Gibbs quantum statistical mechanics II – ideal gases

An ideal gas is treated as a system of noninteracting particles confined in a potential box shown in Fig. 1.

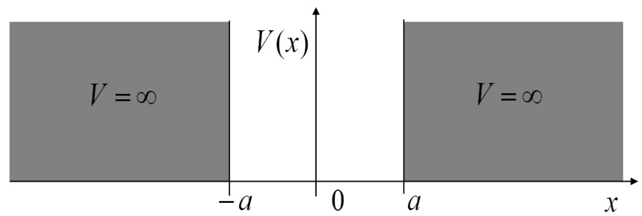

Figure 1: One-dimensional potential box

Particle in a box

- Since the wave function vanishes in the regions of infinite potential, the wave function also vanishes (due to the continuity condition) at $x = -a$ and $x = a$, see Fig. 1. Consequently, there are allowed only such wavelengths in the box that

$$n_x \frac{\lambda}{2} = L, \qquad n_x = 1,\ 2,\ \ldots \tag{1}$$

where $L \equiv 2a$, see Fig. 2

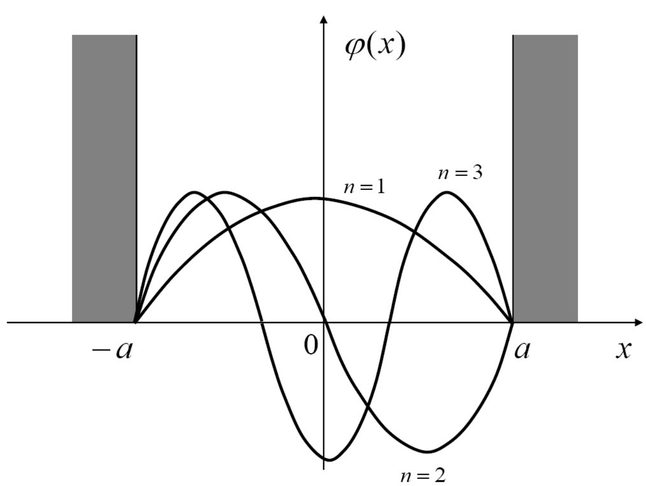

Figure 2: De Broglie waves in a box

- Keeping in mind that

$$\lambda = \frac{h}{p_x} = \frac{2\pi\hbar}{p_x}, \tag{2}$$

the $x-$component of particle's momentum equals

$$p_x = \frac{\pi\hbar}{L} n_x, \qquad n_x = 0,\ 1,\ 2,\ \ldots \tag{3}$$

- As we deal with a three-dimensional box, the momentum is

$$\mathbf{p} = (p_x, p_y, p_z) = \frac{\pi\hbar}{L}\,(n_x, n_y, n_z), \qquad n_x, n_y, n_z = 0,\ 1,\ 2,\ \dots \tag{4}$$

  and the particle's energy equals

$$\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2}\,(n_x^2 + n_y^2 + n_z^2). \tag{5}$$

- Although the reasoning, which is leads to the energy levels (5), is attractively simple and the final result agrees with that one obtained solving the Schrödinger equation, the formulas (2, 3, 4) should be treated with a reservation, as **p** given by Eq. (4) is not, strictly speaking, a momentum of a particle in a box[1].

Fermions & bosons

- In nature all particles are either fermions or bosons.
- Fermions have half odd integer spin ($\frac{1}{2}\hbar,\ \frac{3}{2}\hbar,\ \frac{5}{2}\hbar,\ \dots$) and obey the Pauli exclusion principle. Consequently, fermions follow the Fermi-Dirac statistics.
- Bosons have integer spin ($0,\ \hbar,\ 2\hbar,\ \dots$) and do not obey the Pauli principle. Consequently, bosons follow the Bose-Einstein statistics.
- The energy of a system of non-interacting particles is

$$U = \epsilon_{\mathbf{p}_1} n_{\mathbf{p}_1} + \epsilon_{\mathbf{p}_2} n_{\mathbf{p}_2} + \dots, \tag{6}$$

  where $n_{\mathbf{p}_i}$ is the number of particles with momentum $\mathbf{p}_i$ and

$$n_{\mathbf{p}_i} = \begin{cases} 0,\ 1,\ 2\ \dots & \text{for bosons,} \\ 0,\ 1 & \text{for fermions.} \end{cases} \tag{7}$$

- If a fermion has the number $N_{\rm dof}$ of internal degrees of freedom, for example due to spin, the maximal number of fermions with the momentum $\mathbf{p}_i$ is not 1 but $N_{\rm dof}$.

