7

Bose–Einstein statistics and condensation

- The physics community's acceptance of the photon idea did not come about until the discovery and analysis of Compton scattering in 1923. We present a short introduction to this subject. The remainder of this chapter is devoted to the statistical analysis of photons as identical bosons.

- Just about all of Einstein's principal contributions to quantum theory are statistical in nature: his first paper on the photon, his work on specific heats, on stimulated and spontaneous radiative processes, and now on quantum statistics. This last effort was prompted by a paper that S. Bose sent to him in 1924.

- Bose was dissatisfied with the logical foundation of Planck's radiation theory. He presented a derivation of Planck's distribution using the particle approach from the very beginning. We present Bose's derivation in detail so as to understand the implicit assumptions he made in this pioneering work.

- In the meantime de Broglie put forth his idea that matter, under certain circumstance, could behave like waves. This inspired Einstein to extend Bose's analysis of radiation to systems of matter particles. Here he made the discovery of the astounding possibility of Bose–Einstein condensation (BEC).

- The papers of de Broglie and Einstein directly influenced Schrödinger in his creation of the Schrödinger equation. This prompted Pais to bestow onto Einstein the title of "godfather of wave mechanics".

- The ultimate understanding of Planck's spectral distribution came about in modern quantum mechanics with its notion of indistinguishable particles. A multiparticle system must be described by a wavefunction that is either symmetric or antisymmetric under the interchange of two identical particles. The spin-statistics theorem instructs us that particles with half-integer spin obey Fermi–Dirac statistics and particles with integer spin (like photons) obey Bose–Einstein statistics.

- Section 7.4 is devoted to some basics of Bose–Einstein condensation. In particular we show that this phenomenon of a macroscopic number of particles "condensing" into the momentum space ground state can only take place when the particles' wavefunctions start to overlap. The

> production of BEC and a demonstration of its macroscopic quantum behavior in the laboratory setting was achieved in the 1990s. We briefly describe this success.
> - In SuppMat Section 7.5, we discuss radiation pressure resulting from photon collisions with the enclosure. In SuppMat Section 7.6, we show why, in the context of modern quantum statistics, Planck found the right answer using the statistical weight he wrote down in 1900. In SuppMat Section 7.7, we discuss the role of particle indistinguishability, making it possible for BEC to take place.

As we have already recounted previously, there was persistent resistance to Einstein's 1905 photon proposal. This lasted till 1923 when Arthur H. Compton (1892–1962) performed X-ray scattering off a graphite target and provided the analysis showing that a light quantum has not only energy but also momentum. This brought about the general acceptance of the photon idea. Arnold Sommerfeld (1868–1951), one of the leading lights in physics, had this to say about the result of Compton scattering (Sommerfeld 1924): "It is probably the most important discovery which could have been made in the current state of physics." With this general acceptance, the investigation of radiation made further progress with the first correct statistical analysis of radiation as a specific case of Bose–Einstein quantum statistics. These will be the main topics of this chapter.

7.1 The photon and the Compton effect

Compton carried out experiments with X-rays scattering on a graphite target. In the classical theory, these incoming electromagnetic waves cause electrons in the carbon atoms to oscillate with the same frequency as the incident waves and re-emit the final state waves with the same frequency. In the particle picture of light, a photon carries momentum as well as energy. The energy E and momentum p are related[1] by $\epsilon = pc$, which is the $m = 0$ case of the general relativistic energy and momentum relation $\epsilon^2 = (pc)^2 + (mc^2)^2$. For a quantized photon energy $\epsilon = h\nu$, one has the simple relation between photon momentum and wavelength

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}. \tag{7.1}$$

The particle description of this scattering of light by electrons leads to a distinctive result.[2] From momentum–energy conservation, one expects the final state photon to have a smaller momentum than the incident photon, hence a longer wavelength. The exact relation between this shift of wavelength and scattering angle can easily be worked out (see Fig. 7.1). One starts with the energy conservation relation:

$$\epsilon + mc^2 = \epsilon' + \sqrt{(p_e c)^2 + (mc^2)^2}$$

[1] This is compatible with a classical radiation field with field energy density (u) given by $u = (E^2 + B^2)/2$ and field momentum density given by the Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{B}/c$, with their magnitudes related by $u = cS$, because, in an electromagnetic wave, the electric and magnetic field strengths are equal, $E = B$.

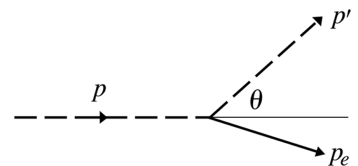[2] This analysis was independently worked out by Compton (1923) and Debye (1923).

Fig. 7.1 The momentum diagram of Compton scattering: A photon with momentum **p** scatters off an electron to produce another photon (**p'**) with the recoil electron having momentum **p**$_e$.

which, after using $(\epsilon - \epsilon') = (p - p')c$, can be written as

$$\left[(p - p')c + mc^2\right]^2 = \left(p_e c\right)^2 + (mc^2)^2. \tag{7.2}$$

The corresponding momentum conservation relation can similarly be written down, with the electron recoil momentum being $\mathbf{p}_e = \mathbf{p} - \mathbf{p}'$. This implies an equation among the magnitudes of the various momenta,

$$p_e^2 = p^2 + p'^2 - 2pp' \cos\theta. \tag{7.3}$$

Eliminate p_e^2 from Eqs. (7.2) and (7.3), we immediately obtain the correlation between wavelength shift and scattering angle as

$$\lambda' - \lambda = \lambda_c(1 - \cos\theta). \tag{7.4}$$

We have used the definition of the **Compton wavelength** $\lambda_c = h/mc$, which is a very small length $\lambda_c = 0.0024$ nm even for an electron mass. In order to see such a tiny wavelength shift, it helps to work with an electromagnetic wave having short wavelength in the first place. This explains why the effect was discovered in the scattering experiment involving X-rays. Still, it was remarkable that Compton was able, in the first experiment making measurements at scattering angles of 45°, 90°, and 135°, to determine the Compton wavelength λ_c to an accuracy that was less than one percent off the modern value. Compton concluded his paper (Compton 1923) this way: "The experimental support of the theory indicates very convincingly a radiation quantum carries with it directed momentum as well as energy."

We have in Section 3.4.3 derived the result for radiation pressure and radiation energy density $p = u/3$ by way of thermodynamic arguments. It may be easier for a modern-day reader to understand this result from the viewpoint of momentum changes as suffered by photons after collisions with the enclosure wall (cf. SuppMat Section 7.5). In the next few sections we shall see how the idea of the photon would finally lead to a more consistent and deeper understanding of blackbody radiation.

