

The Bose–Einstein condensation

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1 Non-interacting gases

We consider here an **quantum gas of identical bosons**. The system is supposed to be confined in a volume V within which the particles can move freely. Unless otherwise stated, the particles are **non-interacting**.

1.1 Origin of the phenomenon

Let us consider the average occupation number of the single-particle states, given by the Bose–Einstein distribution:

$$\langle N_\lambda \rangle = \frac{1}{\exp[-\beta(\varepsilon_\lambda - \mu)] - 1} .$$

This law only yields positive values of the average occupation number if the chemical potential μ is restricted to the interval $]-\infty; \varepsilon_0[$, where ε_0 denotes the energy of the single-particle ground state λ_0 . In the following we will often replace the chemical potential by the **fugacity**, defined by

$$z \equiv \exp[\beta(\mu - \varepsilon_0)] .$$

The fugacity is restricted to the interval $[0; 1[$.

$\langle N_\lambda \rangle$ is an increasing function of μ . In the limit where μ tends to $-\infty$, the occupation numbers of every single particle state λ tends to 0 and hence also the total particle number:

$$\lim_{\mu \rightarrow -\infty} \langle N_\lambda \rangle = 0 , \quad \forall \lambda , \quad \text{implying} \quad \lim_{\mu \rightarrow -\infty} \langle N \rangle = 0 .$$

In the limit where μ tends to ε_0 , the occupation number of the ground state tends to $+\infty$ while the other occupation numbers remain finite:

$$\lim_{\mu \rightarrow \varepsilon_0} \langle N_0 \rangle = +\infty , \quad \lim_{\mu \rightarrow \varepsilon_0} \langle N_{\lambda \neq \lambda_0} \rangle = \frac{1}{\exp[-\beta(\varepsilon_\lambda - \varepsilon_0)] - 1} .$$

Even though the total number of excited states $\lambda \neq \lambda_0$ may itself be infinite, it turns out that the **total population of the excited states**, $\sum_{\lambda \neq \lambda_0} \langle N_\lambda \rangle \equiv \langle N_{\text{exc}} \rangle$, **does remain finite**. We can show this property by making use of the continuous limit and writing:

$$\langle N_{\text{exc}} \rangle = \int \frac{d^3\mathbf{r} d^3\mathbf{p}}{(2\pi\hbar)^3} \frac{1}{\exp[\beta(\varepsilon(\mathbf{p}) - \mu)] - 1}, \quad \text{with } \varepsilon(\mathbf{p}) = \mathbf{p}^2/2m.$$

In order to calculate the integral, we first rewrite the integrand in the form

$$\frac{1}{\exp[\beta(\varepsilon - \mu)] - 1} = \frac{z \exp(-\beta\varepsilon)}{1 - z \exp(-\beta\varepsilon)},$$

which we then expand in a Taylor series:

$$\frac{z \exp(-\beta\varepsilon)}{1 - z \exp(-\beta\varepsilon)} = z \exp(-\beta\varepsilon) \sum_{i=0}^{+\infty} [z \exp(-\beta\varepsilon)]^i = \sum_{j=1}^{+\infty} [z \exp(-\beta\varepsilon)]^j.$$

We now perform the integration and obtain:

$$\langle N_{\text{exc}} \rangle = \sum_{j=1}^{+\infty} \left[z^j \int \frac{d^3\mathbf{r} d^3\mathbf{p}}{(2\pi\hbar)^3} \exp(-j\beta\mathbf{p}^2/2m) \right] = V \left(\frac{mk_{\text{B}}T}{2\pi\hbar^2} \right)^{3/2} \sum_{j=1}^{+\infty} \frac{z^j}{j^{3/2}}.$$