Partition function

- The partition function equals

$$Q_N(T, V) \equiv \sum_n e^{-\beta E_n}, \tag{8}$$

  where the sum is over the energy eigenstates.
- Using Eq. (6), the partition function of ideal gas of N particles is

$$\begin{aligned} Q_N(T,V) &= \underbrace{\sum_{n_{\mathbf{p}_1}} \sum_{n_{\mathbf{p}_2}} \dots}_{N = n_{\mathbf{p}_1} + n_{\mathbf{p}_2} + \dots} \; e^{-\beta(\epsilon_{\mathbf{p}_1} n_{\mathbf{p}_1} + \epsilon_{\mathbf{p}_2} n_{\mathbf{p}_2} + \dots)} \\ &= \sum_{n_{\mathbf{p}_1}} \sum_{n_{\mathbf{p}_2}} \dots \; e^{-\beta(\epsilon_{\mathbf{p}_1} n_{\mathbf{p}_1} + \epsilon_{\mathbf{p}_2} n_{\mathbf{p}_2} + \dots)} \delta_N^{n_{\mathbf{p}_1} + n_{\mathbf{p}_2} + \dots}. \end{aligned} \tag{9}$$

  The sum should be performed in such a way that $n_{\mathbf{p}_1} + n_{\mathbf{p}_2} + \dots = N$ which greatly complicates the computational problem.

[1] I am grateful to Andrea Bevilacqua for calling my attention to the problem.

Grand partition function

- The grand partition function Ξ equals

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} z^N Q_N(T,V), \tag{10}$$

where $z \equiv e^{\beta\mu}$.

- Using the expression (9), the grand partition function becomes

$$\begin{aligned}\Xi(T,V,\mu) &= \sum_{N=0}^{\infty}\sum_{n_{\mathbf{p}_1}}\sum_{n_{\mathbf{p}_2}}\dots\ e^{-\beta\Big((\epsilon_{\mathbf{p}_1}-\mu)n_{\mathbf{p}_1}+(\epsilon_{\mathbf{p}_2}-\mu)n_{\mathbf{p}_2}+\dots\Big)}\delta_N^{n_{\mathbf{p}_1}+n_{\mathbf{p}_2}+\dots} \\ &= \sum_{n_{\mathbf{p}_1}}\sum_{n_{\mathbf{p}_2}}\dots\ e^{-\beta\Big((\epsilon_{\mathbf{p}_1}-\mu)n_{\mathbf{p}_1}+(\epsilon_{\mathbf{p}_2}-\mu)n_{\mathbf{p}_2}+\dots\Big)}. \end{aligned}\tag{11}$$

The sum over N effectively removes the constraint $n_{\mathbf{p}_1} + n_{\mathbf{p}_2} + \cdots = N$.

- The grand partition function factorizes as

$$\Xi(T,V,\mu) = \sum_{n_{\mathbf{p}_1}} e^{-\beta(\epsilon_{\mathbf{p}_1}-\mu)n_{\mathbf{p}_1}} \sum_{n_{\mathbf{p}_2}} e^{-\beta(\epsilon_{\mathbf{p}_2}-\mu)n_{\mathbf{p}_2}} \dots . \tag{12}$$

- In case of fermions $n_{\mathbf{p}_i} = 0,\ 1$ and

$$\sum_{n_{\mathbf{p}_i}} e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)n_{\mathbf{p}_i}} = 1 + e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}. \tag{13}$$

- In case of bosons, $n_{\mathbf{p}_i} = 0,\ 1,\ 2,\ \dots$ and

$$\sum_{n_{\mathbf{p}_i}} e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)n_{\mathbf{p}_i}} = \frac{1}{1 - e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}}. \tag{14}$$

- The results (13, 14) can be written as

$$\sum_{n_{\mathbf{p}_i}} e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)n_{\mathbf{p}_i}} = \big(1 \pm e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}\big)^{\pm 1}, \tag{15}$$

where the upper sign is for fermions and lower one for bosons.

