INTRODUCTORY THEORY OF BOSE EINSTEIN CONDENSATION

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March 4, 2025

Abstract

We present the simple theory of Bose Einstein condensation, suitable for an introductory undergraduate physics course. In the interests of clarity, we include an estimate of the chemical potential μ at low temperature in a finite gas, avoiding self-contradictory claims of "$\mu = 0$". We also treat the two-dimensional gas, and a gas in a harmonic potential well. Some widely misunderstood features, such as the ground state occupation at the transition temperature, are clarified. The pressure and heat capacity are also discussed.

1 Preliminaries

The starting-point of our discussion is the notion of motional states described by their wave vectors $\mathbf{k}$, and the mean occupation number of a single-particle quantum state i, given by the Bose-Einstein distribution function,

$$\langle n_i \rangle = \frac{1}{\exp(\beta(\epsilon_i - \mu) - 1)}. \tag{1}$$

The label i here refers to a quantum state $|i\rangle$ available to particles in a gas. There are many particles, and n_i is the number of them which are in the state i at any given time. The average, $\langle n_i \rangle$, is a time-average of the expectation value of this number in conditions of thermal equilibrium. We will treat the case where the total number of particles in the gas, N, is constant, and large.

First let us note that there is are two natural energy scales associated with any quantum gas: the *energy gap* ΔE and the *quantum energy* ϵ_Q. The former (ΔE) is the gap between the ground state and first excited state of the gas. The latter (ϵ_Q) is a characteristic energy scale, which in the case of Fermions is the Fermi energy, and in the case of Bosons is the transition temperature (times $k_{\rm B}$) up to a numerical constant which we will obtain.

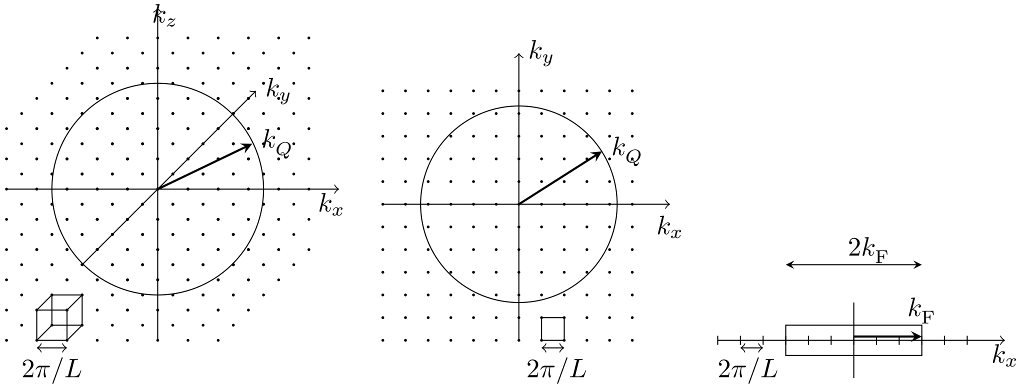

Figure 1: Obtaining the characteristic k-vector, in 3, 2 and 1 dimensions. $k_{\rm Q}$ takes a value such that the number of states in the sphere or circle or line, respectively, is equal to the number of particles, N.

First let us obtain ΔE.

Consider a gas in a cubic box of side L. The states of motion available to any single particle are described by wavefunctions $\sin(k_x x)\sin(k_y y)\sin(k_z z)$ (unnormalized). The lowest-lying state has $k_x = k_y = k_z = \pi/L$ and hence an energy $(\hbar k)^2/(2m) = (\hbar^2/2m)3(\pi/L)^2$ where m is the mass of one particle. One of the first excited states (there are 3 of them) has $k_x = 2\pi/L$, $k_y = k_z = \pi/L$, leading to energy $(\hbar^2/2m)6(\pi/L)^2$. Hence the energy gap is

$$\Delta E = \frac{\hbar^2}{2m}\frac{3\pi^2}{L^2}. \tag{2}$$

For example, $\Delta E \simeq 2.5 \times 10^{-37}$ joule for helium gas in a 1 centimetre box; the equivalent temperature is $\Delta E/k_{\rm B} \sim 10^{-14}$ K. A similar calculation for a square box in 2 dimensions gives the same result.

Next let us find the characteristic quantum energy ϵ_Q. For this purpose it is convenient to adopt periodic boundary conditions, such that the available motional states are distributed throughout k-space as shown in Fig. 1. The energy we want is $\epsilon_Q \equiv (\hbar k_Q)^2/2m$ where k_Q has a size such that the number of states in the sphere (in 3d) or the circle (in 2d) or line (in 1d) is equal to the number of particles:

$$k_Q^3 = \frac{N}{V}6\pi^2, \qquad k_Q^2 = \frac{N}{A}4\pi, \qquad k_Q = \frac{N}{L}\pi, \qquad \text{(3d, 2d, 1d.)} \tag{3}$$

Hence in the 3d case one finds

Characteristic energy scale, gas in a 3d box

$$\epsilon_Q = \frac{\hbar^2}{2m}\left(6\pi^2 n\right)^{2/3} \tag{4}$$

$$\begin{aligned}
2/(6\pi^2)^{1/3} &\simeq 0.513112975 \\
\zeta(3/2) &\simeq 2.612375348685488343348567567924 \\
\zeta(5/2) &\simeq 1.341487257250917179756769693348 \\
(1/2)\sqrt{\pi}\,\zeta(3/2) &\simeq 2.315157373394117000425819469118 \\
\big((3/4)\sqrt{\pi}\,\zeta(3/2)\big)^{-2/3} &\simeq 0.436065922441332967553717470315
\end{aligned}$$

Table 1: Some numerical values that crop up in the study of BEC. $\zeta(s)$ is the Riemann zeta function.

where $n = N/V$ is the number density. It will be useful to note that

$$\epsilon_Q = 0.513 \; N^{2/3} \Delta E. \tag{5}$$

Thus, for large N the characteristic energy is large compared to the energy gap (just as $k_Q \gg \Delta k$ when $N \gg 1$, as a glance at Fig. 1 makes clear).

We now introduce a related energy which will be important in the following. It is useful to define it in terms of a temperature T_0:

BEC transition temperature, 3d gas in a box

$$k_{\rm B} T_0 \equiv \frac{\hbar^2}{2m} 4\pi \left(n/\zeta(3/2) \right)^{2/3} \;=\; 0.436066 \, \epsilon_Q \tag{6}$$

where $\zeta(s)$ is the Riemann zeta function. A more precise statement of the numerical factor in the relationship to ϵ_Q is provided in table 1. A major aim of the analysis to follow is to show that the three-dimensional Bose gas in a box undergoes a phase transition at the temperature T_0, even when the interaction energies between the particles are negligible.

Choosing the zero of energy. The physics of a gas at low temperature depends on the gaps between the energy levels, but not on the value of the ground state energy itself. This is illustrated by the fact that the energy levels ϵ_i do not appear on their own in the distribution function (1), but in company with the chemical potential, in the term $\beta(\mu - \epsilon_i)$. If we shift the zero of energy, both μ and ϵ_0 will move and $\langle n_i \rangle$ is unaffected. It is customary, and convenient, to choose as zero energy the single-particle ground state energy. Thus if single-particle state number 1 is the ground state then $\epsilon_1 = 0$. With this choice of zero energy, the first excited single-particle state has energy $\epsilon_2 = \Delta E$ and this is the choice we shall make from now on (c.f. Fig 4).

