Chapter 14

Ideal Bose gas

In this chapter, we shall study the thermodynamic properties of a gas of non-interacting bosons. We will show that the symmetrization of the wavefunction due to the indistinguishability of particles has important consequences on the behavior of the system. The most important consequence of the quantum mechanical symmetrization is the Bose-Einstein condensation, which is in this sense a special phase transition as it occurs in a system of *non-interacting* particles. We shall consider, as an example, a gas of photons and a gas of phonons.

14.1 Equation of state

We consider a gas of non-interacting bosons in a volume V at temperature T and chemical potential μ. The system is allowed to interchange particles and energy with the surroundings. The appropriate ensemble to treat this many-body system is the grand canonical ensemble.

Non-relativistic Bosons. Our bosons are *non-relativistic* particles with spin s, whose one-particle energies $\epsilon(\mathbf{k})$

$$\epsilon(\mathbf{k}) \,=\, \epsilon(k) \,=\, \frac{\hbar^2 k^2}{2m}, \qquad\qquad \epsilon_0 \,=\, \epsilon(0) \,=\, 0$$

include only the kinetic energy term.

Negative chemical potential. The chemical potential obeys, as discussed in Sect. 12.5.1,

$$-\infty \,<\, \mu \,<\, \epsilon_0, \qquad\qquad \epsilon_0 \,=\, 0 \ .$$

A chemical potential larger than the lowest energy state would lead to nonphysical level occupation.

$$n(\epsilon_r) \,=\, \langle \hat{n}_r \rangle \,=\, \frac{1}{e^{\beta(\epsilon_r-\mu)}-1} \ .$$

Approaching the thermodynamic limit. We consider a situation when the gas is in a box with volume $V = L_x L_y L_z$ and subject to periodic boundary conditions, as we did for the case of fermions in Sect. 13.1.

In the thermodynamic limit ($N \to \infty$, $V \to \infty$, with $n = N/V = \text{const}$), the sums over the wavevector $\vec{k}$ can be replaced by integrals as in the case of the Fermi gas.

However, here we have to be careful when μ happens to approach the value 0. In order to see what kind of trouble we then might get into, let us calculate the ground state occupation.

Occupation of the lowest energy state. We consider the expectation value of the ground state for μ approaching zero from below, viz when $-\beta\mu \ll 1$:

$$n(\epsilon_0) = \frac{1}{e^{-\beta\mu}-1} = \frac{1}{(1-\beta\mu+\ldots)-1} \approx -\frac{1}{\beta\mu}, \qquad \epsilon_0 = 0 \,,$$

which means that $n(\epsilon_0) = \langle \hat{n}_{r=0}\rangle$ diverges. The lowest energy state may hence by occupied *macroscopically*. This is the case when

$$\frac{1}{|\mu|\beta} \sim N, \qquad |\mu| \sim \frac{k_B T}{N}, \qquad 1-z \sim \frac{1}{N} \,. \tag{14.1}$$

Density of states. The density of states $D(E)$, which has the same expression (13.20) as for fermionic systems,

$$D(E) \sim \sqrt{E}, \qquad \lim_{E\to 0} D(E) = 0,$$

vanishes for $E \to 0$. This is where we are going to encounter a problem: if we replace

$$\frac{1}{V}\sum_r \quad \to \quad \int dE\; D(E)$$

we will get that the ground state has zero weight even though, as we have just shown that it can be macroscopically occupied. Fermionic systems do not encounter this problem due to the Pauli principle, which imposes that $\langle \hat{n}_r\rangle \in [0,1]$.