- Substituting the formula (15) into Eq. (12), the grand partition function is

$$\begin{aligned}\Xi(T,V,\mu) = \prod_i \big(1 \pm e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}\big)^{\pm 1} &= \exp\ln\Big[\prod_i \big(1 \pm e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}\big)^{\pm 1}\Big] \\ &= \exp\Big[\pm\sum_i \ln\big(1 \pm e^{-\beta(\epsilon_{\mathbf{p}_i}-\mu)}\big)\Big]. \end{aligned}\tag{16}$$

- Particle's momentum in a box is quantized but the distance between neighbor levels, which is

$$\Delta p_x = \frac{\pi\hbar}{L}, \tag{17}$$

tends to zero when $L \to \infty$. Therefore, the sum over momenta in Eq. (16) can be replaced by the integral over momentum when $L \to \infty$.

- So, we write

$$\sum_i f(\mathbf{p}_i) = \frac{1}{\Delta p_x \Delta p_y \Delta p_z} \sum_i \Delta p_x \Delta p_y \Delta p_z f(\mathbf{p}_i) = \Big(\frac{L}{\pi\hbar}\Big)^3 \sum_i \Delta p_x \Delta p_y \Delta p_z f(\mathbf{p}_i), \tag{18}$$

where the formula (17) is used. With $V = L^3$ the sum is

$$\sum_i f(\mathbf{p}_i) = 2^3 V \sum_i \frac{\Delta p_x}{2\pi\hbar}\frac{\Delta p_y}{2\pi\hbar}\frac{\Delta p_z}{2\pi\hbar} f(\mathbf{p}_i). \tag{19}$$

- Now we change the sum into the integral as

$$\sum_i \frac{\Delta p_x}{2\pi\hbar}\frac{\Delta p_y}{2\pi\hbar}\frac{\Delta p_z}{2\pi\hbar} f(\mathbf{p}_i) \to \int \frac{d^3p}{(2\pi\hbar)^3} f(\mathbf{p}) \tag{20}$$

and we get

$$\sum_i f(\mathbf{p}_i) = V \int \frac{d^3p}{(2\pi\hbar)^3} f(\mathbf{p}), \tag{21}$$

where the factor 2^3 is ignored or included in V.

- Let us note how differently the volume enters into the classical and quantum formulations of statistical mechanics. In the classical case the volume results from the integration over particle's possible positions. In the quantum case the volume shows up via the momentum quantization condition. There appears a subtle issue about a shape of the box. One shows that the shape does not matter in the thermodynamical limit when $V \to \infty$ and $N/V = \text{const}$.

- Substituting the result (21) into Eq. (16), the grand partition function is

$$\Xi(T,V,\mu) = \exp\Big[\pm V \int \frac{d^3p}{(2\pi\hbar)^3} \ln(1 \pm e^{-\beta(\epsilon_\mathbf{p}-\mu)})\Big] \tag{22}$$

or

$$\Xi(T,V,z) = \exp\Big[\pm V \int \frac{d^3p}{(2\pi\hbar)^3} \ln(1 \pm z e^{-\beta\epsilon_\mathbf{p}})\Big]. \tag{23}$$

Thermodynamical quantities

- The internal gas energy, average number of particles and pressure are given as

$$U = -\frac{\partial}{\partial\beta} \ln \Xi(T,V,z) = V \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\epsilon_\mathbf{p}}{z^{-1}e^{\beta\epsilon_\mathbf{p}} \pm 1}, \tag{24}$$

$$\langle N \rangle = z\frac{\partial}{\partial z} \ln \Xi(T,V,z) = V \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{z^{-1}e^{\beta\epsilon_\mathbf{p}} \pm 1}, \tag{25}$$

$$p = \frac{k_B T}{V} \ln \Xi(T,V,z) = \pm k_B T \int \frac{d^3p}{(2\pi\hbar)^3} \ln(1 \pm z e^{-\beta\epsilon_\mathbf{p}}), \tag{26}$$

where the upper signs are for fermions and the lower ones for bosons.

- How the internal degrees of freedom of gas constituents change the formulas?

- When we have, say, gas of electrons of spin 1/2, there are two internal degrees of freedom: spin up and spin down. The gas can be treated as a mixture of the two types of particles. Since the partition function of the mixture is a product of partition functions of each component, and the thermodynamic functions are determined by a logarithm of the partition function, there appear extra factors of 2 in the formulas. The reasoning can be extended to any number of internal degrees of freedom and for bosons as well. Therefore, Eqs. (24, 25, 26) can be rewritten as

$$U = -\frac{\partial}{\partial\beta}\ln\Xi(T,V,z) = gV\int\frac{d^3p}{(2\pi\hbar)^3}\frac{\epsilon_{\mathbf{p}}}{z^{-1}e^{\beta\epsilon_{\mathbf{p}}}\pm 1}, \tag{27}$$

$$\langle N\rangle = z\frac{\partial}{\partial z}\ln\Xi(T,V,z) = gV\int\frac{d^3p}{(2\pi\hbar)^3}\frac{1}{z^{-1}e^{\beta\epsilon_{\mathbf{p}}}\pm 1}, \tag{28}$$

$$p = \frac{k_BT}{V}\ln\Xi(T,V,z) = \pm gk_BT\int\frac{d^3p}{(2\pi\hbar)^3}\ln(1\pm ze^{-\beta\epsilon_{\mathbf{p}}}), \tag{29}$$

  where g is the number of internal degrees of freedom of gas constituents.

