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Density matrix

1.1 Statistical average

Quantum average value of operator $\hat{G}$ in a state $\psi_k(x,t)$

$$\left\langle \hat{G} \right\rangle = \int \psi_k^* \hat{G} \psi_k \mathrm{d}\tau = \left\langle \psi_k \middle| \hat{G} \middle| \psi_k \right\rangle \tag{1.1}$$

Statistical ensemble consists of N hypothetical physical systems of the same Hamiltonian whose states are determined by the wave functions $\psi_k(x,t)$, where $x = \boldsymbol{r},\ \boldsymbol{p}$ symbolizes a generalized variable. We use such a statistical ensemble to calculate a statistical average value

$$\left\langle \bar{\hat{G}} \right\rangle = \frac{1}{N} \sum_{k=1}^{N} \left\langle \psi_k \middle| \hat{G} \middle| \psi_k \right\rangle = \frac{1}{N} \sum_{k=1}^{N} \int \psi_k^* \hat{G} \psi_k \mathrm{d}\tau \tag{1.2}$$

We have here two types of averaging: quantum and statistical over a given ensemble.

1.2 Density matrix

Chosing a complete system of orthonormal functions $\varphi_n(x)$ we can represent

$$\psi_k(x,t) = \sum_n a_n^k(t) \varphi_n(x) \tag{1.3}$$

and write the statistical average of $\hat{G}$

$$\left\langle \bar{\hat{G}} \right\rangle = \frac{1}{N}\sum_{k=1}^{N}\sum_{n,m} a_n^{k*} a_m^{k} \int \underbrace{\psi_n^* \hat{G} \psi_m \mathrm{d}\tau}_{G_{n,m}} =$$

$$= \sum_{n,m} \frac{1}{N}\sum_{k=1}^{N} a_m^k a_n^{k*} G_{nm} = \sum_{n,m} \rho_{mn} G_{nm} = \mathrm{Tr}(\hat{\rho}\hat{G}) \quad (1.4)$$

where we have defined a density matrix $\hat{\rho}$ in a certain representation, that is for a given set of basis functions $\{\psi_n\}$

$$\rho_{mn} = \frac{1}{N}\sum_{k=1}^{N} a_m^k a_n^{k*} \quad (1.5)$$

Although $\hat{\rho}$ is defined for a certain choice of $\{\psi_n\}$, the average value - an observable quantity - does not depend on this choice, what one can easily show transforming $\{\psi_n\}$ into another orthonormal and complete basis $\{\psi_n'\}$

$$\begin{bmatrix} \psi_1' \\ \vdots \\ \psi_n' \\ \vdots \end{bmatrix} = \hat{U} \begin{bmatrix} \psi_1 \\ \vdots \\ \psi_n \\ \vdots \end{bmatrix} \quad (1.6)$$

where $\hat{U}$ is a unitary operator. In this new representation the density matrix reads

$$\hat{\rho}' = \hat{U}^{-1}\rho\hat{U} \quad (1.7)$$

and

$$\hat{G}' = \hat{U}^{-1}\hat{G}\hat{U} \quad (1.8)$$

The averaged $\hat{G}'$ value

$$\mathrm{Tr}\left(\hat{\rho}'\hat{G}'\right) = \mathrm{Tr}\left(\hat{U}^{-1}\hat{U}\hat{U}^{-1}\hat{G}\hat{U}\right) = \mathrm{Tr}\left(\hat{U}^{-1}\hat{\rho}\hat{G}\hat{U}\right) =$$

$$= \mathrm{Tr}\left(\hat{\rho}\hat{G}\hat{U}\hat{U}^{-1}\right) = \mathrm{Tr}\left(\hat{\rho}\hat{G}\right) \quad (1.9)$$

is the same as the the averaged $\hat{G}$. Therefore, we have shown that the averaging does not depend on a particular choice of a basis representation. Summarizing, we have defined a quantum – statistical average of an operator $\hat{G}$

$$\left\langle \bar{\hat{G}} \right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{G}\right) \tag{1.10}$$

where $\hat{\rho}$ is a density matrix. We note that the normalization condition

$$\langle \psi_k \,|\, \psi_k \rangle = 1, \ \left\langle \varphi_n^k \,\middle|\, \varphi_m^k \right\rangle = \delta_{nm} \tag{1.11}$$

leads to

$$1 = \langle \psi_k \,|\, \psi_k \rangle = \sum_{n,m} a_n^k a_m^k \left\langle \varphi_n^k \,\middle|\, \varphi_m^k \right\rangle = \sum_{n,m} a_n^{k*} a_m^k \delta_{nm} = \sum_n \left| a_n^k \right|^2 \tag{1.12}$$

and in consequence to

$$\mathrm{Tr}\hat{\rho} = \sum_n \frac{1}{N} \sum_{k=1}^{N} \left| a_n^k \right|^2 = \frac{1}{N} \sum_{k=1}^{N} \sum_n \left| a_n^k \right|^2 = \frac{1}{N} \sum_{k=1}^{N} 1 = 1 \tag{1.13}$$

which means that $\hat{\rho}$ can be regarded as a probability density matrix. Let's consider a density matrix of a pure state ψ when all wave functions of a statistical ensemble are identical, i.e., $\psi_k = \psi$ and

$$\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} a_m a_n^* = a_m a_n^* \tag{1.14}$$

Calculating $\hat{\rho}^2$ matrix element

$$\begin{aligned}(\hat{\rho}^2)_{mn} = \sum_l \rho_{ml} \rho_{\mathrm{ln}} = \sum_l a_m a_l^* a_l a_n^* = \\ = a_m \left(\sum_l a_l^* a_l \right) a_n^* = a_m a_n^* = \hat{\rho}_{mn}\end{aligned} \tag{1.15}$$

we obtain $\hat{\rho}^2 = \hat{\rho}$ for a pure state system. If we take the energy representation, that is a set of eigenfunctions φ_n

$$\hat{H}\varphi_n = \mathcal{E}\varphi_n \tag{1.16}$$

$$H_{ml} = \left\langle \varphi_m \,\middle|\, \hat{H} \,\middle|\, \varphi_l \right\rangle = \mathcal{E}\delta_{ml} \tag{1.17}$$

the time evolution of $\hat{\rho}$

$$\mathtt{i}\hbar\frac{\partial\hat{\rho}}{\partial t}=\left[\hat{H},\hat{\rho}\right]=\left[\hat{H},\hat{\rho}\left(\hat{H}\right)\right]=0 \tag{1.18}$$

that is for any matrix element ρ_{mn}

$$\begin{aligned}0=\mathtt{i}\hbar\frac{\partial\rho_{mn}}{\partial t}&=\left[\hat{H},\hat{\rho}\right]_{mn}=\left\langle\varphi_m\left|\hat{H}\hat{\rho}\right|\varphi_n\right\rangle-\left\langle\varphi_m\left|\hat{\rho}\hat{H}\right|\varphi_n\right\rangle=\\&=\sum_l\left(\left\langle\varphi_m\left|\hat{H}\right|\varphi_l\right\rangle\langle\varphi_l\,|\,\hat{\rho}\,|\,\varphi_n\rangle-\langle\varphi_m\,|\,\hat{\rho}\,|\,\varphi_l\rangle\left\langle\varphi_l\left|\hat{H}\right|\varphi_n\right\rangle\right)=\\&=\sum_l\left(H_{ml}\rho_{ln}-\rho_{ml}H_{ln}\right)=\sum_l\left(\mathcal{E}_m\delta_{lm}\rho_{ln}-\rho_{ml}\mathcal{E}_n\delta_{ln}\right)=\\&=(\mathcal{E}_m-\mathcal{E}_n)\rho_{mn}\end{aligned} \tag{1.19}$$

and for nondegenerate states we get a diagonal density matrix

$$\rho_{mn}=\delta_{mn}\rho_n \tag{1.20}$$

where

$$\rho_n=\rho_{nn}=\frac{1}{N}\sum_{k=1}^{N}\left|a_n^k\right|^2 \tag{1.21}$$

ρ_n is a probability of finding among the statistical ensemble a system in a state $|\varphi_n\rangle$, in other words, it is a probability that a system resides in a quantum state $|\varphi_n\rangle$. Therefore, in a basis of energy eigenfunctions we can represents $\hat{\rho}$ as

$$\hat{\rho}=\sum_n|\varphi_n\rangle\,\rho_n\,\langle\varphi_n| \tag{1.22}$$

We will use the energy representation of the density matrix throughout this book. At the end let us note that $0\leqslant\left|a_n^k\right|^2\leqslant 1$ for each k and according to (1.21) we have $0\leqslant\rho_n\leqslant 1$. The density matrix element takes its maximal value, $\rho_n=1$, only if $\left|a_n^k\right|^2=1$ for each k, that is when all systems of the statistical ensemble are in the state $|\varphi_n\rangle$ and this means a pure state system for which

$$\hat{\rho}=\left[\begin{array}{c|ccc}1&0&\cdots&0\\\hline 0&0&\cdots&0\\\vdots&\vdots&\ddots&\vdots\\0&0&\cdots&0\end{array}\right] \tag{1.23}$$

Note, that for $\rho_n=1$ also $\rho_n^2=1$ and $\hat{\rho}^2=\hat{\rho}$.

Chapter 2

Entropy

The entropy can be thought off as a measure of the disorder in a system and is obtained by state counting. The entropy of an N particle system is proportional to the logarithm of the number of states available to the system and is defined by the Gibbs formula

$$S = -k_B \mathrm{Tr}(\hat{\rho} \ln \hat{\rho}) \tag{2.1}$$

where $k_B = 1.38 \cdot 10^{-23}$ [J/K] is the Boltzmann constant. In the energy representation we have

$$S = -k_B \sum_{n,m} \rho_{nm} \ln \rho_{mn} = -k_B \sum_{n,m} \rho_n \delta_{mn} \ln(\rho_n \delta_{mn}) \tag{2.2}$$

and the entropy is given by a straight summation over the energy states

$$S = -k_B \sum_{n} \rho_n \ln \rho_n \tag{2.3}$$

Very often it is more convenient to perform an integration instead of a summation using a substitution for a sum over the states of an N-particle system

$$\sum_{n} \longrightarrow \frac{(2s+1)V}{h^{3N}} \int \mathrm{d}^{3N} p \tag{2.4}$$

where V is a volume of a system and s is a particle spin, we can rewrite (2.3) in a form

$$S = -k_B \frac{(2s+1)V}{h^{3N}} \int \rho(p) \ln \rho(p) \mathrm{d}^{3N} p \tag{2.5}$$

where $p = (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$. The density matrix, which becomes a continuous momentum function $\rho(p)$, obeys a normalization condition

$$\frac{(2s+1)V}{h^{3N}} \int \mathrm{d}^{3N} p \rho(p) = 1 \tag{2.6}$$

and can be called a probability density in the $3N$-dimensional momentum space. We need to elucidate that applying the replacement (2.4) one must pay a particular attention to possible singularities of an integrated function and while a use of an integral is allowed for fermions or classical particles in a case of bosons one must include the lowest energy state element in addition to an integral (2.4). This issue will be discussed thoroughly in Chapters 7 and 10. The entropy definition (2.5) is very usefull, as it can be applied after a slight modification to quantum as well as classical systems. Although all particles obey quantum laws, a classical approach is a convenient approximation for systems whose quantum features can be neglected. Therefore, one must use an appropriate classical states counting procedure to have the same number of states as in a quantum system and because a single quantum state of N particles corresponds to $N!$ states of distinguishable classical particles the number of classical states should be diminished by a factor $N!$ which accounts for a number of N particles permutations. For that purpose we introduce a coefficient c_N of an action units which discriminates quantum and classical systems: $c_N = h^{3N}$ for quantum, $c_N = N!h^{3N}$ for classical. We can now introduce a probability density $\rho(p, r)$, where $r = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$, in the $6N$-dimensional momentum and position space, that is the Γ-space, which gives a probability of finding a classical system in a state with particles momenta and positions given by p and r vectors respectively, and for a quantum system is defined as $\rho(p, r) = \rho(p)$. The normalization condition on the Γ-space reads

$$\int \frac{\mathrm{d}p \mathrm{d}r}{c_N} \rho(p, r) = 1, \tag{2.7}$$

where we have used a simplified notation $p = \boldsymbol{p}_{3N}$, $r = \boldsymbol{r}_{3N}$. We note, that in a quantum system the probability density is solely a momentum function and the position integral gives simply volume to the N-th power, which together with the c_N coefficient form the density of states in the momentum space V^N/h^{3N}. According to (3.9) the entropy is defined

$$S = -k_B \int \frac{\mathrm{d}p \mathrm{d}r}{c_N} \rho(p, r) \ln \rho(p, r) \tag{2.8}$$

Chapter 3

Thermodynamics

3.1 Fundamental laws

We will use the first law of thermodynamics, that is the energy conservation law,

$$\mathrm{d}U = \delta Q - P\mathrm{d}V + \mu\mathrm{d}N \tag{3.1}$$

and the second law of thermodynamics

$$\mathrm{d}S \geqslant \frac{\delta Q}{T} \tag{3.2}$$

where the equality holds if changes in the thermodynamic state are reversible, and the inequality applies to spontaneus or irreversible process. In this book we deal with reversible processes, except for the last paragraph, and we have

$$\mathrm{d}S = \frac{\delta Q}{T} \tag{3.3}$$

unless it is not otherwise stated. Therefore, we can combine both thermodynamic laws into a single equation

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V - \mu\mathrm{d}N \tag{3.4}$$

which determines a basic thermodynamic function - the entropy.

3.2 Thermodynamic functions

A thermodynamic definition of the entropy in the relation (3.4) yields

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N \tag{3.5}$$

We note, that the entropy $S = S(U, V, N)$ is a function of three variables: internal energy U, volume V and number of particles N, hence an infinitesimal change of the entropy

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,V} \mathrm{d}N \tag{3.6}$$

yields the following thermodynamic identities

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \tag{3.7}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T} \tag{3.8}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} \tag{3.9}$$

A change of the internal energy U, which according to Eq. (3.4) reads

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{3.10}$$

defines U as a three variable function $U = U(S, V, N)$. Therefore, its differential

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,N} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \mathrm{d}V + \left(\frac{\partial U}{\partial N}\right)_{S,V} \mathrm{d}N \tag{3.11}$$

is determided by the following relations

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \tag{3.12}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P \tag{3.13}$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \tag{3.14}$$

Subsequently, we define the Helmholtz free energy

$$F = U - TS \tag{3.15}$$

whose differential change

$$\mathrm{d}F = \mathrm{d}(U - TS) = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \tag{3.16}$$

depends on the internal energy differential (3.10) and reads

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \tag{3.17}$$

Therefore, we have the free energy as a function of T, V, and N variables $F = F(T, V, N)$ and its differential

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{V,N} \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_{T,N} \mathrm{d}V + \left(\frac{\partial F}{\partial N}\right)_{T,V} \mathrm{d}N \tag{3.18}$$

leads to the following thermodynamic identities

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \tag{3.19}$$

$$\left(\frac{\partial F}{\partial V}\right)_{T,N} = -P \tag{3.20}$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu \tag{3.21}$$

A thermodynamic definition of the grand potential (thermodynamic potential)

$$\Omega(T, V, \mu) = F - \mu N \tag{3.22}$$

combined with Eq. (3.17) gives a differential change of the grand potential

$$\mathrm{d}\Omega = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu \tag{3.23}$$

which is a function of T, V, and μ. A differential of a three variable function $\Omega = \Omega(T, V, \mu)$

$$\mathrm{d}\Omega = \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \mathrm{d}T + \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \mathrm{d}V + \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \mathrm{d}\mu \tag{3.24}$$

leads to thermodynamic identities

$$\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = -S \tag{3.25}$$

$$\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -P \tag{3.26}$$

$$\left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V} = -N \tag{3.27}$$

Up to now, we have defined the differentials of the internal energy, entropy, free energy and thermodynamic potential. Using a scaling property of extensive quantities we will derive an explicit internal energy formula and subsequently obtain the rest of defined thermodynamic functions. First, we note that the internal energy $U = U(S, V, N)$ is a function of extensive quantities: S, V, N which are proportional to the mass and a size of a system, therefore U itself is also an extensive quantity. Let us do a scaling transformation of the system by extending the size of a system λ times

$$\begin{array}{ccc} S & \longrightarrow & \lambda S \\ V & \longrightarrow & \lambda V \\ N & \longrightarrow & \lambda N \end{array}$$

which also gives

$$U \longrightarrow \lambda U$$

We may write this transformation as follows

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \tag{3.28}$$

Taking a derivative with respect to λ at $\lambda = 1$ of the right-hand side of (3.28)

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}U(\lambda S, \lambda V, \lambda N) = \frac{\mathrm{d}}{\mathrm{d}\lambda}\lambda U(S, V, N) = U(S, V, N) \tag{3.29}$$

and of its left-hand side

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\lambda}U(\lambda S, \lambda V, \lambda N) = &\left(\frac{\partial}{\partial \lambda S}U(\lambda S, \lambda V, \lambda N)\right)_{V,N}\left(\frac{\mathrm{d}\lambda S}{\mathrm{d}\lambda}\right) + \\ &\left(\frac{\partial}{\partial \lambda V}U(\lambda S, \lambda V, \lambda N)\right)_{S,N}\left(\frac{\mathrm{d}\lambda V}{\mathrm{d}\lambda}\right) +\end{aligned}$$

$$\left(\frac{\partial}{\partial \lambda N}U(\lambda S, \lambda V, \lambda N)\right)_{V,S}\left(\frac{\mathrm{d}\lambda N}{\mathrm{d}\lambda}\right) \tag{3.30}$$

that is

$$\frac{\mathrm{d}}{\mathrm{d}\lambda}U(\lambda S, \lambda V, \lambda N) = \left(\frac{\partial}{\partial \lambda S}U(\lambda S, \lambda V, \lambda N)\right)_{V,N} S + \left(\frac{\partial}{\partial \lambda V}U(\lambda S, \lambda V, \lambda N)\right)_{S,N} V + \left(\frac{\partial}{\partial \lambda N}U(\lambda S, \lambda V, \lambda N)\right)_{V,S} N \tag{3.31}$$

Hence, we obtain

$$U(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{V,N} N \tag{3.32}$$

and using the thermodynamic identities (3.12)-(3.14) we finally get a formula which defines the internal energy

$$U(S,V,N) = TS - PV + \mu N \tag{3.33}$$

which yields the explicit formulas for the Helmholtz free energy

$$F = U - TS = -PV + \mu N \tag{3.34}$$

and the thermodynamic potential

$$\Omega = F - \mu N = -PV \tag{3.35}$$

or

$$\Omega = F - \mu N = U - TS - \mu N \tag{3.36}$$

The entropy function is to be determined microscopically within the statistical physics approach.

Chapter 4

Microcanonical ensemble

4.1 Density matrix

A microcanonical ensemble consists of all available states of an isolated system, that is states of a constant energy E and a fixed number of particles N. We define the density matrix $\hat{\rho}$ in the energy representation $\{\varphi_n\}$, $\hat{H}\varphi_n = E_n\varphi_n$, for which $\rho_{mn} = \rho_n\delta_{mn}$ and the diagonal elements read

$$\rho_n = \frac{\delta_{E_n,E}}{\Gamma(E)} \tag{4.1}$$

where $\Gamma(E) = \sum\limits_n \delta_{E_n,E}$ is a number of the energy E states. Taking into account a small, compared to the energy, discernibility of the energy measurement, $\Delta \ll E$, we write a physically justified definition of the microcanonical ensemble density matrix

$$\rho_n = \begin{cases} \dfrac{1}{\Gamma(E)} & \text{for } E < E_n < E + \Delta \\ 0 & \text{otherwise} \end{cases} \tag{4.2}$$

where now $\Gamma(E)$ is a number of states in the energy interval $E < E_n < E + \Delta$. We note, that

$$\mathrm{Tr}\hat{\rho} = \sum_n \rho_n = \frac{1}{\Gamma(E)} \sum_n \delta_{E_n,E} = \frac{\Gamma(E)}{\Gamma(E)} = 1 \tag{4.3}$$

which means that $\hat{\rho}$ is a properly defined probability density matrix. We shall see that the microcanonical ensemble extremizes the Gibbs entropy, that is obeys the second law of thermodynamics. We use the Langrage multipliers method to look for an extremum of the entropy (2.8) for a constant energy states

$$S = -k_B \int\limits_{E<H(\boldsymbol{p},\boldsymbol{r})<E+\Delta} \frac{\mathrm{d}p\mathrm{d}r}{c_N} \rho(p,r) \ln \rho(p,r) \tag{4.4}$$

subject to the normalization condition (2.7)

$$\int\limits_{E<H(\boldsymbol{p},\boldsymbol{r})<E+\Delta} \frac{\mathrm{d}p\mathrm{d}r}{c_N} \rho(p,r) = 1, \tag{4.5}$$

For the sake of simplicity, from now on we will drop off the limits in the integral notation minding that all integrals are taken in the same limits as in (4.5) unless other limits are specified. We take a variation

$$\delta \left[S(\rho) + \alpha \left(\int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \rho(p,r) - 1 \right) \right] = 0, \tag{4.6}$$

which reads

$$\int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \left[-k_B \ln \rho(p,r) - k_B + \alpha \right] \delta\rho(p,r) = 0. \tag{4.7}$$

Since $\delta\rho$ is an arbitrary quantity, we have

$$\rho(p,r) = \mathrm{e}^{\frac{\alpha - k_B}{k_B}} = const \tag{4.8}$$

A Lagrange multiplier α is determined from the normalization condition (4.5) which for a constant density matrix gives

$$\rho(p,r) = \left(\int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \right)^{-1} = \Gamma^{-1}(E) \tag{4.9}$$

where $\Gamma(E)$ is a number of states of the energy E.Therefore we have obtained the microcanonical ensemble probability density (4.2).

4.2 Entropy

The Gibbs entropy can be now straightforwardly evaluated

$$S = -k_B \int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \rho(p,r) \ln \rho(p,r) =$$
$$- k_B \int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \Gamma^{-1}(E) \ln \Gamma^{-1}(E) = k_B \ln \Gamma(E) \quad (4.10)$$

and concluding, we may say that we have obtained a useful formula for the entropy in the microcanonical ensemble

$$S = k_B \ln \Gamma(E) \quad (4.11)$$

We can also rederive the entropy formula by taking a trace in the Gibbs definition (2.3)

$$S = -k_B \sum_n \rho_n \ln \rho_n =$$
$$- k_B \sum_n \rho_n \ln \frac{1}{\Gamma(E)} = k_B \ln \Gamma(E) \sum_n \rho_n = k_B \ln \Gamma(E) \quad (4.12)$$

4.2.1 Useful formulas

Sometimes it is more convenient to use a volume $\Omega(E)$ occupied by the available states of the energy E in the Γ-space instead of a number of states $\Gamma(E)$, that is $\Omega(E)$ is a thin shell volume

$$\Omega = \int\limits_{E<H(\boldsymbol{p},\boldsymbol{r})<E+\Delta} \mathrm{d}p\mathrm{d}r \quad (4.13)$$

In such a notation we have

$$S = k_B \ln \frac{\Omega(E)}{c_N} \quad (4.14)$$

We shall now present a somewhat more convenient method of computing the entropy by defining a volume $\Phi(E)$ in the Γ-space occupied by the states of the energy not exceeding the energy E, which is usually easier to evaluate than $\Omega(E)$

$$\Phi(E) = \Phi(E,V,N) = \int\limits_{H(p,r)\leqslant E} \mathrm{d}p\mathrm{d}r, \quad (4.15)$$

which can be represented by a sum of the E_i energy thin shell volumes (Fig. 4.1)

$$\Phi(E,V,N) = \sum_{i=1}^{\frac{E}{\Delta}} \Omega(E_i,V,N) \quad (4.16)$$

where $\Omega(E_i, V, N)$ is the energy E_i thin shell volume. We note that the largest shell volume $\Omega(E_i, V, N)$ is that within the energy interval $(E, E + \Delta)$, thus we can write

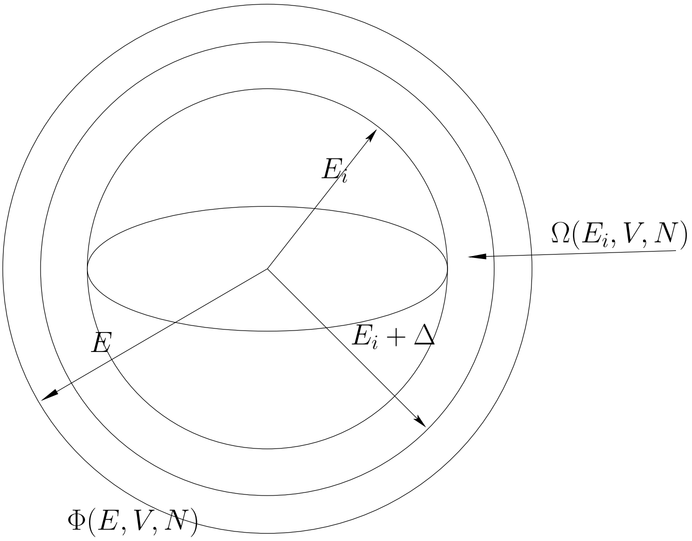


Figure 4.1: $\Omega(E_i, V, N)$ shell volume and $\Phi(E, V, N)$ volume of states of the energy not exceeding E

$$\Omega(E, V, N) \leqslant \Phi(E, V, N) \leqslant \frac{E}{\Delta}\Omega(E, V, N), \tag{4.17}$$

or by taking a logarithm which is a monotonic function

$$\ln \Omega(E) \leqslant \ln \Phi(E) \leqslant \ln \Omega(E) + \ln \frac{E}{\Delta}. \tag{4.18}$$

Because $\Phi(E)$ is a volume in the $6N$-dimensional space $\ln \Phi(E) \sim N$ and the energy E of a system is also proportional to the number of particles $\ln \dfrac{E}{\Delta} \sim \ln N$ we get in the thermodynamic limit

$$\frac{\ln \dfrac{E}{\Delta}}{\ln \Phi(E)} \sim \frac{\ln N}{N} \xrightarrow[\substack{N\to\infty \\ V\to\infty}]{} 0, \tag{4.19}$$

and

$$\ln \Phi(E) = \ln \Omega(E). \tag{4.20}$$

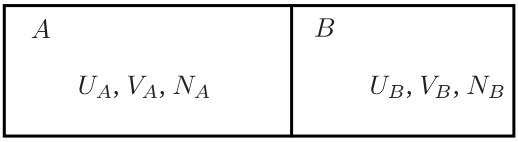
Therefore in the thermodynamic limit the entropy (4.14) reads

$$S = k_B \ln \frac{\Phi(E, V, N)}{c_N} \tag{4.21}$$

where $\Phi(E, V, N)$ is volume of states of the energy not exceeding E.