Special treatment for the ground state. The problem with the potentially macroscopic occupation of the ground state can be solved by giving it via

$$\beta\Omega(T,V,z) = \sum_r \ln\left[1 - e^{-\beta(\epsilon_r-\mu)}\right] \tag{14.2}$$

$$= (2s+1)\frac{V}{(2\pi)^3}4\pi\int_0^\infty dk\; k^2\; \ln\left(1 - z e^{-\beta\epsilon(k)}\right)$$

$$+ \underbrace{(2s+1)\ln(1-z)}_{\substack{\text{occupation of the}\\ \text{ground state } \epsilon(0)=0}} \,. \tag{14.3}$$

a special treatment. Starting from the expression (12.35) for the bosonic grand canonical potential $\Omega(T,V,\mu)$ we have split the $\sum_r$ into an integral over all states, as in (13.3) for the case of fermions, and into the ϵ_0 contribution (the last term).

'Irrelevance' of condensate. The ground state contribution (14.3) to the grand canonical potential Ω is formally irrelevant in the thermodynamic limit as a consquence of the scaling (14.1) of the chemical potential:

$$\lim_{V\to 0}\frac{\ln(1-z)}{V}\;\approx\;\lim_{V\to 0}\frac{-\ln(N)}{V}\;\to\;0\;.$$

We note, however, that the size of the *condensate*, that is the number of particles occupying the ground state, determines how many particles occupy energiers $E > E_0$, viz the density of the *normal fluid*.

Dimensionless variables. With the dimensionless variable x and the thermal de Broglie wavelength λ,

$$x\;=\;\hbar k\sqrt{\frac{\beta}{2m}},\qquad\qquad \lambda\;=\;\sqrt{\frac{2\pi\beta\hbar^2}{m}},$$

we write (14.3) as

$$\beta\Omega(T,V,z)\;=\;\frac{2s+1}{\lambda^3}\frac{4V}{\pi}\int_0^\infty dx\,x^2\,\ln\left(1-ze^{-x^2}\right), \tag{14.4}$$

all in parallel to the transformations performed for the Fermi gas. Compare Eq. (13.4)

Taylor expansion. We recall that the Taylor series expansion

$$\ln(1-y)\;=\;-\sum_{n=1}^{\infty}\frac{y^n}{n},\qquad\qquad |y|<1$$

may be used, as done previously in Sect. 13.1.1, to express the integral

$$\int_0^\infty dx\,x^2\,\ln\left(1-ze^{-x^2}\right)\;=\;-\frac{\sqrt{\pi}}{4}\sum_{n=1}^{\infty}\frac{z^n}{n^{5/2}}$$

in terms of

$$g_{5/2}(z)\;=\;-\frac{4}{\sqrt{\pi}}\int_0^\infty dx\,x^2\,\ln\left(1-ze^{-x^2}\right)\;=\;\sum_{n=1}^{\infty}\frac{z^n}{n^{5/2}}\;. \tag{14.5}$$

Note that $g_{5/2}(z)$ and $f_{5/2}(z)$, as defined in (13.5), differ by a sign $(-1)^{n+1}$ in the summand. For later uses we also define $g_{3/2}(z)$ as

$$g_{3/2}(z)\;=\;z\frac{d}{dz}g_{5/2}(z)\;=\;\sum_{n=1}^{\infty}\frac{z^n}{n^{3/2}}\;. \tag{14.6}$$

Note that $f_{3/2}(z)$ was defined analogously in (13.10) as $zd(f_{5/2})/dz$.

Bosonic grand canonical potential. With (14.5), the grand canonical potential (14.4) takes the form

$$\boxed{\beta\Omega(T,V,z)=-\frac{2s+1}{\lambda^3}V\,g_{5/2}(z)}\;. \tag{14.7}$$

Except for the extra term on the right-hand side, and for an exchange $g_{5/2} \leftrightarrow f_{5/2}$, it has the same form as the expression (13.6) for the Fermi gas.

Pressure. From $\Omega = -PV$ and (14.7) we get

$$\boxed{\beta P \;=\; \frac{2s+1}{\lambda^3} g_{5/2}(z)} \;, \tag{14.8}$$

in analogy to (13.7).

