

# G25.2651: Statistical Mechanics

## Notes for Lecture 20

### I. THE IDEAL BOSON GAS: INTRODUCTION

For the bosonic ideal gas, one must solve the equations

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

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

in order to obtain the equation of state. Examination of these equations, however, shows an immediate problem: The term  $\mathbf{n} = (0, 0, 0)$  is divergent both for the pressure and the average particle number. These terms need to be treated carefully, and so we split them off from the rest of the sum, giving:

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

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

where  $\sum'$  means that the  $\mathbf{n} = (0, 0, 0)$  term is excluded. With these divergent terms split off, the thermodynamic limit can be taken and the remaining sums converted to integrals as was done in the fermion case. Thus, for the pressure, we find

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

where the change of variables

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

has been made. Using the expansion

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

the pressure equation becomes

$$\frac{P\lambda^3}{gkT} = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{5/2}} - \frac{\lambda^3}{V} \ln(1 - \zeta)$$

and by a similar procedure, the average particle number becomes

$$\frac{\rho\lambda^3}{g} = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{3/2}} + \frac{\lambda^3}{V} \frac{\zeta}{1 - \zeta}$$

In this equation, the term that has been split off represents the average occupation of the ground ( $\mathbf{n} = (0, 0, 0)$ ) energy state:

$$\langle f_0 \rangle = \frac{\zeta}{1 - \zeta}$$

Since  $\langle f_0 \rangle$  must be greater than or equal to 0, it can be seen that there are restrictions on the allowed values of  $\zeta$ . Firstly, since  $\zeta = \exp(\beta\mu)$ ,  $\zeta$  must be a positive number. However, in order that the average occupation of the ground state be positive,

$$0 \leq \zeta < 1$$

from which it follows that

$$\mu < 0$$

The fact that as  $\zeta \rightarrow 1$  causes  $\langle f_0 \rangle$  to diverge will have interesting consequences to be discussed below. However, let us first consider the low density limit with  $\zeta \ll 1$ .

## II. LOW DENSITY, SMALL $\zeta$ LIMIT

In a manner completely analogous to what was done for the fermion case, the low density limit can be treated by perturbation theory. Note that if  $\zeta$  is not close to 1, then the divergent terms, which have a  $\lambda^3/V$  prefactor accompanying them, will vanish in the thermodynamic limit. Thus, for the proceeding analysis, these terms can be neglected.

As before, we assume the fugacity can be expanded as

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

Then the equation for the density becomes

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

By equating like powers of  $\rho$  on both sides, the coefficients  $a_1, a_2, a_3, \dots$  can be determined as they were for the fermion gas. Working to first order in  $\rho$  gives

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

and the equation of state is

$$\frac{P}{kT} = \rho$$

which is just the classical ideal gas equation. To second order, however, we find

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

and the second order equation of state becomes

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

The second virial coefficient can be read off and is given by

$$B_2(T) = -\frac{1}{2^{5/2}g}\lambda^3 = -\frac{0.1768}{g}\lambda^3 < 0$$

Interestingly, in contrast to the fermionic system, the pressure is actually decreased from its classical value as a result of bosonic spin statistics. Thus, it appears that there is an “effective attraction” between the particles. This fact is not entirely unexpected, given that any number of bosons can occupy the same quantum state.

### III. THE HIGH DENSITY, $\zeta \rightarrow 1$ LIMIT

The  $\zeta \rightarrow 1$  limit is the limit of maximum chemical potential, which is expected at high density. However, since  $\mu < 0$ , maximum chemical potential will be the limit  $\mu \rightarrow 0$ . In this limit, the full problem, including the divergent terms, must be solved:

$$\frac{P\lambda^3}{gkT} = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{5/2}} - \frac{\lambda^3}{V} \ln(1 - \zeta)$$

$$\frac{\rho\lambda^3}{g} = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{3/2}} + \frac{\lambda^3}{V} \frac{\zeta}{1 - \zeta}$$

We will need to refer to these two sums often in this section, so let us define them to be

$$g_{3/2}(\zeta) = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{3/2}}$$

$$g_{5/2}(\zeta) = \sum_{l=1}^{\infty} \frac{\zeta^l}{l^{5/2}}$$

Thus, the problem becomes one of solving

$$\frac{P\lambda^3}{gkT} = g_{5/2}(\zeta) - \frac{\lambda^3}{V} \ln(1 - \zeta)$$

$$\frac{\rho\lambda^3}{g} = g_{3/2}(\zeta) + \frac{\lambda^3}{V} \frac{\zeta}{1 - \zeta}$$