7.2   Towards Bose–Einstein statistics

The Compton scattering result was obtained in 1923. This had finally established the reality of photons for the general community of physicists. In 1924 Einstein received a letter from Satyendranath Bose (1894–1974) of Kolkata asking his opinion of an enclosed paper,[3] in which Bose used the particle properties of a photon (having the energy–momentum relation of $\epsilon = pc$ with $p^2 = p_x^2 + p_y^2 + p_z^2$) to obtain another derivation of Planck's spectral distribution of blackbody radiation. He stated that he was motivated by the observation that Planck's derivation was not logically self-consistent. Planck arrived at a non-classical physics result of energy quantization while using a relation between radiation density $\rho(\nu, T)$ and average energy U of an oscillator,

$$\rho = \frac{8\pi\nu^2}{c^3}U, \tag{7.5}$$

[3]The paper was written in English and sumitted to *Philosophical Magazine* in 1923. After its rejection by that journal, Bose sent it to Einstein who translated it into German and arranged its publication in *Zeitschrift der Physik* (Bose 1924). A re-translation back into English can be found in the *American Journal of Physics* (Bose 1976).

deduced by a classical electromagnetic calculation (cf. Section 3.2.1). In Section 4.1.3 this result was obtained by a counting of wave states. Bose set out with a particle approach from the very beginning.

After deriving this density of states, Bose proceeded to deduce Planck's distribution. Bose's approach is to adhere closely to Boltzmann's procedure. In contrast to Planck's method (cf. Sections 3.3.1 and 3.3.2), his statistical analysis involves a counting of phase space cells. But to have the calculation ending in Planck's distribution, rather than Boltzmann's, clearly he had to deviate from the latter's procedure. In order to see all this, we shall first provide a brief review of Boltzmann's statistical program.

7.2.1   Boltzmann statistics

Boltzmann's analysis proceeded by identifying particles with cells in position–momentum phase space. He also used the device of discrete energy packets ϵ, but would set $\epsilon = 0$ at the end of a calculation in order to recover a continuous energy. One regards the P energy packets as forming $P + 1$ energy levels, with the lowest level having zero energy $\epsilon_0 = 0$, the second level having energy $\epsilon_1 = \epsilon$, so on up to the highest level $\epsilon_P = P\epsilon$. The N particles (cells) can have various energies; such a configuration (label it as σ) can be described by a set of cell numbers $(N_0, N_1, N_2, \ldots, N_P)$. N_0 is the number of cells at the ground level ϵ_0, N_1 is the number at the next level ϵ_1, etc. Namely, we have the total number of particles and total energy as given by

$$N = \sum_{j=0}^{P} N_j, \qquad U = \sum_{j=0}^{P} \epsilon_j N_j = \sum_{j=0}^{P} j\epsilon N_j. \qquad (7.6)$$

The probability complexion for such a macrostate configuration σ is calculated by counting the number of ways N cells can have different energies (i.e. N is divided into different sets of cells). We note that the number of ways we can select out N_0 cells from the total N is $N!/[N_0!(N - N_0)!]$, then the number of ways to select out N_1 cells from the remaining $N - N_0$ is $(N - N_0)!/[N_1!(N - N_0 - N_1)!]$, etc. Thus the total number of ways one can divide up N oscillators into a distribution of $(N_0, N_1, N_2, \ldots, N_P)$ is the product[4]

$$
\begin{aligned}
W_\sigma &= \frac{N!}{N_0!(N - N_0)!} \times \frac{(N - N_0)!}{N_1!(N - N_0 - N_1)!} \times \cdots \\
&= \frac{N!}{N_0! N_1! \ldots N_P!},
\end{aligned} \qquad (7.7)
$$

leading to the entropy

$$
\begin{aligned}
S = k_{\mathrm{B}} \ln W_\sigma &= k_{\mathrm{B}} \left(\ln N! - \sum_j \ln N_j! \right) \\
&\approx k_{\mathrm{B}} \left(N \ln N - \sum_j N_j \ln N_j \right),
\end{aligned}
$$

[4] In the so-called "correct Boltzmann counting" procedure, one would insert the ad hoc factor of $1/N!$ in order to make the resultant entropy an extensive thermodynamical function. This is ultimately justified by quantum mechanics with its concept of identical particles. We do not make this insertion here because this feature is irrelevant for our present discussion.

where we have approximated the factorial logarithms by Stirling's formula (cf. Appendix A, Section A.3). One then maximizes the entropy, under the constraint of the two conditions given in (7.6), to find the configuration that corresponds to the equilibrium state:

$$0 = \delta \sum_j \left(N_j \ln N_j + A N_j + B \epsilon_j N_j \right)$$

$$= \sum_j \delta N_j \left(\ln N_j + 1 + A + B \epsilon_j \right)$$

where we have used the Lagrangian multipliers A and B to incorporate the two constraint conditions (cf. Appendix A, Section A.4). For an independent variation δN_j, the coefficient must vanish

$$\ln N_j = -\alpha - \beta \epsilon_j + \text{constant} \tag{7.8}$$

giving the primitive form of the Boltzmann distribution, $N_j \propto \exp(-\alpha - \beta \epsilon_j)$. One then has to appeal to analysis of other systems such as an ideal gas to fix the parameters of α and $\beta = 1/k_B T$, etc.

7.2.2 Bose's counting of photon states

Bose obtained the relation (7.5) by a counting of the photon states (instead of wave states as done by Rayleigh). His approach was to count the cells in the particle's position–momentum phase space, which is quantized in units of Planck's constant h^3. First, we will show that quantum theory naturally tells us that the phase space volume for an oscillator is quantized in this way.

As we have already shown in Eq. (3.55) in SuppMat Section 3.5.1, the energy equation of a 1D harmonic oscillator with frequency ν traces out an elliptical curve in the 2D phase space $dqdp$, with an area equal to the ratio of the oscillator energy to its frequency U/ν. In quantum theory, the oscillator energy (above the zero-point energy) is quantized, $U_n = nh\nu$. Thus, each oscillator state occupies an elliptical area of h. Clearly for 3D oscillators with phase space $d^3\mathbf{q} d^3\mathbf{p}$, the 6D volume has a volume of h^3—each oscillator state occupies a phase space volume of h^3.