2 Bose-Einstein condensation

The Bose gas shows an interesting behaviour at low temperature: a special type of phase transition occurs in the three-dimensional case, but not in the two-dimensional case (in the limit of a large box

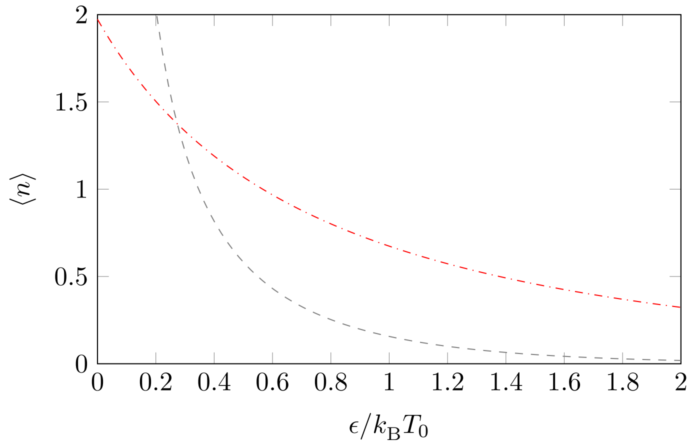

Figure 2: The Bose-Einstein distribution function at two example temperatures. We plot the mean occupation of a state of energy ϵ, as a function of $\epsilon/k_\mathrm{B}T_0$ where T_0 is the BEC transition temperature (see text). The curve for $T = 0$ would be a delta-function spike at $\epsilon = 0$. Gray dashed: $T = 0.5\,T_0$; red dash-dot: $k_\mathrm{B}T = 2\,T_0$. The former case (T below T_0) has μ very close to zero, with the result that the ground state occupation is of order N, a large number. The latter case (T above T_0) has $\mu \simeq -0.82 k_\mathrm{B}T_0$ with the result that none of the quantum states has a macroscopic population.

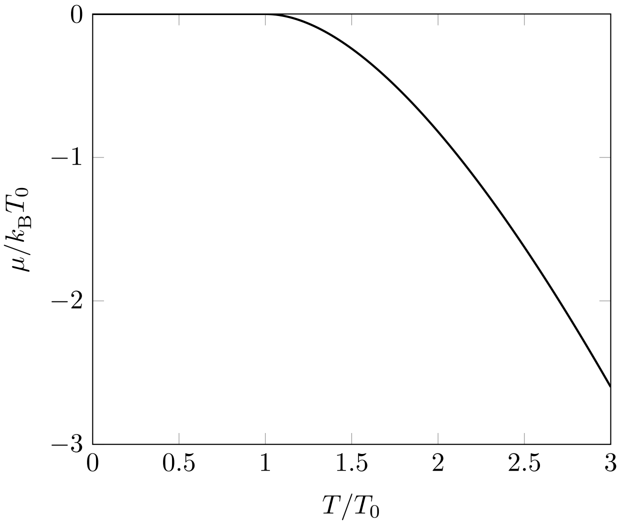

Figure 3: Behaviour of the chemical potential as a function of temperature, for a Bose gas in a 3d box. T_0 is the BEC transition temperature. For bosons in the limit $N \to \infty$ one has $\mu = 0$ for $T \leq T_0$. At high temperatures μ has a $-T \ln T$ dependence on temperature.

and a large number of particles). In order to understand this, we need first to consider the behaviour of the chemical potential as a function of temperature. For fixed V and N we have $\mu = \mu(T)$; its behaviour is shown in Fig. 3. *Much of the work of understanding BEC consists in the task of understanding* $\mu(T)$.

The term 'phase transition' here refers to a situation where there is a discontinuity in either $\mu(T)$ or one of its derivatives. We will (eventually) show that there is a discontinuity in $\mathrm{d}^2\mu/\mathrm{dT}^2$ at $T = T_0$ in the limit $N, V \to \infty$ at constant $n = N/V$.

At high temperature μ is large and negative. One can see this by arguing that at high enough temperature all the occupation numbers will be small, and in particular $\langle n_1 \rangle \ll 1$ where 1 labels the ground state. Hence

$$\frac{1}{e^{\beta(\epsilon_1 - \mu)} - 1} \ll 1, \qquad \text{at high } T \tag{7}$$

therefore

$$\begin{aligned} \beta(\epsilon_1 - \mu) &\gg 0 && (8) \\ \Rightarrow \qquad \mu - \epsilon_1 &\ll 0 \qquad \text{at high } T. && (9) \end{aligned}$$

If we take the zero of energy at ϵ_1 (as stated in the opening remarks) then we have that μ is negative at high temperature. (In more detail, one may show that $|\mu|$ has a $(-T \ln T)$ dependence on temperature at high T, which can be derived straightforwardly from $\mu = (\partial F / \partial N)_{T,V}$ where F is the Helmholtz function).

Now let's consider the low temperature behaviour. For bosons it is easy to see that μ must always be negative (i.e. below the ground state energy level), for we have $\langle n_i \rangle \geq 0$ so $\exp(\beta(\epsilon_i - \mu)) > 1$ which gives

$$\mu < \epsilon_i \qquad \text{for all } i, \text{ at any } T \tag{10}$$

and therefore when $\epsilon_1 = 0$ we have

$$\mu < 0. \tag{11}$$

The equation for $\langle n_i \rangle$ can be solved for μ, giving

$$\beta\mu = -\ln(1 + 1/\langle n_1 \rangle) \tag{12}$$

which is valid at all temperatures. We can estimate μ at the lowest temperatures by noting that when T is low enough most of the particles will be in the ground state, so we must have $\langle n_1 \rangle \sim N$ which gives

$$\mu \quad \simeq \quad -\frac{1}{N\beta} = -\frac{k_{\mathrm{B}}T}{N}. \tag{13}$$

This shows that for $N \gg 1$ (the case we are usually interested in), μ approaches very closely to the ground state energy at low temperature. In particular μ is very small compared to the thermal energy $k_{\mathrm{B}}T$.

$$g(\epsilon) = D\epsilon^q \qquad \begin{array}{ccc} \text{dimensions} & D & q \\ 1 & L(2m)^{1/2}/(2\pi\hbar) & -1/2 \\ 2 & A(2m)\,/\,(4\pi\hbar^2) & 0 \\ 3 & V(2m)^{3/2}/(4\pi^2\hbar^3) & 1/2 \end{array} \tag{14}$$

Table 2: Density of states for free particles in a box (without spin).

We can now proceed to a calculation of the ground state population ($\langle n_1 \rangle$) as a function of temperature. We have

$$\begin{aligned} N &= \sum_i \langle n_i \rangle = \sum_{i=1}^{\infty} \frac{1}{\exp(\beta(\epsilon_i - \mu) - 1} \\ &= \frac{1}{e^{-\beta\mu} - 1} + \sum_{i=2}^{\infty} \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned} \tag{15}$$

where so far the expression is exact, and we have taken $\epsilon_1 = 0$. We would like to approximate the sum. We shall do so by converting it into an integral, but since we are concerned with low temperatures we need to check that this is legitimate. We observe from (5) and (6) that $\Delta E \sim N^{-2/3} k_{\rm B} T_0$. It follows that for temperatures of order T_0 the sum will extend over many terms (before the terms become negligible), therefore it can be well approximated by an integral. Furthermore this approximation remains fairly good down to temperatures of order $N^{-2/3} T_0$ (for a mole that's about $10^{-16} T_0$). Hence we obtain

$$N \simeq \frac{1}{e^{-\beta\mu} - 1} + \int_{\Delta E}^{\infty} \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} - 1} {\rm d}\epsilon, \tag{16}$$

where, though not exact, the expression is very precise in practice for a gas in a chamber of ordinary dimensions, and in the rest of the paper we will treat this expression as if it is exact. The function $g(\epsilon)$ is the density of states function, which takes the form

$$g(\epsilon) = D\epsilon^q \tag{17}$$

where D and q are given in table 2.

