Bosons and Fermions in the Grand Canonical Ensemble

Let us apply the Grand canonical formalism—see corresponding section of the Lecture Notes—to ideal Bose and Fermi gases. The effective energy reads

\[ E' = E - \mu N = g \sum_p (\varepsilon_p - \mu) n_p. \]  

(1)

The only difference with the canonical ensemble is the shift of all single-particle energies by one and the same value \( \mu \). A great simplification is that now we have to sum over all possible \( N \)'s, which means that there is no constraint on the total sum of the occupation numbers, so that the latter are absolutely independent and the partition function factorizes:

\[ Z = \prod_g \prod_p Z_p = \left( \prod_p Z_p \right)^g. \]  

(2)

Performing standard summations—that of harmonic oscillator for bosons and that of two-level system for fermions, we get

\[ Z_p = \sum_{n_p} e^{-\frac{(\varepsilon_p - \mu)n_p}{T}} = \begin{cases} 1 + e^{-\frac{\varepsilon_p - \mu}{T}} & \text{(fermions = two-level system)}, \\ 1 - e^{-\frac{\varepsilon_p - \mu}{T}} & \text{(bosons = harmonic oscillator)}. \end{cases} \]  

(3)

\[ \bar{n}_p = -\left( \frac{\partial \Omega_p}{\partial \mu} \right)_{T,V} = \frac{1}{e^{(\varepsilon_p - \mu)/T} \pm 1} \]  

(fermions/bosons). \]  

(4)

Eq. (4) is called *Fermi-Dirac distribution* in the case of fermions, and *Bose-Einstein distribution* in the case of bosons.

To get the pressure, we use the formula \( P = -\frac{\partial \Omega}{\partial V} \) (we replace summation over momenta with integration):

\[ P = \begin{cases} \frac{\pi^2}{3} \int d\varepsilon_p \ln \left[ 1 + e^{-\varepsilon_p/T} \right] & \text{(fermions)}, \\ -\frac{\pi^2}{3} \int d\varepsilon_p \ln \left[ 1 - e^{-\varepsilon_p/T} \right] & \text{(bosons)}. \end{cases} \]  

(5)

There are two ways of getting the number density: either by using the relation \( n = \partial P(\mu, T)/\partial \mu \), or by directly summing up the occupation numbers to find the total number of particles and then dividing it by \( V \). The result is

\[ n = \frac{g}{(2\pi \hbar)^3} \int \frac{d\varepsilon_p}{e^{(\varepsilon_p - \mu)/T} \pm 1} \]  

(fermions/bosons). \]  

(6)

**Classical limit.** Classical limit corresponds to the regime when \( \mu \) is negative and has the absolute value much larger than \( T \):

\[ \gamma = |\mu|/T \gg 1. \]  

(7)

[Note that there is no contradiction with the common wisdom that at a fixed density, classical regime corresponds to large enough temperature. At fixed density, \( \mu \) is a function of temperature, and to reconcile Eq. (7) with the common wisdom we just need to make sure that with increasing temperature, \( |\mu| \) increases much faster than \( T \). And this will be explicitly seen from the expression for \( \mu \) in terms of \( n \) and \( T \).]
We can use the large parameter $\gamma$ to establish the asymptotic form of Eqs. (5) and (6). In Eqs. (5) we have
\[ e^{-(\epsilon_p + |\mu|)/T} \ll 1 , \] (8)
and, using $\ln(1 + x) \approx x$ at $|x| \ll 1$, get (for both bosons and fermions)
\[ P \approx \frac{gT}{(2\pi\hbar)^3} \int \frac{d\mathbf{p}}{(2\pi \hbar)^3} e^{-(\epsilon_p - |\mu|)/T} = gT e^{-|\mu|/T} \int \frac{d\mathbf{p}}{(2\pi \hbar)^3} e^{-p^2/2mT} . \] (9)

In Eq. (6) we have
\[ e^{(\epsilon_p + |\mu|)/T} \gg 1 , \] (10)
and can neglect $\pm 1$ in denominator, which leads to
\[ n \approx g e^{-|\mu|/T} \frac{1}{(2\pi \hbar)^3} \int \frac{d\mathbf{p}}{(2\pi \hbar)^3} e^{-p^2/2mT} . \] (11)