Density of photon states

Recall the relation of radiation energy density ρ in terms of the number of radiation oscillators N and their respective energy U, see Eqs. (3.13) and (4.5); we have $\rho d\nu = (UN/V)d\nu$. Bose counted the number of photon states N by counting the number of cells occupied in the 6D phase space:

$$N d\nu = 2 \frac{d^3\mathbf{q} d^3\mathbf{p}}{h^3} = \frac{2V}{h^3} 4\pi p^2 dp \tag{7.9}$$

where the factor of 2 corresponds to the two polarization states of a photon.[5] The momentum variable p is then replaced by the frequency ν through the relation of $p = \epsilon/c = (h/c)\nu$ so that

$$N d\nu = \frac{8\pi V}{h^3} \left(\frac{h}{c} \right)^3 \nu^2 d\nu \quad \text{or} \quad \rho = \frac{N}{V} U = \frac{8\pi \nu^2}{c^3} U. \tag{7.10}$$

This is Planck's relation (7.5).

[5] Previously this factor of 2 had always been introduced as the two polarizations of the electromagnetic wave. But here Bose in 1924 was inserting it when working with photons. The whole idea that a particle can have intrinsic spin was not proposed until 1925 (for the electron). Nevertheless, Bose introduced this factor of 2 in his derivation with the comment: "it seems required"!

Bose's derivation of the Planck distribution

Just like Planck, Bose then proceeded to a statistical calculation of the complexion that would lead to Planck's spectral distribution. Recall that all Einstein's previous discussions of blackbody radiation had avoided any explicit statistical analysis. In fact he had mildly criticized Planck's statistical approach as being without foundation (cf. Section 3.4.1). But he was supportive of Bose's new analysis.

Bose assumed that there are N^s quanta, distributed among Z^s phase space cells (i.e. potential states that a photon can occupy) at frequency ν^s (the superscript s is a label of the state, having frequency interval $d\nu$). These cells can be at different energy levels. There are w_r^s cells each holding r quanta, having energy $\epsilon_r^s = rh\nu^s$: thus w_0^s cells at ground state $\epsilon_0^s = 0$, w_1^s cells at $\epsilon_1^s = h\nu^s$, and w_2^s cells at $\epsilon_2^s = 2h\nu^s$, etc. In total there are N photons in the frequency interval $d\nu$. Their relations can be expressed as

$$N = \sum_s N^s, \qquad U = \sum_s N^s h\nu^s, \qquad (7.11)$$

$$N^s = \sum_r r w_r^s, \qquad Z^s = \sum_r w_r^s.$$

The number of microstates, according to Bose, should "simply" be the product of the number of ways (for each ν^s) that Z^s cells can be partitioned into a distribution of $(w_0, w_1, w_2, \dots,)$, much like (7.7):

$$W = \prod_s \frac{Z^s!}{w_0^s! w_1^s! w_2^s! \dots}. \qquad (7.12)$$

Just as in Section 7.2.1, one then maximizes the logarithm of this statistical weight $\delta \ln W = 0$ with

$$\ln W = \sum_s Z^s \ln Z^s - \sum_{s,r} w_r^s \ln w_r^s$$

holding the total number of cells Z^s and total energy U fixed. Using the method of Lagrangian multipliers β and λ^s (see Appendix A.3), he obtains the condition[6]

$$\sum_s \sum_r \delta w_r^s \left(\ln w_r^s + 1 + \lambda^s + r\beta h\nu^s \right) = 0 \qquad (7.13)$$

which implies the solution

$$\ln w_r^s = -r\beta h\nu^s + \text{ constant}$$

or $w_r^s = A^s e^{-r\beta h\nu^s}$ with the coefficient A^s related to $Z^s = \sum_r w_r^s$ by:

$$w_r^s = Z^s \left(1 - e^{-\beta h\nu^s} \right) e^{-r\beta h\nu^s}. \qquad (7.14)$$

Bose proceeds to calculate the photon number distribution by[7]

$$N^s = \sum_r r w_r^s = Z^s \left(1 - e^{-\beta h\nu^s} \right) \sum_r r \left(e^{-\beta h\nu^s} \right)^r$$

$$= Z^s \frac{e^{-\beta h\nu^s}}{1 - e^{-\beta h\nu^s}} = \frac{Z^s}{e^{\beta h\nu^s} - 1}. \qquad (7.15)$$

[6]From (7.11), we insert into $\delta \ln W = 0$ the factors $\lambda^s \delta Z^s = \lambda^s \sum_r \delta w_r^s = 0$ and $\beta \delta U = \beta \sum_s \delta N^s h\nu^s = \beta \sum_{s,r} r \delta w_r^s h\nu^s = 0$.

[7]Here one uses the result of $\sum_r r x^r = x/(1 - x)^2$, which can be gotten from the familiar geometric series $\sum_r x^r = 1/(1 - x)$ by a simple differentiation with respect to the variable x.

Using his result (7.10) for the density of states $Z^s = 8\pi \nu^{s2} V/c^3$, Bose deduces the total radiation energy in the interval

$$\frac{U}{V} d\nu = \sum_s \frac{N^s h \nu^s}{V} d\nu = \frac{8\pi \nu^2}{c^3} \frac{h\nu}{e^{\beta h\nu} - 1} d\nu. \tag{7.16}$$

The Lagrangian multiplier can be fixed as $\beta = 1/k_B T$ by noting that the entropy is $S = k_B \ln W$, and differentiating with respect to energy must be identified with the absolute temperature $T = \partial U/\partial S$. In this way Bose arrives at the Planck's distribution:

$$\rho(\nu, T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1}. \tag{7.17}$$

Implicit assumptions in Bose's derivation

Bose's statistical counting method, compared to Planck's, certainly looks more like the traditional Boltzmann procedure. Clearly he had gone beyond the established approach so that he was able to arrive at Planck's distribution instead of the usual Boltzmann result. Apparently Bose did not realize in what fundamental ways his derivation departed from the usual classical statistical mechanical method. He made no comments about these assumptions in his paper. And in later years he remarked that he did not realize "what he did was all that new"!

Instead of counting photons directly, he divided the phase space into cells, and asked how many photons were in a cell (rather than which photons were in a cell) and thus implicitly assumed indistinguishability of photons. He assumed statistical independence of cells. Thus there is no statistical independence of particles. In his calculation he imposed the condition of conservation of phase space cells (i.e. $Z^s = \sum_r w_r^s = $ constant). Since each cell has an indefinite number of photons, he had implicitly assumed photon number nonconservation (i.e. $N = \sum_s N^s \neq$ constant). Interestingly, this constant Z^s condition is actually irrelevant for his result, as we see in the above calculation that the corresponding Lagrangian multiplier λ^s drops out in the result of the cell distribution (7.14). Furthermore, he had also assumed that (in modern language) the photon has intrinsic spin—again without much of a comment.