- Since the integrands in Eq. (27, 28, 29) depend only on $p\equiv|\mathbf{p}|$, the angular integrals are trivial and one gets

$$U = \frac{gV}{4\pi^2\hbar^3 m}\int_0^\infty\frac{dp\,p^4}{z^{-1}e^{\beta\epsilon_{\mathbf{p}}}\pm 1}, \tag{30}$$

$$\langle N\rangle = \frac{gV}{2\pi^2\hbar^3}\int_0^\infty\frac{dp\,p^2}{z^{-1}e^{\beta\epsilon_{\mathbf{p}}}\pm 1}, \tag{31}$$

$$p = \pm\frac{gk_BT}{2\pi^2\hbar^3}\int_0^\infty dp\,p^2\ln(1\pm ze^{-\beta\epsilon_{\mathbf{p}}}), \tag{32}$$

  where $\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}$. (The particle momentum p should not be confused with the pressure p.)

- Performing the partial integration in the formula (32), we find

$$\begin{aligned} p &= \pm\frac{gk_BT}{2\pi^2\hbar^3}\int_0^\infty dp\,p^2\ln(1\pm ze^{-\beta\epsilon_{\mathbf{p}}}) \\ &= \pm\frac{gk_BT}{2\pi^2\hbar^3}\Big[\frac{p^3}{3}\ln(1\pm ze^{-\beta\epsilon_{\mathbf{p}}})\Big|_0^\infty - \int_0^\infty dp\,\frac{p^3}{3}\frac{d}{dp}\ln(1\pm ze^{-\beta\epsilon_{\mathbf{p}}})\Big] \\ &= \frac{g}{6\pi^2\hbar^3 m}\int_0^\infty\frac{dp\,p^4}{z^{-1}e^{\beta\epsilon_{\mathbf{p}}}\pm 1} = \frac{2}{3}\frac{U}{V}, \end{aligned} \tag{33}$$

  which gives

$$pV = \frac{2}{3}U. \tag{34}$$

  So, once we have U, we immediately get p.

- Using the known formulas

$$pV = \langle N\rangle k_BT, \qquad U = \frac{3}{2}\langle N\rangle k_BT. \tag{35}$$

  one checks that the relation (34) is valid for a classical ideal gas.

- Using the dimensionless variable

$$x \equiv \frac{p}{\sqrt{2mk_BT}}, \tag{36}$$

the formulas (30) and (31) can be written as

$$\varepsilon \equiv \frac{U}{V} = \frac{\sqrt{2}g(mk_BT)^{3/2}}{\pi^2\hbar^3} k_BT \int_0^\infty \frac{dx\, x^4}{z^{-1}e^{x^2} \pm 1}, \tag{37}$$

$$\rho \equiv \frac{\langle N \rangle}{V} = \frac{\sqrt{2}g(mk_BT)^{3/2}}{\pi^2\hbar^3} \int_0^\infty \frac{dx\, x^2}{z^{-1}e^{x^2} \pm 1}. \tag{38}$$

Classical limit

- Let us see whether the formulas (37, 38) reproduce the classical results (35) when

$$\rho \left(\frac{\hbar^2}{mk_BT} \right)^{3/2} \ll 1. \tag{39}$$

- For this purpose we compute the integrals (37, 38) when $z^{-1} \gg 1$. Then, we can ignore ± 1 in the integrand's denominators and

$$\varepsilon = \frac{\sqrt{2}g(mk_BT)^{3/2}}{\pi^2\hbar^3} k_BTz \int_0^\infty dx\, x^4 e^{-x^2}, \tag{40}$$

$$\rho = \frac{\sqrt{2}g(mk_BT)^{3/2}}{\pi^2\hbar^3}\, z \int_0^\infty dx\, x^2 e^{-x^2}. \tag{41}$$