Introducing now

$$x \equiv \beta\epsilon, \qquad y \equiv -\beta\mu \tag{18}$$

we have

$$N = \frac{1}{e^y - 1} + D(k_{\rm B}T)^{q+1} \int_{x_2}^{\infty} \frac{x^q}{e^{x+y} - 1} {\rm dx} \tag{19}$$

where $x_2 = \Delta E / k_{\rm B} T$ and we have substituted an equals sign, signifying that the precision is high (explained above).

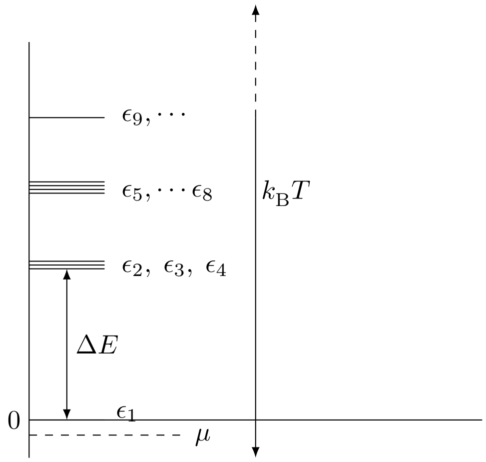

Figure 4: Illustrating the three main energy scales involved in a calculation of properties of a Bose gas at low temperature: $(\epsilon_1 - \mu) \ll (\epsilon_2 - \epsilon_1) \ll k_{\mathrm{B}}T$. The numbers of quantum states at each energy are for illustration only, except that we assume the ground state to be non-degenerate.

In the following, keep in mind that y is to do with μ and we are integrating over x.

As written, (19) has the form of an equation for N in terms of T and y (since D and q are given). But the typical situation is that we already know N and we would like to find y. What happens is that at any given N and T there is just one value of y for which (19) is satisfied. We would like to find that value.

As it stands the integral in (19) is hard to do, because it contains y. It would simplify matters if we could argue that y is sufficiently small that it can be dropped from the integral. This is what we shall do, but the reason this is correct has to be presented carefully because although y is less than x (when $T \le T_0$), it is not always very small compared to x, for values of x appearing in the integral.

We consider the situation at a temperature low enough that the ground state occupation $\langle n_1 \rangle$ is large compared to 1. In this case we can use (12) to obtain

$$y \simeq 1/\langle n_1 \rangle \tag{20}$$

The smallest value of x appearing in the integral is $x_2 = \beta \Delta E$ so we have

$$\frac{y}{x} < \frac{1}{\langle n_1 \rangle \beta \Delta E} \tag{21}$$

For a gas in a box, in either two or three dimensions, (5) gives $\Delta E \simeq 1.9 \epsilon_Q N^{-2/3}$, therefore

$$\frac{y}{x} < \frac{1}{\beta \epsilon_Q} \frac{N^{2/3}}{\langle n_1 \rangle}. \tag{22}$$

We will be interested in temperatures where $\beta\epsilon_Q \geq 1$ so we find $y \ll x$ when the ground state occupation is large compared to $N^{2/3}$. We will show later (eqn (32)) that for the three-dimensional gas it suffices for T to be very slightly below T_0 to satisfy this condition. Right at $T = T_0$, on the other hand, one finds $x_2 \simeq 5.48\,y$ so then y is not negligible compared to x. However, the part of the range of x in which y is not negligible is the part where x is itself very small, and this part only contributes negligibly to the entire integral (c.f. (29)). It follows that at temperatures of order T_0 or less, the integral in (19) is accurately approximated by

$$\int_{x_2}^{\infty} \frac{x^q}{e^{x+y}-1}\mathrm{dx} \simeq \int_{\mathrm{x}_2}^{\infty} \frac{\mathrm{x}^{\mathrm{q}}}{\mathrm{e}^{\mathrm{x}}-1}\mathrm{dx} \tag{23}$$

and the approximation becomes exact in the limit $N \to \infty$ at constant N/V.

The situation is as illustrated in Fig. 4. By this argument we find that for $T \leq T_0$, (19) can be well approximated as

$$N \simeq \frac{1}{e^y - 1} + D(k_{\mathrm{B}}T)^{q+1} \int_{x_2}^{\infty} \frac{x^q}{e^x - 1}\mathrm{dx}. \tag{24}$$

It is now apparent why we separated off the ground state ($i = 1$) term in (15): the approximation of neglecting y does not apply to that term. (If we tried it, we would get $\langle n_1 \rangle \simeq \infty$ which is not a good approximation!).

The step from (19) to (24) is often presented as if we are 'setting the chemical potential to zero', but it is not so. We are merely arguing that $|\mu|$ is small enough that it can be safely neglected in the integral, but not in the other term, for $0 < T \leq T_0$.

A useful way to write (24) is

$$\begin{aligned} N &= \bar{n}_1 + N_{\mathrm{e}} \\ \text{where} \qquad \bar{n}_1 &= \langle n_1 \rangle, \qquad N_{\mathrm{e}} \simeq D(k_{\mathrm{B}}T)^{q+1} \int_{x_2}^{\infty} \frac{x^q}{e^x - 1}\mathrm{dx}. \end{aligned} \tag{25}$$

In this notation the subscript 'e' stands for 'all the excited states'. Our strategy now is to evaluate N_{e} and use it to obtain $\bar{n}_1$.

From now on we need to consider carefully the value of q, because it has a large effect on the integral giving N_{e}. We shall focus attention on two values: $q = 0$, which occurs in the case of a gas in a 2-dimensional box, and $q = 1/2$, which occurs in the case of a gas in a 3-dimensional box.

$$N_{\mathrm{e}} = \begin{cases} D_2 k_{\mathrm{B}} T \displaystyle\int_{x_2}^{\infty} \frac{1}{e^x - 1}\mathrm{dx} & \text{2d} \\ D_3 (k_{\mathrm{B}}T)^{3/2} \displaystyle\int_{x_2}^{\infty} \frac{x^{1/2}}{e^x - 1}\mathrm{dx} & \text{3d} \end{cases} \tag{26}$$

The first integral (2d case) is dominated by the low-x region, which one can see by noting that for $x \ll 1$ the integrand tends to $1/x$ so the integral will diverge as $x_2 \to 0$. The second integrand (3d case), on the other hand, tends to $x^{-1/2}$ at $x \ll 1$ so the second integral does not diverge in the limit $x_2 \to 0$. We estimate the integrals as follows

$$\int_{x_2}^{\infty} \frac{1}{e^x - 1}\mathrm{dx} \quad \simeq \quad -\ln(x_2) \tag{27}$$

$$\int_{x_2}^{\infty} \frac{x^{1/2}}{e^x - 1}\mathrm{dx} \quad \simeq \quad \int_{0}^{\infty} \frac{x^{1/2}}{e^x - 1}\mathrm{dx} \;\simeq\; 2.315157 \tag{28}$$

The numerical value (3d case) is given more fully in table 1.

Let's check the degree of approximation involved in setting the lower limit of the integral to zero in the 3d case. This amounts to adding to the integral an extra contribution of

$$\int_{0}^{x_2} \frac{x^{1/2}}{e^x - 1}\mathrm{dx} \quad \simeq \quad 2\sqrt{x_2} \qquad (x_2 \ll 1). \tag{29}$$

The fractional error introduced is therefore $(2/2.315)\sqrt{x_2}$ which is small when $\Delta E \ll k_\mathrm{B}T$.

Under the approximations which have been made, which include a low (but not vanishing) temperature[1], we have

$$N_\mathrm{e} = \begin{cases} D_2\, k_\mathrm{B}T \ln(k_\mathrm{B}T/\Delta E) & \text{2d} \\ 2.315 D_3\, (k_\mathrm{B}T)^{3/2} & \text{3d} \end{cases} \tag{30}$$

and therefore

$$\frac{\bar{n}_1}{N} = 1 - \frac{N_\mathrm{e}}{N} = \begin{cases} 1 - (m/2\pi\hbar^2 n)\, k_\mathrm{B}T \ln(k_\mathrm{B}T/\Delta E) & \text{2d} \\ 1 - (T/T_0)^{3/2} & \text{3d} \end{cases} \tag{31}$$

where in the 3d case all the constants in (30) have been gathered into T_0. This is how (6) is obtained. The number density $n \equiv N/A$, $n \equiv N/V$ in the 2d, 3d case respectively.