4.2.2 Properties

1. Entropy $S(E) = S(U, V, N)$ is a continuous and differentiable function of U, V, N.
2. Entropy is an additive function, that is, for a system consisting of independent subsystems A, B the entropy $S(U, V, N) = S(U_A, V_A, N_A) + S(U_B, V_B, N_B)$.



Γ_A – number of states in A, Γ_B – number of states in B

Proof: Let us show it for the classical entropy

$$S(U, V, N) = k_B \ln \frac{\Omega_A \Omega_B}{N_A! N_B! h^{3(N_A + N_B)}} = k_B \ln \frac{\Omega_A}{N_A! h^{3N_A}} + k_B \ln \frac{\Omega_B}{N_B! h^{3N_B}} =$$
$$= S(U_A, V_A, N_A) + S(U_B, V_B, N_B). \tag{4.22}$$

3. Entropy is an extensive quantity: $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$, for $\lambda > 0$. Proof: For the classical entropy

$$S(\lambda U, \lambda V, \lambda N) = k_B \ln \frac{\Phi(\lambda U, \lambda V, \lambda N)}{(\lambda N)! h^{3\lambda N}}, \tag{4.23}$$

where $\Phi(\lambda U, \lambda V, \lambda N)$ is a volume in a $6\lambda N$-dimensional Γ-space.

$$\Phi(\lambda U, \lambda V, \lambda N) \sim (\lambda V)^{\lambda N} p_\lambda^{\lambda N} \tag{4.24}$$

since the internal energy

$$U = \sum_{n=1}^{N} p_n^2 \sim N p^2 \tag{4.25}$$

we have

$$p = \left(\frac{U}{N}\right)^{\frac{1}{2}} \tag{4.26}$$

and for the extended system

$$p_\lambda = \left(\frac{\lambda U}{\lambda N}\right)^{\frac{1}{2}} = \left(\frac{U}{N}\right)^{\frac{1}{2}}, \tag{4.27}$$

therefore

$$\Phi(\lambda U, \lambda V, \lambda N) \sim (\lambda V)^{\lambda N} \left(\frac{U}{N}\right)^{\frac{\lambda N}{2}}. \tag{4.28}$$

The entropy of the extended system reads

$$S(\lambda U, \lambda V, \lambda N) = k_B \ln \frac{(\lambda V)^{\lambda N} \left(\frac{U}{N}\right)^{\frac{\lambda N}{2}}}{(\lambda N)! h^{3\lambda N}} \tag{4.29}$$

and using the Stirling's approximation, $\ln N! \approx N \ln N - N$, we have the entropy

$$S(\lambda U, \lambda V, \lambda N) = k_B \lambda \ln \frac{V^N \left(\frac{U}{N}\right)^{\frac{N}{2}}}{h^{3N}} + k_B \lambda N \ln \lambda - k_B \lambda N \ln \lambda N + k_B \lambda N, \tag{4.30}$$

which is equivalent to

$$S(\lambda U, \lambda V, \lambda N) = \lambda k_B \ln \frac{V^N \left(\frac{U}{N}\right)^{\frac{N}{2}}}{N! h^{3N}} = \lambda S(\lambda U, \lambda V, \lambda N)_{\lambda=1} = \lambda S(U, V, N) \tag{4.31}$$

4.3 Ideal classical gas

We use an example of an ideal classical gas to demonstrate the method of the microcanonical ensemble. In order to determine the entropy [3] (pp. 299-300, 348)

$$S = k_B \ln \frac{\Phi(E)}{N! h^3 N} \tag{4.32}$$

we need to compute the volume $\Phi(E)$ in the Γ-space occupied by states of the energy less than E, that is

$$\Phi(E) = \int\limits_V \mathrm{d}\boldsymbol{r}_1 \cdots \int\limits_V \mathrm{d}\boldsymbol{r}_N \int \mathrm{d}\boldsymbol{p}_1 \cdots \int \mathrm{d}\boldsymbol{p}_N \tag{4.33}$$

where the momenta are limited by

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} \leqslant E \tag{4.34}$$

Defining a radius $R = \sqrt{2mE}$ we can write

$$\Phi(E) = V^N \Phi_p, \tag{4.35}$$

where

$$\Phi(E) = \int\limits_{-\infty}^{\infty} \mathrm{d}\boldsymbol{p}_1 \cdots \int\limits_{-\infty}^{\infty} \mathrm{d}\boldsymbol{p}_N \theta \left(R^2 - \sum_{i=1}^{N} p_i^2 \right) \tag{4.36}$$

is a volume enclosed by R in a $3N$-dimensional momentum space, thus it can be represented as

$$\Phi_p = A_{3N} R^{3N}. \tag{4.37}$$

We obtain A_{3N} coefficient by evaluating the integral

$$\int\limits_0^{\infty} \mathrm{d}R \frac{\mathrm{d}\Phi_p}{\mathrm{d}R} \mathrm{e}^{-R^2}, \tag{4.38}$$

where

$$\frac{\mathrm{d}\Phi_p}{\mathrm{d}R} = 3N A_{3N} R^{3N-1}. \tag{4.39}$$

We can do that without using an explicit form of $\frac{\mathrm{d}\Phi_p}{\mathrm{d}R}$ but its definition (4.36)

$$\int\limits_0^{\infty} \mathrm{d}R \frac{\mathrm{d}\Phi_p}{\mathrm{d}R} \mathrm{e}^{-R^2} = \int\limits_0^{\infty} \mathrm{d}R \frac{\mathrm{d}\Phi_p}{\mathrm{d}E} \frac{\mathrm{d}E}{\mathrm{d}R} \mathrm{e}^{-R^2} = \int\limits_0^{\infty} \mathrm{d}E \frac{\mathrm{d}\Phi_p}{\mathrm{d}E} \mathrm{e}^{-R^2} =$$

$$= \int\limits_0^{\infty} \mathrm{d}E \frac{\mathrm{d}}{\mathrm{d}E} \int \mathrm{d}\boldsymbol{p}_1 \cdots \int \mathrm{d}\boldsymbol{p}_N \Theta \left(R^2 - \sum_{i=1}^{N} p_i^2 \right) \mathrm{e}^{-R^2} =$$

$$= \int_0^\infty \mathrm{d}E 2m \int \mathrm{d}\boldsymbol{p}_1 \cdots \int \mathrm{d}\boldsymbol{p}_N \delta\left(R^2 - \sum_{i=1}^N p_i^2\right) \mathrm{e}^{-R^2} =$$

$$= \int_0^\infty \mathrm{d}R^2 \int \mathrm{d}\boldsymbol{p}_1 \cdots \int \mathrm{d}\boldsymbol{p}_N \delta\left(R^2 - \sum_{i=1}^N p_i^2\right) \mathrm{e}^{-R^2} =$$

$$= \int \mathrm{d}\boldsymbol{p}_1 \cdots \int \mathrm{d}\boldsymbol{p}_N \mathrm{e}^{-\sum\limits_{i=1}^N p_i^2} =$$

$$= \int_{-\infty}^\infty \mathrm{d}p_{1x} \int_{-\infty}^\infty \mathrm{d}p_{1y} \int_{-\infty}^\infty \mathrm{d}p_{1z} \cdots \int_{-\infty}^\infty \mathrm{d}p_{Nx} \int_{-\infty}^\infty \mathrm{d}p_{Ny} \int_{-\infty}^\infty \mathrm{d}p_{Nz} \mathrm{e}^{\left(-\sum\limits_{i=1}^N p_{ix}^2 + p_{iy}^2 + p_{iz}^2\right)} =$$

$$= \int_{-\infty}^\infty \mathrm{d}p_{1x} \mathrm{e}^{-p_{1x}^2} \int_{-\infty}^\infty \mathrm{d}p_{1y} \mathrm{e}^{-p_{1y}^2} \int_{-\infty}^\infty \mathrm{d}p_{1z} \mathrm{e}^{-p_{1z}^2} \cdots$$

$$\cdots \int_{-\infty}^\infty \mathrm{d}p_{Nx} \mathrm{e}^{-p_{Nx}^2} \int_{-\infty}^\infty \mathrm{d}p_{Ny} \mathrm{e}^{-p_{Ny}^2} \int_{-\infty}^\infty \mathrm{d}p_{Nz} \mathrm{e}^{-p_{Nz}^2} =$$

$$= \left(\int_{-\infty}^\infty \mathrm{d}p \mathrm{e}^{-p^2}\right)^{3N} = \pi^{\frac{3N}{2}} \quad (4.40)$$

On the other hand using (4.39)

$$\int_0^\infty \mathrm{d}R \frac{\mathrm{d}\Phi_p}{\mathrm{d}R} \mathrm{e}^{-R^2} = 3NA_{3N} \int_0^\infty \mathrm{d}R R^{3N-1} \mathrm{e}^{-R^2} = \frac{3}{2} N A_{3N} \Gamma\left(\frac{3}{2}N\right) \quad (4.41)$$

where

$$\Gamma(x) = \int_0^\infty t^{x-1} \mathrm{e}^{-t} \mathrm{d}t \quad (4.42)$$

is the gamma function. Therefore, comparing (4.40) and (4.41) we get

$$\frac{3}{2} N A_{3N} \Gamma\left(\frac{3}{2}N\right) = \pi^{\frac{3N}{2}}, \quad (4.43)$$

that is

$$A_{3N} = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3}{2}N + 1\right)} \quad (4.44)$$

Therefore, the volume in the momentum space reads

$$\Phi_p = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3}{2}N+1\right)} R^{3N} = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3}{2}N+1\right)} (2mE)^{\frac{3N}{2}} = \frac{(2\pi mE)^{\frac{3N}{2}}}{\Gamma\left(\frac{3}{2}N+1\right)} \tag{4.45}$$

and the volume in the Γ-space

$$\Phi(E) = \frac{V^N (2\pi mE)^{\frac{3N}{2}}}{\Gamma\left(\frac{3}{2}N+1\right)}. \tag{4.46}$$

We are now in a position to calculate the entropy

$$S = k_B \ln\left[\frac{V^N (2\pi mE)^{\frac{3N}{2}}}{N! h^{3N} \Gamma\left(\frac{3}{2}N+1\right)}\right]. \tag{4.47}$$

Because $\Gamma\left(\frac{3}{2}N+1\right) = \left(\frac{3}{2}N\right)!$ and for large N we can use the Stirling's approximation

$$\ln N! \approx N \ln N - N \text{ or } N! \approx \left(\frac{N}{\mathrm{e}}\right)^N, \tag{4.48}$$

we have

$$\Gamma\left(\frac{3}{2}N+1\right) \approx \left(\frac{3N}{2e}\right)^{\frac{3N}{2}} \tag{4.49}$$

and the entropy

$$S = k_B \ln\left[\frac{V^N (2\pi mE)^{\frac{3N}{2}}}{N! h^{3N} \left(\frac{3N}{2e}\right)^{\frac{3N}{2}}}\right] \tag{4.50}$$

The entropy formula can be rearanged, using again the Stirling's approximation as follows

$$\begin{aligned} S &= \frac{3}{2}Nk_B + Nk_B \ln\left[V\left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3}{2}}\right] - k_B \ln N! = \\ &= \frac{3}{2}Nk_B + Nk_B \ln\left[V\left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3}{2}}\right] - Nk_B \ln N + Nk_B = \\ &= \frac{5}{2}Nk_B + Nk_B \ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{\frac{3}{2}}\right] \end{aligned} \tag{4.51}$$

and defining the internal energy $U = E$ the entropy reads

$$S = Nk_B \left[\frac{5}{2} + \ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) \right]. \tag{4.52}$$

We use the above equation to obtain the temperature and pressure. Taking a partial derivative $\frac{\partial}{\partial S}$ of (4.52) at constant V and N we get the equation

$$1 = Nk_B \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right]^{-1} \frac{V}{N} \left(\frac{4\pi m}{3h^2 N} \right)^{\frac{3}{2}} \frac{3}{2} U^{\frac{1}{2}} \left(\frac{\partial U}{\partial S} \right)_{V,N}, \tag{4.53}$$

which simplifies to

$$U = \frac{3}{2} Nk_B \left(\frac{\partial U}{\partial S} \right)_{V,N} = \frac{3}{2} Nk_B T \tag{4.54}$$

where we have used a thermodynamic relation $T = \left(\frac{\partial U}{\partial S} \right)_{V,N}$. We have obtained the internal energy of a monatomic ideal gas

$$U = \frac{3}{2} Nk_B T \tag{4.55}$$

in agreement with the energy equipartition theorem. A similar procedure of taking a partial derivative $\frac{\partial}{\partial V}$ at constant S, N yields a relation

$$0 = \frac{N}{V} \left(\frac{4\pi m U}{3h^2 N} \right)^{-\frac{3}{2}} \left[\frac{1}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} + \frac{V}{N} \left(\frac{4\pi m}{3h^2 N} \right)^{\frac{3}{2}} \frac{3}{2} U^{\frac{1}{2}} \left(\frac{\partial U}{\partial V} \right)_{S,N} \right] \tag{4.56}$$

which is equivalent to

$$-U = \frac{3}{2} V \left(\frac{\partial U}{\partial V} \right)_{S,N} \tag{4.57}$$

Using a thermodynamic identity $P = -\left(\frac{\partial U}{\partial V} \right)_{S,N}$, we get

$$U = \frac{3}{2} PV \tag{4.58}$$

Finally, combining (4.55) and (4.58) we obtain the ideal classical gas equation of state

$$PV = Nk_B T \tag{4.59}$$

We can also find the heat capacity at constant volume

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{3}{2}Nk_BT\right) = \frac{3}{2}Nk_B \tag{4.60}$$

and the Helmholtz free energy

$$\begin{aligned} F = U - TS = -Nk_BT - Nk_BT\ln\left[\frac{V}{N}\left(\frac{2\pi m}{h^2}k_BT\right)^{\frac{3}{2}}\right] = \\ = -Nk_BT - Nk_BT\ln\frac{V}{N} - \frac{3}{2}Nk_BT\ln(2\pi mk_BT) + Nk_BT\ln h^3 \end{aligned} \tag{4.61}$$

which yields the chemical potential

$$\begin{aligned} \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \\ -k_BT - k_BT\ln\frac{V}{N} + k_BT - \frac{3}{2}k_BT\ln(2\pi mk_BT) + k_BT\ln h^3 = \\ k_BT\ln\frac{nh^3}{(2\pi mk_BT)^{\frac{3}{2}}}, \end{aligned} \tag{4.62}$$

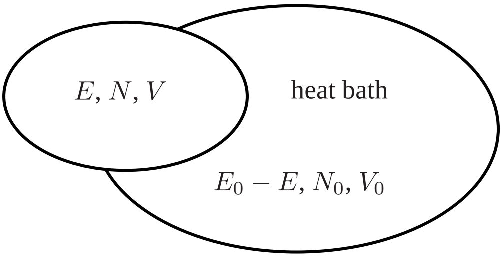
where $n = \frac{N}{V}$ is a particle concentration.

Chapter 5

Canonical ensemble

5.1 Subsystem of a microcanonical system

We consider a system consisting of N particles in a thermal contact with a much larger system containing N_0 particles, $N_0 \gg N$, which we call a heat bath. Although both systems are separate and their particles do not mix, that is particle numbers N and N_0 and volumes of the systems V, V_0 are constant, they can exchange the energy.



The energy E of a smaller system determined by the Hamiltonian $H(p, r) = E$ is much smaller than the energy of the heat bath $E_0 - E$, so in slowly varying energy functions we can assume $E_0 - E \approx E_0 = const$, although E is allowed to change. Both systems can be considered subsystems of a constant energy E_0 system described by a microcanonical ensemble whose number of states $\Gamma_m(E_0)$ because of a spatial separation of the subsystems is a product of the numbers of states Γ and Γ_0 in the $6N$- and $6N_0$-dimensional spaces respectively

$$\Gamma_m(E_0) = \Gamma(E)\Gamma_0(E_0 - E). \tag{5.1}$$

The variation of the microcanonical ensemble entropy $S(E_0) = k_B \ln \Gamma_m(E_0)$ with respect to the energy E must fulfill the extremum condition

$$\delta S(E_0) = 0 \tag{5.2}$$

$$\delta k_B \ln \Gamma_m(E_0) = 0 \tag{5.3}$$

$$\delta \ln [\Gamma(E)\Gamma_0(E_0 - E)] = 0 \tag{5.4}$$

$$\delta \ln \Gamma(E) + \delta \ln \Gamma_0(E_0 - E) = 0 \tag{5.5}$$

$$\left[\frac{1}{\Gamma(E)}\frac{\partial \Gamma(E)}{\partial E} - \frac{1}{\Gamma_0(E_0 - E)}\frac{\partial \Gamma_0(E_0 - E)}{\partial (E_0 - E)}\right] \delta E = 0 \tag{5.6}$$

for an arbitrary δE value, that is,

$$\frac{1}{\Gamma(E)}\frac{\partial \Gamma(E)}{\partial E} - \frac{1}{\Gamma_0(E_0 - E)}\frac{\partial \Gamma_0(E_0 - E)}{\partial (E_0 - E)} = 0 \tag{5.7}$$

$$\frac{1}{\Gamma(E)}\frac{\partial \Gamma(E)}{\partial E} - \frac{\partial}{\partial (E_0 - E)} \ln \Gamma_0(E_0 - E) = 0 \tag{5.8}$$

Because $E_0 \gg E$ we can assume that the energy of the heat bath $E_0 - E \approx E_0$ therefore

$$\frac{1}{\Gamma(E)}\frac{\partial \Gamma(E)}{\partial E} = \frac{1}{k_B}\frac{\partial}{\partial (E_0)} k_B \ln \Gamma_0(E_0). \tag{5.9}$$

On the right-hand side of Eq.(5.9) we have the energy derivative of the heat bath entropy $S_0(E_0) = k_B \ln \Gamma_0(E_0)$ which defines the absolute temperature T of the heat bath

$$\frac{1}{T} = \left(\frac{\partial S_0(E_0)}{\partial E_0}\right)_{N,V}. \tag{5.10}$$

Therefore

$$\frac{1}{\Gamma(E)}\frac{\partial \Gamma(E)}{\partial E} = \frac{1}{k_B T}. \tag{5.11}$$

Let us note that T is a common temperature of both systems since Eq. (5.9) yields

$$\frac{\partial}{\partial E} \ln \Gamma(E) = \frac{\partial}{\partial E_0} \ln \Gamma_0(E_0). \tag{5.12}$$

It means that both systems remain at the same temperature, in other words, the systems are in a thermal equilibrium. Eq. (5.11) is a simple differential equation

$$\frac{\mathrm{d}\Gamma}{\Gamma} = \frac{\mathrm{d}E}{k_B T}, \tag{5.13}$$

which integrated gives

$$\ln\Gamma = \frac{E}{k_B T} + \ln C, \tag{5.14}$$

where C is a constant. Finally, a number of states of the energy E in the $6N$-dimensional space reads

$$\Gamma(E) = C\mathrm{e}^{\frac{E}{k_B T}}. \tag{5.15}$$

If we limit our considerations to the states of a fixed energy E then we still deal with a microcanonical ensemble and the probability density is determined by the normalization condition

$$\sum_n \delta_{E_n,E}\,\rho(E_n) = \int\limits_{H(p,r)=E} \frac{\mathrm{d}p\mathrm{d}r}{c_N}\rho(p,r) = 1 \tag{5.16}$$

where ρ is constant for a constant energy sheet, that is, it reduces to the microcanonical density for a constant energy constraint. We can express this condition by the relation $\rho(p,r) = \rho(H(p,r))$. Therefore, for a given energy we get

$$\rho(p,r) = \Gamma^{-1}(E) \tag{5.17}$$

We can now include all states of the energy E not exceeding the heat bath energy E_0 and based on Eqs. (5.15), (5.17) we write the normalization condition

$$C^{-1} \int\limits_{H(p,r)<E_0} \frac{\mathrm{d}p\mathrm{d}r}{c_N}\mathrm{e}^{-\frac{H(p,r)}{k_B T}} = 1 \tag{5.18}$$

$$C = \int\limits_{H(p,r)<E_0} \frac{\mathrm{d}p\mathrm{d}r}{c_N}\mathrm{e}^{-\frac{H(p,r)}{k_B T}}, \tag{5.19}$$

where we have extended the integral to include all states of the energy smaller than the heat bath energy. Although the above integral should be limited by the energy of the heat bath we can extend it to infinity as in fact only a narrow range of energy matters in the calculation of this integral or in other words we may say that the energy E_0 has been chosen much larger than the energy E of a considered system so we can assume it to be infinite. In summary, we have obtained the probability density

$$\rho(p,r) = \frac{1}{Q_N(V,T)} \mathrm{e}^{-\frac{H(p,r)}{k_B T}}, \tag{5.20}$$

where

$$Q_N(V,T) = C = \int \frac{\mathrm{d}p\mathrm{d}r}{c_N} \mathrm{e}^{-\frac{H(p,r)}{k_B T}} \tag{5.21}$$

is called the partition function or the statistical sum for a system consisting of N particles at the temperature T enclosed in a volume V. The probability density (Eq. (5.20)) defines a canonical statistical ensemble. Concluding, we write $Q_N(V,T)$ explicitely for a classical system

$$Q_N(V,T) = \int \frac{\mathrm{d}p\mathrm{d}r}{N!h^{3N}} \mathrm{e}^{-\frac{H(p,r)}{k_B T}} \tag{5.22}$$

and for a quantum one

$$Q_N(V,T) = V \int \frac{\mathrm{d}p}{h^{3N}} \mathrm{e}^{-\frac{H(p)}{k_B T}} \tag{5.23}$$

5.2 Density matrix

The density matrix elements in the energy representation are given by (5.20) and for the energy E_n state

$$\rho_{mn} = \rho_n \delta_{mn} = \frac{1}{Q_N} \delta_{mn} \mathrm{e}^{-\beta E_n} \tag{5.24}$$

where $\beta = \dfrac{1}{k_B T}$, and the partition function reads

$$Q_N = \underbrace{\sum_n \mathrm{e}^{-\beta E_n}}_{\text{sum over states}} = \underbrace{\sum_{n'} g_{n'} \mathrm{e}^{-\beta E_{n'}}}_{\text{sum over energy levels}}$$

where we have discriminated between two possible summations: over all available states or over all energy levels in which we have included a possible degeneracy of an energy level. We can construct now a density matrix for a normalized and complete set of eigenfunctions φ_n, $\sum\limits_n |\varphi_n\rangle\langle\varphi_n| = 1$,

$$\hat{\rho} = \frac{1}{Q_N}\sum_n |\varphi_n\rangle\,\mathrm{e}^{-\beta E_n}\,\langle\varphi_n| = \frac{1}{Q_N}\mathrm{e}^{-\beta\hat{H}}\sum_n |\varphi_n\rangle\langle\varphi_n| = \frac{1}{Q_N}\mathrm{e}^{-\beta\hat{H}} \qquad (5.25)$$