The series $\sum_j z^j/j^n$ actually defines a regular function called a polylogarithm of order n :

$$g_n(z) \equiv \sum_j \frac{z^j}{j^n}.$$

The polylogarithms of any order are continuously increasing functions of z defined in the interval $[0; 1]$. They are equal to 0 at $z = 0$ and reach the value $\zeta(n)$ at $z = 1$ (ζ is the so-called *zeta*-function). For $n = 3/2$, we have

$$g_{3/2}(1) = \zeta(3/2) \simeq 2.612.$$

Introducing the so-called **thermal de Broglie wavelength**,

$$\lambda_{\text{T}} = \sqrt{\frac{2\pi\hbar^2}{mk_{\text{B}}T}},$$

we can finally write the total number of particles in the excited states as

$$\langle N_{\text{exc}} \rangle = g_{3/2}(z) \frac{V}{\lambda_{\text{T}}^3}$$

and observe that $\langle N_{\text{exc}} \rangle$ reaches a maximum value when μ tends to ε_0 :

$$\lim_{\mu \rightarrow \varepsilon_0} \langle N_{\text{exc}} \rangle \simeq \zeta(3/2) \frac{V}{\lambda_{\text{T}}^3}.$$

The total particle number thus diverges in a very specific way when the chemical potential increases to ε_0 : the number of particles in the excited states $\lambda \neq \lambda_0$ **saturates** and the particles **accumulate in the ground state**. This is the **Bose–Einstein condensation**. At some point, the ground state population becomes dominant and all particles eventually end up in the ground state.

In the following, we will refer to the particles in the ground state as the **condensed particles** and to the particles in the excited states as the **non-condensed particles**. The condensed particles are said to form a **Bose–Einstein condensate**, abbreviated as BEC, while the non-condensed particles are said to form a **thermal gas**. The word “thermal” here means that this part of the system behaves almost like a classical gas because the average occupation numbers of the excited states remain of order 1 or smaller (see the discussion at the end of the first lecture).

Remark: the words “saturation” and “condensation” refer to the usual (and classical) phenomenon of condensation occurring in a saturated vapor.

1.2 Equation of state of the ideal Bose gas

An equation of state is a relation that binds several macroscopic variables together. An easy way to obtain such relation for the ideal Bose gas considered here is to write that the average number of particles is equal to the sum of the average occupation numbers of the single particle states:

$$\langle N \rangle = \sum_{\lambda} \langle N_{\lambda} \rangle = \langle N_0 \rangle + \langle N_{\text{exc}} \rangle ,$$

with

$$\langle N_0 \rangle = \frac{z}{1-z} \quad \text{and} \quad \langle N_{\text{exc}} \rangle = g_{3/2}(z) \frac{V}{\lambda_T^3} .$$

This equation binds together the total number of particles, the volume, the chemical potential (through the fugacity) and the temperature (through the fugacity and the thermal de Broglie wavelength). In terms of particle density, $n \equiv \langle N \rangle / V$, the equation of state reads:

$$n = \frac{1}{V} \frac{z}{1-z} + \frac{g_{3/2}(z)}{\lambda_T^3} .$$

1.3 Threshold for the condensation

The Bose–Einstein condensation is a **phase transition** in the usual meaning of the term (like the liquid-vapour transition, for instance). It is associated with a non-analyticity the heat capacity at a **critical temperature** T_c , marking the appearance of the Bose–Einstein condensate.

Let us suppose that we start with a gas at a temperature higher than the critical temperature and that we lower the temperature at constant density. Initially,

the ground state population is weak and can be neglected in front of the total population of the excited states. We can thus write:

$$n \simeq \frac{g_{3/2}(z)}{\lambda_T^3} \quad \text{when } T > T_c .$$

Lowering the temperature while keeping the density constant requires the fugacity to increase. Once we reach $z = 1$, the relation above can no longer hold, meaning that the ground state becomes macroscopically populated and can no longer be neglected. We must then write:

$$n = \frac{1}{V} \frac{z}{1-z} + \frac{\zeta(3/2)}{\lambda_T^3} \quad \text{when } T < T_c .$$