Now let's look at the two cases.

In both cases the expression for N_e goes above N at high temperature, which means the approximation of setting $\mu = 0$ in the integral is no longer valid. But it is clear that if the expression for N_e exceeds N for $\mu = 0$ then there is some $\mu < 0$ for which N_e is equal to N. Therefore the prediction at higher temperatures is $N_\mathrm{e} \simeq N$ and $\bar{n}_1/N$ is very small. (Indeed it is obvious from the distribution function that once μ falls below the value $-k_\mathrm{B}T \ln 2$ the ground state population falls below 1 so then the ground state population is obviously not macroscopic.)

For lower temperatures, such that $N_\mathrm{e} < N$, the important point is that in 2d the significant energy scale is set by ΔE whereas in 3d it is set by $k_\mathrm{B}T_0$, which can be very much larger than ΔE. Indeed, in the limit of a container of infinite dimensions, $\Delta E \to 0$ but T_0 remains finite if the number density

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[1] A low temperature approximation was invoked when we took $|\mu|$ to be small; nonetheless T is not small compared to $\Delta E/k_\mathrm{B}$ or the sum (15) cannot be approximated by an integral.

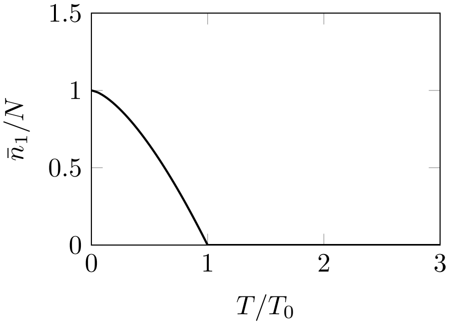

Figure 5: The fraction of particles in the ground state, as a function of temperature, for a Bose gas in a 3-dimensional box. T_0 is the condensation temperature, for $N \gg 1$.

is held constant. In both cases the population accumulates in the ground state as the temperature falls, but in the limit $\Delta E \to 0$ in the 2d case there is no particular temperature (above zero) at which the ground state population starts to rise abruptly as T falls. In the 3d case, on the other hand, the prediction for $\bar{n}_1/N$ is shown in Fig. 5. Once T falls below T_0 the ground state fraction suddenly starts to rise towards 1. This indicates that the particles are 'plunging' into the ground state in large numbers, like lemmings, at a temperature well above $\Delta E/k_{\rm B}$. This is a special property of bosons, expressed loosely by the idea that they 'like' to crowd together[2].

The central result for BEC of a gas in a 3d box is expressed by (31) and (6) which we state again here for emphasis:

Bose-Einstein condensation

$$\frac{\bar{n}_1}{N} = 1 - \left(\frac{T}{T_0}\right)^{3/2}, \qquad k_{\rm B} T_0 = \frac{\hbar^2}{2m} 4\pi \left(\frac{n}{\zeta(3/2)}\right)^{2/3} \tag{32}$$

2.1 Establishing the argument more fully

The previous sections are sufficient for an introductory course (university undergraduate level). For a more thorough study we need to pay attention to various issues which were skimmed-over in the above.[3] For students who only need the introductory level, it is recommended to read this section nevertheless, even if the methods are not required to be learned.

We shall now focus purely on the BEC case, i.e. 3d.

We have given an argument to expect the behaviour shown in Fig. 5 but the reader should be

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[2] More precisely, the probability for a boson to make a transition to a given state is magnified by the occupation number of that state.

[3] . . . but the preceding material is already more careful than some textbook treatments I have seen!

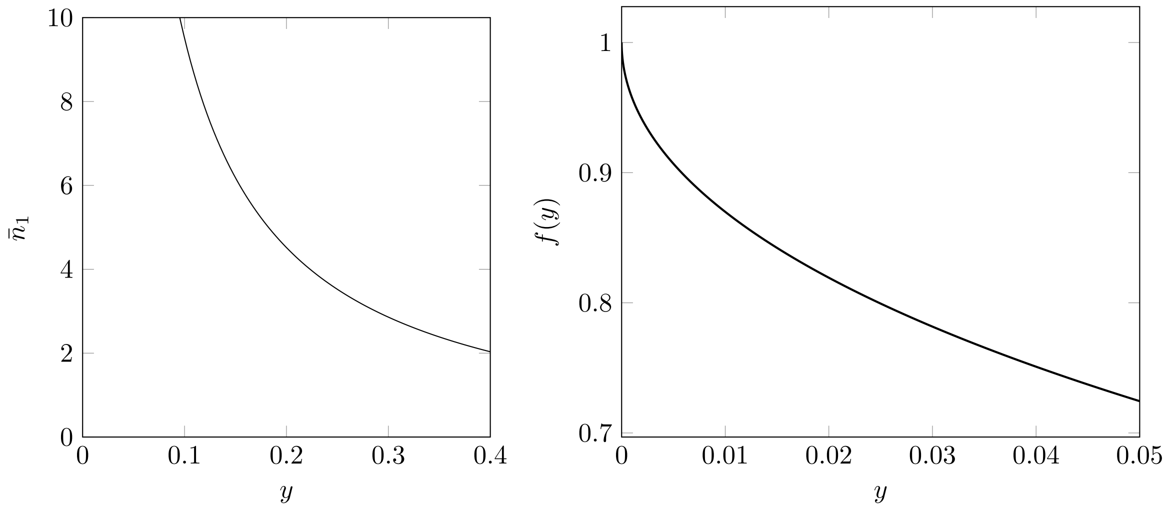

Figure 6: The functions $\bar{n}_1(y)$ and $f(y)$. At large y, $\bar{n}_1 \to e^{-y}$ and $f \to e^{-y}/\zeta(3/2)$.

concerned about three issues:

1. The prediction appears to be that $\bar{n}_1$ goes to zero at $T = T_0$, but according to the distribution function, the ground state population is larger than any other, so we cannot have $\bar{n}_1 = 0$. This puzzle will be answered by showing that $\bar{n}_1(T_0)$ is in fact large, but $\bar{n}_1(T_0)/N \to 0$ in the limit $N \to \infty$.
2. So far we have not obtained $\mu(T)$ except for the limiting case where $\bar{n}_1$ approaches N, leading to (13). It is important also to find the value of μ at temperatures of order T_0 because we need to justify the statement $y < x_2$ which was invoked in order to justify dropping y from the integral when we obtained $N_{\rm e}$.
3. Is there a genuine discontinuity at $T = T_0$ and therefore a phase transition? To answer this we need to discover how μ behaves both at and near T_0.

All these questions will be answered by keeping y in the integral, i.e. we return to the 'exact' (or rather, highly accurate) eqn (19) and proceed from there.

