_BTv}{\lambda^3}\,g_{5/2}(z)$, and for $T > T_c$ we have $n = \dfrac{1}{v} = \dfrac{g_{3/2}(z)}{\lambda^3}$. Using $\mu/k_BT = \ln z$ we then have,

$$\frac{S}{Nk_B} = \frac{5}{2}\frac{v}{\lambda^3}\,g_{5/2}(z) - \ln z = \begin{cases} \dfrac{5}{2}\dfrac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z & \text{for } T > T_c \text{ where } z < 1 \\[2ex] \dfrac{5}{2}\dfrac{v}{\lambda^3}\,g_{5/2}(1), & \text{for } T < T_c \text{ where } z = 1 \end{cases} \tag{3.11.50}$$

Now for $T < T_c$ we had a density of particles $n_0 = n - g_{3/2}(1)/\lambda^3$ in the condensate, and a density $n_n \equiv g_{3/2}(1)/\lambda^3$ in the normal state.

For $T < T_c$, $\dfrac{S}{Nk_B} = \dfrac{5}{2}\left(\dfrac{n_n}{n}\right)\dfrac{g_{5/2}(1)}{g_{3/2}(1)} \to 0$ as $T \to T_c$ (since $n_n \to 0$).

We can thus imagine that each "normal" particle (i.e. a particle *not* in the ground state) caries an entropy $\dfrac{5}{2}k_B\,\dfrac{g_{5/2}(1)}{g_{3/2}(1)}$. The entropy per particle at $T < T_c$ is just the above entropy per "normal" particle, times the fraction of normal particles. This implies that it is only the normal particles that carry the entropy, the condensate has zero entropy.

The entropy difference per particle between the normal state and the condensed state for $T < T_c$ is thus $\dfrac{\Delta S}{N} = \dfrac{5}{2}k_B\,\dfrac{g_{5/2}(1)}{g_{3/2}(1)}$.

We therefore have as the latent heat of condensation,

$$L \equiv T\Delta S = \frac{5}{2}k_B\,\frac{g_{5/2}(1)}{g_{3/2}(1)} \tag{3.11.51}$$

This is the energy released by converting one normal particle into one condensate particle.

The mixed phase is like a coexistence region of a first order phase transition (like water $\leftrightarrow$ ice – one needs to remove energy to turn water into ice). This leads to something known as the "two fluid" model for the mixed phase of the Bose gas. Enough said.