Using the elementary integrals

$$\int_0^\infty dx\, x^2 e^{-x^2} = \frac{\sqrt{\pi}}{4}, \qquad \int_0^\infty dx\, x^4 e^{-x^2} = \frac{3\sqrt{\pi}}{8}, \tag{42}$$

one finds

$$\varepsilon = \frac{3}{2} g \left(\frac{mk_BT}{2\pi\hbar^2} \right)^{3/2} z\, k_BT, \tag{43}$$

$$\rho = g \left(\frac{mk_BT}{2\pi\hbar^2} \right)^{3/2} z. \tag{44}$$

- Eq. (44) shows that the condition $z^{-1} \gg 1$ is equivalent to the classical limit (39).
- Substituting the fugacity z given by Eq. (44) into the formula (43), one finds the energy density as

$$\varepsilon = \frac{3}{2} \rho\, k_BT. \tag{45}$$

- Due to the relation (34) one also finds the equation of state of classical ideal gas.

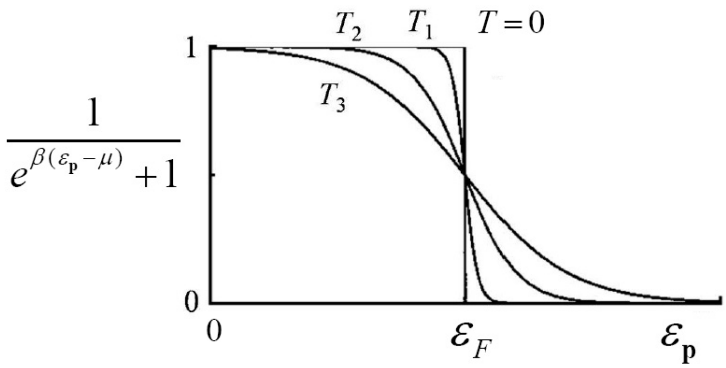

Figure 3: Fermi-Dirac distribution as $T \to 0$

Degenerated Fermi gas

We discuss here a gas of fermions at such high density or low temperature that the condition of classicality (39) is badly violated. Such a gas is called degenerated.

- Let us consider the integrals

$$\rho = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon_{\mathbf{p}}-\mu)}+1}, \tag{46}$$

$$\varepsilon = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\epsilon_{\mathbf{p}}}{e^{\beta(\epsilon_{\mathbf{p}}-\mu)}+1}, \tag{47}$$

in the limit $\beta \to \infty$.

- One observes, see Fig. 3, that

$$\frac{1}{e^{\beta(\epsilon_{\mathbf{p}}-\mu)}+1} \xrightarrow{\beta\to\infty} \Theta(\epsilon_F - \epsilon_{\mathbf{p}}), \tag{48}$$

where $\epsilon_F \equiv \mu(T{=}0)$ that is the chemical potential at zero temperature which is traditionally called the Fermi energy. Due to the step function the states with $\epsilon_{\mathbf{p}} \le \epsilon_F$ are fully occupied and those with $\epsilon_{\mathbf{p}} > \epsilon_F$ completely empty.

- Substituting the step function (48) into the formulas (46, 47), one easily obtains

$$\rho = g \int \frac{d^3p}{(2\pi\hbar)^3} \Theta(\epsilon_F - \epsilon_{\mathbf{p}}) = \frac{g}{2\pi^2\hbar^3} \int_0^{p_F} dp\, p^2 = \frac{g p_F^3}{6\pi^2\hbar^3}, \tag{49}$$

$$\varepsilon = g \int \frac{d^3p}{(2\pi\hbar)^3} \epsilon_{\mathbf{p}} \Theta(\epsilon_F - \epsilon_{\mathbf{p}}) = \frac{g}{4\pi^2\hbar^3 m} \int_0^{p_F} dp\, p^4 = \frac{g p_F^5}{20\pi^2\hbar^3 m} = \frac{3}{5}\rho\, \epsilon_F, \tag{50}$$

where p_F jest is the Fermi momentum related to the Fermi energy as $\epsilon_F = \frac{p_F^2}{2m}$.

- Using Eq. (49), one expresses the Fermi momentum through the particle density as

$$p_F = \hbar \Big(\frac{6\pi^2\rho}{g}\Big)^{1/3}. \tag{51}$$

- The energy density and pressure (the latter is found from the relation (34)), are

$$\varepsilon = \frac{3^{5/3}\pi^{4/3}}{2^{1/3}5} \frac{\hbar^2}{g^{2/3}m} \rho^{5/3}, \qquad p = \frac{1}{5}\Big(\frac{6\pi^2}{g}\Big)^{2/3} \frac{\hbar^2}{m} \rho^{5/3}. \tag{52}$$

- One sees that in contrast to the classical ideal gas, the energy density and pressure do not vanish as $T \to 0$. Due to the Pauli principle only g fermions have vanishing momenta while the remaining ones are in motion and contribute the gas energy and pressure.