In the 3d case, (19) can be written

$$\frac{n_1(y)}{N} + \left(\frac{T}{T_0}\right)^{3/2} f(y) = 1 \tag{33}$$

Bose function; polylogarithm function
The function

$$\mathrm{Li}_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty \mathrm{dx} \frac{\mathrm{x}^{\mathrm{n}-1}}{\mathrm{z}^{-1}\mathrm{e}^{\mathrm{x}} - 1} \tag{38}$$

is called both the *Bose function* and the *polylogarithm function*. One sometimes sees the notation $g_n(z) \equiv \mathrm{Li}_n(z)$ (not to be confused with the density of states). The polylogarithm is related to the zeta function by $\mathrm{Li}_s(1) = \zeta(s)$. Our $f(y)$ can be written

$$f(y) = \mathrm{Li}_{3/2}\left(e^{-y}\right)/\zeta(3/2). \tag{39}$$

For some algebraic manipulations it is useful to introduce the *fugacity* $z \equiv \exp(\beta\mu) = \exp(-y)$. One can show that

$$\mathrm{Li}_n(z) = \sum_{p=1}^{\infty} \frac{z^p}{p^n} \;=\; z + \frac{z^2}{2^n} + \frac{z^3}{3^n} + \cdots . \tag{40}$$

This sum can be a useful way to evaluate the function numerically when $z < 1$. At $z = 1$, on the other hand, the sum converges very slowly and then it is better to evaluate the integral by a suitable numerical method.

where

$$n_1(y) \;=\; (\exp(y) - 1)^{-1}, \tag{34}$$

$$f(y) \;\equiv\; \frac{1}{2.315157\ldots} \int_0^\infty \frac{x^{1/2}}{e^{x+y} - 1} \mathrm{dx} \tag{35}$$

where the prefactor is chosen such that $f(0) = 1$. These functions are plotted in Fig. 6. Here are a few values:

$$\begin{array}{ccc} y & f(y) & n_1(y) \\ 0 & 1 & \infty \\ \ln(3/2) & 0.356166863 & 2 \\ \ln(2) & 0.239183478 & 1 \end{array} \tag{36}$$

In the limit $y \to 0$ one finds[4]

$$f \simeq 1 - 1.3569672\sqrt{y} + 0.559014\, y + \cdots \tag{37}$$

where the coefficient of the $\sqrt{y}$ term is $2\sqrt{\pi}/\zeta(3/2)$.

The value of $y(T)$, and hence $\mu(T)$, is found by solving (33) numerically. Results are shown in Fig. 7 for three values of T/T_0. Having obtained $y(T)$ one may obtain all other information, such as $n_1(T)$.

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[4] This expression may be found either by a fiddly analysis or by evaluating $f(y)$ at a set of y values in the range 0 to 0.01 by numerical integration, then fitting a quartic curve to $1 - f$ as a function of $\sqrt{y}$ and extracting the coefficients of the lowest few terms.

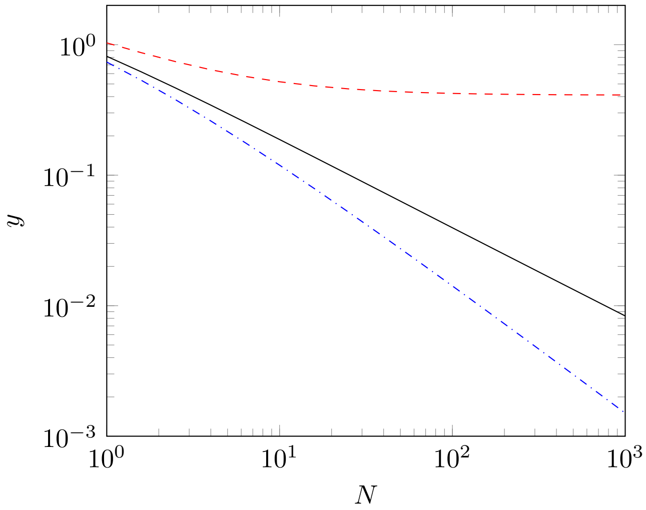

Figure 7: The behaviour of y as a function of N at three values of T. Full curve: $T = T_0$; blue dash-dotted curve: $T = T_0/2$; red dashed curve: $T = 2T_0$. The important point is that in the limit $N \to \infty$, one has $y \to 0$ for $T \le T_0$, and y is non-zero for $T > T_0$.

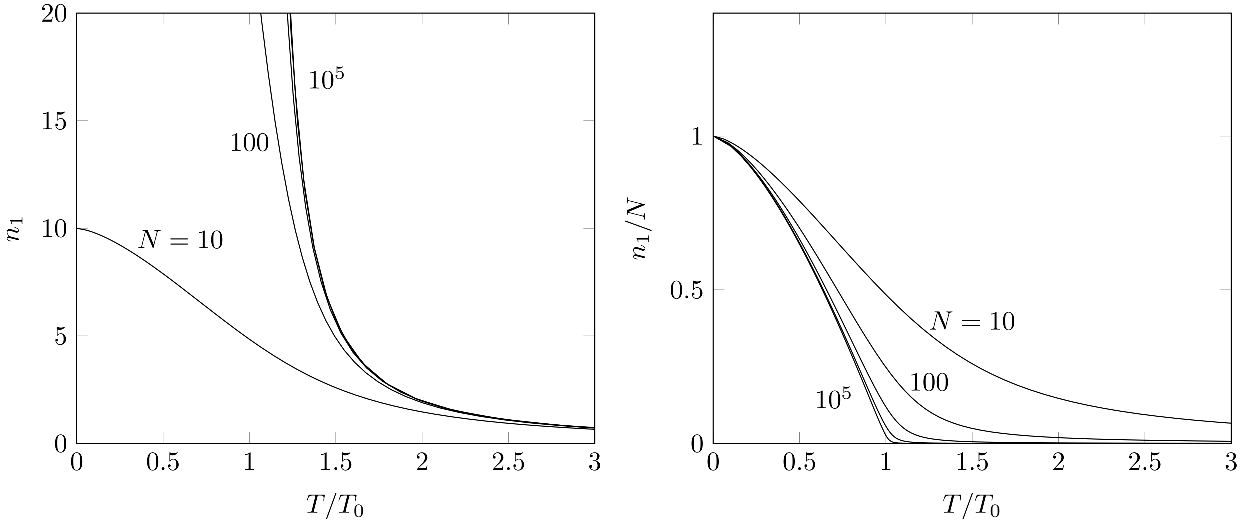

Figure 8: The ground state population n_1 (left) and the ground state fraction n_1/N (right), as a function of temperature, for the values $N = 10^{1,2,\cdots 5}$. The first is independent of N at large T, the second is independent of N at small T.

The result is shown in Fig. 8 for several values of N in the range 10 to 10^6. This study enables one to see how the continuous behaviour at finite N goes over to a discontinuity as $N \to \infty$. Some other features are also noteworthy:

1. $\bar{n}_1/N$ goes to the same value (namely, 1) as $T \to 0$ at all N. This is what we expected.
2. $\bar{n}_1$ itself (as opposed to $\bar{n}_1/N$) is independent of N at high T. This is what one expects when the particles behave independently.
3. $\bar{n}_1 \simeq 2$ at $T = 2T_0$. More precisely, for $N \gg 1$:

$$\begin{array}{c|ccc} \bar{n}_1 & 1 & 2 & 3 \\ T/T_0 & 2.595 & 1.99 & 1.756 \end{array} \tag{41}$$

4. At $T = T_0$, one finds (see below)

$$\bar{n}_1 \simeq (1.35697N)^{2/3} \tag{42}$$

   and therefore $1 \ll \bar{n}_1 \ll N$. Hence it is not true to say that the occupation of the ground state only becomes macroscopic at $T < T_0$, but it is true to say that, in the limit $N \to \infty$, the ground state fraction $(\bar{n}_1/N)$ only rises above zero for $T < T_0$.

To deduce (42) observe that at $T = T_0$, y is small and therefore (37) can be used. The equation for y is then $(\bar{n}_1/N) + f = 1$, or

$$(\exp(y) - 1)^{-1} \simeq 1.35697N\sqrt{y} \tag{43}$$

and by substituting $\exp(y) \simeq 1 - y$, eqn (42) follows.