Comparing (9) and (11), we arrive at the classical equation of state
\[ P = nT . \] (12)

By doing the integral in (11), we find the relation for the chemical potential in terms of temperature and density:
\[ \mu = -T \ln \left( \frac{g}{(2\pi \hbar)^3} \left( \frac{m}{2\pi \hbar^2} \right)^{3/2} / n \right) \text{(classical limit)} . \] (13)

Note that while $\hbar$ enters the expression (as an additive constant), this has nothing to do with quantum effects and only reflects the fact that in classical statistics the chemical potential is defined up to an additive term $\propto T$.

The essentially quantum behavior and, correspondingly, significant difference between bosons and fermions appear at $|\mu| \sim T$. As is seen from a dimensional estimate of the integral (6), or just directly from (13), this regime takes place when
\[ T \sim T_*(n) , \] (14)
where
\[ T_* = \frac{\hbar^2 n^{2/3}}{m} . \] (15)

The condition (14) has a deep quantum mechanical meaning. If we compare the temperature de Broglie wavelength (de Broglie wavelength of a particle with the energy $T$),
\[ \lambda_T = \frac{\hbar}{\sqrt{mT}} , \] (16)
to the typical interparticle separation, $n^{-1/3}$, we see that Eq. (14) is equivalent to
\[ \lambda_T \sim n^{-1/3} . \] (17)

Recalling that de Broglie wavelength is the length below which a particle cannot be localized without substantially changing its energy, we understand that condition (14) implies considerable overlapping of the single-particle wavefunctions, which in its turn leads—due to the symmetrization procedure—to a substantial difference of the behavior of identical particles from that of distinguishable ones.

In the case of a Fermi gas, $T_* \sim \varepsilon_F$, so that the temperature regime $T \sim T_*$ corresponds to the crossover from the Boltzmann statistics of the classical gas to the strongly degenerate fermionic
regime \((T \ll \varepsilon_F)\) which we have analyzed earlier. At \(T \ll \varepsilon_F\) we have \(\mu \approx \varepsilon_F\).

**Bose-Einstein Condensation**

Due to our previous analysis we know very well what happens to fermions in the limit \(T \ll T^*\).—What about bosons?

Suppose we fix some number density \(n\) and decrease the temperature \(T\). Eq. (6), which under these conditions defines the function \(\mu(n, T)\), says that the absolute value of the chemical potential should decrease with temperature to keep \(n\) fixed. It turns out that \(|\mu|\) reaches the zero value at some finite temperature \(T_c(n)\). This temperature can be easily found from Eq. (6) with chemical potential set equal to zero, and the result is

\[
T_c \approx 3.31 \frac{\hbar^2 n^{2/3}}{g^{2/3} m}.
\]

(18)

What happens at \(T < T_c\)? The chemical potential cannot become positive: The integral will diverge! The only reasonable possibility is

\[
\mu \equiv 0 \quad \text{at} \quad T < T_c.
\]

(19)

But then the integral (6) will be equal to

\[
n'(T) = n(T/T_c)^{3/2} < n,
\]

(20)

and the total number of particles is not conserved. The resolution of this paradox is that the rest of the particles “condenses” into the state \(p = 0\), which does not contradict to the distribution (4), provided \(|\mu|\) is macroscopically small. This phenomenon is called Bose-Einstein condensation. The particles in the state \(p = 0\) are called condensate particles, or simply condensate. The rest of the particles, the number density of which is given by (20), are called non-condensate particles. The condensate density thus is given by

\[
n_0 = n - n'(T) = n \left[1 - (T/T_c)^{3/2}\right].
\]

(21)

At \(T < T_c\) the thermodynamics is simple: All the thermodynamic characteristics are density independent and, due to the scale invariance of the function \(\varepsilon_p = p^2/2m\), behave like some powers of temperatures. For example, \(n' \propto (mT)^{3/2}/\hbar^3\). The theory is qualitatively analogous to the theory of equilibrium electromagnetic field. All the integrals are non-dimensionalized leading to some numeric coefficients. Below we list some results.