Therefore, we obtain

$$\hat{\rho} = \frac{1}{Q_N}\mathrm{e}^{-\beta\hat{H}} \qquad (5.26)$$

where the partition function

$$Q_N = \sum_n \mathrm{e}^{-\beta E_n} = \sum_n \left\langle\varphi_n\left|\mathrm{e}^{-\beta\hat{H}}\right|\varphi_n\right\rangle = \\ = \sum_n \left(\mathrm{e}^{-\beta\hat{H}}\right)_{nn} = \mathrm{Tre}^{-\beta\hat{H}} \qquad (5.27)$$

is determined by a trace of the density matrix. Quantum statistical average value of an observable $\hat{G}$: $\left\langle\bar{\hat{G}}\right\rangle = \mathrm{Tr}\left(\hat{\rho}\hat{G}\right)$ is given by a trace of a $\hat{G}$ and $\hat{\rho}$ product

$$\left\langle\bar{\hat{G}}\right\rangle = \mathrm{Tr}\left\{\frac{1}{Q_N}\mathrm{e}^{-\beta\hat{H}}\hat{G}\right\} = \frac{1}{Q_N}\sum_n\left\langle\varphi_n\left|\mathrm{e}^{-\beta\hat{H}}\hat{G}\right|\varphi_n\right\rangle = \\ = \frac{1}{Q_N}\sum_n \mathrm{e}^{-\beta E_n}\left\langle\varphi_n\left|\hat{G}\right|\varphi_n\right\rangle = \frac{1}{Q_N}\sum_n G_{nn}\mathrm{e}^{-\beta E_n} \qquad (5.28)$$

where

$$G_{nn} = \int \varphi_n^*\hat{G}\varphi_n\mathrm{d}\tau = \left\langle\varphi_n\left|\hat{G}\right|\varphi_n\right\rangle \qquad (5.29)$$

and

$$\hat{H}\varphi_n = E_n\varphi_n \qquad (5.30)$$

5.3 Entropy and other thermodynamic functions

A fundamental thermodynamic function - entropy

$$S = -k_B\mathrm{Tr}\left\{\hat{\rho}\ln\hat{\rho}\right\} \qquad (5.31)$$

in the canonical ensemble is given by a relation

$$S = -k_B\mathrm{Tr}\left\{\rho\left(-\ln Q_N - \beta\hat{H}\right)\right\} = \frac{1}{T}\left\langle\bar{\hat{H}}\right\rangle + k_B\ln Q_N \qquad (5.32)$$

where a statistical average of a Hamiltonian represents an average energy of a system, that is an internal energy $U = \left\langle \bar{\hat{H}} \right\rangle$. Therefore, we obtain a relation

$$U = TS - k_B T \ln Q_N \tag{5.33}$$

which compared with a phenomenological thermodynamic definition of the Helmholtz free energy (3.15) gives a statistical definition of the free energy

$$F = -k_B T \ln Q_N(V, T) \tag{5.34}$$

where we have explicitely expressed a particle number N, volume V and temperature T dependence of the free energy. We can use F to express the partition function $Q_N = \mathrm{e}^{-\beta F}$ and the density matrix

$$\hat{\rho} = \mathrm{e}^{\beta(F - \hat{H})} \tag{5.35}$$

A statistical formula for the internal energy follows from its definition

$$U = \mathrm{Tr}\left\{\hat{\rho}\hat{H}\right\} = \underbrace{\sum_n E_n \rho_n}_{\text{sum over states}} = \frac{1}{Q_N}\sum_n E_n \mathrm{e}^{-\beta E_n} \tag{5.36}$$

Using an identity

$$\begin{aligned} \frac{\partial}{\partial T}\ln Q_N = \frac{\partial}{\partial T}\ln\left(\sum_n \mathrm{e}^{-\beta E_n}\right) = \\ = \frac{1}{Q_N}\sum_n \left(-\frac{E_n}{k_B}\right)\left(-\frac{1}{T^2}\right)\mathrm{e}^{-\beta E_n} = \frac{1}{k_B T^2}\frac{1}{Q_N}\sum_n E_n \mathrm{e}^{-\beta E_n} \end{aligned} \tag{5.37}$$

we obtain

$$U = k_B T^2 \frac{\partial}{\partial T}\ln Q_N(V, T) = -\frac{\partial}{\partial \beta}\ln Q_N(V, T) \tag{5.38}$$

Finally, with a use of (5.33) and (5.38) we can derive the entropy formula in the canonical ensemble

$$S = k_B T \frac{\partial}{\partial T}\ln Q_N + k_B \ln Q_N \tag{5.39}$$

which leads

$$S = k_B \frac{\partial}{\partial T}\left(T \ln Q_N(V, T)\right) \tag{5.40}$$

We have shown that the statistical and phenomenological definitions of the thermodynamic functions are consistent. Moreover, using a statistical approach we can confirm some basic thermodynamic identities. Comparing the statistical definitions of the entropy (5.40) and the free energy (5.34), given in the canonical ensemble that is for a constant volume and a constant number of particles, we get

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \tag{5.41}$$

In summary, the thermodynamic functions can be expressed in the canonical ensemble by the statistical sum Q_N

$$F(V,T) = -k_B T \ln Q_N(V,T) \tag{5.42}$$

$$S(U,V) = k_B \frac{\partial}{\partial T} T \ln Q_N(V,T) \tag{5.43}$$

$$U(S,V) = k_B T^2 \frac{\partial}{\partial T} \ln Q_N(V,T) \tag{5.44}$$

5.4 Ideal classical gas

We will use the canonical ensemble method in a discussion of an ideal classical gas defined by the Hamiltonian

$$H = \frac{1}{2m}\sum_{i=1}^{N} p_i^2. \tag{5.45}$$

As the basic quantity that determines the thermodynamic functions is the partition function we start our considerations with an evaluation of $Q_N(V,T)$. The partition function of a system of a volume V

$$Q_N = \frac{V^N}{N!h^{3N}} \int\limits_{-\infty}^{\infty} \exp\left[-\frac{1}{2m}\sum_{i=1}^{N} \frac{\left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2\right)}{k_B T}\right] \mathrm{d}p_{1x}\cdots \mathrm{d}p_{Nx}$$

$$\mathrm{d}p_{1y}\cdots \mathrm{d}p_{Ny}\mathrm{d}p_{1z}\cdots \mathrm{d}p_{Nz} = \frac{V^N}{N!h^{3N}} \left[\int\limits_{-\infty}^{\infty} \mathrm{e}^{-\frac{p^2}{2mk_B T}} \mathrm{d}p\right]^{3N} \tag{5.46}$$

is determined by the Gauss integral

$$\int\limits_{-\infty}^{\infty} \mathrm{d}x \mathrm{e}^{-\lambda x^2} = \sqrt{\frac{\pi}{\lambda}} \tag{5.47}$$

and reads

$$Q_N = \frac{V^N}{N! h^{3N}} \left(2\pi m k_B T\right)^{\frac{3N}{2}} \tag{5.48}$$

For further evaluations we need a logarithm of the partition function

$$\ln Q_N = N \ln V + \frac{3N}{2} \ln\left(2\pi m k_B T\right) - \ln N! - N \ln h^3 \tag{5.49}$$

which for $N \gg 1$ in the Stirling's approximation reads

$$\ln Q_N = N \ln V + \frac{3N}{2} \ln\left(2\pi m k_B T\right) - N \ln N + N - N \ln h^3 \tag{5.50}$$

or

$$\ln Q_N = N \ln \frac{V}{N} + \frac{3}{2} N \ln\left(2\pi m k_B T\right) - N \ln h^3 + N \tag{5.51}$$

Now, we can write down the free energy

$$\begin{aligned} F = -k_B T \ln Q_N = -N k_B T \ln \frac{V}{N} \\ - \frac{3}{2} N k_B T \ln\left(2\pi m k_B T\right) + N k_B T \ln h^3 - N k_B T \end{aligned} \tag{5.52}$$

the internal energy

$$U = k_B T^2 \frac{\partial}{\partial T} \ln Q_N = k_B T^2 \left(\frac{3N}{2}\right) \frac{1}{2\pi m k_B T} 2\pi m k_B = \frac{3}{2} N k_B T \tag{5.53}$$

and the entropy

$$\begin{aligned} S = k_B \frac{\partial}{\partial T} \left(T \ln Q_N\right) = N k_B \ln \frac{V}{N} \\ + \frac{3}{2} N k_B \ln\left(2\pi m k_B T\right) + \frac{3}{2} N k_B - N k_B \ln h^3 + N = \\ = N k_B \ln V + \frac{3}{2} N k_B \ln T + N k_B \left[\ln \frac{\left(2\pi m k_B\right)^{\frac{3}{2}}}{N h^3} + \frac{5}{2}\right]. \end{aligned} \tag{5.54}$$

It is instructive to check that the obtained functions fulfill the thermodynamic relations

$$F = U - TS \quad \text{and} \quad \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} . \tag{5.55}$$

We note also, that the results agree with the ones obtained within the micro-canonical approach.

Chapter 6

Grand canonical ensemble

6.1 Density matrix

We define the grand partition function as a weighted sum of a partition function $Q_N(V,T)$ carried over a varying number of particles N

$$\theta(z,V,T)=\sum_{N=0}^{\infty} z^N Q_N(V,T), \tag{6.1}$$

where $z=\mathrm{e}^{\beta\mu}=\mathrm{e}^{\frac{\mu}{k_BT}}$ is a fugacity and μ is a chemical potential. We may also write

$$\theta(z,V,T)=\sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Q_N(V,T) \tag{6.2}$$

A quantum statistical average of an operator $\hat{G}$ in the grand canonical ensemble is defined also as a weighted average over canonical ensembles corresponding to varying numbers of particles

$$\left\langle \bar{\hat{G}} \right\rangle = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \mathrm{Tr}\left\{\hat{G}\mathrm{e}^{-\beta \hat{H}_N}\right\} \tag{6.3}$$

where $\hat{H}_N$ is a Hamiltonian of an N-particle system. In the energy representation, $\hat{H}_N \left|\varphi_{N,i}\right\rangle = E_{N,i}\left|\varphi_{N,i}\right\rangle$, we have

$$\left\langle \bar{\hat{G}} \right\rangle = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \sum_i \left\langle \varphi_{N,i} \middle| \hat{G} \middle| \varphi_{N,i} \right\rangle \mathrm{e}^{-\beta E_{N,i}}$$

$$= \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \sum_i G_{N,ii}\mathrm{e}^{-\beta E_{N,i}} = \frac{1}{\theta}\sum_{N=0}^{\infty} G_{N,ii}\mathrm{e}^{\frac{\mu N - E_{N,i}}{k_B T}} \tag{6.4}$$

and defining a probability $w_{N,i}$ of an N-particle system to reside in the $E_{N,i}$ energy state

$$w_{N,i} = \frac{1}{\theta}\mathrm{e}^{\dfrac{\mu N - E_{N,i}}{k_B T}} \tag{6.5}$$

where

$$\theta = \sum_{N=0}^{\infty}\sum_i \mathrm{e}^{\frac{\mu N - E_{N,i}}{k_B T}} \tag{6.6}$$

we can write

$$\left\langle \bar{\hat{G}} \right\rangle = \sum_{N=0}^{\infty}\sum_i G_{N,ii} w_{N,i} \tag{6.7}$$

If we assume, that for any N $\left\{\hat{G}, \hat{H}_N\right\} = \hat{G}\hat{H}_N - \hat{H}_N\hat{G} = 0$, that is both operators share the same set of eigenfuctions, we can assign to (6.7) an interpretation of an expected value of $\hat{G}$. Probability $w_{N,i}$ can be regarded as a diagonal element of the density matrix of the grand canonical ensemble

$$\hat{\rho} = \frac{1}{\theta}\mathrm{e}^{-\beta\left(\hat{H} - \mu\hat{N}\right)} \tag{6.8}$$

where we use a symbol $\hat{H}$ for a Hamiltonian with a varying number of particles. In fact, $\hat{\rho}$ fulfills the normalization condition

$$\mathrm{Tr}\hat{\rho} = \frac{1}{\theta}\mathrm{Tr}\mathrm{e}^{-\beta\left(\hat{H} - \mu\hat{N}\right)} = \frac{1}{\theta}\sum_{N=0}^{\infty}\sum_j \left\langle \varphi_{N,j} \middle| \mathrm{e}^{-\beta\left(\hat{H} - \mu\hat{N}\right)} \middle| \varphi_{N,j} \right\rangle =$$

$$\frac{1}{\theta}\sum_{N=0}^{\infty}\sum_j \mathrm{e}^{-\beta(E_{N,j} - \mu N)} = \frac{1}{\theta}\sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N}\sum_j \mathrm{e}^{-\beta E_{N,j}} =$$

$$\frac{1}{\theta}\sum_{N=0}^{\infty} z^N Q_N = 1 \tag{6.9}$$

and using $\hat{\rho}$ we can represent an average value of $\hat{G}$ given by (6.7) as a trace of a product $\hat{G}$ and $\hat{\rho}$ over the energy states of all possible N-particle systems

$$\langle\bar{\hat{G}}\rangle = \mathrm{Tr}\left\{\hat{\rho}\hat{G}\right\} \tag{6.10}$$

Eq. (6.8) defines a density matrix for a grand canonical ensemble. Obviously, for a fixed number of particles $N = N'$

$$\theta(z, V, T) = z^{N'} Q_{N'}(V, T) \tag{6.11}$$

and the grand canonical density matrix

$$\hat{\rho} = \frac{1}{\theta} z^{N'} \mathrm{e}^{-\beta \hat{H}_{N'}} = \frac{1}{z^{N'} Q_{N'}} z^{N'} \mathrm{e}^{-\beta \hat{H}_{N'}} = \frac{1}{Q_{N'}} \mathrm{e}^{-\beta \hat{H}_{N'}} \tag{6.12}$$

reduces to the canonical density matrix, which means that the grand canonical ensemble reduces to the canonical one.

6.2 Entropy and other thermodynamic functions

The entropy in the grand canonical ensemble

$$\begin{aligned} S = -k_B \mathrm{Tr}\left\{\hat{\rho}\left(-\ln\theta - \ln \mathrm{e}^{\beta(\hat{H}-\mu\hat{N})}\right)\right\} = \\ k_B \ln\theta + k_B \mathrm{Tr}\left\{\hat{\rho}\left(\beta(\hat{H}-\mu\hat{N})\right)\right\} = \\ k_B \ln\theta + \frac{1}{T}\left(U - \mu\bar{N}\right) \end{aligned} \tag{6.13}$$

where $U = \mathrm{Tr}\left\{\hat{\rho}\hat{H}\right\}$ represents the internal energy and $\bar{N} = \mathrm{Tr}\left\{\hat{\rho}\hat{N}\right\}$ stands for the average particle number, allows us to formulate a statistical definition of the grand potential (thermodynamic potential) in agreement with (3.36) as

$$\Omega = -k_B T \ln\theta(z, V, T) \tag{6.14}$$

From the above definition we have the grand partition function $\theta = \mathrm{e}^{-\beta\Omega}$ and the density matrix

$$\hat{\rho} = \mathrm{e}^{\beta(\Omega - \hat{H} + \mu\hat{N})} \tag{6.15}$$

Therefore, a quantum statistical average of an operator $\hat{G}$ in the grand canonical ensemble reads

$$\left\langle\bar{\hat{G}}\right\rangle = \mathrm{Tr}\left\{\mathrm{e}^{\beta(\Omega - \hat{H} + \mu\hat{N})}\hat{G}\right\} \tag{6.16}$$

Note that Ω plays the same role for the grand canonical ensemble as F for the canonical ensemble. It is usefull to have an operational formula for the average particle number and the internal energy within the grand canonical ensemble, as we have done it in the canonical ensemble, therefore we evaluate $\bar{N}$ right from the definition using the energy representation

$$\begin{aligned}\bar{N} = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \mathrm{Tr}\left\{\hat{N}\mathrm{e}^{-\beta\hat{H}}\right\} = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N N \sum_i \mathrm{e}^{-\beta E_{N,i}} = \\ \frac{1}{\theta}\sum_{N=0}^{\infty} z^N N Q_N = \frac{1}{\theta} z \frac{\partial}{\partial z}\sum_{N=0}^{\infty} z^N Q_N = \frac{1}{\theta} z \frac{\partial\theta}{\partial z} = z\frac{\partial}{\partial z}\ln\theta \qquad (6.17)\end{aligned}$$

and obtain

$$\bar{N} = z\left(\frac{\partial}{\partial z}\ln\theta(z,V,T)\right)_{T,V} \qquad (6.18)$$

From now on we will use a symbol N instead of $\bar{N}$ for an average particle number. Similarly, we calculate the internal energy

$$\begin{aligned}U = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \mathrm{Tr}\left\{\hat{H}\mathrm{e}^{-\beta\hat{H}}\right\} = \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \sum_i E_{N,i}\mathrm{e}^{-\beta EN,i} = \\ \frac{1}{\theta}\sum_{N=0}^{\infty} z^N \sum_i \left(-\frac{\partial}{\partial\beta}\mathrm{e}^{-\beta EN,i}\right) = \\ -\frac{1}{\theta}\left(\frac{\partial}{\partial\beta}\sum_{N=0}^{\infty} z^N Q_N\right)_{z,V} = -\left(\frac{\partial}{\partial\beta}\ln\theta\right)_{z,V} \qquad (6.19)\end{aligned}$$

and obtain

$$U = -\left(\frac{\partial}{\partial\beta}\ln\theta(z,V,T)\right)_{z,V} \qquad (6.20)$$

or

$$U = k_B T^2\left(\frac{\partial}{\partial T}\ln\theta(z,V,T)\right)_{z,V} \qquad (6.21)$$

Taking into account relations (6.21) and (6.18) formula (6.13) yields

$$\begin{aligned}S = k_B\ln\theta(z,V,T) + \\ k_B T\left(\frac{\partial}{\partial T}(\ln\theta(z,V,T)\right)_{z,V} - \frac{\mu}{T} z\left(\frac{\partial}{\partial z}\ln\theta(z,V,T)\right)_{T,V} \qquad (6.22)\end{aligned}$$

where, as explicitely stated, the grand partition function is considered a function of fugacity and temperature. Applying a fugacity definition, $z = \mathrm{e}^{\beta\mu}$, which involves the temperature and the chemical potential, we can regard $\theta(z, V, T) = \theta(z(\mu, T), V, T) = \theta(\mu, V, T)$ a function of the chemical potential and temperature, whose partial derivative with respect to temperature reads

$$k_B \left(\frac{\partial}{\partial T} (\ln \theta(z(\mu, T), V, T) \right)_{\mu,V} = \left(\frac{\partial}{\partial T} (\ln \theta(z, V, T) \right)_{z,V} + \left(\frac{\partial}{\partial z} (\ln \theta(z, V, T) \right)_{T,V} \left(\frac{\partial z}{\partial T} \right)_{\mu} \tag{6.23}$$

Since $\left(\frac{\partial z}{\partial T} \right)_{\mu} = -\frac{\mu}{k_B T^2} z$, we have

$$k_B \left(\frac{\partial}{\partial T} (\ln \theta(z(\mu, T), V, T) \right)_{\mu,V} = \left(\frac{\partial}{\partial T} (\ln \theta(z, V, T) \right)_{z,V} - \frac{\mu}{k_B T^2} z \left(\frac{\partial}{\partial z} (\ln \theta(z, V, T) \right)_{T,V} \tag{6.24}$$

and the above expression can be used instead of the two last terms on the right-hand side of (6.22) which gives

$$S = k_B \ln \theta(\mu, V, T) + k_B T \left(\frac{\partial}{\partial T} (\ln \theta(\mu, V, T) \right)_{\mu,V} \tag{6.25}$$

so the entropy in the grand canonical ensemble reads

$$S = k_B \frac{\partial}{\partial T} (T \ln \theta(\mu, V, T)) \tag{6.26}$$

We can also get rid of the z variable in the formula (6.18) which determines an average particle number and use a μ variable instead

$$N = z \left(\frac{\partial}{\partial \mu} \ln \theta \right)_{T,V} \left(\frac{\partial \mu}{\partial z} \right)_{T} = z \left(\frac{\partial}{\partial \mu} \ln \theta \right)_{T,V} \frac{k_B T}{z} = k_B T \left(\frac{\partial}{\partial \mu} \ln \theta \right)_{T,V} \tag{6.27}$$

where we have used $\left(\dfrac{\partial z}{\partial \mu}\right)_T = \beta z$. Taking into account a definition of the thermodynamic potential (6.14) we obtain

$$N = k_B T \frac{\partial}{\partial \mu} \ln \theta \tag{6.28}$$

and equations (6.14), (6.26) and (6.28) yield the thermodynamic identities

$$\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -S, \tag{6.29}$$

$$\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = -N \tag{6.30}$$

which agree with a phenomenological definition of Ω. Applying the grand canonical ensemble method we can also study the N dependence of the free energy searching for the entropy extremum with respect to N. Taking a variation of $\theta(z, V, T)$ with respect to N, which also extremizes the entropy (6.22), where

$$\theta(z, V, T) = \sum_{N=0}^{\infty} \mathrm{e}^{\frac{\mu N - F(T,V,N)}{k_B T}} \tag{6.31}$$

we obtain

$$\delta\theta = \frac{1}{k_B T} \sum_{N=0}^{\infty} \left[\mu - \left(\frac{\partial F}{\partial N}\right)_{V,T}\right] \mathrm{e}^{\frac{\mu N - F}{k_B T}} \delta N \tag{6.32}$$

The extremum condition $\delta\theta = 0$ for any δN leads to

$$\left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu \tag{6.33}$$

which is consistent with phenomenological thermodynamics.