3 The two phases; energy, heat capacity, pressure, entropy

We have now established that there is a discontinuity in the quantity

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\bar{n}_1}{N}\right) \tag{44}$$

at $T = T_0$ in the limit $N \to \infty$. We have

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\bar{n}_1}{N}\right) = \left\{ \begin{array}{cl} -3/(2T_0) & \text{at } T = T_0 - |\delta| \\ 0 & \text{at } T = T_0 + |\delta| \end{array} \right. \text{ in the limit } \delta \to 0. \tag{45}$$

It follows that there is also a discontinuity in other quantities. In the subsequent section we will show that $\mathrm{d}^2\mu/\mathrm{dT}^2$ is discontinuous, and also that U and $C_V = \mathrm{dU/dT}$ are continuous, but $\mathrm{dC_V/dT} = \mathrm{d^2U/dT^2}$ is not. The change of behaviour as T falls below T_0, for the 3d Bose gas, is a *phase transition*. It is called **Bose-Einstein condensation** or BEC. The two 'phases' are the two groups of particles:

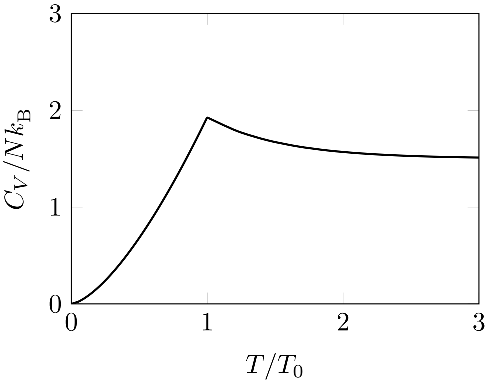

Figure 9: The heat capacity of a Bose gas at low temperature.

one is the group in the ground state, the other is spread over the excited states. The ground state part is called the *condensate*, the remaining part has no special name but may be loosely referred to as the 'normal' part. At the transition temperature (T_0) it is not the case that *all* of the system immediately changes phase, but rather the condensate starts to be a substantial fraction of the total, and grows as T is lowered further. This type of phase transition is called a *continuous phase transition.*

We can calculate the low-temperature heat capacity as follows:

$$\begin{aligned} U &= \int_0^\infty \frac{\epsilon g(\epsilon)}{e^{\beta\epsilon}-1}\mathrm{d}\epsilon \qquad \text{for T} \le \mathrm{T_0} \\ &= D\int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta\epsilon}-1}\mathrm{d}\epsilon \\ &= D(k_\mathrm{B}T)^{5/2}\int_0^\infty \frac{x^{3/2}}{e^{x}-1}\mathrm{dx} \\ &= \frac{3\,\zeta(5/2)}{2\,\zeta(3/2)} N k_\mathrm{B} T_0 \left(\frac{T}{T_0}\right)^{5/2} \\ &\simeq 0.77027 N k_\mathrm{B} T_0\,(T/T_0)^{5/2} \end{aligned} \tag{46}$$

hence

$$C_V = 1.92567 N k_\mathrm{B} (T/T_0)^{3/2}. \tag{47}$$

This is accurate all the way up to $T = T_0$ because the approximation $|\mu| \ll k_\mathrm{B}T$ holds throughout this range. At $T = T_0$ we note that C_V reaches a value a little higher than the high-temperature value of $1.5Nk_\mathrm{B}$; the overall behaviour is as shown in Fig. 9. The discontinuity in $\mathrm{dC_V/dT}$ will be derived in the next section. This cusp is an observable signature of the BEC phase transition (though not necessarily the first thing one notices in the laboratory).

Next let's examine the pressure and hence the equation of state. For this purpose we invoke (without derivation here) the grand partition function $\mathcal{Z}$ and its relation to the grand potential Ω. For any

'pV' system we have

$$\Omega = U - TS - \mu N = -k_{\rm B} T \ln \mathcal{Z} \tag{48}$$

and for a Bose gas

$$\mathcal{Z} = \prod_i \frac{1}{1 - e^{\beta(\mu - \epsilon_i)}}. \tag{49}$$

General thermodynamic arguments lead to the Euler relation which gives $G = \mu N$ where the Gibbs function $G = U - TS - pV$. But from the definitions we have $\Omega = G - \mu N - pV$ and thus one obtains

$$pV = -\Omega = k_{\rm B} T \ln \mathcal{Z}. \tag{50}$$

Hence

$$\begin{aligned} pV &= -k_{\rm B} T \sum_i \ln\left(1 - e^{\beta(\mu - \epsilon_i)}\right) \\ &\simeq k_{\rm B} T \int_0^\infty {\rm d}\epsilon\, {\rm g}(\epsilon) \ln\left(1 - {\rm e}^{\beta(\mu - \epsilon_{\rm i})}\right) \end{aligned} \tag{51}$$

where the approximation requires only the modest assumption $k_{\rm B} T \gg \Delta E$. (We have not assumed small μ here: the result is valid at all temperatures above $\Delta E / k_{\rm B}$). Carrying out an integration by parts, using $g(\epsilon) = D\epsilon^{1/2}$, one obtains $\int g(\epsilon){\rm d}\epsilon = (2/3)\epsilon {\rm g}(\epsilon)$ and hence

$$\begin{aligned} pV &= \frac{2}{3} k_{\rm B} T \int {\rm d}\epsilon \frac{\epsilon {\rm g}(\epsilon)}{1 - {\rm e}^{\beta(\mu - \epsilon)}} \beta {\rm e}^{\beta(\mu - \epsilon)} \\ &= \frac{2}{3} \int {\rm d}\epsilon \frac{\epsilon {\rm g}(\epsilon)}{{\rm e}^{\beta(\epsilon - \mu)} - 1} \\ &= \frac{2}{3} U. \end{aligned} \tag{52}$$

This remarkably simple formula announces that the pressure is simply equal to the two-thirds of the energy density, whether or not the gas is in the condensation regime.

By using (46) we find that for $T \le T_0$

$$p = \frac{\zeta(5/2)}{\zeta(3/2)} n k_{\rm B} T_0 \left(\frac{T}{T_0}\right)^{5/2}. \tag{53}$$

Recalling now that $T_0 \propto n^{2/3}$ (eqn (6)), a useful way to write this result is

$$p = \left(\frac{2m}{4\pi\hbar^2}\right)^{3/2} \zeta(5/2)\, (k_{\rm B} T)^{5/2}. \tag{54}$$

Hence *the pressure depends on temperature alone (independent of the density)* in the condensation regime. The situation is as shown in Fig. 10. On an indicator diagram, the isotherms have a

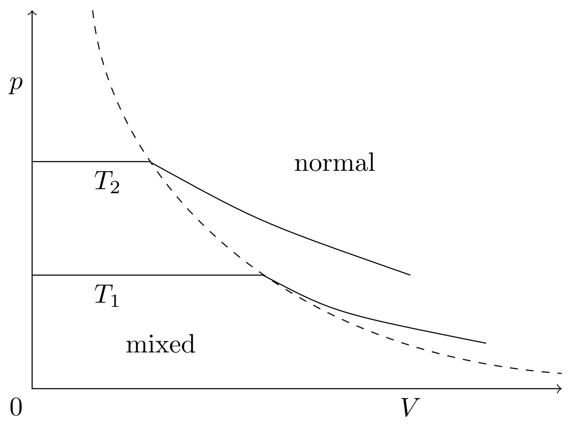

Figure 10: Indicator diagram for a Bose gas. Two isotherms are shown, with $T_1 < T_2$. The dashed line shows the boundary of the mixed-phase region. It is described by $p \propto T^{5/2}$ with $T_0 \propto n^{2/3}$ therefore $p \propto V^{-5/3}$ at fixed N.

behaviour qualitatively similar to those of any ordinary fluid such as water in the liquid/vapour mixed-phase regime: above the phase transition, the pressure increases as the volume falls (at any given temperature) and then after the transition point the pressure stays constant as the volume falls; the condensate fraction is then growing.