\[
P = 0.0851 \frac{g m^{3/2} T^{5/2}}{\hbar^3}.
\]

(22)

\[
E = 0.128 \frac{g m^{3/2} T^{5/2}}{\hbar^3} V.
\]

(23)

\[
C_V = \frac{5E}{2T}.
\]

(24)
Similarity of the Equation of State. Scaling Functions

In the case of an ideal gas of distinguishable particles, the equation of state has a very simple power-law form. This fact is due to the scale invariance of the single-particle problem. The problem of quantum distinguishable particles is different, and now $P(n, T)$ is a non-trivial function. However, there is still a circumstance that allows us to reduce the complexity of this function from two independent variables to just one. Namely, the absence of separate scales for energy and density. Typical temperature $T_*$ is expressed in terms of density, and vice versa: if we fix some temperature and estimate a density at which the quantum behavior sets in, we will arrive at the same relation, $\hbar^2 n^{5/3}/m \sim T$. This means that the temperature dependence of pressure can be represented as

$$P \propto f(T/T_*(n)),$$

where $f(x)$ is some dimensionless function of a dimensionless argument $x$. It is easy to figure out that the dimensional coefficient in (25) should be $\propto \hbar^2 n^{5/3}/m$, so that we can write

$$P = \frac{\hbar^2 n^{5/3}}{m} f(T/T_*(n)).$$

(26)

This situation is called similarity. The behavior of the system as a function of, say, temperature at different densities is basically one and the same, up to a proper scaling of the variables. This example illustrates the practical importance of revealing similarities in physical problems. A word which is used in the context of the situation of similarity is scaling. The function $f$ the relations like Eq. (26) is called scaling function. Scaling functions describe relationships between dimensionless variables. In Eq. (26), the function $f$ describes the relation

$$y = f(x)$$

between two dimensionless variables: $x = mT/\hbar^2 n^{2/3}$ and $y = mP/\hbar^2 n^{5/3}$. Such variables are called scaling variables.

**Problem 41.**

(a) On the basis of dimensional analysis combined with the analysis of intensive and extensive quantities, find proper scaling variables and introduce—just introduce, do not evaluate(!)—corresponding scaling function describing the dependence of the entropy of a quantum gas on the following three variables: $N$, $V$, and $T$.

(b) Do the same for $C_V$ as a function of the same variables.

**Problem 42.** Find numerically the functions $f_B(x)$ and $f_F(x)$, Eqs. (26),(27)—for bosons and fermions with $g = 1$. *Hint:* Use non-dimensionalized Eqs. (5) and (6) to numerically obtain $y = f(x)$ in a parametric form, the dimensionless parameter being $\gamma = \mu/T$. Carefully check that the functions do demonstrate the proper limiting behavior:

(a) $f(x) \to x$ at $x \gg 1$ (classical limit),

(b) Fermions: the $x \ll 1$ case corresponding to the degenerate situation discussed previously, where the pressure and its finite temperature correction were found,

(c) Bosons: Equivalence to Eq. (22) at $x < x_c = 3.31$; continuity at $x = x_c$.

To help you with numerics, below I provide tables of the values of the following integrals.

$$I_{B1} = -\int_0^\infty d\xi \xi^2 \ln \left[1 - e^{-(\xi^2 - \gamma)}\right], \quad I_{B2} = \int_0^\infty \frac{d\xi \xi^2}{e^{(\xi^2 - \gamma)} - 1},$$