Chapter 7

Ideal quantum gas

7.1 Fermi-Dirac and Bose-Einstein distributions

A state of an ideal gas can be defined by a set of occupancy numbers $\{n_{\boldsymbol{p}}\}$, where $n_{\boldsymbol{p}}$ is a number of particles in a single particle state $\boldsymbol{p}$. For spinless particles $\{n_{\boldsymbol{p}}\}$ uniquely defines the state of a system

$$n_{\boldsymbol{p}} = \begin{cases} 0, 1, 2, \ldots & \text{(bosons)} \\ 0, 1 & \text{(fermions)} \end{cases} \tag{7.1}$$

Therefore, we can use a summation over all possible sets $\{n_{\boldsymbol{p}}\}$ in a calculation of a total energy of a system

$$E\{n_{\boldsymbol{p}}\} = \sum_{\boldsymbol{p}} \mathcal{E}_{\boldsymbol{p}} n_{\boldsymbol{p}} \tag{7.2}$$

total particle number

$$N = \sum_{\boldsymbol{p}} n_{\boldsymbol{p}} \tag{7.3}$$

which yield the partition function Q_N and the grand partition function θ. We obtain for the partition function

$$Q_N(V,T) = \sum_n \mathrm{e}^{-\beta E_n} = \sum_{\{n_{\boldsymbol{p}}\}} \mathrm{e}^{-\beta E\{n_{\boldsymbol{p}}\}} \tag{7.4}$$

and for the grand partition function

$$\theta(z,V,T)=\sum_{N=0}^{\infty} z^N Q_N(V,T)=$$
$$\sum_{N=0}^{\infty} z^N \sum_{\{n_{\boldsymbol{p}}\}} \mathrm{e}^{-\beta\sum\limits_{\boldsymbol{p}}\mathcal{E}_{\boldsymbol{p}} n_{\boldsymbol{p}}}=\sum_{N=0}^{\infty}\sum_{\{n_{\boldsymbol{p}}\}}\prod_{\boldsymbol{p}}\left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}} \tag{7.5}$$

A double summation $\sum\limits_{N=0}^{\infty}\sum\limits_{\{n_{\boldsymbol{p}}\}}$ is equivalent to independent summations over each $n_{\boldsymbol{p}}$, therefore we get

$$\theta(z,V,T)=\sum_{n_0}\sum_{n_1}\dots\left[\left(z\mathrm{e}^{-\beta\mathcal{E}_0}\right)^{n_0}\left(z\mathrm{e}^{-\beta\mathcal{E}_1}\right)^{n_1}\dots\right]=$$
$$=\left[\sum_{n_0}\left(z\mathrm{e}^{-\beta\mathcal{E}_0}\right)^{n_0}\right]\left[\sum_{n_1}\left(z\mathrm{e}^{-\beta\mathcal{E}_1}\right)^{n_1}\right]\dots=\prod_{\boldsymbol{p}}\left[\sum_{n_{\boldsymbol{p}}}\left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}}\right] \tag{7.6}$$

The feature of substituting a summation over sets of occupancy numbers with a series of independent summations over the occupancy numbers, that we have used above in the evaluation of the grand partition function is really clear in the second quantization language in which the grand partition function

$$\theta=\mathrm{Tr}\left\{\mathrm{e}^{-\beta(\hat{H}-\mu\hat{N})}\right\} \tag{7.7}$$

in the Fock space reads

$$\theta=\sum_{n_1,\dots,n_\infty}\langle n_1,\dots,n_\infty|\mathrm{e}^{\beta(\mu\hat{N}-\hat{H})}|n_1,\dots,n_\infty\rangle \tag{7.8}$$

Using the energy representation and assuming that $\hat{H}$ and $\hat{N}$ share the same set of ortonormal eigenstates we have

$$\theta=\sum_{n_1,\dots,n_\infty}\langle n_1,\dots,n_\infty|\exp\left[\beta\left(\mu\sum_i n_i-\sum_i\mathcal{E}_i n_i\right)\right]|n_1,\dots,n_\infty\rangle \tag{7.9}$$

and finally

$$\theta=\sum_{n_1,\dots,n_\infty}\prod_i\mathrm{e}^{-\beta(\mathcal{E}_i n_i-\mu n_i)}=\prod_i\sum_{n_i}\mathrm{e}^{-\beta(\mathcal{E}_i n_i-\mu n_i)} \tag{7.10}$$

For a Bose gas

$$\sum_{n_{\boldsymbol{p}}} \left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}} = \sum_{n_{\boldsymbol{p}}=0}^{\infty} \left(z\mathrm{e}^{-\beta\mathcal{E}_{p}}\right)^{n_{\boldsymbol{p}}} \tag{7.11}$$

we deal with a geometric series in (7.6) and under the condition that $z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}} < 1 \Leftrightarrow z < \mathrm{e}^{\beta\mathcal{E}_{\boldsymbol{p}}}$ for any $\mathcal{E}_{\boldsymbol{p}} > 0$, that is $z \leq e^0 = 1$, we obtain

$$\sum_{n_{\boldsymbol{p}}} \left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}} = \frac{1}{1 - z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}} = \frac{1}{1 - \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}} \tag{7.12}$$

We note, that for bosons in order to keep a finite value of the grand partition function we had to limit the fugacity $\mathrm{e}^{\beta\mu} \leq 1$ which yields a nonpositive chemical potential $\mu \leq 0$. In a case of a Fermi gas we are left with a two number summation in (7.6)

$$\sum_{n_{\boldsymbol{p}}} \left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}} = \sum_{n_{\boldsymbol{p}}=0}^{1} \left(z\mathrm{e}^{-\beta\mathcal{E}_{p}}\right)^{n_{\boldsymbol{p}}} \tag{7.13}$$

and obtain

$$\sum_{n_{\boldsymbol{p}}} \left(z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)^{n_{\boldsymbol{p}}} = 1 + z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}} = 1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})} \tag{7.14}$$

We can now write down the grand partition function for quantum particles (7.6)

$$\theta(z, V, T) = \begin{cases} \prod\limits_{\boldsymbol{p}} \dfrac{1}{1 - z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}} & \text{(bosons)} \\ \prod\limits_{\boldsymbol{p}} \left(1 + z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right) & \text{(fermions)} \end{cases} \tag{7.15}$$

Having the grand partition function we obtain the equation of state

$$\frac{PV}{k_B T} = \ln\theta(z, V, T) = \begin{cases} -\sum\limits_{\boldsymbol{p}} \ln(1 - z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}) & \text{(bosons)} \\ \sum\limits_{\boldsymbol{p}} \ln(1 + z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}) & \text{(fermions)} \end{cases} \tag{7.16}$$

and the average number of particles

$$N = z\frac{\partial}{\partial z}\ln\theta(z, V, t) = \begin{cases} \sum\limits_{\boldsymbol{p}} \dfrac{z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}}{1 - z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}} & \text{(bosons)} \\ \sum\limits_{\boldsymbol{p}} \dfrac{z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}}{1 + z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}} & \text{(fermions)} \end{cases} \tag{7.17}$$

The average number of particles N can be regarded as a sum over states of the average state occupancy numbers $\langle n_{\boldsymbol{p}} \rangle$

$$N = \sum_{\boldsymbol{p}} \langle n_{\boldsymbol{p}} \rangle \tag{7.18}$$

therefore, with a notation

$$\langle n_{\boldsymbol{p}} \rangle = n(\boldsymbol{p}) = f(\boldsymbol{p}) \tag{7.19}$$

where $f(\boldsymbol{p})$ is called a distribution function, we write the average occupancy numbers

$$f(\boldsymbol{p}) = \begin{cases} \dfrac{1}{\mathrm{e}^{\beta(\mathcal{E}_{\boldsymbol{p}}-\mu)} - 1} & \text{bosons} \\ \dfrac{1}{\mathrm{e}^{\beta(\mathcal{E}_{\boldsymbol{p}}-\mu)} + 1} & \text{fermions} \end{cases} \tag{7.20}$$

For bosons $f(\boldsymbol{p})$ is called the Bose-Einstein distribution, whereas for fermions - the Fermi-Dirac distribution function. The average occupation number can be also obtained in a direct calculation. If we consider a system consisting of a single state $\boldsymbol{p}$ and construct a grand canonical ensemble which corresponds to different occupations of this state, then the average occupation number $\langle n_{\boldsymbol{p}} \rangle$ using the grand canonical method of averaging reads

$$\langle n_{\boldsymbol{p}} \rangle = \frac{1}{\theta_{\boldsymbol{p}}} \sum_{n_{\boldsymbol{p}}} z^{n_{\boldsymbol{p}}} n_{\boldsymbol{p}} \mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}} n_{\boldsymbol{p}}} \tag{7.21}$$

where

$$\theta_{\boldsymbol{p}} = \sum_{n_{\boldsymbol{p}}} z^{n_{\boldsymbol{p}}} \mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}} n_{\boldsymbol{p}}} \tag{7.22}$$

and the sum runs over possible occupancy numbers. It is straightforward to see that

$$\langle n_{\boldsymbol{p}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \mathcal{E}_{\boldsymbol{p}}} \ln \theta_{\boldsymbol{p}} \tag{7.23}$$

As the sum for fermions consists only of two terms $n_{\boldsymbol{p}} = 0, 1$ we get $\theta_{\boldsymbol{p}} = 1 + z\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}}$ and $\langle n_{\boldsymbol{p}} \rangle = (z^{-1}\mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}}} + 1)^{-1}$. For bosons the partition function becomes a sum of an infinite geometric series, $n_{\boldsymbol{p}} = 0, 1, 2, ...$, and reads $\theta_{\boldsymbol{p}} = (1 - z\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}})^{-1}$, then the relation (7.23) yields $\langle n_{\boldsymbol{p}} \rangle = (z^{-1}\mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}}} - 1)^{-1}$.

7.2 Equation of state

We are particulary interested in the thermodynamic limit of the above equations, that is, for $V \longrightarrow \infty$, $N \longrightarrow \infty$ with $n = \dfrac{N}{V}$ kept constant. For a large volume of a system we can replace a sum over momenta and spin s projections σ with an integral

$$\sum_{\boldsymbol{p},\sigma} \longrightarrow \frac{(2s+1)V}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \tag{7.24}$$

Therefore, in the thermodynamic limit we can write, for fermions

$$\frac{P}{k_B T} = \frac{(2s+1)}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \ln\left(1 + z\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}}\right) \tag{7.25}$$

which constitutes the equation of state and

$$\frac{1}{v} = \frac{(2s+1)}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \frac{1}{z^{-1}\mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}}+1}} \tag{7.26}$$

which presents the equation for the chemical potential, where $v = n^{-1}$ is a proper volume, that is, a volume per particle. For bosons, we obtain respectively

$$\frac{P}{k_B T} = -\frac{(2s+1)}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \ln\left(1 - z\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}}\right) - \frac{(2s+1)}{V} \ln\left(1 - z^{-1}\mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}=0}}\right) \tag{7.27}$$

and

$$\frac{1}{v} = \frac{(2s+1)}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \frac{1}{z^{-1}\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}} - 1} + \frac{(2s+1)}{V} \frac{1}{z^{-1}\mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}=0}} - 1}. \tag{7.28}$$

We have separated here terms of the lowest energy, that is $\mathcal{E}_{\boldsymbol{p}=0}$, before replacing a sum with an integral. It is obvious that both terms aside the integrals in (7.27) and (7.28) can be divergent and their values can be significant, however when integrated they may vanish since the assigned measure weight in the integral is proportional to $p^2 \mathrm{d}p$ and vanishes for $p = 0$.The real physical spectrum is discrete and the integral is only a useful approximation which simplifies the calculations, nevertheless its application cannot hide a real physics. There is no need to pay such a particular attention to a zero momentum terms for fermions as they do not lead to any singularity. Note, that we have not assumed any dispersion relation yet.

7.3 Density of states

Momentum integrals

$$\frac{(2s+1)V}{(2\pi\hbar)^3}\int\limits_{-\infty}^{\infty} \mathrm{d}^3p F(\mathcal{E}(\boldsymbol{p})) \tag{7.29}$$

can be converted into the energy integrals which involve a density of states function $\nu(\mathcal{E})$ which counts a number of states per an energy unit

$$\int\limits_{0}^{\infty} F(\mathcal{E})\nu(\mathcal{E})\mathrm{d}\mathcal{E} \tag{7.30}$$

With a use of the density of states function we can express the equations which determine the state of a system. As they look different for fermions and bosons we will specify them for each kind of particles separately. For fermions, the chemical potential equation

$$n = \int\limits_{0}^{\infty} \frac{\nu(\mathcal{E})\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} \tag{7.31}$$

which yields $\mu = \mu(\beta, n)$ or determines a particle concentration, and the equation

$$\frac{P}{k_BT} = \int\limits_{0}^{\infty} \ln(1+z\mathrm{e}^{-\beta\mathcal{E}})\nu(\mathcal{E})\mathrm{d}\mathcal{E} \tag{7.32}$$

yield the equation of state. For bosons, we obtain respectively

$$n = \int\limits_{0}^{\infty} \frac{\nu(\mathcal{E})\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}-1} + \frac{(2s+1)}{V}\frac{z}{1-z} \tag{7.33}$$

and

$$\frac{P}{k_BT} = -\int\limits_{0}^{\infty} \ln(1-z\mathrm{e}^{-\beta\mathcal{E}})\nu(\mathcal{E})\mathrm{d}\mathcal{E} - \frac{(2s+1)}{V}\ln(1-z) \tag{7.34}$$

Since, quite often we will work within such an approach, below we derive the density of states function for various dimensionalities of a system.

7.3.1 Three-dimensional density of states

For a three-dimensional gas of noninteracting particles with a spin s and a dispersion relation $\mathcal{E} = p^2/2m$ we have

$$
\begin{aligned}
&\frac{(2s+1)V}{(2\pi\hbar)^3}\int\limits_{-\infty}^{\infty} \mathrm{d}^3 p F(\mathcal{E}(\boldsymbol{p})) = \frac{(2s+1)V}{(2\pi\hbar)^3} 4\pi \int\limits_{0}^{\infty} F(\mathcal{E}(\boldsymbol{p}))p^2 \mathrm{d}p = \\
&\quad \frac{(2s+1)V}{(2\pi\hbar)^3} 4\pi \int\limits_{0}^{\infty} pF(\mathcal{E}(\boldsymbol{p}))p\mathrm{d}p = 4\pi \frac{(2s+1)V}{(2\pi\hbar)^3} \int\limits_{0}^{\infty} F(\mathcal{E})\sqrt{2m\mathcal{E}}\, m\mathrm{d}\mathcal{E} = \\
&\qquad 4\sqrt{2}\pi \frac{(2s+1)V}{(2\pi\hbar)^3} m^{\frac{3}{2}} \int\limits_{0}^{\infty} F(\mathcal{E})\mathcal{E}^{\frac{1}{2}}\mathrm{d}\mathcal{E} = \int\limits_{0}^{\infty} F(\mathcal{E})\nu(\mathcal{E})\mathrm{d}\mathcal{E}
\end{aligned}
\tag{7.35}
$$

where

$$
\nu(\mathcal{E}) = \nu_{3D}(\mathcal{E}) = \alpha_{3D} V \sqrt{\mathcal{E}} \tag{7.36}
$$

is a density of states function for an isotropic three-dimensional system and

$$
\alpha_{3D} = \frac{4\sqrt{2}}{h^3}\pi m^{\frac{3}{2}}(2s+1) \tag{7.37}
$$

7.3.2 Two-dimensional density of states

For a two-dimensional gas with a parabolic dispersion:

$$
\begin{aligned}
\sum_{\boldsymbol{p},\sigma} F(\mathcal{E}\boldsymbol{p})) = \frac{(2s+1)}{(2\pi\hbar)^2} S \int\limits_{-\infty}^{\infty} F(\mathcal{E}(\boldsymbol{p}))\mathrm{d}^2 p &= \\
\frac{(2s+1)}{(2\pi\hbar)^2} 2\pi S \int\limits_{0}^{\infty} F(\mathcal{E}(\boldsymbol{p}))p\mathrm{d}p &= \\
\frac{(2s+1)}{(2\pi\hbar)^2} 2\pi S \int\limits_{0}^{\infty} F(\mathcal{E}) m\mathrm{d}\mathcal{E} &= \int\limits_{0}^{\infty} F(\mathcal{E})\nu_{2D}(\mathcal{E})\mathrm{d}\mathcal{E}
\end{aligned}
\tag{7.38}
$$

where S is a system surface area and

$$
\nu_{2D}(\mathcal{E}) = \alpha_{2D} S \tag{7.39}
$$

is a density of states function for an isotropic two-dimensional system and

$$\alpha_{2D} = \frac{2\pi m}{h^2}(2s+1) \tag{7.40}$$

7.3.3 One-dimensional density of states

For a one-dimensional gas with a parabolic dispersion:

$$\sum_{\boldsymbol{p},\sigma} F(\mathcal{E}\boldsymbol{p})) = \frac{(2s+1)}{(2\pi\hbar)} L \int\limits_{-\infty}^{\infty} F(\mathcal{E}\boldsymbol{p}))\mathrm{d}p = 2\frac{(2s+1)}{2\pi\hbar} L \int\limits_{0}^{\infty} F(\mathcal{E}\boldsymbol{p}))\mathrm{d}p =$$

$$2\frac{(2s+1)}{(2\pi\hbar)} L \int\limits_{0}^{\infty} F(\mathcal{E})\frac{m\mathrm{d}\mathcal{E}}{\sqrt{2m\mathcal{E}}} = \int\limits_{0}^{\infty} F(\mathcal{E})\nu_{1D}(\mathcal{E})\mathrm{d}\mathcal{E} \tag{7.41}$$

where L is a system length and

$$\nu_{1D}(\mathcal{E}) = \alpha_{1D} L \mathcal{E}^{-\frac{1}{2}} \tag{7.42}$$

is a density of states function for an isotropic one-dimensional system and

$$\alpha_{1D} = \frac{\sqrt{2m}}{h}(2s+1) \tag{7.43}$$

7.4 Thermodynamics

In this section we will derive basic thermodynamic functions for a three dimensional gas of free particles which obey a parabolic dispersion relation $\mathcal{E}(\boldsymbol{p}) = \dfrac{p^2}{2m}$. We start, however, with the equation of state for fermions and bosons.

7.4.1 Equation of state

For the Fermi gas

$$\frac{P}{k_B T} = (2s+1)\frac{4\pi}{h^3}\int\limits_{0}^{\infty} \mathrm{d}p p^2 \ln(1 + z\mathrm{e}^{-\frac{\beta p^2}{2m}}) \tag{7.44}$$

$$\frac{1}{v} = (2s+1)\frac{4\pi}{h^3}\int\limits_{0}^{\infty} \mathrm{d}p p^2 \frac{1}{z^{-1}\mathrm{e}^{\frac{\beta p^2}{2m}} + 1} \tag{7.45}$$

Defining fermionic functions

$$f_{\frac{5}{2}}(z) \equiv \frac{4}{\sqrt{\pi}} \int\limits_0^\infty \mathrm{d}x x^2 \ln\left(1 + z\mathrm{e}^{-x^2}\right) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{\frac{5}{2}}} \tag{7.46}$$

$$f_{\frac{3}{2}}(z) \equiv z\frac{\partial}{\partial z} f_{\frac{5}{2}}(z) = \frac{4}{\sqrt{\pi}} \int\limits_0^\infty \mathrm{d}x x^2 \frac{1}{z^{-1}\mathrm{e}^{x^2} + 1} = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{\frac{3}{2}}} \tag{7.47}$$

we can write the state equation and the chemical potential equation respectively

$$\frac{P}{k_B T} = \frac{1}{\lambda_s^3} f_{\frac{5}{2}}(z) \tag{7.48}$$

$$\frac{1}{v} = \frac{1}{\lambda_s^3} f_{\frac{3}{2}}(z) \tag{7.49}$$

where we have introduced a thermal wavelength

$$\lambda_s = \frac{1}{(2s+1)^{\frac{1}{3}}} \frac{h}{\sqrt{2\pi m k_B T}} \tag{7.50}$$

which sets a length scale of the order of magnitude of the de Broglie wavelength

$$\lambda_{\mathrm{d}B} = \frac{h}{p} = \frac{h}{\sqrt{2m\mathcal{E}(\boldsymbol{p})}} \sim \frac{h}{\sqrt{2mk_B T}} \sim \lambda_s \tag{7.51}$$

Note, that λ_s agrees with a formerly introduced thermal wavelength λ_0 for classical spinless particles when $s = 0$. Similarly for a Bose gas

$$\frac{P}{k_B T} = -(2s+1)\frac{4\pi}{h^3} \int\limits_0^\infty \mathrm{d}p p^2 \ln(1 - z\mathrm{e}^{-\frac{\beta p^2}{2m}}) - \frac{(2s+1)}{V} \ln(1-z) \tag{7.52}$$

and

$$\frac{1}{v} = (2s+1)\frac{4\pi}{h^3} \int\limits_0^\infty \mathrm{d}p p^2 \frac{1}{z^{-1}\mathrm{e}^{\frac{\beta p^2}{2m}} - 1} + \frac{(2s+1)}{V} \frac{z}{1-z} \tag{7.53}$$

or expressed with a use of the bosonic functions

$$g_{\frac{5}{2}}(z) \equiv -\frac{4}{\sqrt{\pi}} \int\limits_0^\infty \mathrm{d}x x^2 \ln\left(1 - z\mathrm{e}^{-x^2}\right) = \sum_{l=1}^{\infty} \frac{z^l}{l^{\frac{5}{2}}} \tag{7.54}$$

$$g_{\frac{3}{2}}(z) \equiv z\frac{\partial}{\partial z} g_{\frac{5}{2}}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{\frac{3}{2}}} \tag{7.55}$$

we have

$$\frac{P}{k_B T} = \frac{1}{\lambda_s^3} g_{\frac{5}{2}}(z) - \frac{(2s+1)}{V}\ln(1-z) \tag{7.56}$$

$$\frac{1}{v} = \frac{1}{\lambda_s^3} g_{\frac{3}{2}}(z) + \frac{(2s+1)}{V}\frac{z}{1-z} \tag{7.57}$$

We note, that the equations for a Fermi gas (7.48) and (7.49) do not change when we take a thermodynamic limit, however, such a limiting procedure requires a separate analysis in the case of bosons. Although we will discuss this issue thoroughly in Chapter 10, we just briefly state here, that the logarithm term in (7.56) vanishes for $V \longrightarrow \infty$ and it turns out that the second term on the right hand side of (7.57) vanishes in the thermodynamic limit for any z but $z = 1$ for which it gives a finite value. Concluding, we can write the state equation for bosons in the thermodynamic limit

$$\frac{P}{k_B T} = \frac{1}{\lambda_s^3} g_{\frac{5}{2}}(z) \tag{7.58}$$

$$\frac{1}{v} = \frac{1}{\lambda_s^3} g_{\frac{3}{2}}(z) + \lim_{V\to\infty} \frac{(2s+1)}{V}\frac{z}{1-z} \tag{7.59}$$

7.4.2 Thermodynamic potential and internal energy

A thermodynamic definition of the thermodynamic potential $\Omega = -PV$ gives us a formula

$$\frac{\Omega}{V} = \begin{cases} \dfrac{-k_B T}{\lambda_S^3} f_{\frac{5}{2}}(z) & \text{(fermions)} \\ \dfrac{-k_B T}{\lambda_S^3} g_{\frac{5}{2}}(z) + \dfrac{(2s+1)}{V} k_B T \ln(1-z) & \text{(bosons)} \end{cases} \tag{7.60}$$

If we calculate the thermodynamic potential directly using its statistical definition

$$\Omega = -k_B T \ln \theta(z, V, T) = \\ -k_B T \ln \prod_{\boldsymbol{p}} \left(1 + z\mathrm{e}^{-\beta\mathcal{E}(\boldsymbol{p})}\right) = -k_B T \sum_{\boldsymbol{p}} \ln\left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E}(\boldsymbol{p}))}\right) \tag{7.61}$$

then we get it determined by an integral

$$\Omega = \mp k_B T \alpha V \int_0^\infty \ln\left(1 \pm z\mathrm{e}^{-\beta\mathcal{E}}\right)\sqrt{\mathcal{E}}\,\mathrm{d}\mathcal{E} \tag{7.62}$$

where the upper sign concerns fermions and the lower sign corresponds to bosons. Integrating by parts we get

$$\begin{aligned}\int_0^\infty \ln\left(1 \pm z\mathrm{e}^{-\beta\mathcal{E}_{\boldsymbol{p}}}\right)\sqrt{\mathcal{E}}\,\mathrm{d}\mathcal{E} &= \frac{2}{3}\int_0^\infty \left(\mathcal{E}^{\frac{3}{2}}\right)' \ln\left(1 \pm z\mathrm{e}^{-\beta\mathcal{E}}\right)\mathrm{d}\mathcal{E} = \\ &= \frac{2}{3}\mathcal{E}^{\frac{3}{2}}\ln\left(1 \pm z\mathrm{e}^{-\beta\mathcal{E}}\right)\Big|_0^\infty \pm \frac{2}{3}\beta\int_0^\infty \mathcal{E}^{\frac{3}{2}}\frac{z\mathrm{e}^{-\beta\mathcal{E}}}{1 \pm \mathrm{e}^{-\beta\mathcal{E}}}\mathrm{d}\mathcal{E} = \\ &= \pm\frac{2}{3}\beta\int_0^\infty \frac{\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E}}{z^{-1}\mathrm{e}^{\beta\mathcal{E}} \pm 1} = \pm\frac{2}{3}\beta\int_0^\infty f(\mathcal{E})\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E}\end{aligned} \tag{7.63}$$

therefore

$$\Omega = -\frac{2}{3}\alpha V\int_0^\infty f(\mathcal{E})\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E} \tag{7.64}$$

and when we compare it to the internal energy

$$\begin{aligned}U = \sum_{\boldsymbol{p}}\mathcal{E}(\boldsymbol{p})n_{\boldsymbol{p}} = \sum_{\boldsymbol{p}}\frac{\mathcal{E}(\boldsymbol{p})}{z^{-1}\mathrm{e}^{\beta\mathcal{E}(\boldsymbol{p})} \pm 1} = \\ \alpha V\int_0^\infty \frac{\mathcal{E}}{z^{-1}\mathrm{e}^{\beta\mathcal{E}} \pm 1}\sqrt{\mathcal{E}}\,\mathrm{d}\mathcal{E} == \alpha V\int_0^\infty f(\mathcal{E})\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E}\end{aligned} \tag{7.65}$$

we see that

$$\Omega = -\frac{2}{3}U \tag{7.66}$$

and also obtain a relation between pressure and the internal energy

$$PV = \frac{2}{3}U \tag{7.67}$$

Finally, we can write the internal energy

$$\frac{U}{V}=\begin{cases}\dfrac{3k_BT}{2\lambda_s^3}f_{\frac{5}{2}}(z) & \text{(fermions)}\\ \dfrac{3k_BT}{2\lambda_s^3}g_{\frac{5}{2}}(z)-\dfrac{3}{2}\dfrac{(2s+1)}{V}k_BT\ln(1-z) & \text{(bosons)}\end{cases} \tag{7.68}$$

Concerning our discussion of the equation of state, we can write the thermodynamic potential and the internal energy in the thermodynamic limit

$$\frac{\Omega}{V}=\begin{cases}\dfrac{-k_BT}{\lambda_S^3}f_{\frac{5}{2}}(z) & \text{(fermions)}\\ \dfrac{-k_BT}{\lambda_S^3}g_{\frac{5}{2}}(z) & \text{(bosons)}\end{cases} \tag{7.69}$$

$$\frac{U}{V}=\begin{cases}\dfrac{3k_BT}{2\lambda_s^3}f_{\frac{5}{2}}(z) & \text{(fermions)}\\ \dfrac{3k_BT}{2\lambda_s^3}g_{\frac{5}{2}}(z) & \text{(bosons)}\end{cases} \tag{7.70}$$