7.2.3   Einstein's elaboration of Bose's counting statistics

Einstein arranged the publication of Bose's paper and he also sent in a related contribution (Einstein 1924), extending Bose's case of photon statistics to the general case of noninteracting particles (i.e. atoms and molecules). In the meantime (1923–24) Louis de Broglie made his suggestion that matter, under certainly circumstances, could have wave-like behavior. Einstein was very enthusiastic about this idea. His paper (Einstein 1925) was the first of anyone who actually referred to de Broglie's new suggestion of matter waves. He justifies his application of Bose's photon counting method to matter particles by saying that if particles can be waves, they should obey similar statistics to photons.

Density of nonrelativistic particle states

To count the nonrelativistic gas particle states, Einstein followed Bose by calculating the corresponding phase space volume in units of h^3 as in (7.9):

$$N d\nu = \frac{d^3\mathbf{q} d^3\mathbf{p}}{h^3} = \frac{V}{h^3} 4\pi p^2 dp. \tag{7.18}$$

Instead of photons, we have nonrelativistic particles with the momentum p related to the kinetic energy ϵ by $p = \sqrt{2m\epsilon}$ so that

$$N d\nu = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon = \mathcal{Z}(\epsilon) \, d\epsilon. \tag{7.19}$$

The particle density (number per unit energy) $\mathcal{Z}(\epsilon)$ is given by

$$\mathcal{Z}(\epsilon) = 2V \sqrt{\frac{\epsilon}{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2}. \tag{7.20}$$

Particles obeying Bose–Einstein statistics are called bosons.

Distribution of identical bosons

Einstein improved upon Bose's method in his derivation of the distribution of gas particles. Recall our comment that it is irrelevant to impose the condition $Z^s = \sum_r w_r^s = $ constant. Instead of working with the statistical weight of (7.12), Einstein wrote down the complexion in a form more similar to Planck's Eq. (3.38):

$$W = \prod_s \frac{(N^s + Z^s - 1)!}{N^s!(Z^s - 1)!} \simeq \prod_s \frac{(N^s + Z^s)!}{N^s! Z^s!}. \tag{7.21}$$

This is a counting of the ways that one can distribute N^s identical particles into Z^s cells.[8] Einstein then maximizes $\ln W$ under the constraint of holding the particle number $N = \Sigma N^s$ and the energy $U = \Sigma N^s \epsilon^s$ fixed—by using two Lagrangian multipliers, which can eventually be identified with $1/k_B T$ and the chemical potential μ:

$$N^s = \frac{1}{e^{(\epsilon^s - \mu)/k_B T} - 1}. \tag{7.22}$$

[8]Recall in Eq. (3.34) that Planck was counting the ways of distributing P quanta into N oscillators.

This came to be known as Bose–Einstein statistics. Because photon number is not conserved (that is, photons can be freely emitted and absorbed), there is not the requirement of $N = \Sigma N^s$, and the Lagrangian multiplier μ, identified with the chemical potential, is absent (or, $\mu = 0$):

$$N^s = \frac{1}{e^{\epsilon^s/k_B T} - 1}. \tag{7.23}$$

This is the correct distribution for photons as discussed in Section 7.2.2.

Using the expression for the density of states obtained in (7.20), the total number density is

$$
\begin{aligned}
N &= \int \frac{\mathcal{Z}(\epsilon) \, d\epsilon}{e^{(\epsilon^s - \mu)/k_B T} - 1} \\
&= \frac{2V}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} \int \frac{\epsilon^{1/2} d\epsilon}{e^{(\epsilon^s - \mu)/k_B T} - 1}.
\end{aligned}
\tag{7.24}
$$

The discovery of Bose–Einstein condensation

For the case of the ground state (with $\epsilon^s = 0$) we have from (7.22):

$$N_0 = \frac{1}{e^{-\mu/k_\mathrm{B}T} - 1}.$$

The requirement that $N_0 > 0$ (i.e. $e^{-\mu/k_\mathrm{B}T} > 1$) implies that the chemical potential μ must in general be nonpositive. Einstein discovered that when the temperature drops below a certain temperature (called the condensation temperature T_c) when the chemical potential approaches zero (from below) the above expression for the ground state population becomes macroscopic in size:

$$N_0 = \frac{k_\mathrm{B}T}{-\mu} \ggg 1. \qquad (7.25)$$

Einstein commented on this remarkable result:

I maintain that, in this case, a number of molecules steadily growing with increasing density goes over in the first quantum state (which has zero kinetic energy) while the remaining molecules distribute themselves according to the parameter value of $\mu = 0 \ldots$ A separation is effected; one part condenses, the rest remains a 'saturated ideal gas'.

Einstein had discovered a purely statistically induced phase transition, which we now call "Bose–Einstein condensation". In Section 7.4 we shall provide a more detailed discussion of this condensation phenomenon.

7.3   Quantum mechanics and identical particles

Modern quantum mechanics came into being in 1925–26. In this new theory physical states are identified with vectors and physical observables with operators of the Hilbert space. These vectors and operators may appear rather differently depending on what basis vectors one chooses to represent this geometric space. This is reflected in the two separate discoveries of quantum mechanics. In the spring of 1925 Werner Heisenberg, following his study of dispersion relations, had proposed a rather abstract version of a quantum theory, which came to be known as *matrix mechanics*. At the end of 1925 Erwin Schrödinger wrote down his wave equation thus initiated *wave mechanics*. The hydrogen spectrum was obtained in both matrix and wave mechanics. Soon, in 1926, P.A.M. Dirac, and independently Heisenberg and Schrödinger, had shown that wave and matrix mechanics are equivalent to each other: they were just two different representations of the same theory. In the following discussion we shall mostly use the more accessible language of wave mechanics.

7.3.1   Wave mechanics: de Broglie–Einstein–Schrödinger

In 1924 Louis de Broglie proposed in his doctoral thesis that, associated with every matter particle (with momentum p) there was also a wave with

wavelength $\lambda = h/p$ (de Broglie 1924). Recall that Einstein had introduced the idea of light quanta—particle-like properties of radiation; he stated his general motivation as wanting to have a more symmetric description of matter and radiation. In fact de Broglie explicitly acknowledges that his matter wave idea was inspired by this particle–wave dualism[9] as stated in Einstein's 1905 photon paper. Thus we should not be surprised that de Broglie's matter wave idea received Einstein's enthusiastic support. The question: What would be the equation that governs the behavior of this matter wave? It is also of historical interest to note that Erwin Schrödinger first became aware of de Broglie's idea from reading Einstein's 1924–25 papers. This led directly to the creation of his wave equation, which immediately came to be known as the Schrödinger equation, at the end of 1925.