The critical temperature is reached when:

$$n = \frac{\zeta(3/2)}{\lambda_T^3} = \zeta(3/2) \left(\frac{mk_B T_c}{2\pi\hbar^2} \right)^{3/2} ,$$

yielding

$$T_c = \frac{2\pi\hbar^2}{mk_B} \left(\frac{n}{\zeta(3/2)} \right)^{2/3} .$$

If, instead of tuning the temperature at fixed density, we tune the density at fixed temperature, we find that the Bose–Einstein condensation occurs when the density becomes larger than the critical value

$$n_c = \frac{\zeta(3/2)}{\lambda_T^3} .$$

1.4 Condensate fraction

The fraction of particles in the BEC, $f_0 \equiv n_0/n$, is called the **condensate fraction**. Above the condensation threshold, it is obviously equal to zero. Below the condensation threshold, it is given by

$$f_0 = \frac{n - n_c}{n} = 1 - \frac{n_c}{n} = 1 - \left(\frac{T}{T_c} \right)^{3/2} ,$$

where we have used the fact that $n_{\text{exc}} = n_c$ to write the first equality and we have used the expression n_c as a function of T and that of T_c as a function of n to derive the second inequality.

The condensate fraction may be viewed as an **order parameter** for the phase transition. It is equal to 0 on the high-temperature side of the transition (called the *disordered phase*) and finite on the low-temperature side of the transition (called the *ordered phase*). The reduced temperature T/T_c plays the role of a *control parameter* for the phase transition. The exponent to which it is raised (here 3) is called a *critical exponent*. At the transition point, the derivative of f_0 with respect to T is discontinuous. This *kink* at $T = T_c$ is another typical feature of a phase transition.

1.5 Bimodality of the momentum distribution

The BEC and the thermal gas have distinct features that make it possible to *distinguish between them experimentally*. One of these features is the momentum distribution, which we examine here.

Since the single-particle energy eigenstates of our free gas are also momentum eigenstates, we know that the momentum distribution in the ground state is a narrow peak centered on $\mathbf{p} = \mathbf{0}$. The width of this peak will be set by the Heisenberg uncertainty principle $\sim \hbar/V^{1/3}$, where $V^{1/3}$ gives the size of the system.

The momentum distribution of the excited state population is given by the Bose–Einstein distribution:

$$\langle N(\mathbf{p}) \rangle = \frac{1}{\exp[\beta(\mathbf{p}^2/2m - \mu)] - 1} .$$

The width of the latter distribution will be of order $\sqrt{mk_B T}$, much larger than $\hbar/V^{1/3}$. The momentum distribution of the gas is therefore *bimodal*, with a sharp peak containing the condensed particles and sitting on a broad pedestal containing the non-condensed particles.

1.6 Trapped gases

While we have treated so far the case of a gas of free particles enclosed in a volume with sharp boundaries, the gases studied in most experiments are confined in a smooth external potential, which can be approximated by a harmonic potential in the vicinity of its minimum:

$$U(\mathbf{r}) = \frac{1}{2}m\omega^2\mathbf{r}^2 .$$

Such trapped system are no longer homogeneous, which makes their study a little bit more difficult. Following the same reasoning as for homogeneous gases, we can however show that Bose–Einstein condensation still occurs when the temperature reaches the critical value

$$T_c = \frac{\hbar\omega}{k_B} \left(\frac{\langle N \rangle}{g_3(1)} \right)^{1/3} \quad \text{with} \quad g_3(1) = \zeta(3) \simeq 1.202 .$$

Instead of a critical density, one obtains a critical particle number for these non-homogenous gases. It is given by

$$N_c = \zeta(3) \left(\frac{k_B T}{\hbar\omega} \right)^3 .$$

Interestingly, when the critical particle number is reached, the *local* density at the minimum of the trapping potential is precisely equal to the critical density

of the homogeneous gas:

$$n(\mathbf{r} = \mathbf{0}) = \frac{\zeta(3/2)}{\lambda_T^3} \quad \text{when} \quad \langle N \rangle = N_c .$$

Finally, the condensate fraction below the condensation threshold now obeys the equation

$$f_0 = 1 - \left(\frac{T}{T_c} \right)^3 .$$

One sees that it behaves similarly to the case of homogeneous gases, but with a different critical exponent.