Particle density. For the particle density N/V we derived in Sect. 10.3.1 the relation

$$\frac{\langle N\rangle}{V} \;=\; \frac{1}{\beta V}\left[\frac{\partial}{\partial \mu}\ln \mathcal{Z}\right] \;=\; \frac{z}{V}\left[\frac{\partial}{\partial z}\ln \mathcal{Z}\right] \;=\; -\frac{\beta z}{V}\left[\frac{\partial}{\partial z}\Omega\right],$$

where we used (12.25), namely that $\beta\Omega = -\ln \mathcal{Z}$. In this case the condensate term (14.3) contributes. We then find

$$\boxed{n \;=\; \frac{2s+1}{\lambda^3} g_{3/2}(z) + \frac{2s+1}{V}\frac{z}{1-z}} \tag{14.9}$$

for the density of particles $n = \langle \hat{N}\rangle/V$ in terms of the fugacity z, where where we have used (14.7) and (14.6). The thermal equation of states then results from combining (14.8) and (14.9).

Ground state occupation. The term

$$n_0 = \frac{2s+1}{V}\frac{z}{1-z} \tag{14.10}$$

in (14.9) describes the contribution of the ground state to the particle density n. When n_0 becomes macroscopically large on speaks of a *Bose-Einstein condensation.*

Internal energy. The internal energy U is given by

$$U \;=\; -\left(\frac{\partial}{\partial \beta}\ln \mathcal{Z}(T,z,V)\right)_{z,V} \;=\; \left(\frac{\partial}{\partial \beta}\beta\Omega(T,V,z)\right)_{z,V} \;. \tag{14.11}$$

Note that the fugactity z is kept constant in above expression. Our result (14.7) states that

$$\beta\Omega(T,V,z) \;\sim\; -\lambda^{-3} \;\sim\; -\beta^{-3/2} \;,$$

which then leads with (14.11) to

$$\boxed{\frac{U}{V} \;=\; \frac{3k_BT}{2}\frac{2s+1}{\lambda^3} g_{5/2}(z)} \;. \tag{14.12}$$

This expression is the same as the one for the Fermi gas when $f_{5/2}(z)$ is substituted by $g_{5/2}(z)$. The reason is that the ground state energy ϵ_0 vanishes, $\epsilon_0 = 0$. It does hence not matter how many particle occupy the lowest energy level.

Caloric equation of state. Combining (14.12) with (14.8) one can derive the caloric equation of state:

$$\boxed{U = \frac{3}{2}PV} ,$$

which is identical to the one obtained for the ideal Fermi gas. Compare Eq. (13.13).

14.2 Classical limit

The classical limit (non-degenerate Bose gas) corresponds to low particle densities and high temperatures. The fugacity is then small,

$$z = e^{\beta\mu} \ll 1 ,$$

with the Bose-Einstein distribution

$$\langle \hat{n}_r \rangle = \frac{1}{z^{-1}e^{\beta\epsilon_r} - 1} = \frac{ze^{-\beta\epsilon_r}}{1 - ze^{-\beta\epsilon_r}} \approx ze^{-\beta\epsilon_r} \ll 1$$

reducing to the Maxwell-Boltzmann distribution, just as for a fermionic system. The differences between Bose-, Fermi- and Boltzmann statistics are in next order of the order $1/z$ and hence small.

Expansion in the fugacity. As $z \ll 1$, it is sufficient to retain only the first two terms of the series for $g_{5/2}(z)$ and $g_{3/2}(z)$:

$$g_{5/2}(z) \approx z + \frac{z^2}{2^{5/2}}, \qquad g_{3/2}(z) \approx z + \frac{z^2}{2^{3/2}} .$$

With that, the particle density (14.9) takes the following form:

$$n \approx \frac{2s+1}{\lambda^3} z \left(1 + \frac{z}{2^{3/2}}\right) + \frac{2s+1}{V}\frac{z}{1-z} \tag{14.13}$$

Irrelevance of the ground-state contribution. We note that the ground-state contribution (14.10) vanishes generically in the thermodynamic limit, being proportional to $1/V$. The number of particles occupying the ground state is finite only for $z \to 1$. For the case of small fugacities considered here we can neglect it generically, obtaining

$$n \approx \frac{2s+1}{\lambda^3} z \left(1 + \frac{z}{2^{3/2}}\right) . \tag{14.14}$$

Convergence radius. That ground state contributions can be generically neglected at elevated temperatures follows also from the following consideration.