- The above formulas have been derived for $T = 0$ but according to Eq. (48) the results hold under the condition $e^{\beta\epsilon_F} \gg 1$ which is equivalent to

$$k_B T \ll \epsilon_F. \tag{53}$$

  Using Eq. (51) the condition (53) becomes

$$k_B T \ll \frac{\hbar^2 \rho^{2/3}}{m}. \tag{54}$$

  The gas is degenerated when its temperature is sufficiently low or its density sufficiently high.

- Due to the condition (54), we often deal with a degenerated gas at temperatures which are relatively high. The is the case of conduction electrons in metals.

- After nuclear fuel is burnt out a star can become a *white dwarf* which is supported by the electron degeneracy pressure against the gravitational collapse. At extremely high densities the Fermi momentum, according to Eq. (51), becomes not only relativistic but ultra-relativistic ($p_F \gg m$) and electrons can be treated as massless. Then, $\epsilon_{\mathbf{p}} = |\mathbf{p}|c$ and one easily shows that the pressure grows with the density not as $\rho^{5/3}$ but as $\rho^{4/3}$. Subrahmanyan Chandrasekhar (1910 - 1995) showed in 1930 that because of the equation-of-state softening the white dwarfs heavier than 1.44 of solar mass, which is now known as the Chandrasekhar limit, are not stable as the electron degeneracy pressure cannot counteract the gravitational collapse. Chandrasekhar actually foresaw an existence of black holes.

Bose-Einstein condensate

We are going to discuss a gas of bosons at very low temperatures when a surprising quantum phenomenon shows up.

- Let us consider the density of bosons

$$\rho = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon_{\mathbf{p}} - \mu)} - 1}. \tag{55}$$

- Since the density of particles with any momentum is nonnegative, the denominator of the integrand must be nonnegative as well. This means that the chemical potential μ cannot be positive. One observes that the density (55) grows as $\mu \to 0$, and consequently the density is maximal for $\mu = 0$. It equals

$$\rho_c = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta\epsilon_{\mathbf{p}}} - 1} = \frac{g}{2\pi^2\hbar^3} \int_0^\infty \frac{dp\, p^2}{e^{\frac{p^2}{2mk_BT}} - 1}, \tag{56}$$

  where the trivial angular integral is performed.

- Introducing the dimensionless variable

$$x \equiv \frac{p}{\sqrt{2mk_BT}} \tag{57}$$

and using the formula

$$\int_0^\infty \frac{dx\, x^2}{e^{x^2}-1} = \frac{\sqrt{\pi}}{4}\,\zeta(3/2), \tag{58}$$

where $\zeta(z)$ is the zeta Riemann function ($\zeta(3/2) \approx 2.612$), one finds

$$\rho_c = g\Big(\frac{mk_BT}{2\pi\hbar^2}\Big)^{3/2}\zeta(3/2). \tag{59}$$

- What happens when the density is bigger than ρ_c?
- To clarify the problem we must return to Eq. (16) where the sum over momenta was replaced by the integral. The particle number is

$$\langle N\rangle = z\frac{\partial}{\partial z}\ln \Xi(T,V,z) = -z\frac{\partial}{\partial z}\sum_i \ln(1 - ze^{-\beta\epsilon_{\mathbf{p}_i}}) = \sum_i \frac{ze^{-\beta\epsilon_{\mathbf{p}_i}}}{1-ze^{-\beta\epsilon_{\mathbf{p}_i}}}. \tag{60}$$

The term corresponding to $\mathbf{p} = 0$ equals

$$\langle N_0\rangle = \frac{z}{1-z}. \tag{61}$$

When $\mu \to 0$ or $z \to 1$, the number of bosons with zero momentum becomes infinite.