Next we find the entropy, which can conveniently be obtained from $G = U - TS + pV = \mu N$ so

$$\begin{aligned} S &= \frac{1}{T}(U + pV - \mu N) \qquad \text{any } T \\ &= \frac{5}{3}\frac{U}{T} \qquad T \le T_0 \end{aligned} \tag{55}$$

using (52).

Observe now that in the condensation regime $S \propto T^{3/2} \propto N_{\rm e}$. We can interpret the outcome by inferring that the entropy is entirely owing to the normal part of the gas, and the condensate has no entropy at all. Each normal particle contributes an entropy $(5/2)k_{\rm B}\,\zeta(5/2)/\zeta(3/2) \simeq 1.28\,k_{\rm B}$. (This is reminiscent of the entropy of about $3.6\,k_{\rm B}$ per photon in thermal radiation).

For a monatomic gas in the classical limit one has $U = (3/2)Nk_{\rm B}T$ and $p = (N/V)k_{\rm B}T$, so one may say there is an energy $(3/2)k_{\rm B}T$ per particle and a pressure $k_{\rm B}T/V$ per particle. In the condensation regime we have that both U/T and p/T are proportional to $N_{\rm e}$. It follows that we can interpret the overall situation by saying the condensate has neither entropy nor energy nor pressure, and the normal component has an amount of all three quantities similar to what one might expect. These conclusions are legitimate in the limit $V \to \infty$. (At finite volume one has that the ground state energy is a function of volume so the condensate will exert a little pressure, but this is usually negligible compared to that of the normal component).

4 The approach to T_0 from above

This section is more advanced than previous sections and would normally be omitted for an introductory course.

In order to study the situation $T > T_0$ we need to evaluate functions such as $f(y)$ and $U(T)$ for $y \neq 0$. For this purpose it will be useful to have $y(T)$ (which then immediately gives $\mu(T)$). For given N and T, one finds $y(T)$ by solving (33). Above the transition temperature we can neglect the n_1/N term in the limit $N \gg 1$ and then we have

$$f(y) = (T/T_0)^{-3/2} \qquad (T \geq T_0) \tag{56}$$

For small y (i.e. close to the transition) (37) gives $f = 1 - a\sqrt{y} + O(y)$ where $a = 2\sqrt{\pi}/\zeta(3/2) \simeq 1.357$ so we have

$$1 - a\sqrt{y} + O(y) = (T/T_0)^{-3/2} \tag{57}$$

and therefore

$$y + O(y^{3/2}) = \frac{1}{a^2}\left(1 - t^{-3/2}\right)^2 \tag{58}$$

where we introduced $t \equiv T/T_0$ in order to reduce clutter. We now drop the $O(y^{3/2})$ term in order to find the following results which are valid when $y \ll 1$:

$$\frac{\mathrm{d}y}{\mathrm{d}T} = \frac{3}{a^2 T_0}\left(1 - t^{-3/2}\right) t^{-5/2}, \tag{59}$$

$$\frac{\mathrm{d}^2 y}{\mathrm{d}T^2} = \frac{3}{a^2 T_0^2}\left(-\frac{5}{2}t^{-7/2} + 4t^{-5}\right). \tag{60}$$

At the transition (where $t = 1$) we therefore find $y = 0$, $\mathrm{dy/dT} = 0$ and

$$\frac{\mathrm{d}^2 y}{\mathrm{d}T^2} = \frac{9}{2a^2 T_0^2}. \tag{61}$$

By a similar analysis for $\mu = -k_{\mathrm{B}} T\, y$ one finds, at the transition (approached from above)

$$\frac{\mathrm{d}\mu}{\mathrm{d}T} = 0, \qquad \frac{\mathrm{d}^2\mu}{\mathrm{d}T^2} = -\frac{9k_{\mathrm{B}}}{2a^2 T_0}. \tag{62}$$

We therefore deduce that the non-analytic behaviour in the chemical potential appears in its second derivative (since for temperatures approaching T_0 from below one has $\mu = 0$ with all derivatives zero).

Next we consider energy. For any temperature we have

$$U = D(k_{\mathrm{B}}T)^{5/2}\int_0^\infty \frac{x^{3/2}}{e^{x+y} - 1}\mathrm{dx}. \tag{63}$$

To reduce clutter let's introduce $\tilde{D} \equiv k_{\rm B}^{5/2} D$ and

$$I(y) = \int_0^\infty \frac{x^{3/2}}{e^{x+y} - 1} {\rm dx}, \tag{64}$$

then we have

$$U = \tilde{D} T^{5/2} I(y). \tag{65}$$

In conditions of constant V and N the heat capacity is

$$C_V = \frac{{\rm d}U}{{\rm d}T} = \frac{5}{2} \tilde{D} T^{3/2} I(y) + \tilde{D} T^{5/2} \frac{{\rm d}y}{{\rm d}T} \frac{{\rm d}I}{{\rm d}y}. \tag{66}$$

When $T \le T_0$ we have $y = 0$ and ${\rm dy/dT} = 0$ so just the first term in (66) contributes, and it gives (47). We can now observe that the second term tends to zero in the limit $y \to 0$ (we will prove this shortly) and therefore we have the same C_V at $T = T_0^+$ as at $T = T_0^-$: the heat capacity is a continuous function of T.

Next we proceed to the gradient of the heat capacity:

$$\frac{{\rm d}C_V}{{\rm d}T} = \frac{{\rm d}^2 U}{{\rm d}T^2} = \frac{15}{4} \tilde{D} T^{1/2} I(y) + \tilde{D} \left[\frac{5}{2} T^{3/2} \frac{{\rm d}y}{{\rm d}T} + T^{5/2} \frac{{\rm d}^2 y}{{\rm d}T^2} \right] \frac{{\rm d}I}{{\rm d}y} + \tilde{D} T^{5/2} \left(\frac{{\rm d}y}{{\rm d}T} \right)^2 \frac{{\rm d}^2 I}{{\rm d}y^2} \tag{67}$$

This is exact. We now take an interest in the limit $y \to 0$ (with y always positive). We showed above that in this limit ${\rm dy/dT} \to 0$ and furthermore we will show in a moment that it does so fast enough to suppress a divergence in ${\rm d^2I/dy^2}$, hence we find that the abrupt change in ${\rm dC_V/dT}$ at the transition is given by the ${\rm d^2y/dT^2}$ term. Therefore

$$\frac{\Delta({\rm dC_v/dT})}{{\rm dC_V/dT}} = \frac{6}{5a^2} \frac{{\rm dI/dy}}{I} \tag{68}$$

where we used (61) and the integrals should be evaluated at $y = 0$. We have $I(y) = \Gamma(5/2) {\rm Li}_{5/2}(z)$ where $z = e^{-y}$. By using the series expression (40) one obtains

$$\frac{{\rm dLi}_n(z)}{{\rm d}z} = \frac{1}{z} {\rm Li}_{n-1}(z) \tag{69}$$

and therefore ${\rm dI/dy} = -\Gamma(5/2){\rm Li_{3/2}(z)}$. Hence

$$\frac{\Delta({\rm dC_v/dT})}{{\rm dC_V/dT}} = -\frac{3(\zeta(3/2))^3}{10\pi\zeta(5/2)} \simeq -1.269087 \tag{70}$$

(The slope changes from $2.8885\, N k_{\rm B}/T_0$ at T_0^- to $-0.77726\, N k_{\rm B}/T_0$ at T_0^+).