[9]Recall our discussion in Section 6.1 of Einstein's 1909 investigation of radiation fluctuation leading him to the notion of particle–wave duality. In a paper submitted at the beginning of 1925 Einstein showed that a relation, just like Eq. (6.16), holds as well for his quantum gas of material particles as discussed in Section 7.2.3.

7.3.2 Identical particles are truly identical in quantum mechanics

The concept of identical particles in quantum mechanics is qualitatively different from any analogous notion in classical physics. In classical physics ultimately no particles can be identical. Two electrons with identical charge and mass can still be distinguished because we can in principle follow their individual trajectories and tell apart which is which particle. In quantum mechanics, it is impossible to have precise particle trajectories. In classical physics we can also in principle distinguish two particles by putting labels on them (e.g. paint them different colors) without interfering with their motion. In quantum mechanics, on the other hand, it is not possible to keep track of particle trajectories or to put extra labels involving an incompatible observable.[10] Thus identical particles are truly identical in quantum mechanics. The interchange of any two identical particles leaves no observable consequence—no change in the measurement probability. The wavefunction, being the probability amplitude, must therefore be either symmetric or antisymmetric with respect to such an exchange of identical particles. As we commented at the end Section 6.4, quantum field theory can account for symmetry properties of the identical particle nature of a field's quanta. The commutation relation discussed in Eq. (6.47) is just the elegant mathematical device needed to bring about this required symmetry.

[10]Because observables are represented by operators. Two observables are said to be incompatible if their respective operators do not commute, $\hat{A}\hat{B} - \hat{B}\hat{A} \equiv [\hat{A}, \hat{B}] \neq 0$. This leads to an uncertainty relation of their observable values, $\Delta A \Delta B \geq \hbar$. The 'extra label' that one would wish to place on a particle must be an incompatible one as a particle has already been labeled by a complete set of compatible observables.

7.3.3 Spin and statistics

In the meantime the quantum mechanical concept of particle spin had emerged.[11] It was then proposed that there is a direct relation between the particle spin and the symmetry property of a wavefunction, and hence the statistical properties of such identical particles. A system of particles having integer spin (e.g. photons with spin 1) must have a symmetric wavefunction and obey Bose–Einstein statistics; these particles are called bosons. A system of particles with half-integer spin (e.g. electrons with spin 1/2) must have an antisymmetric wavefunction, and obey Fermi–Dirac statistics. They are called fermions. The spin-statistics theorem was proven by Wolfgang Pauli and others

[11]Electron spin was first proposed by Uhlenbeck and Goudsmit (1925).

in the framework of quantum field theory (based on quantum mechanics and special relativity) (Pauli 1940).

7.3.4   The physical implications of symmetrization

The physical implications of the concept of indistinguishable particles are remarkable. The antisymmetric property of the fermionic wavefunction means that two identical fermions cannot be in the same state. This explains Pauli's exclusion principle—crucial, among other consequences, in the explication of the structure of multi-electron atoms. The totally symmetric wavefunction of a boson system also leads to highly counter-intuitive results. Just consider the calculation of statistical weight. Boltzmann's statistics (7.7) would yield results that are in accord with our intuition. For instance, compare the two cases of distributing 10 (distinguishable) particles into two cells: in one case 10 particles are in one cell and none in the other cell, and in the other case each cell has five particles. The ratio of weights for these two cases is

$$\frac{10!}{10!0!} : \frac{10!}{5!5!} = 1 : 252.$$

This is to be contrasted with the quantum distribution of 10 identical bosons yielding the rather counter-intuitive result of the statistical weight for each case being unity—hence the ratio 1 : 1 for the above-considered situation. In each case there is only one totally symmetric wavefunction. When Einstein first worked out the Bose–Einstein (BE) counting, he commented:

The BE counting "expresses indirectly certain hypothesis on the mutual influences of the molecules which for the time being is of a quite mysterious nature."

While we now know that this is just the correlation induced by the requirement of a totally symmetric wavefunction,[12] on a deeper physical level this mutual influence is still no less mysterious today.

[12] For a discussion of the role of particle indistinguishability making BE condensation possible, see SuppMat Section 7.7.

The final resolution of the counting schemes of Bose (1924), Einstein (1905), and Planck (1900)

We have seen how quantum Bose–Einstein statistics naturally explains how Bose's implicit assumptions are all justified. It also justifies Einstein's original classical statistical mechanical argument of Wien radiation being a gas of photons. Even though Einstein avoided making an explicit calculation of the statistical weight, since he used the analogy of a classical ideal gas, implicitly he had assumed the Boltzmann statistics of (7.7). However we can justify it now because in the Wien limit ($\epsilon^s \gg k_B T$) the average photon number (7.23) is vanishing small: $N^s = e^{-\epsilon^s/k_B T} \simeq 0$. Thus in this limit, the statistical weight of Boltzmann counting (7.7) is indistinguishable from Bose–Einstein ($W = 1$). The Planck spectral distribution is of course understood as the consequence of BE statistics. Nevertheless it is useful to work out the way of seeing how Planck's statistical analysis can lead to the correct result. This calculation can be found in the SuppMat Section 7.6.

7.4 Bose–Einstein condensation

Let the energies of the first excited and the (lowest energy) ground states be ϵ_1 and $\epsilon_0 = 0$ so that they have the energy gap $\triangle\epsilon = \epsilon_1$. If the available thermal energy is not much bigger than this energy gap $k_B T \lesssim \triangle\epsilon$, it would not surprise us to find many molecules in their ground state. On the other hand, Bose–Einstein condensation (BEC) is the phenomenon that, at a temperature below some critical value T_c, a macroscopic number of molecules would stay in ("condense into") the ground state, even though the available thermal energy $k_B T$ is much bigger than the energy gap, $k_B T \gg \triangle\epsilon$. What Einstein had shown was that the chemical potential can be extremely small ($|\mu| \ll \epsilon_1$) in the low-temperature regime $T < T_c$. For example, liquid helium has an energy gap of $\epsilon_1 \simeq 10^{-18}$ eV. But below a temperature of $\lesssim O(1\ \text{K})$, i.e. a thermal energy of $\lesssim O(10^{-4}\ \text{eV})$, the chemical potential of helium[13] has such a small value $\mu \simeq -10^{-26}$ eV that the Bose–Einstein distribution (7.22) would imply

$$N_1 = \frac{1}{e^{(\epsilon_1 - 0)/k_B T} - 1} \simeq \frac{k_B T}{\epsilon_1}. \tag{7.26}$$

Comparing this to the ground state occupation number given in (7.25), one finds that most of the molecules would condense into the ground state,

$$\frac{N_0}{N_1} = \frac{\epsilon_1}{-\mu} \gg 1. \tag{7.27}$$

One must bear in mind this is condensation in momentum space (rather than the everyday condensation in configuration space).