7.4.3 Entropy

The thermodynamic potential or the internal energy can be used to determine the entropy

$$S=-\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}=-\left(\frac{\partial}{\partial T}\left(-\frac{2}{3}U\right)\right)_{V,\mu}=\frac{2}{3}\left(\frac{\partial U}{\partial T}\right)_{V,\mu} \tag{7.71}$$

For fermions we have

$$S=Vk_B\left(\frac{\partial}{\partial T}\left[\frac{T}{\lambda_s^3}f_{\frac{5}{2}}(z)\right]\right)_{V,\mu}= \\ Vk_B\left[\frac{5}{2}\frac{1}{\lambda_s^3}f_{\frac{5}{2}}(z)+\frac{T}{\lambda_s^3}\frac{1}{z}f_{\frac{3}{2}}(z)\left(\frac{\partial z}{\partial T}\right)_{V,\mu}\right] \tag{7.72}$$

and since

$$\left(\frac{\partial z}{\partial T}\right)_{V,\mu}=\left(\frac{\partial}{\partial T}\mathrm{e}^{\frac{\mu}{k_BT}}\right)_{V,\mu}=-\frac{\mu}{k_BT^2}z=-\frac{1}{T}z\ln z \tag{7.73}$$

we obtain

$$S = Nk_B \frac{v}{\lambda_s^3} \left[\frac{5}{2} f_{\frac{5}{2}}(z) - f_{\frac{3}{2}}(z) \ln z \right] \tag{7.74}$$

For bosons

$$\begin{aligned} S = Vk_B \left(\frac{\partial}{\partial T} \left[\frac{T}{\lambda_s^3} g_{\frac{5}{2}}(z) - \frac{2s+1}{V} T \ln(1-z) \right] \right)_{V,\mu} = \\ Vk_B \left[\frac{5}{2} \frac{1}{\lambda_S^3} g_{\frac{5}{2}}(z) - \frac{1}{\lambda_s^3} g_{\frac{3}{2}}(z) \ln z - \right. \\ \left. \frac{2s+1}{V} \ln(1-z) - \frac{2s+1}{V} \frac{z}{1-z} \ln z \right] \end{aligned} \tag{7.75}$$

therefore

$$\begin{aligned} S = Nk_B \frac{v}{\lambda_s^3} \left[\frac{5}{2} g_{\frac{5}{2}}(z) - g_{\frac{3}{2}}(z) \ln z \right] - \\ (2s+1) k_B \left[\ln(1-z) + \frac{z}{1-z} \ln z \right] \end{aligned} \tag{7.76}$$

In summary, we can write the entropy formula

$$\frac{S}{Nk_B} = \begin{cases} \frac{v}{\lambda_s^3} \left[\frac{5}{2} f_{\frac{5}{2}}(z) - f_{\frac{3}{2}}(z) \ln z \right] & \text{(fermions)} \\ \frac{v}{\lambda_s^3} \left[\frac{5}{2} g_{\frac{5}{2}}(z) - g_{\frac{3}{2}}(z) \ln z \right] - \frac{2s+1}{N} \left[\ln(1-z) + \frac{z}{1-z} \ln z \right] & \text{(bosons)} \end{cases} \tag{7.77}$$

Finally, in the thermodynamic limit we get

$$\frac{S}{Nk_B} = \begin{cases} \frac{v}{\lambda_s^3} \left[\frac{5}{2} f_{\frac{5}{2}}(z) - f_{\frac{3}{2}}(z) \ln z \right] & \text{(fermions)} \\ \frac{v}{\lambda_s^3} \left[\frac{5}{2} g_{\frac{5}{2}}(z) - g_{\frac{3}{2}}(z) \ln z \right] & \text{(bosons)} \end{cases} \tag{7.78}$$

7.4.4 Free energy

The internal energy and the entropy determine the free energy, $F = U - TS$, which reads for fermions and bosons, respectively

$$\frac{F}{Nk_BT} = \begin{cases} \dfrac{v}{\lambda_s^3}\left[-f_{\frac{5}{2}}(z) - f_{\frac{3}{2}}(z)\ln z\right] & \text{(fermions)} \\[2ex] \dfrac{v}{\lambda_s^3}\left[-g_{\frac{5}{2}}(z) - g_{\frac{3}{2}}(z)\ln z\right] - \dfrac{2s+1}{N}\left[\dfrac{5}{2}\ln(1-z) + \dfrac{z}{1-z}\ln z\right] & \text{(bosons)} \end{cases} \tag{7.79}$$

and in the thermodynamic limit

$$\frac{F}{Nk_BT} = \begin{cases} \dfrac{v}{\lambda_s^3}\left[-f_{\frac{5}{2}}(z) - f_{\frac{3}{2}}(z)\ln z\right] & \text{(fermions)} \\[2ex] \dfrac{v}{\lambda_s^3}\left[-g_{\frac{5}{2}}(z) - g_{\frac{3}{2}}(z)\ln z\right] & \text{(bosons)} \end{cases} \tag{7.80}$$

7.4.5 Heat capacity C_V

A heat capacity at a constant volume C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,n} \tag{7.81}$$

for fermions is given by

$$C_V = \frac{3}{2}Vk_B\left(\frac{\partial}{\partial T}\left[\frac{T}{\lambda_s^3}f_{\frac{5}{2}}(z)\right]\right)_{V,n} = \\ \frac{3}{2}Vk_B\left[\frac{5}{2}\frac{1}{\lambda_s^3}f_{\frac{5}{2}}(z) + \frac{T}{\lambda_s^3}\frac{1}{z}f_{\frac{3}{2}}(z)\left(\frac{\partial z}{\partial T}\right)_{V,n}\right] \tag{7.82}$$

where we have used a property

$$\frac{\partial}{\partial z}f_{\frac{5}{2}}(z) = \frac{1}{z}f_{\frac{3}{2}}(z) \tag{7.83}$$

A partial derivative $\left(\dfrac{\partial z}{\partial T}\right)_{V,n}$ we obtain from the condition

$$n = \frac{1}{\lambda_s^3}f_{\frac{3}{2}}(z), \tag{7.84}$$

for a constant n as $\left(\frac{\partial n}{\partial T}\right)_{V,n} = 0$ and using

$$\frac{\partial}{\partial z} f_{\frac{3}{2}}(z) = \frac{1}{z} f_{\frac{1}{2}}(z) \tag{7.85}$$

we get

$$\frac{3}{2}\frac{1}{T\lambda_s^3} f_{\frac{3}{2}}(z) + \frac{1}{\lambda_s^3}\frac{1}{z} f_{\frac{1}{2}}(z) \left(\frac{\partial z}{\partial T}\right)_{V,n} = 0 \tag{7.86}$$

which yields

$$\left(\frac{\partial z}{\partial T}\right)_{V,n} = -\frac{3}{2}\frac{z}{T}\frac{f_{\frac{3}{2}}(z)}{f_{\frac{1}{2}}(z)} \tag{7.87}$$

and finally, the heat capacity of a Fermi gas at a constant volume reads

$$C_V = \frac{3}{2} N k_B \frac{v}{\lambda_s^3}\left[\frac{5}{2} f_{\frac{5}{2}}(z) - \frac{3}{2}\frac{f^2_{\frac{3}{2}}(z)}{f_{\frac{1}{2}}(z)}\right] \tag{7.88}$$

Following the same rules for bosons we have

$$\begin{aligned} C_V = \frac{3}{2} V k_B \left(\frac{\partial}{\partial T}\left[\frac{T}{\lambda_s^3} g_{\frac{5}{2}}(z) - \frac{2s+1}{V} T \ln(1-z)\right]\right)_{V,n} = \\ \frac{3}{2} V k_B \left[\frac{5}{2}\frac{1}{\lambda_s^3} g_{\frac{5}{2}}(z) + \frac{T}{\lambda_s^3}\left(\frac{\partial}{\partial z} g_{\frac{5}{2}}(z)\right)\left(\frac{\partial z}{\partial T}\right)_{V,n}\right. \\ \left. - \frac{2s+1}{V}\ln(1-z) + \frac{2s+1}{V}\frac{T}{1-z}\left(\frac{\partial z}{\partial T}\right)_{V,n}\right] \end{aligned} \tag{7.89}$$

and similarly to fermions we have used $\frac{\partial}{\partial z} g_{\frac{5}{2}}(z) = \frac{1}{2} g_{\frac{3}{2}}(z)$. Again, a partial derivative $\left(\frac{\partial z}{\partial T}\right)_{V,n}$ is determined by the chemical potential equation

$$n = \frac{1}{\lambda_s^3} g_{\frac{3}{2}}(z) + \frac{2s+1}{V}\frac{z}{1-z} = \frac{1}{\lambda_s^3} g_{\frac{3}{2}}(z) + \frac{2s+1}{V}\frac{1}{1-z} - \frac{2s+1}{V} \tag{7.90}$$

for $\left(\frac{\partial n}{\partial T}\right)_{V,n} = 0$ it yields

$$0 = \frac{3}{2}\frac{1}{T\lambda_s^3} g_{\frac{3}{2}}(z) + \frac{1}{\lambda_s^3}\frac{1}{z} g_{\frac{1}{2}}(z)\left(\frac{\partial z}{\partial T}\right)_{V,n} + \frac{2s+1}{V}\frac{1}{(1-z)^2}\left(\frac{\partial z}{\partial T}\right)_{V,n} \tag{7.91}$$

and

$$\begin{aligned}\left(\frac{\partial z}{\partial T}\right)_{V,n} &= -\frac{3}{2}\frac{1}{T\lambda_s^3}g_{\frac{3}{2}}(z)\left[\frac{1}{\lambda_s^3}\frac{1}{z}g_{\frac{1}{2}}(z)+\frac{2s+1}{V}\frac{1}{(1-z)^2}\right]^{-1} = \\ &= -\frac{3}{2}\frac{z}{T}g_{\frac{3}{2}}(z)\left[g_{\frac{1}{2}}(z)+\frac{2s+1}{V}\lambda_s^3\frac{z}{(1-z)^2}\right]^{-1}\end{aligned} \tag{7.92}$$

therefore

$$\begin{aligned}C_V = \frac{3}{2}Nk_B\Bigg[&\frac{5}{2}\frac{v}{\lambda_s^3}g_{\frac{5}{2}}(z)-\frac{2s+1}{N}\ln(1-z)- \\ &\frac{3}{2}\frac{v}{\lambda_s^3}g_{\frac{3}{2}}(z)\frac{\frac{v}{\lambda_s^3}g_{\frac{3}{2}}(z)+\frac{2s+1}{N}\frac{z}{1-z}}{\frac{v}{\lambda_s^3}g_{\frac{1}{2}}(z)+\frac{2s+1}{N}\frac{z}{(1-z)^2}}\Bigg]\end{aligned} \tag{7.93}$$

Concluding, we gather the formulas for the heat capacity at a constant volume of free fermions and bosons

$$\frac{C_V}{Nk_B} = \begin{cases}\dfrac{3}{2}\dfrac{v}{\lambda_s^3}\left[\dfrac{5}{2}f_{\frac{5}{2}}(z)-\dfrac{3}{2}\dfrac{f^2_{\frac{3}{2}}(z)}{f_{\frac{1}{2}}(z)}\right] & \text{(fermions} \\[2ex] \dfrac{3}{2}\dfrac{v}{\lambda_s^3}\left[\dfrac{5}{2}g_{\frac{5}{2}}(z)-\dfrac{3}{2}g_{\frac{3}{2}}(z)\dfrac{\frac{v}{\lambda_s^3}g_{\frac{3}{2}}(z)+\frac{2s+1}{N}\frac{z}{1-z}}{\frac{v}{\lambda_s^3}g_{\frac{1}{2}}(z)+\frac{2s+1}{N}\frac{z}{(1-z)^2}}-\dfrac{2s+1}{N}\ln(1-z)\right] & \text{(bosons)}\end{cases} \tag{7.94}$$

One can show, that in the thermodynamic limit (7.94) reduces to

$$\frac{C_V}{Nk_B} = \begin{cases}\dfrac{3}{2}\dfrac{v}{\lambda_s^3}\left[\dfrac{5}{2}f_{\frac{5}{2}}(z)-\dfrac{3}{2}\dfrac{f^2_{\frac{3}{2}}(z)}{f_{\frac{1}{2}}(z)}\right] & \text{(fermions)} \\[2ex] \dfrac{3}{2}\dfrac{v}{\lambda_s^3}\left[\dfrac{5}{2}g_{\frac{5}{2}}(z)-\dfrac{3}{2}\dfrac{g^2_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)}\right] & \text{(bosons)}\end{cases} \tag{7.95}$$

Chapter 8

Degenerate quantum gas

A gas degeneracy means a deviation from the classical gas behavior and occurrence of quantum features. It starts when a particle de Broglie wavelength λ_{dB} is of the order of magnitude of an average interparticle distance d

$$\lambda_{dB} \sim d \tag{8.1}$$

therefore when the de Broglie waves of particles begin to overlap and interfere. Weakly degenerate gas for which

$$\lambda_{dB} \ll d \tag{8.2}$$

reveals small quantum corrections to the equation of state which very often are negligible and the system can be considered classical. On the other hand for a strongly degenerate gas we have

$$\lambda_{dB} \gg d \tag{8.3}$$

and the quantum effects prevail. Strongly degenerate quantum system is described solely by a quantum statistics. Knowing that the de Broglie wavelength λ_{dB} is of the order of magnitude of the thermal wavelength λ_s we can use a modified degeneracy criterion with (λ_s/d) as a degeneracy parameter

$$\frac{\lambda_s}{d} \ll 1 \quad \text{weak degeneracy} \tag{8.4}$$

$$\frac{\lambda_s}{d} = 1 \quad \text{degeneracy} \tag{8.5}$$

$$\frac{\lambda_s}{d} \gg 1 \quad \text{strong degeneracy} \tag{8.6}$$

A degeneracy condition $\lambda_s = d$ defines a moment when a significant degeneracy of a system takes place and physics is no longer determined by a mere small correction to classical equations but it obeys quantum laws. The degeneracy condition yields a degeneracy temperature T_e

$$1 = \frac{\lambda_s}{V} = \frac{nh^3}{(2s+1)\left(2\pi m k_B T_e\right)^{\frac{3}{2}}} \tag{8.7}$$

$$k_B T = \frac{1}{(2s+1)^{\frac{2}{3}}} \frac{\hbar}{m} n^{\frac{2}{3}} \sim \frac{\hbar^2}{m} n^{\frac{2}{3}} \tag{8.8}$$

For temperatures $T \leqslant T_e$ we have a degenerate gas (electrons in metal), while for $T \gg T_e$ we have a weakly degenerate gas or even an ideal classical gas. The average interparticle distance d determines a proper volume v, that is a volume occupied by a single particle, $v = d^3$ or a particle concentration $n = \frac{1}{v} = d^{-3}$, and becomes large for a low particle concentration

$$d = n^{-\frac{1}{3}} \xrightarrow{n \to 0} \infty \tag{8.9}$$

The thermal wavelength is small for high temperatures

$$\lambda_s \sim \frac{1}{\sqrt{T}} \xrightarrow{T \to \infty} 0 \tag{8.10}$$

Therefore, a weak degeneracy condition

$$\left(\lambda_s \sim \frac{1}{T}\right) \ll \left(d \sim n^{-\frac{1}{3}}\right) \tag{8.11}$$

is achieved in systems of a low particle concentration at high temperatures. The opposite case of a strongly degenerate gas determined by a constraint

$$\left(\lambda_s \sim \frac{1}{\sqrt{T}}\right) \gg \left(d \sim n^{-\frac{1}{3}}\right) \tag{8.12}$$

corresponds to low temperatures

$$\lambda_s \sim \frac{1}{\sqrt{T}} \xrightarrow{T \to 0} \infty \tag{8.13}$$

and high particle concentrations

$$d \sim n^{-\frac{1}{3}} \xrightarrow{n \to \infty} 0 \tag{8.14}$$

Having the degeneracy parameter λ_s/d we can write the chemical potential equations for fermions and bosons, respectively

$$\frac{\lambda_s^3}{v} = f_{\frac{3}{2}}(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{\frac{3}{2}}} \tag{8.15}$$

$$\frac{\lambda_s^3}{v}\left(1 - \frac{(2s+1)}{N}\frac{z}{1-z}\right) = g_{\frac{3}{2}}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{\frac{3}{2}}} \tag{8.16}$$

and based on these equations we can obtain an equivalent degeneracy condition determined by a value of the fugacity z. We see that the weak degeneracy, $\lambda_s \ll d$, for both fermions and bosons corresponds to $z \ll 1$ which means a negative chemical potential $\mu < 0$ and $|\mu|/k_B T \gg 1$. For a weak degeneracy limit we can neglect a term proportional to N^{-1} in the Bose gas equation as it is negligibly small for a large N and vanishes in the thermodynamic limit when $N \to \infty$. From now on, as far as the weak degeneracy limit is concerned, we will drop off this small term and consider a modified equation

$$\frac{\lambda_s^3}{v} = g_{\frac{3}{2}}(z) \tag{8.17}$$

A strong degeneracy, $\lambda_s \gg d$, corresponds to $z \gg 1$ for fermions, that is to $\mu/k_B T \gg 1$. We note, that for bosons $z \leq 1$ and the left hand side of the chemical potential equation (8.17) is upper bounded

$$\frac{\lambda_s^3}{v}\left(1 - \frac{(2s+1)}{N}\frac{z}{1-z}\right) = g_{\frac{3}{2}}(1) \simeq 2.612 \tag{8.18}$$

Therefore, we see that in order to fulfill $\lambda_s \gg d$ criterion we need $z \simeq 1$ and in the thermodynamic limit $z = 1$.

8.1 Weak degeneracy

For a weak degeneracy

$$z = \mathrm{e}^{\beta\mu} \ll 1 \tag{8.19}$$

and we can easily evaluate the integral, where the upper sign concerns fermions and the lower sign corresponds to bosons,

$$\int\limits_0^\infty \frac{\sqrt{\mathcal{E}}\mathrm{d}\mathcal{E}}{z^{-1}\mathrm{e}^{\beta\mathcal{E}} \pm 1} = \int\limits_0^\infty \frac{z\mathrm{e}^{-\beta\mathcal{E}}\sqrt{\mathcal{E}}\mathrm{d}\mathcal{E}}{1 \pm z\mathrm{e}^{\beta\mathcal{E}}} =$$

$$= z\int\limits_0^\infty \mathrm{e}^{-\beta\mathcal{E}}\left[1 \mp z\mathrm{e}^{-\beta\mathcal{E}} + \ldots\right]\sqrt{\mathcal{E}}\mathrm{d}\mathcal{E} =$$

$$= z\beta^{-\frac{3}{2}}\int\limits_0^\infty \left[\sqrt{x}\mathrm{e}^{-x} \mp z\sqrt{x}\mathrm{e}^{-2x} + \ldots\right]\mathrm{d}x = /x = \beta\mathcal{E}/ =$$

$$= z\beta^{-\frac{3}{2}}\frac{\sqrt{\pi}}{2}\left[1 \mp \frac{z}{2^{\frac{3}{2}}} + \ldots\right] \qquad (8.20)$$

thus, neglecting the higher order terms, we have

$$n = \frac{\sqrt{\pi}}{2}\beta^{-\frac{3}{2}}\alpha z\left[1 \mp \frac{z}{2^{\frac{3}{2}}}\right] \text{ (fermions/bosons)} \qquad (8.21)$$

In the zeroth order approximation $z = z_0$

$$n = \frac{\sqrt{\pi}}{2}\beta^{-\frac{3}{2}}\alpha z_0, \qquad (8.22)$$

which gives

$$z_0 = \frac{2n}{\sqrt{\pi}\alpha}\beta^{\frac{3}{2}} = \frac{nh^3}{(2s+1)(2\pi m k_B T)^{\frac{3}{2}}} \qquad (8.23)$$

Therefore in the zeroth order of approximation

$$z_0 = n\lambda_s^3 \qquad (8.24)$$

Fugacity in the first order approximation

$$n = \frac{\sqrt{\pi}}{2}\beta^{-\frac{3}{2}}az\left[1 \mp \frac{z}{2^{\frac{3}{2}}}\right] \qquad (8.25)$$

$$z = \frac{2n}{\sqrt{\pi}a(k_B T)^{\frac{3}{2}}}\left[1 \mp \frac{z}{2^{\frac{3}{2}}}\right]^{-1} = z_0\left[1 \mp \frac{z}{2^{\frac{3}{2}}}\right]^{-1} =$$

$$= \frac{z_0}{1 \mp \frac{z_0}{2^{\frac{3}{2}}}} = z_0 \left[1 \pm \frac{z_0}{2^{\frac{3}{2}}} \right] \tag{8.26}$$

therefore the chemical potential

$$\mu = k_B T \left[\ln z_0 + \ln \left(1 \pm \frac{z_0}{2^{\frac{3}{2}}} \right) \right] = k_B T \left[\ln z_0 \pm \frac{z_0}{2^{\frac{3}{2}}} \right] \tag{8.27}$$

which is the chemical potential in the first order approximation (first iteration). In this approximation

$$z_0 = \mathrm{e}^{\frac{\mu}{k_B T}} \tag{8.28}$$

thus

$$\mu = \mu_0 \pm \frac{1}{2^{\frac{3}{2}} k_B T \mathrm{e}^{\frac{\mu_0}{k_B T}}} \tag{8.29}$$

where

$$\mu_0 = k_B T \ln z_0 = k_B T \ln \frac{n h^3}{(2s+1)\left(2\pi m k_B T\right)^{\frac{3}{2}}} \tag{8.30}$$

8.2 Strong degeneracy

For a strongly degenerate Fermi gas

$$z = \mathrm{e}^{\beta\mu} \gg 1 \tag{8.31}$$

which yields $\mu > 0$ and $\mu \gg k_B T$. We start with the evaluation of an integral

$$\int_0^\infty F(\mathcal{E}) \frac{\partial f}{\partial \mathcal{E}} \mathrm{d}\mathcal{E} \tag{8.32}$$

where $F(\mathcal{E})$ is a differentiable slowly varying function of the energy which can be approximated by the expansion

$$F(\mathcal{E}) = F(\mu) + (\mathcal{E} + \mu) F'(\mu) + \frac{(\mathcal{E} - \mu)^2}{2} F''(\mu) \tag{8.33}$$

$f(\mathcal{E})$ is the Fermi-Dirac distribution function

$$f(\mathcal{E}) = \frac{1}{\mathrm{e}^{\beta(\mathcal{E} - \mu)} + 1} \tag{8.34}$$

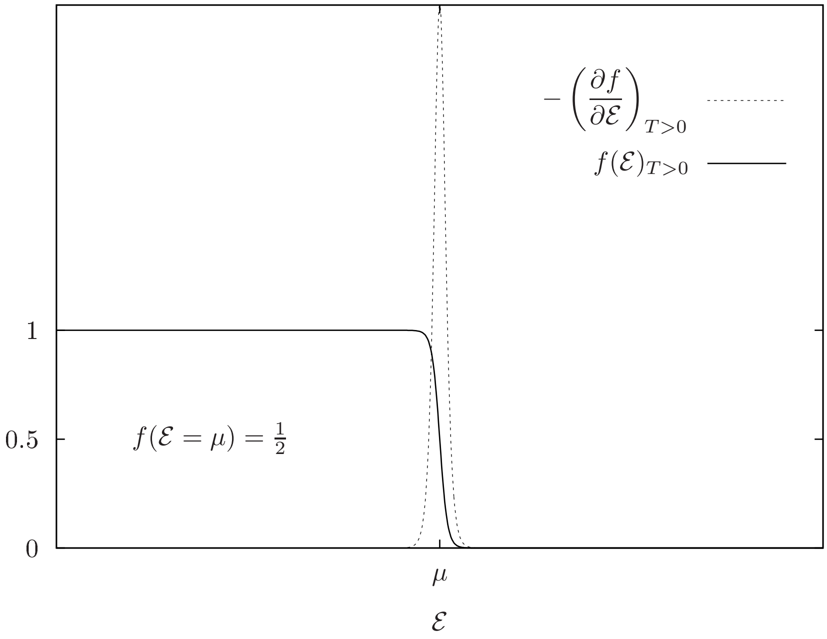


Figure 8.1: Fermi-Dirac distribution and its derivative

which for a degenerate gas is plotted in Fig. 8.1

$$\frac{\partial f}{\partial \mathcal{E}} = -\frac{\beta \mathrm{e}^{\beta(\mathcal{E}-\mu)}}{\left(\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1\right)^2} = \\ -\frac{1}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}} \frac{\beta \mathrm{e}^{\beta(\mathcal{E}-\mu)}}{\left(\mathrm{e}^{\frac{1}{2}\beta(\mathcal{E}-\mu)}+\mathrm{e}^{-\frac{1}{2}\beta(\mathcal{E}-\mu)}\right)^2} = -\frac{\beta}{4}\cosh^{-2}\left[\frac{\beta}{2}(\mathcal{E}-\mu)\right] \quad (8.35)$$