4.1 Mathematical detail

It remains to confirm that the final term in (67) is indeed zero in the limit $y \to 0$. This is a little fiddly; the reader may skip this section if they wish simply to trust the claim. Using (69) and that y

is quadratic in T, the final term in (67) is proportional to

$$y^2 \int_0^\infty \frac{x^{-1/2}}{e^{x+y}-1} \mathrm{dx}. \tag{71}$$

The integrand is divergent at $(x+y)=0$ so let's examine

$$y^2 \int_0^\epsilon \frac{x^{-1/2}}{e^{x+y}-1} \mathrm{dx} \tag{72}$$

for some small ϵ. The rest of the integral is finite so it obviously gives zero contribution when $y \to 0$. We just need to check this portion near $x=0$. Since both x and y are small we have

$$y^2 \int_0^\epsilon \frac{x^{-1/2}}{x+y+O((x+y)^2)} \mathrm{dx}. \tag{73}$$

As we take the limit $y \to 0$ we can take, for example, $\epsilon = y^2$ and therefore $\epsilon \ll y$. In this case $y \gg x$ in the integrand and we have

$$y^2 \int_0^\epsilon \frac{x^{-1/2}}{y+O(y^2)} \mathrm{dx}. \tag{74}$$

This form of the integral is finite. We deduce that there exists a way to take the limit $y \to 0$ such that the expression (71) tends to zero in the limit.

5 Gas in a harmonic well

So far we discussed a gas confined in a box, meaning a confining potential with hard walls, with particles moving freely away from the walls. Another way to study low-temperature gases is to confine them in some other potential, such as a harmonic potential well, with potential energy $V = (1/2)m\omega^2 r^2$ where r is the distance from the centre of the well and ω (the natural frequency) is a constant. Study of the quantum harmonic oscillator gives the energy levels and degeneracies

dim	ϵ_n	g_n	q
1d	$(n+1/2)\hbar\omega$	1	0
2d	$(n+1)\hbar\omega$	$n+1$	1
3d	$(n+3/2)\hbar\omega$	$1+n(n+3)/2$	2

(75)

It follows that, for energies $\epsilon \gg \hbar\omega$ the density of states has the form $D\epsilon^q$ with the values of q as shown in the table. With this information one can revisit the arguments of the previous sections and discover the main facts about BEC in a harmonic well. One finds now that there is a phase transition in both the 2D and 3D cases, because $q > 0$. Below the transition temperature the condensate fraction is $n_1/N = 1 - (T/T_0)^{q+1}$.

When one studies low-temperature gases in the laboratory, many parameters can in principle act as a signature of the BEC transition. For a gas in a harmonic well, notable properties include

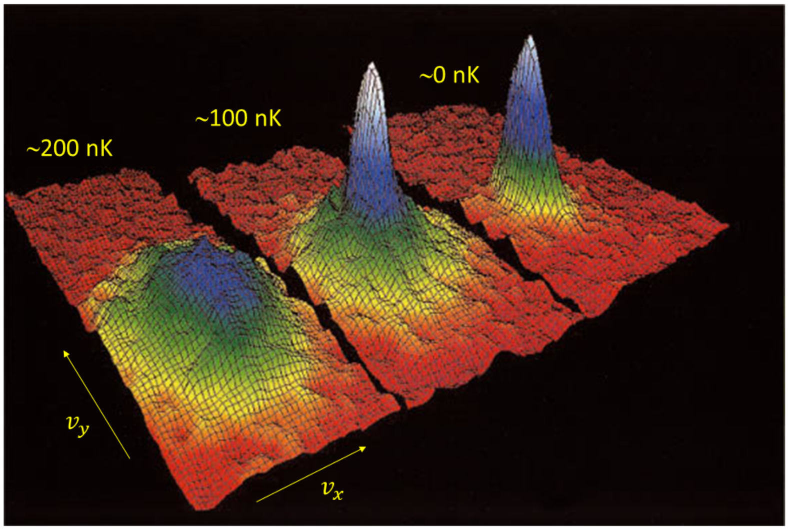

Figure 11: Data from the laboratory of Eric Cornell and Carl Wieman, revealing the appearance of a condensate of rubidium atoms. The plot shows the measured velocity distribution at three temperatures attained in different stages of cooling. The cooling method involves some loss of atoms by a process akin to evaporation.

the density and velocity distributions. The ground state of the well has a gaussian wavefunction $\psi(r)$, giving a probability distribution $|\psi(r)|^2$. The standard deviation in any one direction is then $\Delta x_1 = (\hbar/2m\omega)^{1/2}$. For a cloud in a well at high temperature, on the other hand, the mean potential energy has a contribution $(1/2)k_{\rm B}T$ for each direction of motion, so we find $\Delta x_T = (k_{\rm B}T/m\omega^2)^{1/2}$. Hence

$$\frac{\Delta x_1}{\Delta x_T} = \sqrt{\frac{\hbar\omega}{k_{\rm B}T}}. \tag{76}$$

The transition temperature T_0 will satisfy $k_{\rm B}T_0 \gg \hbar\omega$ when $N \gg 1$ so $\Delta x_1 \ll \Delta x_T$. When the temperature T reaches the transition temperature and falls below it, one therefore expects to find a density distribution made of a sum of two gaussians with different widths. The narrow part appears as a peak which grows rapidly in height, but not in width, as the temperature falls, and this is what is seen experimentally.

In practice it may be easier to probe the velocity distribution in the first instance. This is done, for example, by switching off the trapping potential. The cloud then falls under gravity and expands as it falls. One takes a snapshot of the cloud (using laser fluorescence) after it has expanded for about 0.1 seconds. The observed spatial distribution in the horizontal plane now maps the velocity distribution of the cloud when it was released. The condensate appears in momentum space as a peak of width $\hbar/2\Delta x_1$. Therefore in the condensation regime one expects a velocity distribution in the form of a narrow peak superimposed on a broader (also gaussian) background. The narrow peak is owing to the condensate. Its appearance and growth as T falls is a clear signature of BEC—c.f. Fig. 11.

6 Liquid Helium; ultracold atomic vapours

There are two main physical systems where Bose Einstein condensation, or a process closely related to it, have been studied experimentally. The first is liquid helium, the second is ultracold atomic vapours trapped in a harmonic potential well.

The case of liquid helium is relevant because the helium-4 atoms are bosons and they have two further relevant properties: the interactions between the atoms are weak and the atoms are light, which results in a high kinetic energy (compared with heavier particles) when the particles are confined. In consequence helium does not solidify at ordinary pressures when it is cooled, and furthermore one can regard the liquid as, to a rough approximation, quite like a cold gas. It is observed that liquid helium undergoes a transition at 2.17 K. This transition is called the *lambda point*, a reference to the fact that the graph of C_V as a function of temperature has a spike at the transition which resembles a greek letter λ. Above the lambda point helium it is a normal liquid, called helium I. Below the transition it is another form called helium II, and the latter is well modelled as a mixture of two liquids, one of which is normal and the other is superfluid (having zero viscosity). The superfluid fraction grows as the temperature is further reduced below the lambda point.

These observations led London to suggest that the transition in liquid helium is, or is like, a Bose-Einstein condensation. The transition temperature predicted from the observed density is 3.13 K which is quite close to the observed value at the lambda point. The superfluid fraction can be modelled, to first approximation, as the ground state fraction in the BEC picture.

In fact liquid helium is not a gas; the atomic interactions cannot be neglected in an accurate model. This results in differences between BEC and the lambda point in liquid helium, but it is clear that the lambda point is owing to the quantum nature of the helium atoms, especially their indistinguishability and bosonic nature.

A transition which can be called a true BEC occurs in experiments with ultracold (nanokelvin) atomic vapours at low density. The vapour in these experiments is typically of modest size (say some millions of atoms) but the low density makes it a very good approximation to ignore the particle interactions in the first instance, and the BEC theory can be tested precisely. A series of largely experimental developments led to these remarkable results, including laser cooling to milliKelvin temperatures (1978), followed after some years to an experimental breakthrough attaining microKelvin temperatures (1997 Nobel prize) and then a further insight called evaporative cooling leading to nanoKelvin temperatures and BEC which was first observed in 1995. The 2001 Nobel prize was awarded for this and related work.