- The change of sum into the integral is a legitimate operation if every term of the sum provides an infinitesimally small contribution to the sum. The term $\langle N_0\rangle$ instead can be as large as $\langle N\rangle$. So, it requires a special treatment: when $\rho > \rho_c$ the term must be included in the density (55). The term represents the Bose-Einstein condensate.
- The Bose-Einstein condensation occurs when $\rho > \rho_c$ or when $T < T_c$ where the critical temperature corresponds to the critical density

$$T_c = \frac{2\pi\hbar^2}{mk_B}\Big(\frac{\rho}{g\zeta(3/2)}\Big)^{2/3}. \tag{62}$$

- In the presence of the condensate $\mu = 0$ or $z = 1$.
- The number of particles with zero momentum is

$$\frac{\langle N_0\rangle}{\langle N\rangle} = \begin{cases} 0, & \text{for} \quad \rho < \rho_c, \\ 1 - \frac{\rho_c}{\rho} & \text{for} \quad \rho > \rho_c. \end{cases} \tag{63}$$

or

$$\frac{\langle N_0\rangle}{\langle N\rangle} = \begin{cases} 0, & \text{gdy} \quad T > T_c, \\ 1 - \big(\frac{T}{T_c}\big)^{3/2} & \text{gdy} \quad T < T_c. \end{cases} \tag{64}$$

The dependences (63, 64) are shown in Fig. 4.

- We note that the Bose-Einstein condensate does not occur in two- and one-dimensional systems. In such a case, the factor p^2 in the integrand (56) is replaced by p or 1, the integral is divergent as $\mu \to 0$ and all bosons have thermal distribution of momentum.

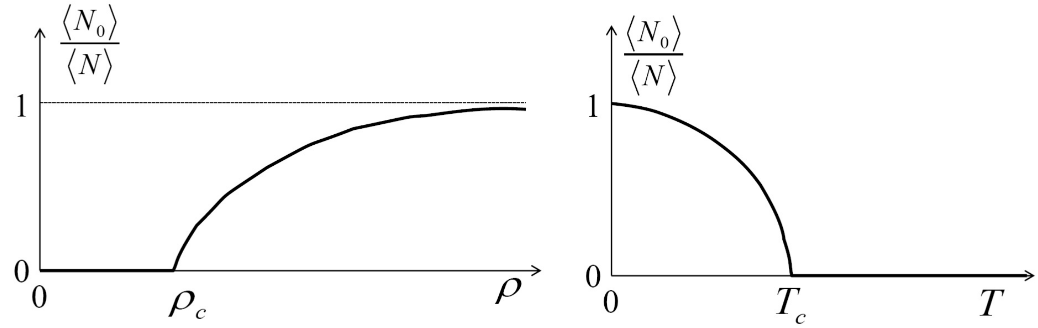

Figure 4: Relative number of particles in the condensate as a function of density and temperature

- Let us compute the gas energy density when $T < T_c$. Since $\mu = 0$ and particles with zero momentum do not contribute to the system's energy we have

$$\varepsilon = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\epsilon_{\mathbf{p}}}{e^{\beta\epsilon_{\mathbf{p}}} - 1} = \frac{g}{4\pi^2\hbar^3 m} \int_0^\infty \frac{dp\, p^4}{e^{\frac{p^2}{2mk_BT}} - 1} = \frac{g(2mk_BT)^{5/2}}{4\pi^2\hbar^3 m} \int_0^\infty \frac{dx\, x^4}{e^{x^2} - 1}. \tag{65}$$

Using the formula

$$\int_0^\infty \frac{dx\, x^4}{e^{x^2} - 1} = \frac{3\sqrt{\pi}}{8}\, \zeta(5/2), \tag{66}$$

where $\zeta(5/2) \approx 1.342$, the energy density is found to be

$$\varepsilon = \frac{3}{2} k_B T\, g \Big(\frac{m k_B T}{2\pi\hbar^2}\Big)^{3/2} \zeta(5/2). \tag{67}$$

- The heat capacity is

$$C_V \equiv \Big(\frac{\partial U}{\partial T}\Big)_V = \frac{15}{4} k_B\, g \Big(\frac{m k_B T}{2\pi\hbar^2}\Big)^{3/2} \zeta(5/2) V \tag{68}$$

and it vanishes as $T \to 0$ in agreement with the third principle of thermodynamics.

- The liquid helium ^{4}He, which becomes superfluid below $T_c = 2.18$ K, is often given as an example of the Bose-Einstein condensate. In the liquid helium, however, the atoms cannot be treated as noninteracting.

- In 1995 Eric Cornell and Carl Wieman managed to confine atoms of rubidium in a magnetic trap and cool the system down to $T = 1.7 \cdot 10^{-7}$ K. The Bose-Einstein condensate was observed through a measurement of velocity distribution of atoms. Wolfgang Ketterle performed a similar experiment with atoms of sodium at the same time. In both cases the densities were low that the atoms were almost noninteracting and the effect could be assigned to the Bose-Einstein statistics. Cornell, Wieman and Ketterle were awarded the Nobel prize in 2001.