Bose–Einstein condensation as a macroscopic quantum state   That a macroscopic number of molecules are in one quantum state would lead to quantum mechanical behavior on the macroscopic scale. This was first pointed out in 1928 by Fritz London (1900–54). London suggested that superfluid helium was an example of a Bose–Einstein condensate. His related work on superconductivity also decidedly influenced the later development of BCS theory in which electron pairs (the Cooper pairs) form the Bose–Einstein condensate.[14]

7.4.1   Condensate occupancy calculated

To calculate the condensation temperature, below which a macroscopic fraction of the particles are in the ground state, we must know how to add up the occupancy for every state. Only then can we compare the occupancy in the ground state with those in the excited states. In general the total particle number N is given by (7.24) where the discrete sum can be replaced by integration using the density of states $\mathcal{Z}(\epsilon)$. This replacement, while applicable for the excited states, is not valid for the ground state, as $\mathcal{Z}(\epsilon = 0) = 0$. We will simply separate out the ground state with its occupancy labeled N_0:

$$N = N_0 + N_{\text{ex}}$$
$$= \frac{1}{e^{-\mu/k_B T} - 1} + \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{3/2} V \int_0^\infty \frac{\sqrt{\epsilon}\, d\epsilon}{e^{(\epsilon - \mu)/k_B T} - 1}. \tag{7.28}$$

[13] Helium exhibits superfluid behavior below the critical temperature of 2.17 K. We can estimate the size of its chemical potential by the relation (7.25), $-\mu = k_B T/N_0$, with the approximation $N_0 \simeq N$ because a significant fraction of all molecules would have condensed into the ground state. We then obtain a value $-\mu = \left(10^{-4}\ \text{eV} \cdot \text{K}^{-1}\right) \times (1\ \text{K}) \times 10^{-22} = 10^{-26}$ eV.

[14] London later substantiated his original suggestion by showing that the phase change of superfluid helium had properties consistent with a BEC transition (London 1938). The BCS theory is named after its originators: John Bardeen, Leon Cooper, and Robert Schrieffer.

As we have already discussed, the chemical potential is extremely small in the region $T < T_c$. Nevertheless, μ must be kept in N_0 because $\epsilon_0 = 0$, while setting $\mu = 0$ in N_{ex},

$$N = -\frac{k_B T}{\mu} + \frac{2}{\sqrt{\pi}}\left(\frac{2\pi m}{h^2}\right)^{3/2} V \int_0^\infty \frac{\sqrt{\epsilon}d\epsilon}{e^{\epsilon/k_B T} - 1}. \tag{7.29}$$

Let us carry out the calculation for N_{ex} with a change of integration variable $x = \epsilon/kT$:

$$N_{ex} = \left(\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}dx}{e^x - 1}\right)\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V = 2.612\frac{V}{v_Q} \tag{7.30}$$

[15]The quantum volume is the cube of the quantum length $v_Q = l_Q^3$ with $l_Q = h/(2\pi m k_B T)^{1/2}$, also called the "de Broglie thermal wavelength" because, except for a $O(1)$ factor of $\sqrt{\pi}$, it is the de Broglie wavelength associated with the thermal momentum $p = (2mk_B T)^{1/2}$.

where $v_Q = \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}$ is the particle's quantum volume.[15] Rewriting this in terms of the particle's physical volume $v = V/N$, we have

$$\frac{N_{ex}}{N} = 2.612\frac{v}{v_Q}. \tag{7.31}$$

In other words, the fraction of particles in the excited states is directly proportional to how small a particle's quantum volume has become with respect to its physical volume.

7.4.2 The condensation temperature

Because of the absence of a significant number of molecules in the ground state when $T > T_c$, we can define the condensation temperature T_c by $N_{ex}(T_c) \equiv N$. Namely, we have the relation

$$N_{ex} = 2.612\left(\frac{2\pi m k_B T_c}{h^2}\right)^{3/2} V = N \tag{7.32}$$

or

$$T_c = \frac{h^2}{2\pi m k_B}\left(\frac{N}{2.612V}\right)^{2/3}. \tag{7.33}$$

Furthermore, taking the ratio of Eq. (7.30) and Eq. (7.32), we have

$$\frac{N_{ex}}{N} = \left(\frac{T}{T_c}\right)^{3/2}, \tag{7.34}$$

which is plotted in Fig. 7.2.

T_c for noninteracting helium Let us use (7.33) to calculate the condensation temperature for the He system: one mole $N = N_A = 6 \times 10^{23}$ of helium with molar volume $V = 27.6$ cm^3. This yields $T_c(\text{He}) = 3.1$ K, which is not too far off from the experimental value of 2.17 K, considering that we have completely ignored mutual interactions, which are rather complicated collisions involving many particles.
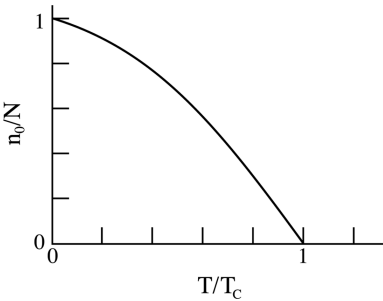

Fig. 7.2 Fractional ground state as a function of temperature.

Behavior of the chemical potential when $T \lesssim T_c$

From (7.34) we can also see the behavior of the chemical potential

$$N = N_0 + N_{\text{ex}} = -\frac{k_B T}{\mu} + N\left(\frac{T}{T_c}\right)^{3/2} \quad \text{or} \quad \frac{k_B T/N}{\mu} = \left(\frac{T}{T_c}\right)^{3/2} - 1. \tag{7.35}$$

Thus

$$\mu(T) = \frac{\frac{k_B T}{N}}{\left(\frac{T}{T_c}\right)^{3/2} - 1} = \begin{cases} -\dfrac{k_B T}{N} & \text{for } T \to 0 \\[2mm] -\dfrac{k_B T_c}{N}\dfrac{2T_c}{3\delta T} & \text{for } T \to (T_c - \delta T). \end{cases} \tag{7.36}$$

Namely, the chemical potential, which started out being extremely small in magnitude at low temperature, suddenly increases at the condensation temperature (as shown by the factor $T_c/\delta T$). It is this behavior that brings about the phase transition at T_c.