We compute the integral (8.32) using a new variable

$$x = \beta(\mathcal{E}-\mu) \quad (8.36)$$

$$\mathcal{E} = \frac{x}{\beta}+\mu \quad (8.37)$$

$$\mathrm{d}\mathcal{E} = \frac{1}{\beta}\mathrm{d}x \quad (8.38)$$

$$\frac{\partial f}{\partial \mathcal{E}} = \frac{\partial f}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}\mathcal{E}} = \beta \frac{\partial f}{\partial x} \tag{8.39}$$

hence

$$\int\limits_{0}^{\infty} F(\mathcal{E})\frac{\partial f}{\partial \mathcal{E}}\mathrm{d}\mathcal{E} = \beta \int\limits_{-\beta\mu}^{\infty} F\left(\frac{x}{\beta}+\mu\right)\frac{\partial f}{\partial x}\frac{\mathrm{d}x}{\beta} = \int\limits_{-\beta\mu}^{\infty} F\left(\mu+\frac{x}{\beta}+\mu\right)\frac{\partial f}{\partial x}\mathrm{d}x \tag{8.40}$$

Because for a strongly degenerate Fermi gas

$$\beta\mu = \frac{\mu}{k_B T} \gg 1 \ \Rightarrow\ -\beta\mu \to -\infty \tag{8.41}$$

we can substitute $-\infty$ for the lower limit in the integral (8.40) which reads

$$\begin{aligned}
\int\limits_{-\infty}^{\infty} F\left(\mu+\frac{x}{\beta}\right)\frac{\partial f}{\partial x}\mathrm{d}x &= \int\limits_{-\infty}^{\infty}\left[F(\mu)+F'(\mu)\frac{x}{\beta}+\frac{1}{2}F''(\mu)\frac{x^2}{\beta^2}\right]\frac{\partial f}{\partial x}\mathrm{d}x = \\
&= F(\mu)\int\limits_{-\infty}^{\infty}\frac{\partial f}{\partial x}\mathrm{d}x + \frac{F'(\mu)}{\beta}\int\limits_{-\infty}^{\infty} x\frac{\partial f}{\partial x}\mathrm{d}x + \frac{1}{2}\frac{F''(\mu)}{\beta^2}\int\limits_{-\infty}^{\infty} x^2\frac{\partial f}{\partial x}\mathrm{d}x = \\
&= F(\mu)\left[f(x=\infty)-f(x=-\infty)\right] - \frac{1}{8}\frac{F''(\mu)}{\beta^2}\int\limits_{-\infty}^{\infty} x^2\cosh^{-2}\frac{x}{2}\mathrm{d}x
\end{aligned} \tag{8.42}$$

where we have used

$$\frac{\partial f}{\partial x} = \frac{1}{\beta}\frac{\partial f}{\partial \mathcal{E}} = -\frac{1}{4}\cosh^{-2}\frac{x}{2} \tag{8.43}$$

and noted that $x\dfrac{\partial f}{\partial x}$ is an odd function

$$\int\limits_{-\infty}^{\infty} x\frac{\partial f}{\partial x}\mathrm{d}x = -\frac{1}{4}\int\limits_{-\infty}^{\infty} x\cosh^{-2}\frac{x}{2}\mathrm{d}x = 0 \tag{8.44}$$

Since $f(x=\infty)=0$ and $f(x=-\infty)=1$ we have

$$F(\mu)\left[f(x=\infty)-f(x=-\infty)\right]-\frac{1}{8}\frac{F''(\mu)}{\beta^2}\int\limits_{-\infty}^{\infty}x^2\cosh^{-2}\frac{x}{2}\mathrm{d}x=$$

$$-F(\mu)-\frac{1}{8}\frac{F''(\mu)}{\beta^2}\int\limits_{-\infty}^{\infty}x^2\cosh^{-2}\frac{x}{2}\mathrm{d}x=$$

$$-F(\mu)-\frac{1}{8}\frac{F''(\mu)}{\beta}\int\limits_{-\infty}^{\infty}4y^2\cosh^{-2}y\mathrm{d}(2y)=$$

$$-F(\mu)-\frac{F''(\mu)}{\beta^2}\int\limits_{-\infty}^{\infty}\frac{y^2}{\cosh^{-2}y}\mathrm{d}y=-f(\mu)-\frac{\pi^2}{6}\frac{F''(\mu)}{\beta^2}\tag{8.45}$$

where we have used

$$\int\limits_{-\infty}^{\infty}\frac{y^2}{\cosh^2 y}\mathrm{d}y=\frac{\pi^2}{6}\tag{8.46}$$

Therefore, we have obtained

$$\int\limits_{0}^{\infty}F(\mathcal{E})\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E}=-F(\mu)-\frac{\pi^2}{6}k_B^2T^2F''(\mu)\tag{8.47}$$

In the zeroth order approximation in temperature

$$\int\limits_{0}^{\infty}F(\mathcal{E})\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E}=-F(\mu)\tag{8.48}$$

so we may write $\dfrac{\partial f}{\partial\mathcal{E}}=-\delta(\mathcal{E}-\mu)$. In the second order approximation

$$\int\limits_{0}^{\infty}F(\mathcal{E})\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E}=-F(\mu)-\frac{\pi^2}{6}k_B^2T^2F''(\mu)\tag{8.49}$$

where $\dfrac{k_BT}{\mu}$ is a small parameter. If F is a power function of the energy, like $\mathcal{E}^{\frac{1}{2}}$ in a calculation of the number of particles or $\mathcal{E}^{\frac{3}{2}}$ in the internal energy calculation, we can estimate a second derivative with respect to the energy $F''(\mu) \sim F(\mu)/\mu^2$ and obtain the order of magnitude of the second order term

$$-\frac{\pi^2}{6}k_B^2T^2F''(\mu) \sim F(\mu)\left(\frac{k_BT}{\mu}\right)^2 \tag{8.50}$$

8.2.1 Chemical potential and particle concentration

The condition for the chemical potential reads

$$n = \alpha\int\limits_0^\infty \frac{\sqrt{\mathcal{E}}\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} \tag{8.51}$$

and we can easily evaluate this integral

$$\begin{aligned}\int\limits_0^\infty \frac{\sqrt{\mathcal{E}}\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} = \int\limits_0^\infty \frac{\left(\frac{2}{3}\mathcal{E}^{\frac{3}{2}}\right)'\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} = \frac{2}{3}\int\limits_0^\infty \left(\mathcal{E}^{\frac{3}{2}}\right)' f(\mathcal{E})\mathrm{d}\mathcal{E} = \\ \frac{2}{3}\mathcal{E}^{\frac{3}{2}}f(\mathcal{E})\Big|_0^\infty - \frac{2}{3}\int\limits_0^\infty \mathcal{E}^{\frac{3}{2}}\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E} = \frac{2}{3}\mu^{\frac{3}{2}} + \frac{2}{3}\frac{1}{6}\pi^2k_B^2T^2\left(\mathcal{E}^{\frac{3}{2}}\right)''_{\mathcal{E}=\mu} = \\ \frac{2}{3}\mu^{\frac{3}{2}} + \frac{2}{3}\frac{1}{6}\pi^2k_B^2T^2\frac{3}{4}\frac{1}{\sqrt{\mu}} = \frac{2}{3}\mu^{\frac{3}{2}} + \frac{2}{3}\frac{\pi^2}{12}\frac{k_B^2T^2}{\sqrt{\mu}}\end{aligned} \tag{8.52}$$

Therefore

$$n = \alpha\left[\frac{2}{3}\mu^{\frac{3}{2}} + \frac{\pi^2}{12}\frac{k_B^2T^2}{\sqrt{\mu}}\right] \tag{8.53}$$

We define the chemical potential μ_0 in the zeroth order approximation (for $T = 0$)

$$n = \alpha\frac{2}{3}\mu_0^{\frac{3}{2}} \tag{8.54}$$

that is

$$\mu_0 = \left(\frac{3n}{2\alpha}\right)^{\frac{2}{3}} \tag{8.55}$$

and substitute

$$a = \frac{4\sqrt{2}}{h^3}\pi m^{\frac{3}{2}}(2s+1) \tag{8.56}$$

which gives us

$$\mu_0 = \left(\frac{3nh^3}{2\cdot 4\sqrt{2}\pi m^{\frac{3}{2}}(2s+1)}\right)^{\frac{2}{3}} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \tag{8.57}$$

Note, that we can obtain the same result by taking a direct product of the density of states in the momentum space and the volume occupied by the ground state in the momentum space

$$N = \frac{2V}{(2\pi\hbar)^3}\frac{4}{3}\pi p_F^3 \tag{8.58}$$

$$N = \frac{2V}{h^3}\frac{4}{3}\pi p_F^3 \tag{8.59}$$

$$n = \frac{8\pi}{3}\frac{p_F^3}{h^3} \tag{8.60}$$

where p_F is the Fermi momentum

$$p_F = h\left(\frac{3n}{8\pi}\right)^{\frac{1}{3}} \tag{8.61}$$

$$\mu_0 = \frac{p_F^2}{2m} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \tag{8.62}$$

The Fermi energy $\mathcal{E}_F = \mu_0 = \mu(T=0)$ is the maximal energy of occupied states at $T = 0$, states with energy larger than $\mathcal{E}_F$ are empty, see Fig 8.2,

$$\langle n_{\boldsymbol{p}}\rangle_{T=0} = \lim_{T\to 0}\frac{1}{\mathrm{e}^{\frac{\mathcal{E}_{\boldsymbol{p}}-\mu}{k_BT}}+1} = \lim_{T\to 0}\frac{1}{\mathrm{e}^{\frac{\mathcal{E}_{\boldsymbol{p}}-\mathcal{E}_F}{k_BT}}+1} =$$

$$\theta(\mathcal{E}_F - \mathcal{E}_{\boldsymbol{p}}) = \begin{cases} 1 & \text{for } \mathcal{E}_{\boldsymbol{p}} < \mathcal{E}_F \\ 0 & \text{for } \mathcal{E}_{\boldsymbol{p}} > \mathcal{E}_F \end{cases} \tag{8.63}$$

8.2.2 Fermi temperature and Fermi energy

We apply the following condition for a gas degeneracy

$$z \ll e \text{ – classical or weakly degenerate electron gas} \tag{8.64}$$

$$z \geqslant \mathrm{e} = 2.71 \sim 1 \text{ – degenerate electron gas} \tag{8.65}$$

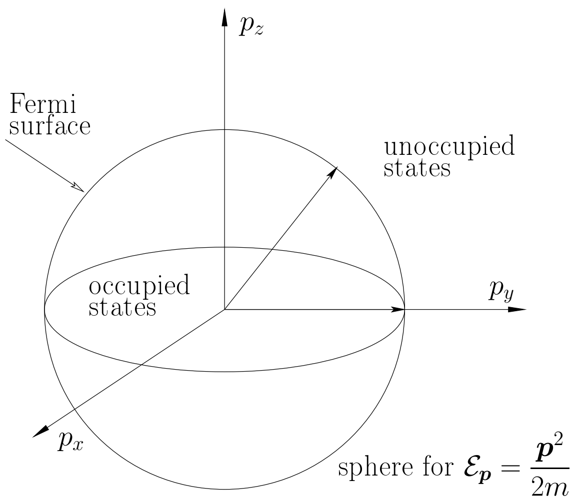


Figure 8.2: Fermi sphere

$$z \gg e \sim 1 \text{ – strongly degenerate electron gas} \tag{8.66}$$

$$z = \mathrm{e}^{\frac{\mu_0}{k_B T}} \geqslant \mathrm{e} = \mathrm{e}^{\frac{\mu_0}{k_B T_F}} \tag{8.67}$$

where $\dfrac{\mu_0}{k_B T_F} = 1$ and T_F is the Fermi temperature

$$k_B T_F = \mu_0 = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \tag{8.68}$$

Note, that

$$k_B T_F = \frac{h^2}{m} n^{\frac{2}{3}} \cdot \frac{1}{2}\left(\frac{3}{8\pi}\right) \sim \frac{h^2}{m} n^{\frac{2}{3}} \sim k_B T_e. \tag{8.69}$$

Therefore, gas is degenerate for temperatures

$$T \leqslant T_F \text{ – degenerate electron gas} \tag{8.70}$$

and gas is classical (weakly degenerate) for

$$T \gg T_F \text{ – classical electron gas} \tag{8.71}$$

For metals the Fermi energy

$$\mathcal{E}_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \tag{8.72}$$

with one free electron per atom and an interatomic distance $a = 1.5$ Å $= 1.5 \cdot 10^{-10}$ m

$$n = \frac{1}{a^3} = \frac{1}{(1.5)^3} \cdot 10^{30}\ \mathrm{m}^{-3}, \tag{8.73}$$

electron mass $m = 9.11 \cdot 10^{-31}$ kg, $h = 6.63 \cdot 10^{-34}$ Js, $k_B = 1.38 \cdot 10^{-23} \frac{\mathrm{J}}{\mathrm{K}}$ we get

$$\mathcal{E}_F \approx 0.26 \cdot 10^{-17}\ \mathrm{J} \approx 10\ \mathrm{eV} \tag{8.74}$$

and

$$T_F = \frac{\mathcal{E}_F}{k_B} = \frac{0.26 \cdot 10^{-17}}{1.38 \cdot 10^{-23}}\ \mathrm{K} \approx 1.9 \cdot 10^4\ \mathrm{K} \sim 10^4\ \mathrm{K} \tag{8.75}$$

Conclusion: electrons in metals form a degenerate electron gas.

8.2.3 Temperature dependence of the chemical potential

In the second order approximation, that is when we keep terms of the order of magnitude $\left(\frac{k_B T}{\mu}\right)^2$ we have the following condition for the chemical potential μ:

$$n = a\left[\frac{2}{3}\mu^{\frac{3}{2}} + \frac{\pi^2}{12}\frac{k_B^2 T^2}{\sqrt{\mu}}\right] = a\frac{2}{3}\mu^{\frac{3}{2}}\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right] \tag{8.76}$$

which yields

$$\mu = \left(\frac{3n}{2a}\right)^{\frac{2}{3}}\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right]^{-\frac{2}{3}} = \mu_0\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right]^{-\frac{2}{3}} \tag{8.77}$$

We have obtained a self-consistent equation for the chemical potential which can be solved through a series expansion with respect to a small term $\left(\frac{k_B T}{\mu}\right)^2 \approx \left(\frac{k_B T}{\mu_0}\right)^2 = \left(\frac{T}{T_F}\right)^2 \ll 1$

$$\mu = \mu_0 \left[1 + \underbrace{\frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2}_{\text{small}} \right]^{-\frac{2}{3}} \approx \mu_0 \left[1 + \left(-\frac{2}{3}\right)\frac{\pi^2}{8}\left(\frac{k_B T}{\mu_0}\right)^2 \right] =$$

$$\mu_0 \left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\mu_0}\right)^2 \right] \tag{8.78}$$

Therefore, we have obtained a temperature dependence of the chemical potential with the order of magnitude of $\left(\frac{k_B T}{\mu_0}\right)^2 = \left(\frac{T}{T_F}\right)^2$.

8.3 Role of system dimensionality

8.3.1 Two-dimensional ideal gas

The chemical potential equation

$$n = \alpha_{2D} \int_0^\infty \frac{\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)} \pm 1} \tag{8.79}$$

where we have used a two-dimensional density of states, $\nu_{2D}(\mathcal{E}) = \alpha_{2D} V$ with $V = S$ representing the system surface area, is easily integrated for fermions

$$n = -\frac{\alpha_{2D}}{\beta} \ln\left[\mathrm{e}^{\beta(\mu-\mathcal{E})} + 1\right]\Big|_0^\infty = \alpha_{2D} k_B T \ln[1+z] \tag{8.80}$$

and for bosons

$$n = \frac{\alpha_{2D}}{\beta} \ln\left[\mathrm{e}^{\beta(\mu-\mathcal{E})} - 1\right]\Big|_0^\infty = -\alpha_{2D} k_B T \ln[1-z] \tag{8.81}$$

where we note, that $n > 0$ since $0 > z > 1$. We have obtained the above equations for an arbitary value of the fugacity, which means that we can easily establish the chemical potential for an ideal two-dimensional gas based on an analytical formula. Then we can obtain the equation of state through a relation

$$P = \pm k_B T \alpha_{2D} \int_0^\infty \ln\left(1 \pm z\mathrm{e}^{-\beta\mathcal{E}}\right) \mathrm{d}\mathcal{E} \tag{8.82}$$

When we introduce an average interparticle distance d

$$n = \frac{1}{v} = d^{-2} \tag{8.83}$$

and define a two-dimensional system the thermal wavelength

$$\lambda_{s_{2D}} = \frac{1}{(2s+1)^{\frac{1}{2}}} \frac{h}{\sqrt{2\pi m k_B T}}. \tag{8.84}$$

we can write the chemical potential equation in the form

$$\left(\frac{\lambda_{S_{2D}}}{d}\right)^2 = \ln\left[1 \pm z\right] \tag{8.85}$$

where we have used a relation between the density of states and the thermal wavelength $\alpha_{2D} k_B T = \lambda_{S_{2D}}^{-2}$ and note that

$$\alpha_{2D} k_B T = \frac{2\pi m}{h^2}(2s+1) k_B T = \lambda_{s_{2D}}^{-2}, \tag{8.86}$$

We see that the weak degeneracy limit corresponds to $z \ll 1$ whereas the strong degeneracy is determined by $z \gg 1$ for fermions and $z \approx 1$ for bosons. For a weak degeneracy, $z \ll 1$,

$$\left(\frac{\lambda_{s_{2D}}}{d}\right)^2 = z \mp \frac{z^2}{2} \tag{8.87}$$

and solving this equation in an iterative way keeping up to the second order terms in $\left(\frac{\lambda_{s_{2D}}}{d}\right)^2$ we get

$$z = \left(\frac{\lambda_{s_{2D}}}{d}\right)^2 \pm \frac{1}{2}\left(\frac{\lambda_{s_{2D}}}{d}\right)^4 \tag{8.88}$$

and the chemical potential

$$\mu = k_B T \left[\ln z_0 + \ln\left(1 \pm \frac{1}{2} z_0\right)\right] \approx k_B T \left[\ln z_0 \pm \frac{1}{2} z_0\right] \tag{8.89}$$

where

$$z_0 = \left(\frac{\lambda_{s_{2D}}}{d}\right)^2 = \frac{\lambda_{S_{2D}}^2}{v} \tag{8.90}$$

is the fugacity in the zeroth order approximation and corresponds to μ_0

$$\mu_0 = k_B T \ln z_0 = k_B T \ln \frac{nh^2}{(2s+1)2\pi m k_B T}. \tag{8.91}$$

Therefore, one can write the chemical potential

$$\mu = \mu_0 \pm \frac{1}{2} k_B T \mathrm{e}^{\frac{\mu_0}{k_B T}} \tag{8.92}$$

The equation of state for a weakly degenerate gas is obtained by an expansion with respect to a small term $z\mathrm{e}^{-\beta\mathcal{E}}$ of (8.82)

$$P = \pm k_B T \alpha_{2D} \int\limits_0^\infty \left(\pm z\mathrm{e}^{-\beta\mathcal{E}} \mp \frac{1}{2} z^2 \mathrm{e}^{-2\beta\mathcal{E}} \right) \mathrm{d}\mathcal{E} \tag{8.93}$$

and rearanged into

$$\frac{P}{k_B T} = \alpha_{2D} z \int\limits_0^\infty \left(\mathrm{e}^{-\beta\mathcal{E}} \mp \frac{1}{2} z \mathrm{e}^{-2\beta\mathcal{E}} \right) \mathrm{d}\mathcal{E} \tag{8.94}$$

Substituting $z = z_0$ we obtain

$$\frac{P}{k_B T} = \frac{1}{v} \left[\int\limits_0^\infty \mathrm{e}^{-x} \mathrm{d}x \mp \frac{1}{2} z_0 \int\limits_0^\infty \mathrm{e}^{-2x} \mathrm{d}x \right] \tag{8.95}$$

and after the integral the equation of state of a weakly degenerate gas reads

$$\frac{Pv}{k_B T} = 1 \mp \frac{z_0}{2^2} \tag{8.96}$$

or written for N particles

$$\frac{PV}{N k_B T} = 1 \mp \frac{z_0}{2^2}. \tag{8.97}$$

A quantum correction to the classical equation of state $PV = N k_B T$ reads $N k_B T z_0/4$ and since $z_0 \sim (k_B T)^{-1}$ is temperature independent.

8.3.2 One-dimensional ideal gas

Applying a one-dimensional density of states

$$\nu_{1D}(\mathcal{E}) = \alpha_{1D} V \mathcal{E}^{-\frac{1}{2}}, \tag{8.98}$$

where $V = L$ is the system length yields the chemical potential equation

$$n = \alpha_{1D} \int\limits_0^\infty \frac{\mathcal{E}^{-\frac{1}{2}} \mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)} \pm 1} \tag{8.99}$$

where the upper sign concerns fermions and the lower sign corresponds to bosons. Introducing the interparticle distance $d = n^{-1}$ and the thermal wavelength in one dimension

$$\lambda_{s_{1D}} = \frac{1}{(2s+1)} \frac{h}{\sqrt{2\pi m k_B T}} \tag{8.100}$$

we have

$$\frac{\lambda_{s_{1D}}}{d} = \frac{z}{\sqrt{\pi}} \int\limits_0^\infty \frac{x^{-\frac{1}{2}} \mathrm{d}x}{\mathrm{e}^x \pm z} \tag{8.101}$$

where we have used a relation $\alpha_{1D} = \left(\sqrt{\pi k_B T \lambda_{s_{1D}}}\right)^{-1}$. We note, that again a weak degeneracy corresponds to $z \ll 1$ and for a weakly degenerate gas we have

$$\begin{aligned} \frac{z}{\sqrt{\pi}} \int\limits_0^\infty \frac{x^{-\frac{1}{2}} \mathrm{d}x}{\mathrm{e}^x \pm z} &\approx \frac{z}{\sqrt{\pi}} \left[\int\limits_0^\infty x^{-\frac{1}{2}} \mathrm{e}^{-x} \mathrm{d}x \mp z \int\limits_0^\infty x^{-\frac{1}{2}} \mathrm{e}^{-2x} \mathrm{d}x \right] \\ &= \frac{z}{\sqrt{\pi}} \Gamma\left(\frac{1}{2}\right) \left[1 \mp \frac{1}{\sqrt{2}} z\right] = z \left[1 \mp \frac{1}{\sqrt{2}} z\right] \end{aligned} \tag{8.102}$$

Thus we have

$$\frac{\lambda_{s_{1D}}}{d} = z \left[\mp \frac{1}{\sqrt{2}} z\right] \tag{8.103}$$

and an iterative solution for z yields

$$z = \left(\frac{\lambda_{s_{1D}}}{d}\right) \pm \frac{1}{\sqrt{2}} \left(\frac{\lambda_{s_{1D}}}{d}\right)^2 \tag{8.104}$$

and the chemical potential

$$\mu = k_B T \left[\ln z_0 + \ln \left(1 \pm \frac{1}{\sqrt{2}} z_0 \right) \right] \approx k_B T \left[\ln z_0 \pm \frac{1}{\sqrt{2}} z_0 \right] \tag{8.105}$$

where $z_0 = \left(\frac{\lambda_{s_{1D}}}{d} \right)$ is the fugacity in the zeroth order approximation and corresponds to μ_0

$$\mu_0 = k_B T \ln \frac{nh}{(2s+1)\sqrt{2\pi m k_B T}} \tag{8.106}$$

Therefore, one can write the chemical potential

$$\mu = \mu_0 \pm \frac{1}{\sqrt{2}} k_B T \mathrm{e}^{\frac{\mu_0}{k_B T}} \tag{8.107}$$

Equation of state of a weakly degenerate gas

$$\frac{Pv}{k_B T} = \frac{1}{\sqrt{\pi}} \left[\int_0^\infty x^{-\frac{1}{2}} \mathrm{e}^{-x} \mathrm{d}x \mp \frac{1}{2} z_0 \int_0^\infty x^{-\frac{1}{2}} \mathrm{e}^{-2x} \mathrm{d}x \right] \tag{8.108}$$

after the integral reads

$$\frac{Pv}{k_B T} = \frac{1}{\sqrt{\pi}} \Gamma \left(\frac{1}{2} \right) \left[1 \mp \frac{z_0}{2^{\frac{3}{2}}} \right] \tag{8.109}$$

and since $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$ we have

$$\frac{Pv}{k_B T} = 1 \mp \frac{z_0}{2^{\frac{3}{2}}}, \tag{8.110}$$

where the quantum correction to the classical equation of state

$$k_B T \frac{z_0}{2^{\frac{3}{2}}} \sim k_B T \left(k_B T \right)^{-\frac{1}{2}} \sim \sqrt{k_B T} \tag{8.111}$$

vanishes at zero temperature.