We examine, first the density equation. The second term will diverge at  $\zeta = 1$ . It is instructive to ask what is the behavior of the first term  $g_{3/2}(\zeta)$  at  $\zeta = 1$ . In fact  $g_{3/2}(1)$  is nothing but a Riemann zeta-function:

$$g_{3/2}(1) = \sum_{l=1}^{\infty} \frac{1}{l^{3/2}} = R(3/2)$$

In general, a Riemann zeta-function  $R(n)$  is given by

$$R(n) = \sum_{l=1}^{\infty} \frac{1}{l^n}$$

and the values of this function are given in many standard math tables. The particles value of  $R(3/2)$  is approximately 2.612... Moreover, from the form of  $g_{3/2}(\zeta)$ , it is clear that, since  $\zeta < 1$ ,  $g_{3/2}(1)$  is the maximum value of  $g_{3/2}(\zeta)$ . A plot of  $g_{3/2}(\zeta)$  is given below:

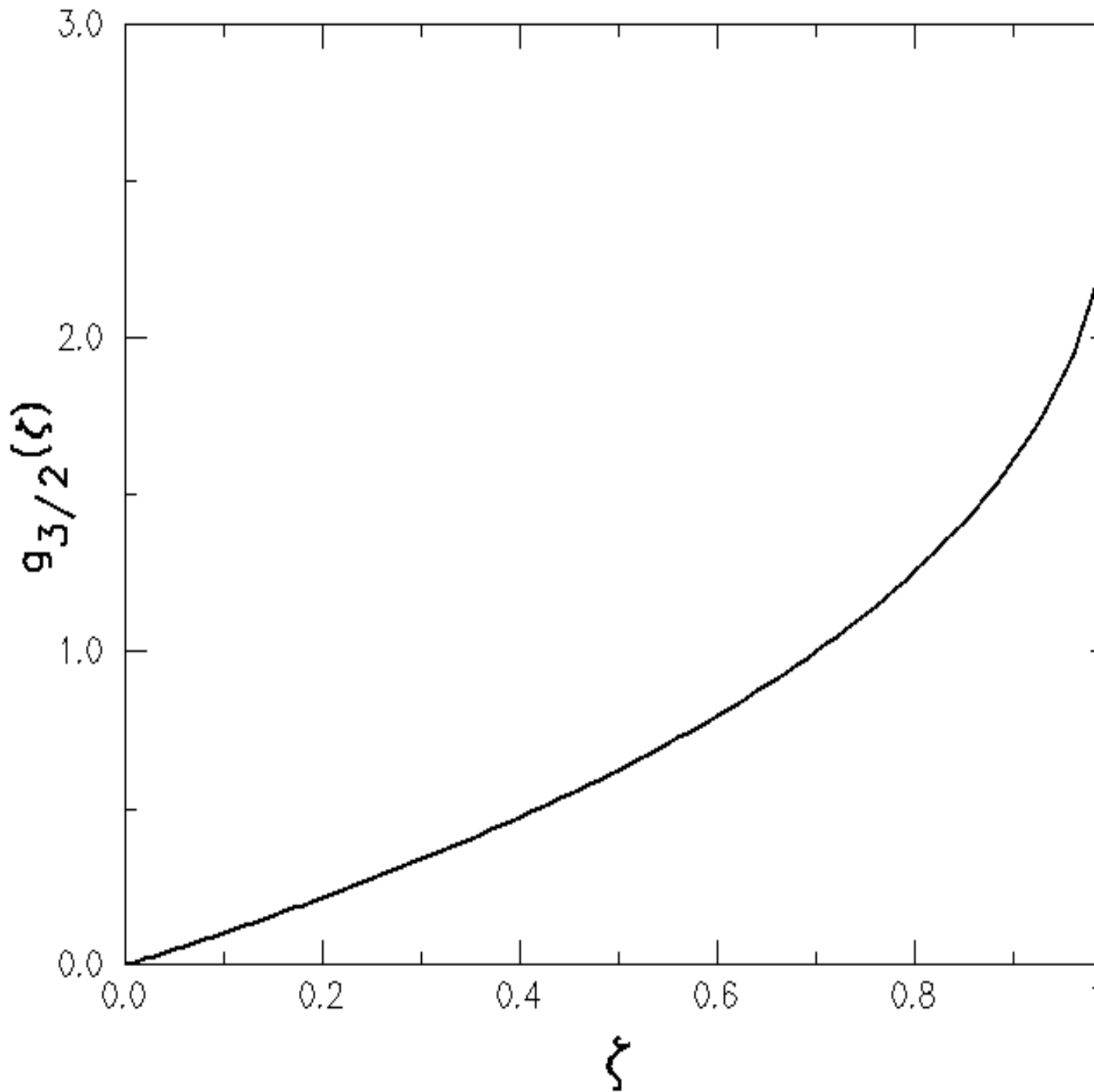


FIG. 1.