- An expansion in a physical parameter, like z or β, converges only as long as one one remains within the same phase, here the high-temperature quasi-classical gas phase.

- An expansion *diverges* once a phase boundary is encountered, in our case the transition to a phase with macroscopically occupied ground-state level. A condensed low-temperature state can therefore not be described within a high-temperature expansion.

Classical limit. In the strict classical limit we retain only the the terms $\sim z$ on the right-hand side of (14.14) We thus have that

$$n\lambda^3 \approx (2s+1)z^{(0)}, \qquad \boxed{z^{(0)} \approx \frac{n\lambda^3}{2s+1}}\ . \tag{14.15}$$

in the zeroth approximation.

Classical equation of state. We note that (14.15) is identical to corresponding expression (13.15) for Fermions. The expression (14.8) for the pressure reduces then with $g_{5/2} \to z^{(0)}$ to the equation of state for classical particles:

$$\beta P = \frac{2s+1}{\lambda^3}\frac{n\lambda^3}{2s+1}, \qquad VP = \langle\hat{N}\rangle k_B T, \qquad n = \langle\hat{N}\rangle/V\ .$$

First order correction. We solve (14.15),

$$\frac{n\lambda^3}{2s+1} \approx z^{(0)} \approx z^{(1)}\left(1+\frac{z^{(1)}}{2^{3/2}}\right) \approx z^{(1)}\left(1+\frac{z^{(0)}}{2^{3/2}}\right)$$

for $z^{(1)}$, obtaining

$$z^{(1)} \approx \frac{z^{(0)}}{1+\frac{z^{(0)}}{2^{3/2}}} \approx z^{(0)}\left(1-\frac{z^{(0)}}{2^{3/2}}\right)\ , \tag{14.16}$$

which may be substituted in the pressure equation (14.8) for the ideal Bose gas:

$$\beta P \approx \frac{2s+1}{\lambda^3} g_{5/2}(z) \approx \frac{2s+1}{\lambda^3} z^{(1)}\ . \tag{14.17}$$

Quantum correction. Taking all together, (14.17), (14.16) and (14.15), gives us

$$\boxed{PV = \langle\hat{N}\rangle k_B T\left[1-\frac{n\lambda^3}{4\sqrt{2}(2s+1)}\right]}\ . \tag{14.18}$$

The last term in this expression are the *quantum corrections.*

- Equation of states for a real gas, like the van der Waals equation (6.11), posses “similar” additive corrections with respect to the ideal case, which are however due to the interaction between particles. The additive terms present in (14.18) originate on the other side from the indistinguishability principle and *not* from the interaction among particles.

- The correcting term for the ideal Fermi gas quasi-classical equation of state (13.16) is positive, contributing as a “repulsion” among particles. For the Bose gas, the additive term is negative and therefore contributes as an ”attraction” among particles.

Quantitatively, the quantum corrections are much smaller than terms coming from the interaction among particles.

14.3 Bose-Einstein condensation

We consider now the limit of *high* particle densities and low temperatures (quantum limit), where one finds important qualitative differences between bosons, fermions and classical particles.