$$I_{F1} = \int_0^\infty d\xi \xi^2 \ln \left[1 + e^{-(\xi^2 - \gamma)}\right], \quad I_{F2} = \int_0^\infty \frac{d\xi \xi^2}{e^{(\xi^2 - \gamma)} + 1}.$$
<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$I_{B1}$</th>
<th>$I_{B2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0001</td>
<td>0.594</td>
<td>1.142</td>
</tr>
<tr>
<td>-0.0003</td>
<td>0.594</td>
<td>1.131</td>
</tr>
<tr>
<td>-0.001</td>
<td>0.593</td>
<td>1.109</td>
</tr>
<tr>
<td>-0.002</td>
<td>0.592</td>
<td>1.089</td>
</tr>
<tr>
<td>-0.003</td>
<td>0.591</td>
<td>1.073</td>
</tr>
<tr>
<td>-0.005</td>
<td>0.589</td>
<td>1.050</td>
</tr>
<tr>
<td>-0.01</td>
<td>0.584</td>
<td>1.007</td>
</tr>
<tr>
<td>-0.02</td>
<td>0.574</td>
<td>0.948</td>
</tr>
<tr>
<td>-0.05</td>
<td>0.548</td>
<td>0.839</td>
</tr>
<tr>
<td>-0.075</td>
<td>0.527</td>
<td>0.776</td>
</tr>
<tr>
<td>-0.1</td>
<td>0.509</td>
<td>0.725</td>
</tr>
<tr>
<td>-0.15</td>
<td>0.474</td>
<td>0.645</td>
</tr>
<tr>
<td>-0.2</td>
<td>0.444</td>
<td>0.583</td>
</tr>
<tr>
<td>-0.25</td>
<td>0.416</td>
<td>0.531</td>
</tr>
<tr>
<td>-0.3</td>
<td>0.391</td>
<td>0.487</td>
</tr>
<tr>
<td>-0.4</td>
<td>0.3455</td>
<td>0.4157</td>
</tr>
<tr>
<td>-0.5</td>
<td>0.3069</td>
<td>0.3591</td>
</tr>
<tr>
<td>-0.6</td>
<td>0.2734</td>
<td>0.3130</td>
</tr>
<tr>
<td>-0.8</td>
<td>0.2183</td>
<td>0.2418</td>
</tr>
<tr>
<td>-1.0</td>
<td>0.1754</td>
<td>0.1898</td>
</tr>
<tr>
<td>-1.2</td>
<td>0.1415</td>
<td>0.1506</td>
</tr>
<tr>
<td>-1.5</td>
<td>0.1031</td>
<td>0.1078</td>
</tr>
<tr>
<td>-1.75</td>
<td>0.07953</td>
<td>0.08224</td>
</tr>
<tr>
<td>-2.0</td>
<td>0.06148</td>
<td>0.06307</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$I_{F1}$</th>
<th>$I_{F2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.5</td>
<td>0.0953</td>
<td>0.0919</td>
</tr>
<tr>
<td>-1.0</td>
<td>0.1536</td>
<td>0.1453</td>
</tr>
<tr>
<td>-0.5</td>
<td>0.245</td>
<td>0.225</td>
</tr>
<tr>
<td>-0.3</td>
<td>0.294</td>
<td>0.266</td>
</tr>
<tr>
<td>0.0</td>
<td>0.384</td>
<td>0.339</td>
</tr>
<tr>
<td>0.5</td>
<td>0.591</td>
<td>0.495</td>
</tr>
<tr>
<td>1.0</td>
<td>0.887</td>
<td>0.698</td>
</tr>
<tr>
<td>1.5</td>
<td>1.297</td>
<td>0.950</td>
</tr>
<tr>
<td>2.0</td>
<td>1.846</td>
<td>1.251</td>
</tr>
<tr>
<td>2.5</td>
<td>2.556</td>
<td>1.598</td>
</tr>
<tr>
<td>3.0</td>
<td>3.451</td>
<td>1.988</td>
</tr>
<tr>
<td>4.0</td>
<td>5.876</td>
<td>2.885</td>
</tr>
<tr>
<td>5.0</td>
<td>9.267</td>
<td>3.919</td>
</tr>
<tr>
<td>7.0</td>
<td>19.45</td>
<td>6.332</td>
</tr>
<tr>
<td>10.0</td>
<td>44.76</td>
<td>10.67</td>
</tr>
<tr>
<td>15.0</td>
<td>119.4</td>
<td>19.47</td>
</tr>
</tbody>
</table>