The figure also indicates that the derivative  $g'_{3/2}(\zeta)$  diverges at  $\zeta = 1$  despite the fact that the value of the function is finite. Note that, since  $\zeta < 1$

$$g_{3/2}(\zeta) < g_{5/2}(\zeta)$$

It is possible to solve the density equation for  $\zeta$  by noting that unless  $\zeta$  is very close to 1, the divergent term will still vanish in the thermodynamic limit as a result of its  $\lambda^3/V$  prefactor. How close to 1 must it be for this term to dominate? It can only be different from 1 by an amount on the order of  $1/V$ . Thus, let us take  $\zeta$  to be of the form

$$\zeta = 1 - \frac{a}{V}$$

where  $a$  is a positive constant. Substituting this ansatz into the equation for the density gives

$$\frac{\rho\lambda^3}{g} = g_{3/2}(1 - a/V) + \frac{\lambda^3}{V} \frac{1 - a/V}{a/V}$$

Since  $g_{3/2}(\zeta)$  does not change its value much if  $\zeta$  is displaced just a little from 1, we can replace the first term by  $R(3/2)$ . Then,

$$\frac{\rho\lambda^3}{g} \approx g_{3/2}(1) + \frac{\lambda^3}{V} \frac{1 - a/V}{a/V}$$

can be solved for  $a$  to yield

$$a = \frac{\lambda^3}{\frac{\rho\lambda^3}{g} - R(3/2)}$$

where we have neglected a term  $\lambda^3/V$ , which vanishes in the thermodynamic limit. Since  $a$  must be positive, this solution is only valid for  $\rho\lambda^3/g > R(3/2)$ . For  $\rho\lambda^3/g < R(3/2)$ ,  $\zeta$  will be different from 1 by more than an amount  $1/V$  so in this regime, the  $\zeta/(1-\zeta)$  term can be neglected, leaving the problem of solving  $\rho\lambda^3/g = g_{3/2}(\zeta)$ . Therefore, the solution for  $\zeta$  can be expressed as

$$\zeta = \begin{cases} 1 - \frac{\lambda^3/V}{\frac{\rho\lambda^3}{g} - R(3/2)} & \frac{\rho\lambda^3}{g} > R(3/2) \\ \text{root of } g_{3/2}(\zeta) = \frac{\rho\lambda^3}{g} & \frac{\rho\lambda^3}{g} < R(3/2) \end{cases}$$

which, in the thermodynamic limit, becomes

$$\zeta = \begin{cases} 1 & \frac{\rho\lambda^3}{g} > R(3/2) \\ \text{root of } g_{3/2}(\zeta) = \frac{\rho\lambda^3}{g} & \frac{\rho\lambda^3}{g} < R(3/2) \end{cases}$$

A plot of  $\zeta$  vs.  $v/\lambda^3 = V/\langle N \rangle \lambda^3$  is shown below:

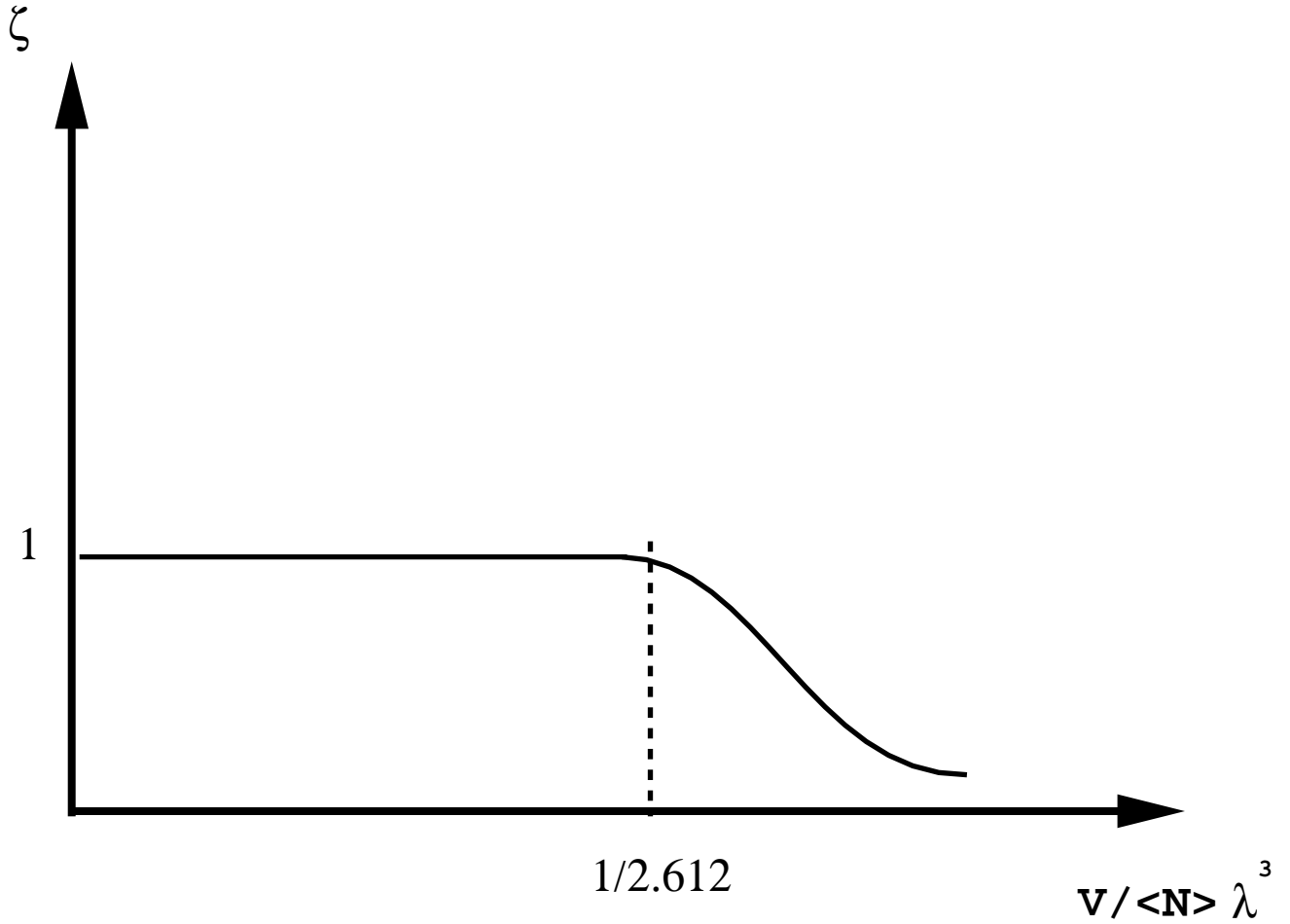


FIG. 2.

Clearly, point  $R(3/2)$  is special, as  $\zeta$  undergoes a transition there to a constant value of 1. Recall that the occupation of the ground state is

$$\langle f_0 \rangle = \frac{\zeta}{1 - \zeta}$$

Thus, for  $\zeta = 1 - a/V$ , this becomes

$$\langle f_0 \rangle \approx \frac{V}{a} = \frac{V}{\lambda^3} \left( \frac{\rho \lambda^3}{g} - R(3/2) \right)$$

for  $\rho \lambda^3 / g > R(3/2)$ . At  $\rho \lambda^3 / g = R(3/2)$  the occupation of the ground state becomes 0. To what temperature does this correspond? We can find this out by solving

$$\begin{aligned} \frac{\rho \lambda^3}{g} &= R(3/2) \\ \frac{\rho}{g} \left( \frac{2\pi \hbar^2}{mkT_0} \right)^{3/2} &= R(3/2) \\ kT_0 &= \left( \frac{\rho}{gR(3/2)} \right)^{2/3} \frac{2\pi \hbar^2}{m} \end{aligned}$$

so that for temperatures less than  $T_0$  the occupation of the ground state becomes

$$\langle f_0 \rangle = \frac{\rho V}{g} \left[ 1 - \frac{g}{\rho \lambda^3} R(3/2) \right]$$

$$\begin{aligned}
&= \frac{\langle N \rangle}{g} \left[ 1 - \frac{g}{\rho \lambda^3} R(3/2) \right] \\
&= \frac{\langle N \rangle}{g} \left[ 1 - \frac{g R(3/2)}{\rho} \left( \frac{mkT}{2\pi \hbar^2} \right)^{3/2} \left( \frac{kT_0}{kT} \right)^{3/2} \right] \\
\frac{\langle N \rangle}{g} \left[ 1 - \left( \frac{T}{T_0} \right)^{3/2} \right] \\
\frac{\langle f_0 \rangle}{\langle N \rangle} &= \frac{1}{g} \left[ 1 - \left( \frac{T}{T_0} \right)^{3/2} \right]
\end{aligned}$$

Thus, at  $T = 0$

$$\langle f_0 \rangle = \frac{\langle N \rangle}{g}$$

which is equivalent to

$$\langle f_{\mathbf{n}=(0,0,0),m} \rangle = \frac{\langle N \rangle}{g}$$

If we sum both sides over  $m$ , this gives

$$\begin{aligned}
\sum_m \langle f_{\mathbf{n}=(0,0,0),m} \rangle &= \sum_m \frac{\langle N \rangle}{g} \\
\langle \bar{f}_0 \rangle &= \langle N \rangle
\end{aligned}$$

where  $\langle \bar{f}_0 \rangle$  indicates that the spin degeneracy has been summed over. For  $T > T_0$ ,  $\rho \lambda^3 / g < R(3/2)$  and  $\zeta$  is not within  $1/V$  of 1. This means that  $\zeta / (1 - \zeta)$  is finite and

$$\frac{\langle f_0 \rangle}{\langle N \rangle} = \frac{1}{\langle N \rangle} \frac{\zeta}{1 - \zeta} \rightarrow 0$$

as  $\langle N \rangle \rightarrow \infty$ . Therefore, we have, for the occupation of the ground state:

$$\frac{\langle f_0 \rangle}{\langle N \rangle} = \begin{cases} 1 - (T/T_0)^{3/2} & T < T_0 \\ 0 & T > T_0 \end{cases}$$

which is shown in the figure below:

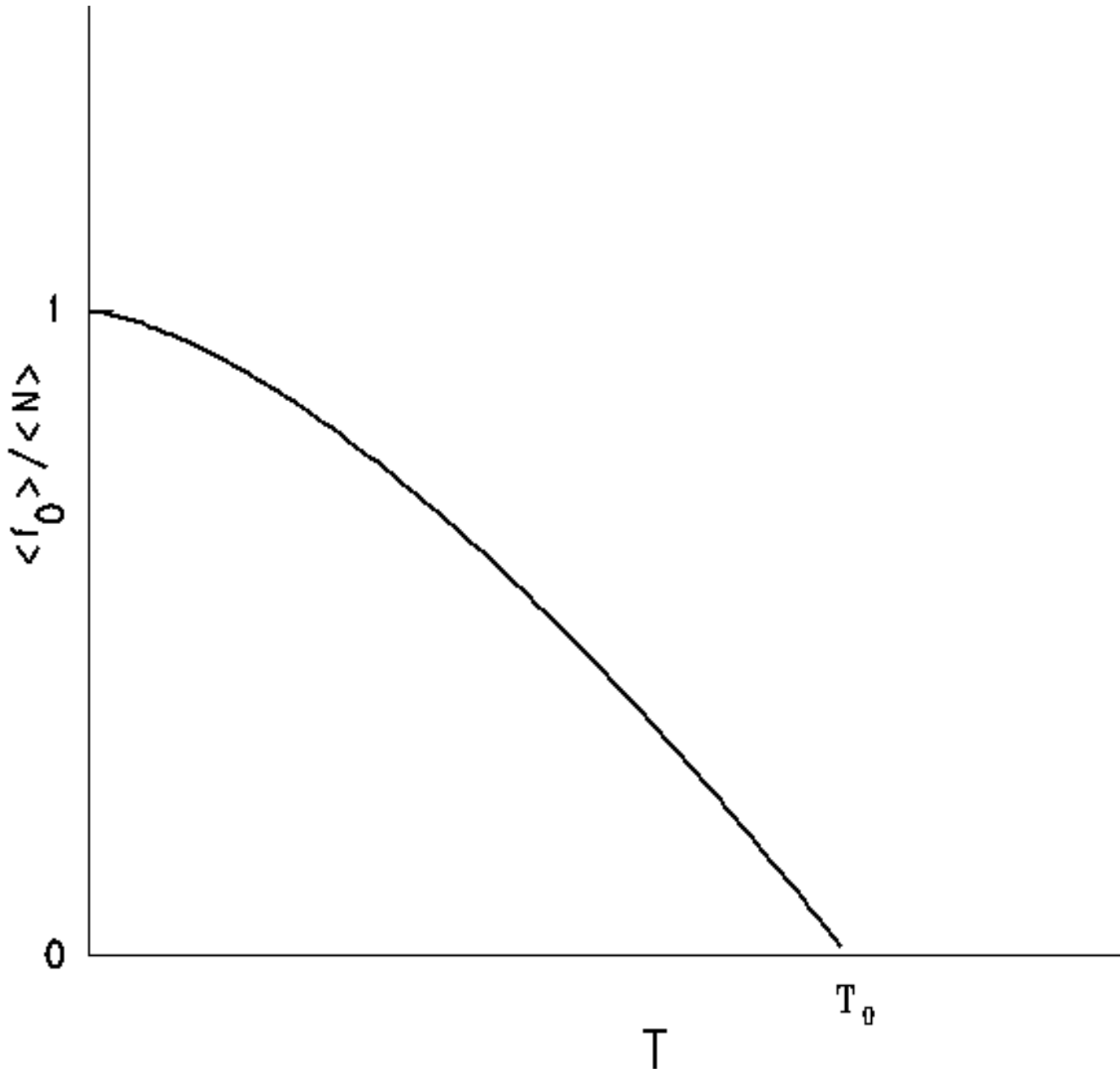


FIG. 3.

The occupation of the ground state undergoes a transition from a finite value to 0 at  $T = T_0$  and for all higher temperatures, remains 0. Now,  $\langle f_0 \rangle / \langle N \rangle$  represents the probability that a particle will be found in the ground state. It also represents the fraction of the total number of particles that will be found in the ground state. For  $T \ll T_0$ , this number is very close to 1, and at  $T = 0$ , it becomes exactly 1, implying that at  $T = 0$  all particles will be found in the ground state. This is a phenomenon known as *Bose-Einstein* condensation. The occupation number of the ground state as a function of temperature is shown in the plot below:

Note that there is also a critical density corresponding to this temperature. This will be given by the solution of

$$\frac{\rho \lambda^3}{g} = R(3/2)$$

which can be solved to yield

$$\rho = \frac{gR(3/2)}{\lambda^3} = gR(3/2) \left( \frac{mkT_0}{2\pi\hbar^2} \right)^{3/2} \equiv \rho_0$$

and the occupation number, expressed in terms of the density is

$$\frac{\langle \bar{f}_0 \rangle}{\langle N \rangle} = \begin{cases} 1 - (\rho_0/\rho) & \rho > \rho_0 \\ 0 & \rho < \rho_0 \end{cases}$$

The term in the pressure equation

$$-\frac{\lambda^3}{V} \ln(1 - \zeta)$$

becomes, for  $\zeta$  very close to 1

$$\frac{\lambda^3}{V} \ln(V/a) \sim \frac{\ln V}{V}$$

which clearly vanishes in the thermodynamic limit, since  $V \sim \langle N \rangle$ . This allows to deduce the equation of state as

$$\frac{P}{gkT} = \begin{cases} \frac{g_{5/2}(1)}{\lambda^3} & \rho > \rho_0 \\ \frac{g_{5/2}(\zeta)}{\lambda^3} & \rho < \rho_0 \end{cases}$$

where  $\zeta$  in the above equation comes from the actual solution of  $\rho\lambda^3/g = g_{3/2}(\zeta)$ . What is particularly interesting to note about the equation of state is that the pressure is independent of the density for  $\rho > \rho_0$ . Isotherms of the ideal Bose gas are shown below:

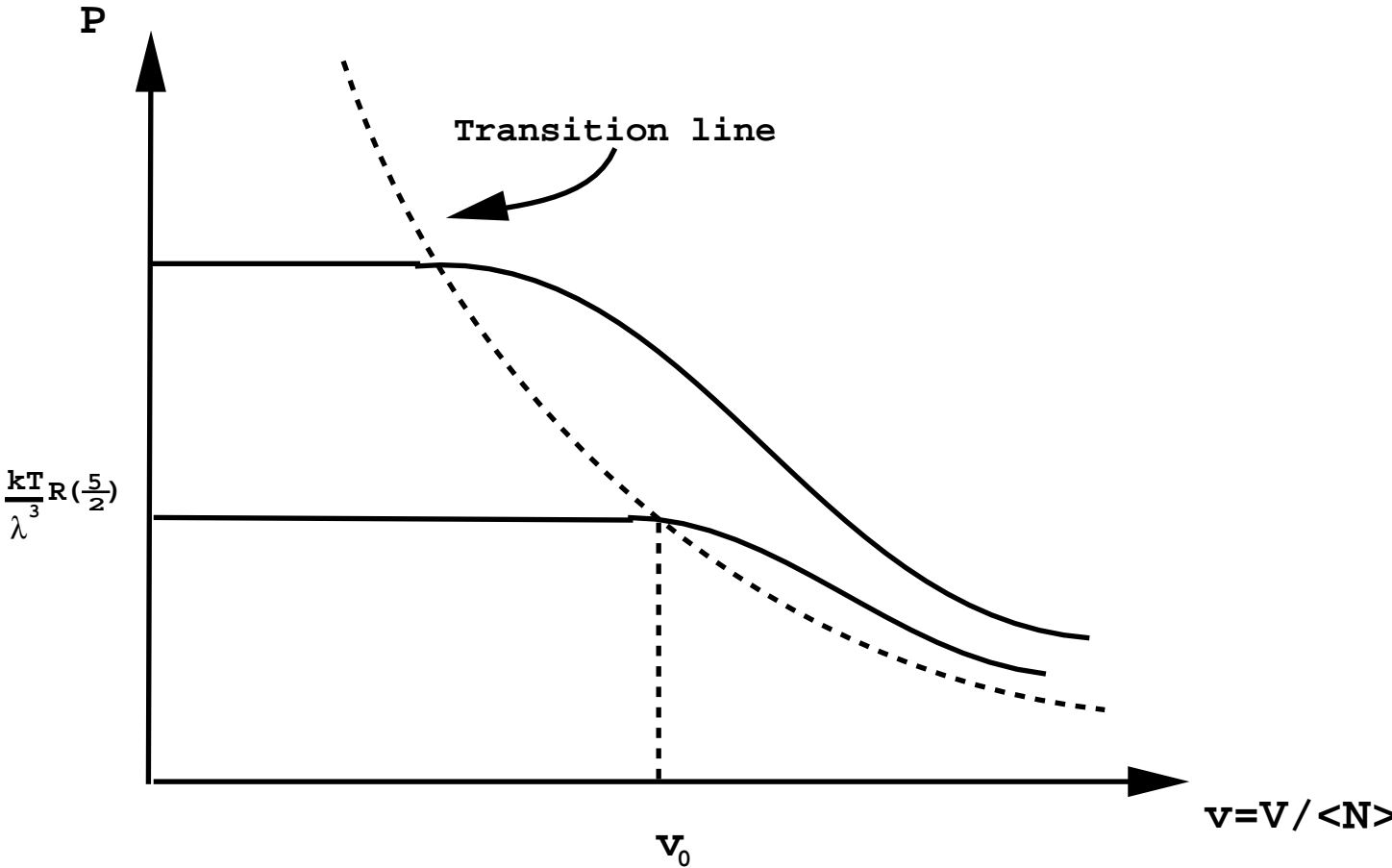


FIG. 4.