1.7 Condensate wave function

All condensed particles occupy the same single particle state λ_0 and share the same wave function $\psi_0(\mathbf{r})$. For instance, a gas confined in a harmonic potential will condense in the wave function:

$$\psi_0^{\text{ho}}(\mathbf{r}) = \frac{1}{(\sqrt{\pi}a_{\text{ho}})^{3/2}} \exp(-\mathbf{r}^2/2a_{\text{ho}}) , \quad \text{with} \quad a_{\text{ho}} = \sqrt{\frac{\hbar}{m\omega}} .$$

One can thus think of the BEC as a **macroscopic matter wave** and introduce the **condensate wave function**:

$$\Psi(\mathbf{r}) = \sqrt{\langle N_0 \rangle} \psi_0(\mathbf{r}) ,$$

whose squared modulus represents the condensate density:

$$|\Psi(\mathbf{r})|^2 = n_0(\mathbf{r}) .$$

One thus sees that a BEC is a fully **phase coherent** matter wave, with a well defined phase across the entire system:

$$\Psi(\mathbf{r}) = \sqrt{n_0(\mathbf{r})} \exp(i\varphi) .$$

2 Weakly interacting gases

We end this lecture with a glimpse into the more realistic case of (weakly) interacting gases. Taking interactions into account when treating an N -body problem is always a challenging task. In the vast majority of cases, there is no analytic solution and one must rely on various types of approximations.

Here, we will treat interactions in the **mean field** approximation, meaning that we add to the non-interacting single-particle energies a term proportional to the particle density:

$$\varepsilon_\lambda^{\text{mf}} = \varepsilon_\lambda^{\text{ni}} + \gamma n .$$

We must however take care of one subtlety, namely that the constant γ differs when considering condensed or non-condensed particles. In short, the mean field from non-condensed particles is twice as strong as the the mean field from condensed particle. The result, which stems from the symmetrization against the permutation of particles, is not obvious and we won't demonstrate it here. We thus define the **interaction strength** g such that

$$\begin{cases} \gamma = 2g & \text{for the mean field of non-condensed particles,} \\ \gamma = g & \text{for the mean field of condensed particles.} \end{cases}$$

2.1 Bose–Einstein condensation in the presence of interactions

The saturation of the excited state population persists in the presence of the mean field, as can be seen by considering the expression

$$\langle N_{\text{exc}}^{\text{mf}} \rangle = \int \frac{d^3 \mathbf{r} d^3 \mathbf{p}}{(2\pi\hbar)^3} \frac{1}{\exp[\beta(\mathbf{p}^2/2m + 2gn_{\text{exc}}^{\text{mf}} - \mu)] - 1}.$$

The mean field effect is simply to shift the chemical potential by $-2gn_{\text{exc}}^{\text{mf}}$, and we can adapt the ideal gas result accordingly to write:

$$\langle N_{\text{exc}}^{\text{mf}} \rangle = g_{3/2}(\tilde{z}) \frac{V}{\lambda_{\text{T}}^3} \quad \text{with} \quad \tilde{z} = \exp[\beta(\mu - 2gn_{\text{exc}})].$$

Within this approximation, the saturation of the excited states occurs at the same critical temperature as in the ideal gas and the Bose–Einstein condensation takes place in the same way.

Here a **word of caution** is necessary: the mean field approximation presented here predicts the same critical temperature for the weakly-interacting gas as for the non-interacting gas. This result is actually incorrect, as the critical temperature for the weakly-interacting gas is in reality slightly smaller than that of the non-interacting gas.

2.2 Gross–Pitaevskii equation for the condensate wave function

Note: the content of this and the following sections are adapted from Castin (2001).

We consider now a *deeply condensed* gas, that is a gas where the density of non-condensed particles is much lower than the density of condensed particles and can be neglected. We seek the effect of the interactions on the condensate wave function. The effect is relevant for trapped, inhomogeneous gases, where interactions are expected to inflate the condensate wave function so as to minimize the interaction energy.

The total energy of the condensed particles can be written as an energy functional of the condensate wave function:

$$E[\Psi_0, \Psi^*] = \int d^3\mathbf{r} \left[\frac{1}{2m} |\hbar\nabla\Psi(\mathbf{r})|^2 + U(\mathbf{r})|\Psi(\mathbf{r})|^2 + \frac{1}{2}g|\Psi(\mathbf{r})|^4 \right].$$

The first term in the integrand represents the kinetic energy. The second term stands for the potential energy in the presence of a trapping potential. The third and last term is the mean field interaction with $\gamma = g$. The factor 1/2 in front of the mean field energy ensures that the interaction energy is counted only once for each pair of particle. Since the condensate wave function is a priori complex valued, its real and imaginary parts are independent functions. Instead of these variables, we choose here instead Ψ and its complex-conjugate Ψ^* .