Overlap of wavefunctions when $T \lesssim T_c$

Instead of μ, it is useful to have a more direct way to understand the meaning of the condensation temperature. From Eq. (7.31) $N_{\text{ex}}/N = 2.6 \left(a/l_Q\right)^3$ where a and l_Q are the interatomic separation $\left(v = a^3\right)$ and the quantum length $\left(v_Q = l_Q^3\right)$, respectively. Thus at $T = T_c$ when $N_{\text{ex}} = N$, we have $a \simeq l_Q$. Namely, the condensation temperature is the low temperature when the thermal de Broglie wavelength $\sim 1/\sqrt{T}$, hence the effective quantum size of atoms, becomes so large that atomic wavefunctions begin to overlap. As the temperature falls below T_c the overlap is enhanced, more particles condense into the ground state, and N_0 becomes ever increasing.

7.4.3   Laboratory observation of Bose–Einstein condensation

The prediction of BEC is for noninteracting bosons. Thus a dilute gas is much closer to theoretical considerations, rather than the dense helium case. The helium density has the value

$$\left(\frac{N}{V}\right)_{\text{He}} = \frac{6 \times 10^{23}}{27.6} \text{ cm}^{-3} = 2 \times 10^{22} \text{ cm}^{-3}. \tag{7.37}$$

In a modern experiment, using a laser and magnetic cooling techniques, experimenters have achieved the confinement of $O\left(10^4\right)$ atoms (e.g. rubidium 86) in a volume $V = 10^{-9}$ cm^3, thus a density of

$$\left(\frac{N}{V}\right)_{\text{gas}} = \frac{10^4}{10^{-9}} \text{ cm}^{-3} = 10^{13} \text{ cm}^{-3} \tag{7.38}$$

which is a billion times smaller than the helium case. This implies a decrease in condensation temperature, through (7.33),

$$T_c^{\text{gas}} = \frac{m_{\text{He}}}{m_{\text{Rb}}} \left[\frac{(N/V)_{\text{gas}}}{(N/V)_{\text{He}}} \right]^{2/3} T_c^{\text{He}}$$

$$= \frac{4}{86} \left[\frac{10^{13}}{10^{22}} \right]^{2/3} T_c^{\text{He}} \simeq 10^{-7} \text{ K.} \tag{7.39}$$

Given this extremely low condensation temperature the experimental study of BEC of a low-density gas is very difficult. One can use laser cooling and at the same time trap the atoms in a magneto-optical trap. Further manipulation of the trapped atoms by evaporation cooling enables experimentalists to reach the critical temperature when the BEC takes place. The positions of the atoms can be recorded using laser beams. In Fig. 7.3 we display the result of one such experiment. With this technique, the signature of the BEC is the appearance of a sharp peak. The atoms in the condensed phase are in the ground state (of the momentum space) and expand only slowly once released from the trap. The atoms in the excited states move relatively rapidly out of their steady state positions.

The success of producing dilute-gas BEC in the laboratory setting at Boulder, MIT, and elsewhere came about some 70 years after its first theoretical proposal by Einstein. The 2001 Nobel Prize for Physics was awarded to Eric Cornell (1961–), Wolfgang Ketterle (1957–), and Carl Wieman (1951–) for their experimental work in this area.
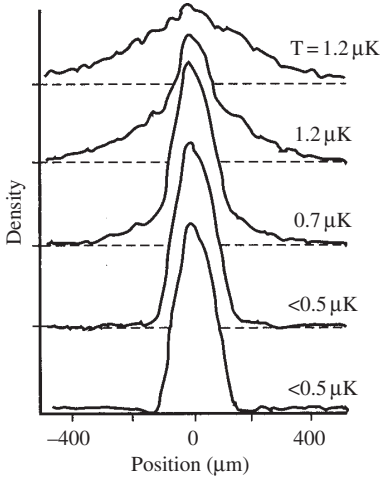

Fig. 7.3 Observation of BEC in a trapped atomic gas with $T_c = 1.7$ μK when a central peak appears representing the probability $|\psi|^2$. As the temperature is lowered, the thermal cloud is depleted, and atoms accumulate in the Bose condensate: the number of particles on the wing-sides (excited state particles) diminishes while the central peak (ground state particles) rises. Reproduction of Fig. 7 from Stenger *et al.* (1998).

7.5   SuppMat: Radiation pressure due to a gas of photons

The pressure ($\mathcal{P}$) is the force per unit area A and the force is the rate of momentum change $\Delta p / \Delta t$:

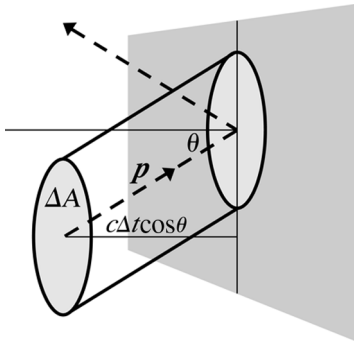$$\mathcal{P} = \frac{\text{force}}{\text{area}} = \frac{1}{\Delta A \Delta t} \Delta p. \tag{7.40}$$

We denote the photon momentum by **p** (not to be confused with the pressure denoted by capital script $\mathcal{P}$). A given photon with energy and momentum of $(\epsilon, \mathbf{p})$ with $\epsilon = cp$, colliding with the wall, imparts a momentum of $\Delta p = 2p_z$, where p_z is the photon momentum component in the direction perpendicular to the wall (call it $\hat{z}$). Let $n(q)$ be the photon density function—the number of photons per unit spatial volume and per unit momentum space volume, in the momentum interval $(p, p + dp)$. The total pressure is the sum of the momenta that all the photons deposit onto the wall; we need to integrate over the momentum and configuration spaces (see Fig. 7.4). The configuration space is the volume of the parallelepiped with base area ΔA and perpendicular height $c\Delta t \cos \theta$, with θ being the angle between the photon momentum and the normal to the area (hence, $p_z = p \cos \theta$). All photons in this volume $[c\Delta t \cos \theta \Delta A]$ would collide with the wall in the interval of Δt. The sum of (7.40) is then

Fig. 7.4 Momentum change of a photon bouncing off a wall.

$$\mathcal{P} = \frac{1}{\Delta A \Delta t} \int n(p) \, \Delta p d^3 \mathbf{p} [c \Delta t \cos \theta \, \Delta A]$$

$$= \int_{g_z > 0} n(p) \, 2p_z d^3 \mathbf{p} \left[c \frac{p_z}{p} \right] = \frac{2}{3} \int_{p_z > 0} [cp] n(p) \, d^3 \mathbf{p}. \qquad (7.41)$$

To reach the last equality on the RHS, we have used the fact that radiation is isotropic $p_x^2 = p_y^2 = p_z^2$ and thus the momentum magnitude squared is $p^2 = p_x^2 + p_y^2 + p_z^2 = 3p_z^2$. Furthermore, the density function $n(p)$ depends only on $p = |\mathbf{p}|$ so that the integrand must be an even function of p; we can extend the integration to the full range of $(-\infty, +\infty)$ and thus remove the factor of 2:

$$\mathcal{P} = \frac{1}{3} \int_{-\infty}^{+\infty} [cp] n(p) \, d^3 \mathbf{p} = \frac{1}{3} \int_{-\infty}^{+\infty} [\epsilon] n(p) \, d^3 \mathbf{p} = \frac{1}{3} u. \qquad (7.42)$$

Namely, the integral is the radiation density—the sum of all photon energies (ϵ) per unit spatial volume—as n is the number per unit spatial and momentum volumes.