Here,  $v_0$  corresponds to the critical density  $\rho_0$ . As a function of temperature, we see that  $P \sim T^{5/2}$ , which is quite different from the classical ideal gas. This is also in contrast to the fermion ideal gas, where as  $T \rightarrow 0$  the pressure remains finite. For the Boson gas, as  $T \rightarrow 0$  the pressure vanishes, in keeping with the notion of an “effective” attraction between the particles.

Other thermodynamic quantities can be determined in a similar manner. The energy can be obtained from  $E = 3PV/2$  straightforwardly:

$$E = \begin{cases} \frac{3}{2} \frac{kTV}{\lambda^3} g_{5/2}(1) & \rho > \rho_0, T < T_0 \\ \frac{3}{2} \frac{kTV}{\lambda^3} g_{5/2}(\zeta) & \rho < \rho_0, T > T_0 \end{cases}$$

and the heat capacity at constant volume from

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

which gives

$$\frac{C_V}{\langle N \rangle K} = \begin{cases} \frac{15}{4} \frac{g_{5/2}(1)}{\rho \lambda^3} & T < T_0 \\ \frac{15}{4} \frac{g_{5/2}(\zeta)}{\rho \lambda^3} - \frac{9}{4} \frac{g_{3/2}(\zeta)}{g_{1/2}(\zeta)} & T > T_0 \end{cases}$$

A plot of the heat capacity exhibits a cusp at  $T = T_0$ :

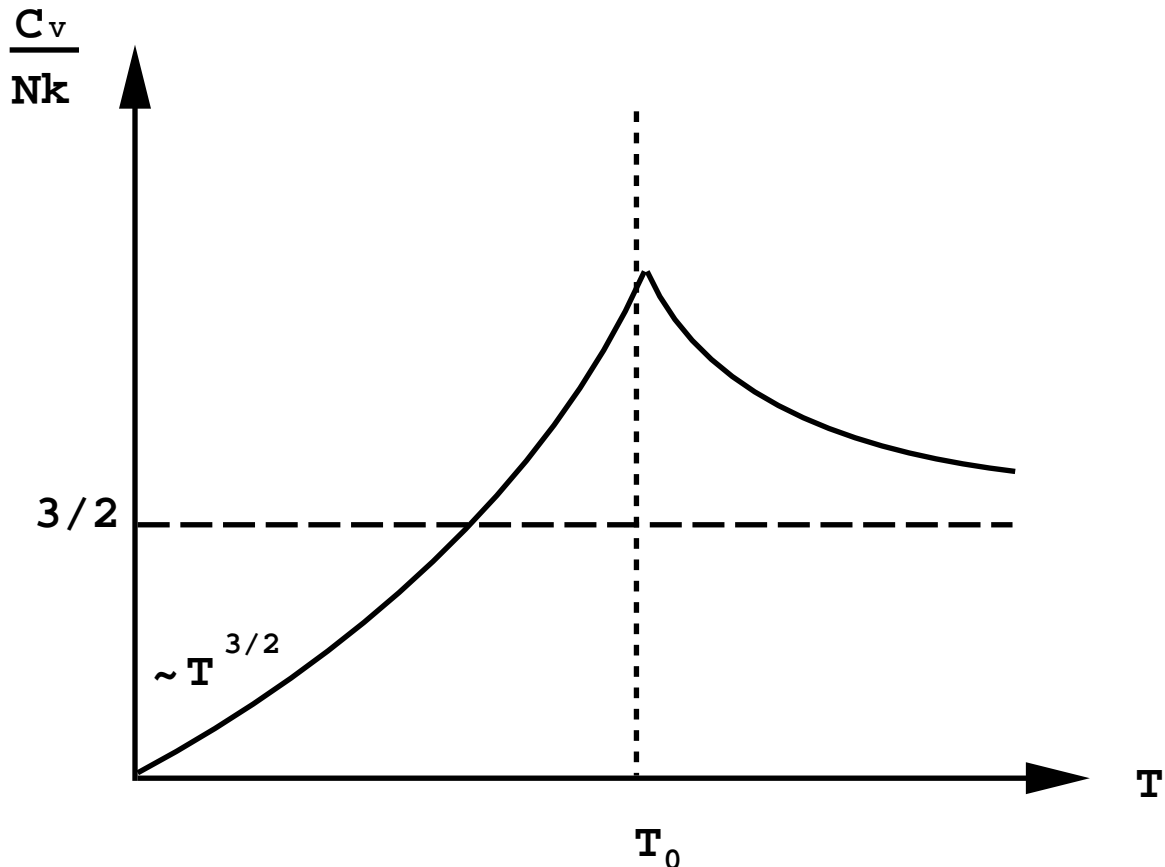


FIG. 5.