Particle density. We rewrite the the particle density (14.9) as

$$n = \int_0^\infty \frac{D(\epsilon)d\epsilon}{e^{\beta(\epsilon-\mu)}-1} + \frac{2s+1}{V}\frac{z}{1-z}\,, \tag{14.19}$$

where the the density of states $D(\epsilon)$ is given by (13.20),

$$D(\epsilon) = A\sqrt{\epsilon}, \qquad A = \frac{2s+1}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\,.$$

Dimensionless variables. The regular contribution to the particle density in (14.19) can be evaluated for $\mu = 0$ as

$$\lim_{\mu\to 0}\int_0^\infty \frac{A\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)}-1} = \frac{A}{\beta^{3/2}}\int_0^\infty \frac{\sqrt{x}dx}{e^x-1} = \frac{A}{\beta^{3/2}}\cdot 2.61\,,$$

where we have used the dimensionless variable $x = \beta\epsilon$. The original expression (14.19) for n then becomes

$$\boxed{n = 2.61A(k_BT)^{3/2} + \frac{2s+1}{V}\frac{1}{e^{-\beta\mu}-1}}\,, \qquad A = \frac{2s+1}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\,. \tag{14.20}$$

This is a mixed representation where we have taken the limes $\mu \to 0$ for the regular contribution, but not for the occupation of the ground state.

Bose-Einstein condensation. It is evident from (14.20) that there is a critical temperature T_c,

$$n = 2.61A(k_BT_c)^{3/2}, \qquad \boxed{n = 2.61\,\frac{2}{\sqrt{\pi}}\frac{2s+1}{\lambda_c^3}}\,, \qquad \lambda_c = \sqrt{\frac{h^2}{2\pi m k_B T_c}} \tag{14.21}$$

for which the regular contribution would fall below the desired particle density n. We have used that $(4\pi)^{3/2}/4\pi^2 = 2/\sqrt{\pi}$.

- T_c is the *Bose-Einstein transition temperature.*
- A non-vanishing negative chemical potential $\mu < 0$ would lead to an even small regular term in (14.19). There is therefore no way that the regular term could account for all particle for $T < T_c$.
- The transition takes place when $n\lambda_c^3/(2s+1) = 2.61 \cdot 2/\sqrt{\pi} \approx 2.9$, viz when the thermal wavelength λ_c is of the order of the inter-particle distance.

Scaling of the chemical potential. Rewriting (14.20) for small $|\mu|$ as

$$n - n_c(T) \sim \frac{2s+1}{V}\frac{k_BT}{-\mu}, \qquad \boxed{(-\mu) \sim \frac{2s+1}{V}\frac{k_BT}{n-n_c(T)}}\,, \tag{14.22}$$

where $n_c(T) = 2.61(2s+1)/\lambda^3$. The chemical potential scales therefore like $1/V$, viz it strictly vanishes only in the thermodynamic limit $V \to \infty$.

First excited state. The energy level are quantized for a particle in a box,

$$\epsilon(\mathbf{k}) = \frac{k_x^2+k_y^2+k_z^2}{2m}, \qquad k_\alpha = \frac{2\pi}{L_\alpha}n_\alpha, \qquad \alpha = x,y,z\ ,$$

as discussed in Sect. 13.1. The volume is with $V = L_xL_yL_z$ the product of the linear dimensions.

Diverging occupation of the first excited state. The energy ϵ_1 of one of the first excited states, corresponding e.g. to $(n_x,n_y,n_z) = (1,0,0)$, then scales as

$$\epsilon_1 \sim \frac{1}{L_x^2} \sim V^{-2/3}, \qquad \epsilon_1 \gg |\mu| \sim V^{-1}\ .$$

The occupation n_1 of the first excited state,

$$n_1 = \frac{1}{e^{\beta(\epsilon_1-\mu)}-1} \approx \frac{1}{e^{\beta\epsilon_1}-1} \approx \frac{1}{1+\beta\epsilon_1-1} \sim V^{2/3},$$

therefore diverges in the thermodynamic limit $V \to \infty$. The ground-state occupation $n_0 \sim V$ diverges in contract to a *macroscopic* value.

> The Bose-Einstein condensation is characterized by divergences in occupation numbers. The ground state is however the only state with a *macroscopic* occupation number.

Experimental verification. The Bose-Einstein condensation was predicted by Satyendra Bose and Albert Einstein in 1924-1925. It took almost 70 years to have an experimental corroboration of this phenomenon with the ultracold gas systems. Previous experiments had been done with ^{4}He as well as with hydrogen.