Chapter 9

Thermodynamics of a Fermi gas

We start with the grand potential

$$\begin{aligned}\Omega = -k_B T \ln \theta(z, V, T) = \\ -k_B T \ln \prod_{\boldsymbol{p}} \left(1 + z\mathrm{e}^{-\beta \mathcal{E}_{\boldsymbol{p}}}\right) = -k_B T \sum_{\boldsymbol{p}} \ln \left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}\right)\end{aligned} \tag{9.1}$$

and using the density of states we can write

$$\Omega = -k_B T \alpha V \int\limits_0^\infty \ln \left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}\right) \sqrt{\mathcal{E}}\, \mathrm{d}\mathcal{E} \tag{9.2}$$

We evaluate the above integral

$$\begin{aligned}\int\limits_0^\infty \ln \left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}\right) \sqrt{\mathcal{E}}\, \mathrm{d}\mathcal{E} = \frac{2}{3} \int\limits_0^\infty \left(\mathcal{E}^{\frac{3}{2}}\right)' \ln \left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}\right) \mathrm{d}\mathcal{E} = \\ = \frac{2}{3} \mathcal{E}^{\frac{3}{2}} \ln \left(1 + \mathrm{e}^{\beta(\mu - \mathcal{E})}\right)\Big|_0^\infty - \int\limits_0^\infty \frac{2}{3} \mathcal{E}^{\frac{3}{2}} \frac{-\beta \mathrm{e}^{\beta(\mu - \mathcal{E})}}{1 + \mathrm{e}^{\beta(\mu - \mathcal{E}_{\boldsymbol{p}})}} \mathrm{d}\mathcal{E} = \\ = \frac{2}{3} \beta \int\limits_0^\infty \frac{\mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}_{\boldsymbol{p}} - \mu)} + 1} = \frac{2}{3} \beta \int\limits_0^\infty f(\mathcal{E}) \mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E}\end{aligned} \tag{9.3}$$

and comparing it with the internal energy

$$U = \sum_{\boldsymbol{p}} \mathcal{E}_{\boldsymbol{p}} \overline{n}_{\boldsymbol{p}} = \sum_{\boldsymbol{p}} \frac{\mathcal{E}_{\boldsymbol{p}}}{\mathrm{e}^{\beta(\mathcal{E}_{\boldsymbol{p}}-\mu)}+1} = \alpha V \int_0^\infty \frac{\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} \sqrt{\mathcal{E}}\,\mathrm{d}\mathcal{E} =$$

$$= \alpha V \int_0^\infty \frac{\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E}}{\mathrm{e}^{\beta(\mathcal{E}-\mu)}+1} = \alpha V \int_0^\infty f(\mathcal{E})\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E} \tag{9.4}$$

we get

$$\Omega = -k_B T \frac{2}{3} \beta U = -\frac{2}{3} U \tag{9.5}$$

From the thermodynamic definition of the grand potential

$$\Omega = -PV \tag{9.6}$$

we have

$$PV = \frac{2}{3} U \tag{9.7}$$

which is the same relation as holds for the Boltzmann gas. Using the identity (9.5) we can represent the entropy as a temperature derivative of the internal energy

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -\left(\frac{\partial}{\partial T}\left(-\frac{2}{3}U\right)\right)_{V,\mu} = \frac{2}{3}\left(\frac{\partial U}{\partial T}\right)_{V,\mu} \tag{9.8}$$

In the following subsections we discuss thermodynamic properties a Fermi gas in a low and strong degenaracy regimes.

9.1 Weak degeneracy

The internal energy is determined by an integral which for a weakly degenerate system can be approximated as follows

$$U = \alpha V \int_0^\infty \frac{\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E}}{z^{-1}\mathrm{e}^{\beta\mathcal{E}}+1} = \alpha V z \int_0^\infty \mathrm{e}^{-\beta\mathcal{E}} \left[1 - z\mathrm{e}^{-\beta\mathcal{E}} + \ldots\right] \mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E} =$$

$$\alpha V z \beta^{-\frac{5}{2}} \int_0^\infty \left[x^{\frac{3}{2}} - z x^{\frac{3}{2}} \mathrm{e}^{-2x} + \ldots\right] \mathrm{d}x = \alpha V \beta^{-\frac{5}{2}} \Gamma\left(\frac{5}{2}\right) z \left[1 - \frac{z}{2^{\frac{5}{2}}}\right] \tag{9.9}$$

where we have used a definition of the gamma function $\Gamma(z) = \int\limits_0^\infty x^{z-1}\mathrm{e}^{-x}\mathrm{d}x$ for the evaluation of the integrals above

$$\int\limits_0^\infty x^{\frac{3}{2}}\mathrm{e}^{-x}\mathrm{d}x = \int\limits_0^\infty x^{\frac{5}{2}-1}\mathrm{e}^{-x}\mathrm{d}x = \Gamma\left(\frac{5}{2}\right) \tag{9.10}$$

$$\int\limits_0^\infty x^{\frac{3}{2}}\mathrm{e}^{-2x}\mathrm{d}x = \int\limits_0^\infty \left(\frac{x}{2}\right)^{\frac{3}{2}}\mathrm{e}^{-y}\frac{\mathrm{d}y}{2} = \frac{1}{2^{\frac{5}{2}}}\int\limits_0^\infty y^{\frac{3}{2}}\mathrm{e}^{-y}\mathrm{d}y = \frac{1}{2^{\frac{5}{2}}}\Gamma\left(\frac{5}{2}\right) \tag{9.11}$$

and $\Gamma\left(\frac{5}{2}\right) = \frac{3}{4}\sqrt{\pi}$. Taking the fugacity in the second order approximation $z = z_0 + \frac{1}{2^{3/2}}z_0^2$, where $z_0 = \frac{2n}{\sqrt{\pi}\,\alpha}\beta^{\frac{3}{2}}$, and keeping up to the first order terms in z_0 we obtain the internal energy

$$U = \frac{3}{2}Nk_BT\left[1 + \frac{z_0}{2^{\frac{5}{2}}}\right] \tag{9.12}$$

and by a virtue of relation (9.5) the equation of state

$$PV = \frac{2}{3}U = Nk_BT\left[1 + \frac{z_0}{2^{\frac{5}{2}}}\right] \tag{9.13}$$

We note that the pressure exceeds that of an ideal classical gas.

9.2 Strong degeneracy

The internal energy integral for a strong degeneracy system can be evaluated by the integration by parts

$$\begin{aligned} U = \alpha V\int\limits_0^\infty f(\mathcal{E})\mathcal{E}^{\frac{3}{2}}\mathrm{d}\mathcal{E} = \alpha V\frac{2}{5}\int\limits_0^\infty f(\mathcal{E})\mathrm{d}\mathcal{E}^{\frac{5}{2}} = \\ \frac{2}{5}\alpha V f(\mathcal{E})\mathcal{E}^{\frac{5}{2}}\Big|_0^\infty - \frac{2}{5}\alpha V\int\limits_0^\infty \mathcal{E}^{\frac{5}{2}}\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E} = -\frac{2}{5}\alpha V\int\limits_0^\infty \mathcal{E}^{\frac{5}{2}}\frac{\partial f}{\partial\mathcal{E}}\mathrm{d}\mathcal{E} = \\ -\frac{2}{5}\alpha V\left[-\mu^{\frac{5}{2}} - \frac{1}{6}\pi^2k_B^2T^2\left(\mathcal{E}^{\frac{5}{2}}\right)''_{\mathcal{E}=\mu}\right] = \frac{2}{5}\alpha V\left[\mu^{\frac{5}{2}} + \frac{1}{6}\pi^2k_B^2T^2\frac{5}{2}\frac{3}{2}\mu^{\frac{1}{2}}\right] \end{aligned} \tag{9.14}$$

Taking into account a temperature dependence of the chemical potential

$$\mu = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 \right] \tag{9.15}$$

and its dependence on the particle concentration

$$\alpha \frac{2}{3} \mu_0^{\frac{3}{2}} = n \tag{9.16}$$

we get, with the order of magnitude of $\left(\frac{k_B T}{\mu_0} \right)^2$

$$U = \frac{3}{5} n V \mu_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 \right] = \frac{3}{5} N \mu_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 \right] \tag{9.17}$$

At $T = 0$ we have $U = U_0 = \frac{3}{5} N \mu_0$ and we can calculate the energy per particle

$$\frac{U_0}{N} = \frac{3}{5} \mu_0 = \frac{3}{5} \mathcal{E}_F = \frac{3h^2}{10m} \left(\frac{3n}{8\pi} \right)^{\frac{2}{3}} \tag{9.18}$$

for electrons ($s = \frac{1}{2}$). Pressure of a degenerate Fermi gas

$$P = \frac{1}{V} \frac{2}{3} U = \frac{2}{5} n \mu_0 \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 \right] \tag{9.19}$$

For $T = 0$ we have $P = P_0$

$$P_0 = \frac{2}{5} n \mu_0 = \frac{1}{5} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} n^{\frac{5}{3}} \tag{9.20}$$

for electrons $s = \frac{1}{2}$. Note a nonzero pressure even for $T = 0$ – Pauli exclusion principle. The entropy of a strongly degenerate Fermi gas

$$\begin{aligned} S &= \frac{2}{3} \alpha V \frac{\partial}{\partial T} \int_0^\infty f(\mathcal{E}) \mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E} = \frac{2}{3} k_B \alpha V \frac{\partial}{\partial (k_B T)} \int_0^\infty f(\mathcal{E}) \mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E} \\ &= \frac{2}{3} k_B \alpha V \int_0^\infty \frac{\partial f(\mathcal{E})}{\partial (k_B T)} \mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E} = \frac{2}{3} k_B \alpha V \int_0^\infty \left(- \frac{\partial f(\mathcal{E})}{\partial (k_B T)} \right) \frac{\mathcal{E} - \mu}{k_B T} \mathcal{E}^{\frac{3}{2}} \mathrm{d}\mathcal{E} \end{aligned} \tag{9.21}$$

and using

$$\frac{\partial f}{\partial k_B T} = -\frac{\mathcal{E}-\mu}{k_B T}\frac{\partial f}{\partial \mathcal{E}} \tag{9.22}$$

we get

$$\begin{aligned} S &= \frac{2}{3}k_B\frac{\alpha V}{k_B T}\left[\int\limits_0^\infty \mathcal{E}^{\frac{5}{2}}\left(-\frac{\partial f}{\partial \mathcal{E}}\right)\mathrm{d}\mathcal{E} - \mu\int\limits_0^\infty \mathcal{E}^{\frac{3}{2}}\left(-\frac{\partial f}{\partial \mathcal{E}}\right)\mathrm{d}\mathcal{E}\right] = \\ &= \frac{2}{3}k_B\frac{\alpha V}{k_B T}\left[\mu^{\frac{5}{2}}\left(1+\frac{5\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right) - \mu^{\frac{5}{2}}\left(1+\frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2\right)\right] = \\ &= \frac{2}{3}k_B\frac{\alpha V}{k_B T}\mu^{\frac{5}{2}}\left[\frac{5}{8}\pi^2\left(\frac{k_B T}{\mu}\right)^2 - \frac{\pi}{8}\pi^2\left(\frac{k_B T}{\mu}\right)^2\right] = \\ &= \frac{\pi^2}{3}k_B\frac{\alpha V}{k_B T}\mu^{\frac{5}{2}}\left(\frac{k_B T}{\mu}\right)^2 = \frac{\pi^2}{3}k_B\alpha V\mu^{\frac{1}{2}}k_B T = \frac{\pi^2}{2}k_B N\left(\frac{k_B T}{\mu_0}\right) \end{aligned} \tag{9.23}$$

$$\alpha\frac{2}{3}\mu_0 = n \tag{9.24}$$

$$\mu = \mu_0 \tag{9.25}$$

Finally

$$S = \frac{\pi^2}{2}k_B N\left(\frac{k_B T}{\mu_0}\right) \tag{9.26}$$

Note, that

$$\lim_{T\to 0} S = 0 \tag{9.27}$$

Heat capacity at a constant volume C_V

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \tag{9.28}$$

$$\mathrm{d}U = \delta Q - \delta W = C_V\mathrm{d}T\ (V = \mathrm{const}) \tag{9.29}$$

$$C_V = \left(\frac{\delta Q}{\mathrm{d}T}\right) = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{9.30}$$

$$U = \frac{3}{2}N\mu_0\left[1+\frac{5\pi^2}{12}\left(\frac{k_B T}{\mu_0}\right)^2\right] \tag{9.31}$$

$$C_V = \frac{3}{5}N\mu_0\frac{5}{6}\pi^2\frac{k_B^2}{\mu_0}T = \frac{\pi^2}{2}Nk_B\frac{k_B T}{\mu_0} \tag{9.32}$$

or alternatively using the entropy for a monatomic Fermi gas (9.26)

$$C_V = T\frac{\mathrm{d}S}{\mathrm{d}T} = T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\pi^2}{2}k_B N\frac{k_B T}{\mu_0}\right) = \frac{\pi^2}{2}Nk_B\frac{k_B T}{\mu_0} \tag{9.33}$$

Chapter 10

Bose-Einstein condensation

10.1 Macroscopic occupancy of the lowest energy level

We assume a spin $s = 0$ and $\mathcal{E}_{\boldsymbol{p}} = \dfrac{p^2}{2m}$, then the state equation reads

$$\frac{P}{k_B T} = \frac{1}{\lambda_0^3} g_{\frac{5}{2}}(z) - \frac{1}{V} \ln(1 - z) \tag{10.1}$$

and the chemical potential (8.17)

$$\frac{1}{v} = \frac{1}{\lambda_0^3} g_{\frac{3}{2}}(z) + \frac{1}{v} \frac{z}{1 - z} \tag{10.2}$$

with the thermal wavelength for spin $s = 0$

$$\lambda_0 = \frac{h}{\sqrt{2\pi m k_B T}} \tag{10.3}$$

the same as for classical spinless particles. We focus now on (10.2). It is easy to see that the last term on the right hand side of the equation is proportional to an average number of particles in the lowest, $p = 0$, energy level

$$\langle n_0 \rangle = \frac{1}{z^{-1} \mathrm{e}^{\beta \mathcal{E}_{\boldsymbol{p}=0}} - 1} = \frac{1}{z^{-1} - 1} = \frac{z}{1 - z} \tag{10.4}$$

therefore we can write

$$\frac{1}{v} = \frac{1}{\lambda_0^3} g_{\frac{3}{2}}(z) + \frac{\langle n_0 \rangle}{V} \tag{10.5}$$

or

$$\lambda_0^3 \frac{\langle n_0 \rangle}{V} = \frac{\lambda_0^3}{v} - g_{\frac{3}{2}}(z) \tag{10.6}$$

The fugacity $z = \mathrm{e}^{\beta\mu}$ for bosons changes in the range $0 \leqslant z \leqslant 1$, that is $\mu \leqslant 0$. For this domain range the $g_{\frac{3}{2}}(z)$ function is a monotonic upper bounded positive function and its upper limit at $z = 1$ can be obtained via a series expansion

$$g_{\frac{3}{2}}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{\frac{3}{2}}} \tag{10.7}$$

which for $z = 1$ gives

$$g_{\frac{3}{2}}(1) = \sum_{l=1}^{\infty} \frac{1}{l^{\frac{3}{2}}} = \zeta\left(\frac{3}{2}\right) \approx 2.612 \tag{10.8}$$

where $\zeta(x)$ is the Riemann zeta function. Note, that a $g_{\frac{3}{2}}(z)$ derivative

$$\frac{\mathrm{d}}{\mathrm{d}z} g_{\frac{3}{2}}(z) = \frac{1}{z} g_{\frac{1}{2}}(z) = \frac{1}{z} \sum_{l=1}^{\infty} \frac{z^l}{\sqrt{l}} \tag{10.9}$$

is divergent at $z = 1$. Since for any $0 \leqslant z \leqslant 1$ we have $g_{\frac{3}{2}}(z) \leqslant g_{\frac{3}{2}}(1) = \zeta\left(\frac{3}{2}\right) \approx 2.612$ we obtain

$$\frac{\lambda_0^3}{v} - g_{\frac{3}{2}}(z) \geqslant \frac{\lambda_0^3}{v} - g_{\frac{3}{2}}(1) \tag{10.10}$$

and if the temperature and volume per particle (the thermal wavelength is temperature and proper volume dependent) fulfill the condition

$$\frac{\lambda_0^3}{v} > g_{\frac{3}{2}}(1) \tag{10.11}$$

then based on (10.6) and (10.10) we get

$$\frac{\langle n_0 \rangle}{V} > 0 \tag{10.12}$$

This result means that a finite fraction of all particles occupies a lowest energy level $\mathcal{E}(\boldsymbol{p} = 0)$. This is the effect of Bose-Einstein condensation (BEC), which is particularly spectacular for the thermodynamic limit, i.e., in large systems when volume $V \longrightarrow \infty$, number of particles $N \longrightarrow \infty$ and a concentration of particles $n = \frac{N}{V} = const$, then

$$\lim_{V\to\infty} \frac{\langle n_0 \rangle}{V} = \lim_{N\to\infty} n \frac{\langle n_0 \rangle}{N} > 0 \tag{10.13}$$

and we obtain

$$\lim_{N\to\infty} \frac{\langle n_0 \rangle}{N} > 0 \tag{10.14}$$

which means that $\langle n_0 \rangle \longrightarrow \infty$, that is the occupancy of the lowest energy level becomes macroscopic, or in other words, a finite $\frac{\langle n_0 \rangle}{N}$ fraction of all particles resides in the lowest energy level. As the occupancy of the lowest energy level is given by

$$\langle n_0 \rangle = \frac{z}{1-z} \longrightarrow \infty \tag{10.15}$$

its divergency leads to the fugacity $z \longrightarrow 1$ or the chemical potential $\mu = \frac{1}{\beta} \ln z \longrightarrow 0$. It means that in our discussion of a Bose-Einstein condensation in the thermodynamic limit we should use $z = 1$. In this case a condition

$$\frac{\lambda_0^3}{v} = g_{\frac{3}{2}}(1) \tag{10.16}$$

defines a moment when the condensation begins, that is a phase transition: Bose gas to BEC takes place. The Eq. (10.16) defines a surface in the P, v, T space which seperates gas and BEC phases. Explicitly, using λ_0 definition the condition (10.16) reads

$$\frac{h^3}{v(2\pi m k_B T)^{\frac{3}{2}}} = \zeta\left(\frac{3}{2}\right) \tag{10.17}$$

At a given particle concentration $n = \frac{1}{v}$ it determines the critical temperature T_C

$$T_C = \frac{h^2 n^{\frac{2}{3}}}{2\pi m k_B \zeta^{\frac{2}{3}}\left(\frac{3}{2}\right)} \tag{10.18}$$

For temperatures $T \leqslant T_C$ a macroscopic occupancy of the lowest energy level takes place. Alternatively, at a given temperature we obtain a critical density

$$n_C = \zeta\left(\frac{3}{2}\right)\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{10.19}$$

or a critical proper volume $v_C = \dfrac{1}{n_C}$ which lead to the BEC phase transition. At the critical temperature T_C the thermal wavelength λ_0 becomes of the order of magnitude of the average interparticle distance d

$$\lambda_0(T_C) = \frac{h}{\sqrt{2\pi mk_BT_C}} = \left(v\zeta\left(\frac{3}{2}\right)\right)^{\frac{1}{3}} = \left(d^3\zeta\left(\frac{3}{2}\right)\right)^{\frac{1}{3}} = \\ d(2.612)^{\frac{1}{3}} \approx 1.377d \tag{10.20}$$

We remember, that $\lambda_0 \sim \lambda_{\mathrm{dB}}$, so at T_C we have $\lambda_{\mathrm{dB}} \sim d$ which means that the de Broglie waves of single particles start to overlap and interfere. As we continue on decreasing the temperature the thermal wavelength increase and the overlap becomes more and more significant until a complete interference into a single wave when the zero temperature is reached. We show this process in Fig. 10.1.

10.2 Uniqueness of the lowest energy level

We will show that the condensation can occur only at the lowest energy level. Although we can always extract a finite number of terms from the integral in (7.28) and instead of Eq. (10.5) deal with

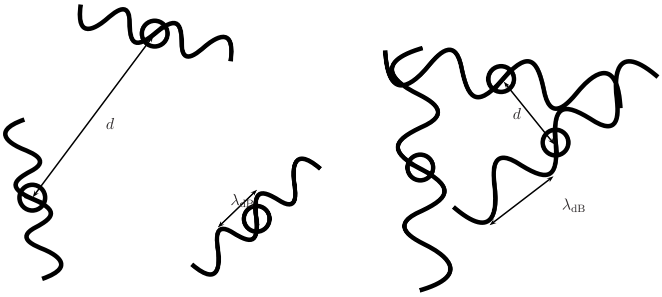
$$n = \frac{1}{\lambda_0^3}g_{\frac{3}{2}}(z) + \frac{\langle n_0\rangle}{V} + \left(\frac{\langle n_1\rangle}{V} + \frac{\langle n_2\rangle}{V} + \cdots + \frac{\langle n_l\rangle}{V}\right) \tag{10.21}$$

in the thermodynamic limit, every but the $\langle n_0\rangle$ term vanishes. If we take, for instance, a term

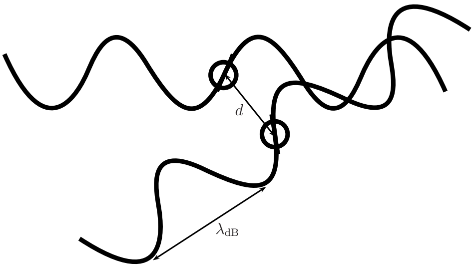
$$\frac{\langle n_m\rangle}{V} = \frac{1}{V}\frac{1}{z^{-1}\mathrm{e}^{\beta\mathcal{E}_m} - 1} \tag{10.22}$$

where $\mathcal{E}_m = \dfrac{\boldsymbol{p}_m^2}{2m}$ is the energy level determined by the quantum number m, then using the relations $z \leqslant 1$ and $\beta\mathcal{E}_m \geqslant 0$ we can establish an upper limit on $\langle n_m\rangle$

$$\frac{\langle n_m\rangle}{V} \leqslant \frac{1}{V}\frac{1}{\mathrm{e}^{\beta\mathcal{E}_m} - 1} \tag{10.23}$$



(a) $d \gg \lambda_{\mathrm{dB}}$, $T > T_C$ (b) $d \sim \lambda_{\mathrm{dB}}$, $T = T_C$



(c) $d \ll \lambda_{\mathrm{dB}}$, $T \ll T_C$

Figure 10.1: Bosons and their de Broglie waves at different temperatures.

which can be upper bounded through a Taylor's expansion

$$\frac{1}{V}\frac{1}{\mathrm{e}^{\beta\mathcal{E}_m}-1} \leqslant \frac{1}{V}\frac{1}{1+\beta\mathcal{E}_m-1} = \frac{1}{V}\frac{k_BT}{\mathcal{E}_m} \tag{10.24}$$

Applying a periodic boundary condition on the plane wave function $\psi(\boldsymbol{r}) = \exp\left(\mathtt{i}\boldsymbol{pr}/\hbar\right)$

$$\psi(\boldsymbol{r}) = \psi(\boldsymbol{r}+\boldsymbol{R}) \tag{10.25}$$

where $\boldsymbol{R}$ is any of the three vectors $(L,\ 0,\ 0)$, $(0,\ L,\ 0)$, $(0,\ 0,\ L)$ and $L^3 = V$ is a volume of system, we obtain the momentum

$$\boldsymbol{p} = \frac{2\pi\hbar}{L}\begin{pmatrix} m_1, & m_2, & m_3\end{pmatrix} \tag{10.26}$$

and the energy

$$\mathcal{E}_m = \frac{(2\pi\hbar)^2}{2m}\frac{m}{V^{\frac{2}{3}}} \tag{10.27}$$

where $m = m_1^2 + m_2^2 + m_3^2$. Therefore, a quantized energy level gives the $\langle n_m \rangle$ occupancy

$$\frac{\langle n_m \rangle}{V} \leqslant \frac{1}{V}\frac{2mk_BTV^{\frac{2}{3}}}{(2\pi\hbar)^2 m} \sim \frac{1}{V^{\frac{1}{3}}} \tag{10.28}$$

which vanishes in the thermodynamic limit

$$\lim_{V\to\infty}\frac{\langle n_m \rangle}{V} = \lim_{V\to\infty} V^{-\frac{1}{3}} = 0 \tag{10.29}$$

It is noteworthy, that the presented limiting procedure does not work in two or one dimensional systems, where particles are spread all over all accessible states and the Bose-Einstein condensation does not take place.