Experiments carried out on liquid  $\text{He}^4$ , which has been observed to undergo Bose-Einstein condensation at around  $T=2.18$  K, have measured an actual discontinuity in the heat capacity at the transition temperature, suggesting that Bose-Einstein condensation is a phase transition known as the  $\lambda$  transition. The experimental heat capacity is shown roughly below:

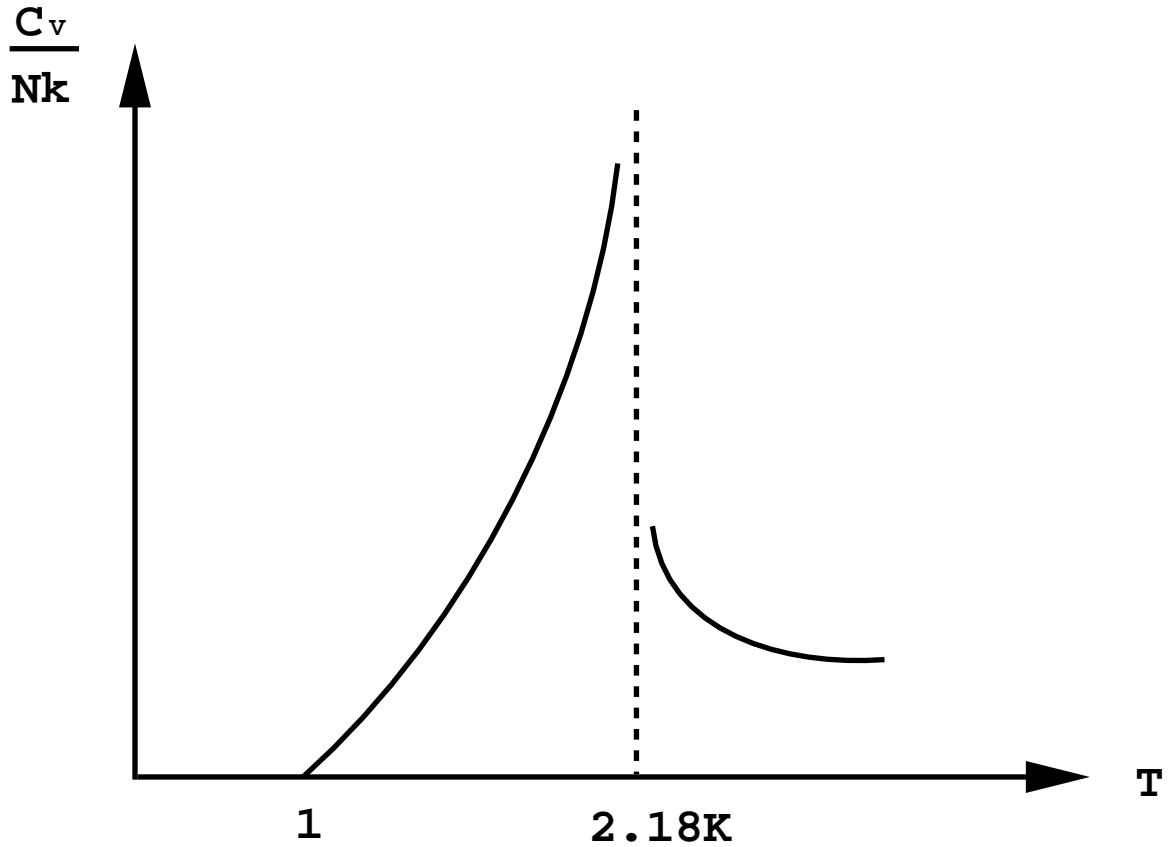


FIG. 6.

By contrast, the ideal Bose gas undergoes a first order phase transition. However, using the mass and density of liquid  $\text{He}^4$  in the expression for  $T_0$  given above, one would predict that  $T_0$  is about 3.14 K, which is not far off the experimental transition temperature of 2.18 K for real liquid helium.

For completeness, other thermodynamic properties of the ideal Bose gas are given as follows: The entropy is

$$\frac{S}{\langle N \rangle K} = \begin{cases} \frac{5}{2} \frac{1}{\rho \lambda^3} g_{5/2}(1) & T < T_0 \\ \frac{5}{2} \frac{1}{\rho \lambda^3} g_{5/2}(\zeta) - \ln \zeta & T > T_0 \end{cases}$$

The Gibbs free energy is given by

$$\frac{G}{\langle N \rangle K} = \begin{cases} 0 & T < T_0 \\ \ln \zeta & T > T_0 \end{cases}$$

It is clear from the analysis of this and the fermion ideal gas that quantum statistics give rise to an enormously rich behavior, even when there are no particle interactions!