7.6   SuppMat: Planck's original analysis in view of Bose–Einstein statistics

We have already explained how Planck's distribution can be derived as the $\mu = 0$ case of the Bose–Einstein statistics (7.21). In the context of later development, it is perhaps still useful to take a closer look at Planck's original statistical weight written down in Eq. (3.34),

$$W_N = \frac{(P+N)!}{P!N!}, \qquad (7.43)$$

to see how it leads at the correct result despite of its unorthodox analysis. Let us recall that P is the total number of quanta in a system of N oscillators. Planck converts this W_N into the entropy of the oscillator $S = S_N/N = (k_B \ln W_N)/N = k_B \ln W$, in term of the statistical weight of a single oscillator $W = (W_N)^{-N}$. Planck does not perform any maximization of the entropy, subject to the energy constraint, but simply makes the substitution $U = (P/N)\epsilon$ and, after a differentiation of $\partial S / \partial U = 1/T$, obtains the distribution

$$U = \frac{\epsilon}{e^{\epsilon/k_B T} - 1}. \qquad (7.44)$$

We now wish to interpret Planck's analysis in view of Bose–Einstein statistics.

Accord to Bose–Einstein statistics, one starts with the statistical weight of (7.21),

$$W_N = \prod_s \frac{(n^s + 1)!}{n^s!}. \qquad (7.45)$$

For our purpose, we have the density of states (degeneracy) $Z^s = 1$, and we have changed the notation for the photon number from N^s to n^s (so as not to have it confused with the oscillator number discussed above). To avoid the maximization of entropy (with Lagrangian multiplier, etc.), we simply impose

the energy condition $U = \Sigma_s n^s \epsilon^s$ in the form of $U = \langle n \rangle \epsilon$, where $\langle n \rangle$ is the average number of photons in a state having energy $\epsilon^s = \epsilon = h\nu$. With this average value, the statistical weight of (7.45) is simplified to

$$W_N = \left[\frac{(\langle n \rangle + 1)!}{\langle n \rangle!} \right]^{\langle n \rangle}. \tag{7.46}$$

Taking its logarithm and using $\langle n \rangle = U/\epsilon$, we have

$$S = k_B \ln W = k_B (\ln W_N)/\langle n \rangle$$

$$= k_B [(\langle n \rangle + 1) \ln(\langle n \rangle + 1) - \langle n \rangle \ln \langle n \rangle]$$

$$= k_B \left[\left(\frac{U}{\epsilon} + 1 \right) \ln \left(\frac{U}{\epsilon} + 1 \right) - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} \right],$$

which is just the entropy expression (3.40) obtained by Planck, leading to Planck's distribution of (7.44) or equivalently, the average photon number:

$$\frac{U}{\epsilon} = \langle n \rangle = \frac{1}{e^{\epsilon/k_B T} - 1}. \tag{7.47}$$

7.7   SuppMat: The role of particle indistinguishability in Bose–Einstein condensation

It will be illuminating to see how Bose–Einstein condensation follows from the indistinguishability of particles.[16] To see such an effect, we shall contrast two cases—in one all particles are somehow distinguishable, while in the other case, they are not.

N distinguishable particles

We shall discuss this case using two different approaches.

The approach of considering one-particle systems separately   This is the most straightforward approach. The partition function

$$Z_1 = \sum_\epsilon e^{-\epsilon/kT} \tag{7.48}$$

is essentially the number of accessible single-particle states. Namely, because higher energy states are exponentially suppressed, it counts all states with energy on the order of kT. Each state is roughly equally probable, hence there is about equal chance $1/Z_1$ for a particle to occupy any one of these states. This situation is not changed when we consider the whole system of N (independent) particles. The ground state being one of these many states, the fraction of particles in the ground state, when compared to the particles in all the excited state, is negligible. There is no BEC.

The approach of considering all *N* particles as a system   The above approach, while straightforward in explaining the absence of BEC for distinguishable particles, does not really highlight the crucial role played by the

particles' distinguishability. Here is an alternative approach of considering the N particles as a whole. For an excited state of this system with energy U, the associated probability[17] is $W(U) = e^{-U/kT}$. While the ground state $U_0 \equiv 0$ has a probability of $W(0) = 1$, a typical excited state with $U = NkT$ has a probability of $W(U) = e^{-N}$. Thus it appears that the ground state probability is overwhelmingly large. This conclusion is incorrect because we have not taken into account the fact that while an individual excited state has small probability, there are an enormous number (ν) of such excited states. This multiplicity ν can be calculated by remembering that each one of the distinguishable particles can be in any one of these Z_1 single-particle states. Thus $\nu = (Z_1)^N$, or $N_{ex} = \nu e^{-N} = (Z_1/e)^N$, which is a large number as long as $Z_1 > e$. [*Comment*: While Z_1 can be large, the likely situation is still $Z_1 \ll N$.] Hence we have the situation that vastly more particles are in the excited state, confirming the above argument that there is no BEC.

[17] Since all the probabilities discussed here have a common partition function in their denominator, we shall not bother to display it.

N indistinguishable particles

The probability of an N-particle system being in each of the excited states is still e^{-N}. However, the number of excited states (of the system as a whole) ν for the case of N indistinguishable particles is much less than that for the distinguishable case. Now ν is the number of ways one can distribute N indistinguishable particles among the various single-particle states (Z_1):

$$\nu = \binom{N + Z_1 - 1}{N} = \frac{(N + Z_1)!}{N! \, Z_1!} \simeq \frac{(N + Z_1)^{N+Z_1}}{N^N Z_1^{Z_1}}, \qquad (7.49)$$

where we have used Stirling's approximation of $X! \simeq X^X$. For $N \gg Z_1$ we have

$$\nu \simeq \frac{N^{N+Z_1}}{N^N Z_1^{Z_1}} = \left(\frac{N}{Z_1}\right)^{Z_1}. \qquad (7.50)$$

While this is still fairly large, but the product $\nu e^{-N} \lesssim 1$, and we expect that it is now possible for a significant fraction of the particles to be in the ground state. This indicates why BEC becomes possible in a system of identical bosons.