Gas of thermal photons

Historically the problem emerged as a black body radiation and its solution by Max Planck (1858 - 1947) initiated the quantum physics in 1900. The term photon was coined by chemist Gilbert N. Lewis only in 1926.

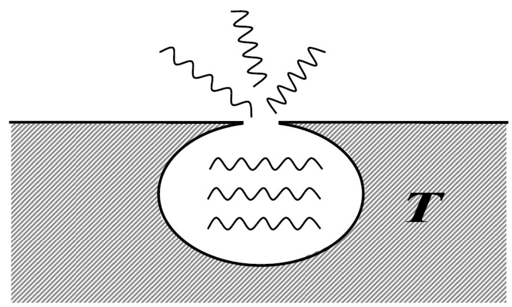

Figure 5: Model of black body radiation

- The photons almost do not interact with each other but do interact with walls of the container. If there is a hole in the container, as shown in Fig. 5, one observes a photon spectrum known as the black body radiation.
- A photon has zero mass and its energy as function of its momentum $\mathbf{p}$ is $\epsilon_{\mathbf{p}} = |\mathbf{p}|c$ where c is the speed of light.
- Since photons do not carry any charge their number is not fixed. The photon chemical potential vanishes as the free energy is independent of the photon number.
- The energy density equals
$$\varepsilon = 2 \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\epsilon_{\mathbf{p}}}{e^{\beta\epsilon_{\mathbf{p}}} - 1} = \frac{c}{\pi^2\hbar^3} \int_0^\infty \frac{dp\, p^3}{e^{\beta cp} - 1} = \frac{(k_BT)^4}{\pi^2\hbar^3c^3} \int_0^\infty \frac{dx\, x^3}{e^x - 1}, \tag{69}$$
where two photon spin states ($g = 2$) are taken into account.
- Using the integral formula
$$\int_0^\infty \frac{dx\, x^3}{e^x - 1} = \frac{\pi^4}{15}, \tag{70}$$
the energy density is
$$\varepsilon = \frac{\pi^2}{15\hbar^3c^3}\, k_B^4 T^4, \tag{71}$$
which is known as the Stefana-Boltzmann law.
- The heat capacity equals
$$C_V \equiv \Big(\frac{\partial U}{\partial T}\Big)_V = \frac{4\pi^2}{15\hbar^3c^3}\, V k_B^4 T^3 \tag{72}$$
and in agreement with the third principle of thermodynamics it vanishes as $T \to 0$.
- It is worth noticing that C_V shows unlimited growth as $T \to \infty$. It reflects the fact that the average number of photons and the number of degrees of freedom grow to infinity as $T \to \infty$.

- The photon pressure found from Eq. (32) equals

$$p = -\frac{k_B T}{\pi^2 \hbar^3} \int_0^\infty dp\, p^2 \ln(1 - e^{-\beta c p}). \tag{73}$$

Performing partial integration one finds

$$p = \frac{1}{3}\, \varepsilon, \tag{74}$$

which holds for any massless particles both bosons and fermions.

- The radiation pressure plays a role in the stellar balance as first noted by the Polish physicist Czesław Białobrzeski (1878 - 1953).

- Let us note that for a gas of non-relativistic (massive) particles Eq. (34) holds that is $p = \frac{2}{3}\, \varepsilon$.

- Photon's energy and momentum can be expressed through the angular frequency ω as $\hbar\omega/c$ and $\hbar\omega$, respectively. The energy density (69) then equals

$$\varepsilon = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{d\omega\, \omega^3}{e^{\beta\hbar\omega} - 1}, \tag{75}$$

and the spectral distribution is

$$\frac{d\varepsilon}{d\omega} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}, \tag{76}$$

which is the famous Planck formula.

- In the long wavelength or small frequency limit we deal with classical electromagnetic waves. Indeed, when $\hbar\omega \ll k_B T$, Eq. (76) gives the classical radiation spectrum

$$\frac{d\varepsilon}{d\omega} = \frac{k_B T}{\pi^2 c^3}\, \omega^2, \tag{77}$$

where the Planck constant is absent.

- The Planck spectrum (76) is rather common in nature. In particular, the cosmic microwave background (CMB) is well described by the Planck formula with $T = 2.7$ K.