Because the condensed particles accumulate in the ground state, the condensate wave function minimizes the energy functional with the constraint of fixed total particle number:

$$\int d^3\mathbf{r} |\Psi(\mathbf{r})|^2 = \langle N_0 \rangle.$$

We take into account this constraint using the method of Lagrange multipliers. We thus introduce the free energy,

$$F = E - \mu \int d^3\mathbf{r} |\Psi(\mathbf{r})|^2,$$

and minimize this quantity without constraint. The constraint can later be taken into account by choosing the value chemical potential appropriately.

We first calculate the variation of the free energy induced by an infinitesimal change in the condensate wave function:

$$\Psi(\mathbf{r}) \rightarrow \Psi(\mathbf{r}) + \delta\Psi(\mathbf{r}), \quad \Psi^*(\mathbf{r}) \rightarrow \Psi^*(\mathbf{r}) + \delta\Psi^*(\mathbf{r}).$$

We find:

$$\delta F = \int d^3\mathbf{r} \left[\frac{\hbar^2}{2m} \nabla\delta\Psi^* \cdot \nabla\Psi + U(\mathbf{r})\delta\Psi^*\Psi + g\delta\Psi^*\Psi^*\Psi^2 - \mu\delta\Psi^*\Psi \right] + \text{c.c.}$$

We modify the kinetic energy term by integrating by part, assuming that the condensate wave function vanishes at infinity:

$$\int d^3\mathbf{r} (\nabla\delta\Psi^* \cdot \nabla\Psi + \text{c.c.}) = - \int d^3\mathbf{r} (\delta\Psi^* \Delta\Psi + \text{c.c.}).$$

Finally, we impose that $\delta F = 0$ for any $\delta\Psi$ and $\delta\Psi^*$. We therefore obtain:

$$\mu\Psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\Delta + U(\mathbf{r}) + g|\Psi(\mathbf{r})|^2 \right] \Psi(\mathbf{r}).$$

This equation is known as the Gross–Pitaevskii equation. It yields the condensate wave function in the presence of an arbitrary trapping potential $U(\mathbf{r})$.

2.2.1 The Thomas–Fermi limit

When the number of condensed particles is large, the interactions are expected to increase the spatial extent of the condensate wave function much beyond the typical size of the non-interacting ground-state wave function. In the specific case of a gas confined by a harmonic potential, the radius R of the interacting condensate should verify:

$$R \gg \sqrt{\frac{\hbar}{m\omega}}.$$

Since the momentum width of the condensate wave function is inversely proportional to the wave function radius, the inequality written above also implies that the kinetic energy can be neglected in front of the potential energy:

$$\frac{E_{\text{kin}}}{E_{\text{pot}}} \sim \frac{\hbar^2/mR^2}{m\omega^2 R^2} = \left(\frac{\hbar}{m\omega R^2}\right)^2 \ll 1.$$

The Gross–Pitevskii equation therefore reduces to:

$$\mu\Psi(\mathbf{r}) = [U(\mathbf{r}) + g|\Psi(\mathbf{r})|^2] \Psi(\mathbf{r}).$$

Taking Ψ to be real, we finally obtain:

$$\Psi^{\text{TF}}(\mathbf{r}) = \sqrt{\frac{\mu - U(\mathbf{r})}{g}},$$

or

$$n_0^{\text{TF}}(\mathbf{r}) = \frac{\mu - U(\mathbf{r})}{g}.$$

This regime where the kinetic energy can be neglected in front of the potential energy because of the strong repulsion between the particles is called the **Thomas–Fermi regime**.

References

- Castin, Yvan. 2001. “Bose-Einstein Condensates in Atomic Gases: Simple Theoretical Results.” *arXiv:Cond-Mat/0105058* 72: 1–136. https://doi.org/10.1007/3-540-45338-5_1.