10.3 Chemical potential

We have established that in the thermodynamic limit the fugacity $z = 1$ for the BEC phase, that is for temperatures determined by a condition

$$\frac{\lambda_0^3}{v} \geqslant \zeta\left(\frac{3}{2}\right) \tag{10.30}$$

In the gas phase, that is when $\frac{\lambda_0^3}{v} < \zeta\left(\frac{3}{2}\right)$, the fugacity is given by a relation

$$\frac{\lambda_0^3}{v} - g_{\frac{3}{2}}(z) = 0 \tag{10.31}$$

Let us note, that due to the above condition there is no finite occupancy of the lowest energy level in a gas phase as

$$\frac{\langle n_0 \rangle}{V} = \frac{\lambda_0^3}{v} - g_{\frac{3}{2}}(z) = 0 \tag{10.32}$$

Summarising we can write

$$z = \begin{cases} 1 & \text{for } \frac{\lambda_0^3}{v} \geqslant \zeta\left(\frac{3}{2}\right) \text{ (BEC)} \\ \text{solution of } \frac{\lambda_0^3}{v} = g_{\frac{3}{2}}(z) & \text{for } \frac{\lambda_0^3}{v} < \zeta\left(\frac{3}{2}\right) \text{ (gas)} \end{cases} \tag{10.33}$$

Finally, using the relation $\mu = k_B T \ln z$ we can determine the temperature dependence of the chemical potential

$$\mu = \begin{cases} 0 & \text{for } T \leqslant T_C \\ \text{solution of } \dfrac{\lambda_0^3}{v} = g_{\frac{3}{2}}\left(\mathrm{e}^{\beta\mu}\right) & \text{for } T > T_C \end{cases} \tag{10.34}$$

where the critical temperature is determined by

$$\frac{\lambda_0^3}{v} = \zeta\left(\frac{3}{2}\right). \tag{10.35}$$

10.4 Condensate

The Bose-Einstein condensate consists of particles in the state of zero momentum whose number $\langle n_0 \rangle$ represents a finite fraction of a number of all particles $N = nV$, where n is a particle concentration. Based on

$$\frac{1}{v} = \frac{\langle n_0 \rangle}{V} + \frac{1}{\lambda_0^3} g_{\frac{3}{2}}(z) \tag{10.36}$$

we obtain the total particle number

$$N = \langle n_0 \rangle + \frac{V}{\lambda_0^3} g_{\frac{3}{2}}(z). \tag{10.37}$$

We know that for the condensate, that is for $T \leqslant T_C$, the fugacity $z = 1$ and a fraction of all particles in the condensate reads

$$\frac{\langle n_0 \rangle}{N} = 1 - \frac{g_{\frac{3}{2}}(1)}{n\lambda_0^3}, \tag{10.38}$$

where $\lambda_0 = \lambda_0(T)$. Since $g_{\frac{3}{2}}(1) = n\lambda_0^3(T_C)$ determines the critical temperature we get the temperature dependence of the lowest energy level occupancy

$$\frac{\langle n_0 \rangle}{N} = 1 - \frac{\lambda_0^3(T_C)}{\lambda_0^3(T)} \tag{10.39}$$

and using $\lambda_0(T) = \dfrac{h}{\sqrt{2mk_B T}}$ we obtain

$$\frac{\langle n_0 \rangle}{N} = 1 - \left(\frac{T}{T_C}\right)^{\frac{3}{2}} \tag{10.40}$$

that is the fraction of all particles in the lowest energy level, in other words, the fraction of particles which create the condensate, see Fig. 10.2 . This result holds when the chemical potential vanishes, whereas there is no condensation for a negative μ. So we can write

$$\frac{\langle n_0\rangle}{N} = \begin{cases} 0 & \text{for } \mu < 0 \\ 1 - \left(\frac{T}{T_C}\right)^{\frac{3}{2}} & \text{for } \mu = 0 \end{cases} \tag{10.41}$$

Similarly, evoking a definition of the critical proper volume

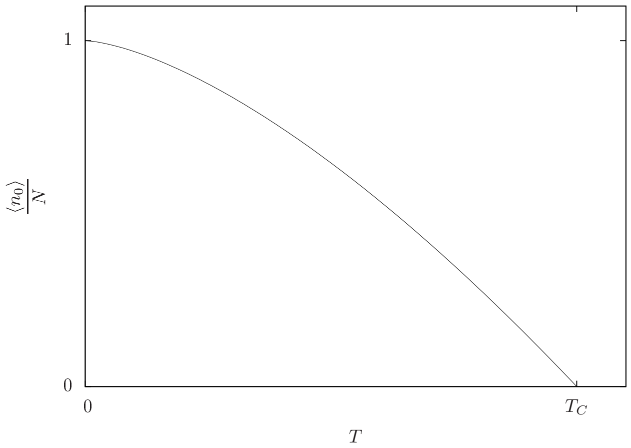


Figure 10.2: Occupancy of the lowest energy level as a function of temperature for a fixed particle concentration

$$\frac{1}{v_C} = \frac{g_{\frac{3}{2}}(1)}{\lambda_0^3} \tag{10.42}$$

we derive using (10.38) a dependence of $\langle n_0\rangle$ on the proper volume $v = \frac{1}{n}$

$$\frac{\langle n_0\rangle}{N} = 1 - \frac{v}{v_C} \tag{10.43}$$

plotted in Fig. 10.3. For an arbitrary chemical potential value we have

$$\frac{\langle n_0\rangle}{N} = \begin{cases} 0 & \text{for } \mu < 0 \\ 1 - \dfrac{v}{v_C} & \text{for } \mu = 0 \end{cases} \tag{10.44}$$

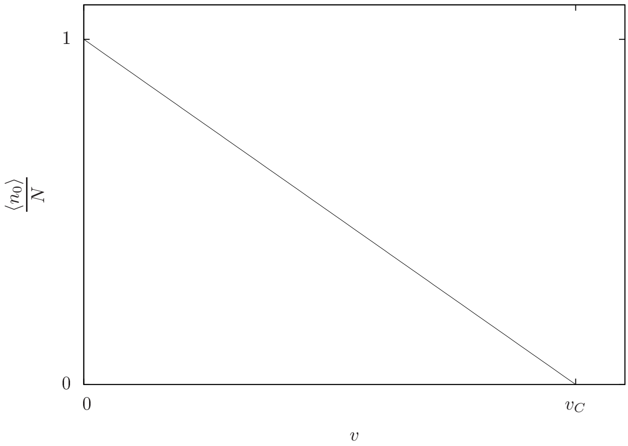


Figure 10.3: Occupancy of the lowest energy level as a function of proper volume for a fixed temperature

10.5 Equation of state

We know, that in general we deal with two phases of a Bose system: a Bose gas and a Bose-Einstein condensate. The phase transition is determined by the critical proper volume v_C for a fixed temperature or by the critical temperature T_C at a given interparticle distance.

$$\text{Phases at a given temperature:} \begin{cases} \text{BEC} & \text{for } v \leqslant v_C \\ \text{Bose gas} & \text{for } v > v_C \end{cases} \tag{10.45}$$

$$\text{Phases at a given proper volume:} \begin{cases} \text{BEC} & \text{for } T \leqslant T_C \\ \text{Bose gas} & \text{for } T > T_C \end{cases} \tag{10.46}$$

We need to elucidate that in a so defined BEC phase the Bose-condensate forms a part of a system and coexists in a thermal equilibrium with a Bose gas until the temperature falls down to zero and the whole system will condensate. We have derived the temperature dependence of the condensate volume in a former section. Presently, we will study the state equation (10.5). To discuss the properties of the system in the thermodynamic limit we need to take a $V \longrightarrow \infty$ ($v = \text{const}$) limit in (10.1)

$$\frac{P}{k_B T} = \frac{1}{\lambda_0^3} g_{\frac{5}{2}}(z) - \lim_{V\to\infty} \frac{1}{V} \ln(1-z). \tag{10.47}$$

Note, that for a gas phase we have $z < 1$ and

$$\lim_{V\to\infty} \frac{1}{V} \frac{z}{1-z} = \frac{\langle n_0 \rangle}{V} = 0 \tag{10.48}$$

therefore the state equation for a Bose gas reads

$$\frac{P}{k_B T} = \frac{1}{\lambda_0^3} g_{\frac{5}{2}}(z) \tag{10.49}$$

Below the Bose-Einstein phase transition, that is for $T < T_C$ or $v < v_C$, the fugacity in the thermodynamic limit, $\lim_{V\to\infty} z = 1$, and we deal with the following limits in (10.1)

$$\lim_{V\to\infty} \frac{1}{V} \ln(1-z) \tag{10.50}$$

In order to evaluate the above expression we evoke the result for the occupancy of the lowest energy level in the BEC phase

$$\lim_{V\to\infty} \frac{1}{V} \frac{z}{1-z} = \lim_{V\to\infty} \frac{\langle n_0 \rangle}{V} < \infty, \tag{10.51}$$

which upper binds the left hand side of Eq.(10.51) and leads to the relation

$$\lim_{V\to\infty} \frac{1}{V} \ln\left(\frac{1}{V} \frac{z}{1-z}\right) = 0 \tag{10.52}$$

Now, when we look at (10.52) as at a sum of three terms

$$\lim_{V\to\infty} \left[-\frac{1}{V} \ln V + \frac{1}{V} \ln z - \frac{1}{V} \ln(1-z) \right] = 0, \tag{10.53}$$

we get immediately that

$$\lim_{V\to\infty}\frac{1}{V}\ln(1-z)=0. \tag{10.54}$$

and the equation of state (10.1) below the BEC phase transition reads

$$\frac{P}{k_BT}=\frac{1}{\lambda_0^3}g_{\frac{5}{2}}(1) \tag{10.55}$$

Summarizing, we have obtained the state equation for bosons in the thermodynamic limit

$$\frac{P}{k_BT}=\begin{cases}\dfrac{1}{\lambda_0^3}g_{\frac{5}{2}}(z) & \text{for } v>v_C \text{ (Bose gas)}\\[2ex] \dfrac{1}{\lambda_0^3}g_{\frac{5}{2}}(1) & \text{for } v\leqslant v_C \text{ (BEC)}\end{cases} \tag{10.56}$$

where $g_{\frac{5}{2}}(1)=\zeta\left(\frac{5}{2}\right)\approx 1.342$.

10.6 Thermodynamic properties

We use general results of Chapter 7 to determine the thermodynamic functions of a Bose gas and a Bose-Einstein condensate phases.

10.6.1 Internal energy

$$\frac{U}{Nk_B}=\begin{cases}\dfrac{3}{2}v\dfrac{1}{\lambda_0^3}Tg_{\frac{5}{2}}(z) & \text{for } v>v_C \text{ (Bose gas)}\\[2ex] \dfrac{3}{2}v\dfrac{1}{\lambda_0^3}Tg_{\frac{5}{2}}(1) & \text{for } v\leqslant v_C \text{ (BEC)}\end{cases} \tag{10.57}$$

In particular, we see that in the BEC phase the internal energy

$$U=\frac{3}{2}V\zeta\left(\frac{5}{2}\right)\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}(k_BT)^{\frac{5}{2}} \tag{10.58}$$

and pressure given by $PV=\frac{2}{3}U$ is only temperature dependent

$$P=\zeta\left(\frac{5}{2}\right)\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}(k_BT)^{\frac{5}{2}} \tag{10.59}$$

For $T > 0$ it is also a pressure of the Bose gas which coexists in a thermal equilibrium with the condensate. Note, that the Bose condensation takes place in a real space (not only in the momentum space), that is, we can distinguish the part of a system which underwent a phase transition. The balance between these two coexisting phases requires a constant pressure throughout the whole system.

10.6.2 Entropy

Using the chemical potential equation for the gas phase, $g_{\frac{3}{2}}(z) = \lambda_0^3/v$, and taking into account that $z = 1$ in the BEC phase we get

$$\frac{S}{Nk_B} = \begin{cases} \frac{5}{2}\frac{v}{\lambda_0^3} g_{\frac{5}{2}}(z) - \ln z & \text{for } v > v_C \text{ (Bose gas)} \\ \\ \frac{5}{2}\frac{v}{\lambda_0^3} g_{\frac{5}{2}}(1) & \text{for } v \leqslant v_C \text{(BEC)} \end{cases} \tag{10.60}$$

For the Bose-Einstein condensate

$$S = \frac{5}{2} V k_B^{\frac{5}{2}} \zeta\left(\frac{5}{2}\right)\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} T^{\frac{3}{2}} \tag{10.61}$$

and at $T = 0$ the entropy $S = 0$ in agreement with the Nernst rule. We may also conclude, that the condensate which is the only existing phase at $T = 0$ has zero entropy, therefore the obtained entropy describes the gas in thermal equilibrium with the condensate. Note, that the entropy is a continuous function of v or T. Both formulas in (10.60) become equal at $z = 1$ that is when we cross v_C or T_C.

10.6.3 Specific heat c_V

$$c_V = \begin{cases} \frac{15}{4}\frac{k_B}{\lambda_0^3} g_{\frac{5}{2}}(z) - \frac{9}{4}\frac{k_B}{v}\frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)} & \text{for } v > v_C \text{ (Bose gas)} \\ \frac{15}{4}\frac{k_B}{\lambda_0^3} g_{\frac{5}{2}}(1) \sim T^{\frac{3}{2}} & \text{for } v \leqslant v_C \text{(BEC)} \end{cases} \tag{10.62}$$

For low temperatures, $T \leqslant T_C$, $c_V \sim T^{\frac{3}{2}}$, whereas when the temperature is high

$$\lim_{T\to\infty} z = \lim_{T\to\infty} \mathrm{e}^{\frac{\mu}{k_B T}} = 0 \tag{10.63}$$

and for $z \to 0$ we may write

$$\lim_{T\to\infty} c_V = \lim_{z\to 0} \frac{k_B}{v}\left[\frac{15}{4}\frac{g_{\frac{5}{2}}(z)}{g_{\frac{3}{2}}(z)} - \frac{9}{4}\frac{g_{\frac{3}{2}}(z)}{g_{\frac{1}{2}}(z)}\right] \tag{10.64}$$

where we have used $\lambda_0^3 = v g_{\frac{3}{2}}(z)$. Because

$$g_{\frac{1}{2}}(z) = z\frac{\mathrm{d}}{\mathrm{d}z} g_{\frac{3}{2}}(z) \tag{10.65}$$

$$g_{\frac{3}{2}}(z) = z\frac{\mathrm{d}}{\mathrm{d}z} g_{\frac{5}{2}}(z) \tag{10.66}$$

and $g_{\frac{1}{2}}(z=0) = g_{\frac{3}{2}}(z=0) = g_{\frac{5}{2}}(z=0) = 0$, we may write

$$\lim_{T\to 0}\left[\frac{15}{4}\frac{g'_{\frac{5}{2}}(z)}{g'_{\frac{5}{2}}(z)} - \frac{9}{4}\frac{g'_{\frac{3}{2}}(z)}{g'_{\frac{3}{2}}(z)}\right] = \frac{3}{2} \tag{10.67}$$

where for shortness we used a notation $g'(z) = \frac{\mathrm{d}}{\mathrm{d}z}g(z)$. We note, that for high temperatures a Bose gas behaves like a monatomic classical gas and obeys the equipartition rule

$$\lim_{T\to\infty} c_V = \frac{1}{V}\lim_{T\to\infty}\left(\frac{\mathrm{d}U}{\mathrm{d}T}\right) = \frac{3}{2}\frac{k_B}{v} \tag{10.68}$$

$$U = \frac{3}{2} N k_B T \tag{10.69}$$

10.6.4 Free energy

Having the internal energy and the entropy we can write down the Helmholtz free energy $F = U - TS$ formula

$$\frac{F}{Nk_B} = \begin{cases} -\frac{v}{\lambda_S^3} T g_{\frac{5}{2}}(z) + T\ln z & \text{for } v > v_C \text{ (Bose gas)} \\ -\frac{v}{\lambda_S^3} T g_{\frac{5}{2}}(1) & \text{for } v \leqslant v_C \text{(BEC)} \end{cases} \tag{10.70}$$

10.7 Role of a system dimensionality [7]

Knowing the physical nature of the BEC we can work out a short and convenient way to obtain the critical parameters. Writing the Eq. (7.28) for $\mu = 0$ we get the equation

$$n = \alpha \int_0^\infty \frac{\sqrt{\mathcal{E}}\,\mathrm{d}\mathcal{E}}{\mathrm{e}^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{10.71}$$

which determines the critical particle concentration $n_C = n_C(T)$ as a function of the temperature or the critical temperature $T_C = T_C(n)$ as a function of the concentration. Introducing $x = \dfrac{\mathcal{E}}{k_B T}$ we get for the critical concentration

$$n_C = \zeta\left(\frac{3}{2}\right)(2s+1)\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{10.72}$$

where we have used

$$\int_0^\infty \frac{\sqrt{x}\,\mathrm{d}x}{\mathrm{e}^x - 1} = \Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right), \tag{10.73}$$

$$\Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \tag{10.74}$$

and

$$\alpha = \frac{4\sqrt{2}}{h^3}\pi m^{\frac{3}{2}}(2s+1). \tag{10.75}$$

Therefore for spinless bosons

$$n_C = \zeta\left(\frac{3}{2}\right)\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{10.76}$$

or

$$T_C = \frac{2\pi\hbar^2}{m k_B}\left(\frac{n}{\zeta\left(\frac{3}{2}\right)}\right)^{\frac{2}{3}} \tag{10.77}$$

We will use the above method of establishing the critical Bose condensation critical parameters in a short discussion of the BEC in arbitrary dimension, that is for a D-dimensional gas of bosons which obey the dispersion relation $\mathcal{E} = A\boldsymbol{p}^{\sigma}$ and carry spin s. The critical concentration

$$n_C = \frac{(2s+1)}{(2\pi\hbar)^D} \int\limits_{-\infty}^{\infty} \frac{\mathrm{d}^D p}{\mathrm{e}^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{10.78}$$

in the D-dimensional spherical coordinates for an isotropic system reads

$$n_C = \frac{(2s+1)^B}{(2\pi\hbar)^D} \int\limits_{0}^{\infty} \frac{p^{D-1}\mathrm{d}p}{\mathrm{e}^{\frac{\mathcal{E}}{k_B T}} - 1} \tag{10.79}$$

where B is a dimension dependent constant which results from the angle integral, and for physically relevant dimensions

$$B = \begin{cases} 2 & \text{for } D = 1, \\ 2\pi & \text{for } D = 2, \\ 4\pi & \text{for } D = 3. \end{cases} \tag{10.80}$$

Using the dispersion relation

$$p = \left(\frac{\mathcal{E}}{A}\right)^{\frac{1}{\sigma}} \tag{10.81}$$

and

$$\mathrm{d}p = \frac{1}{\sigma} A^{-\frac{1}{\sigma}} \mathcal{E}^{\frac{1}{\sigma}-1} \mathrm{d}\mathcal{E} \tag{10.82}$$

we have

$$n_C = \frac{(2s+1)^B}{(2\pi\hbar)^D} \frac{A^{-\frac{1}{\sigma}}}{\sigma} \int\limits_{0}^{\infty} \frac{\mathcal{E}^{\frac{D}{\sigma}-1}\mathrm{d}\mathcal{E}}{\mathrm{e}^{\frac{\mathcal{E}}{k_B T}} - 1}. \tag{10.83}$$

Now, letting $x = \dfrac{\mathcal{E}}{k_B T}$ we obtain the condition (constraint) for the critical concentration

$$n_C = c \int\limits_{0}^{\infty} \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^{x} - 1} \mathrm{d}x \tag{10.84}$$

$$c = \frac{(2s+1)}{(2\pi\hbar)^D} \frac{A^{-\frac{1}{\sigma}}}{\sigma} (k_B T)^{\frac{D}{\sigma}} \tag{10.85}$$

Bose-Einstein condensation occurs if the above formula yields a finite critical concentration n_C, that is only when the integral

$$\int_0^\infty \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^x - 1}\mathrm{d}x < \infty \tag{10.86}$$

is convergent. For its estimation we split (10.86) into two integrals

$$\int_0^\infty \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^x - 1}\mathrm{d}x = \int_0^\delta \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^x - 1}\mathrm{d}x + \int_\delta^\infty \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^x - 1}\mathrm{d}x \tag{10.87}$$

where $\delta > 0$. Obviously, the second integral is convergent,

$$\int_0^\delta \frac{x^{\frac{D}{\sigma}-1}}{\mathrm{e}^x - 1}\mathrm{d}x \sim \int_0^\delta x^{\frac{D}{\sigma}-2}\mathrm{d}x = \begin{cases} \left.\dfrac{x^{\frac{D}{\sigma}-1}}{\dfrac{D}{\sigma}-1}\right|_0^\delta & \text{for } \dfrac{D}{\sigma} \neq 1 \\ \ln x\big|_0^\delta & \text{for } \dfrac{D}{\sigma} = 1 \end{cases} \tag{10.88}$$

We conclude, that for $\dfrac{D}{\sigma} \leqslant 1$ the integral is divergent whereas for $\dfrac{D}{\sigma} > 1$ it is convergent. It means that the Bose-Einstein condensation occurs for $\dfrac{D}{\sigma} > 1$ and there is no such a condensation for $\dfrac{D}{\sigma} \leqslant 1$. The ratio of the dimensionality of the system and the power coefficient in the dispersion relation decides about a possibility of system to Bose-condense.

$$\mathrm{BEC} = \begin{cases} \text{no} & \text{for } \dfrac{D}{\sigma} \leqslant 1 \\ \text{yes} & \text{for } \dfrac{D}{\sigma} > 1 \end{cases} \tag{10.89}$$

If we look now at the gas of parabolic dispersion, $\sigma = 2$, in one, two or three dimensions, we note that for $D = 1$, $\dfrac{D}{\sigma} = \dfrac{1}{2}$, for $D = 2$, $\dfrac{D}{\sigma} = 1$, for $D = 3$, $\dfrac{D}{\sigma} = \dfrac{3}{2}$. Such a gas cannot Bose-condense in $D = 1$ and $D = 2$ dimensions.

Nevertheless, photons whose dispersion $\mathcal{E} = cp$ can condense in $D = 2$ dimensions: $\dfrac{D}{\sigma} = 2$.

Chapter 11

Kinetic equation approach to nonequilibrium processes [5]

11.1 Boltzmann equation and collision integral

We take a quasiclassical approach assuming that particles, although subject to quantum statistics, have a determined momentum as well as a position. Such an approach can be carried out when we discuss the wave packets instead of plane waves. For the quasiclassical particles the distribution function in general depends on particles momenta, positions and time as we speak of nonequilibrium processes, $f = f(\boldsymbol{r}, \boldsymbol{p}, t)$. A time change of the distribution function is set by collisions of particles with lattice defects or impurities, phonons or other particles. These scattering processes, if induced by external fields like an electric field or a temperature gradient, lead to sudden changes in the occupation of allowed states and in this way affect the Fermi-Dirac distribution. Quantitatively a time evolution of the distribution function is determined by a collision integral $I(f)$ through the Boltzmann equation or the kinetic equation which in the most general form reads

$$\frac{\mathrm{d}f}{\mathrm{d}t} = I(f) \tag{11.1}$$

Taking into account the momentum, position and time dependence of the distribution function we can write the kinetic equation in a more explicit form

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \boldsymbol{r}}\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} + \frac{\partial f}{\partial \boldsymbol{p}}\frac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = I(f) \tag{11.2}$$

This equation can be applied for small external perturbations to the system like an electric or magnetic field or an increment in temperature which can be included through a perturbational nonequilibrium correction f_1 to the Fermi-Dirac distribution, i.e., $f = f_0 + f_1$. For a wave packet propagates with a group velocity $\boldsymbol{v} = \dfrac{\partial \boldsymbol{\mathcal{E}}(\boldsymbol{p})}{\partial \boldsymbol{p}}$ we have $\dfrac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{v}$. A time change of a quasiparticle energy $\dfrac{\mathrm{d}\boldsymbol{\mathcal{E}}(\boldsymbol{p})}{\mathrm{d}t} = \dfrac{\partial \boldsymbol{\mathcal{E}}(\boldsymbol{p})}{\partial \boldsymbol{p}}\dfrac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t}$ in an electric field is determined by the Coulomb interaction $\dfrac{\mathrm{d}\boldsymbol{\mathcal{E}}(\boldsymbol{p})}{\mathrm{d}t} = \boldsymbol{v}\cdot e\boldsymbol{E}$ and we can write for a time change of a momentum (quasimomentum) $\dfrac{\mathrm{d}\boldsymbol{p}}{\mathrm{d}t} = e\boldsymbol{E}$. Therefore, the kinetic equation of a nonuniformly heated system in the presence of an electric field reads

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{r}} + e\boldsymbol{E}\frac{\partial f}{\partial \boldsymbol{p}} = I(f) \tag{11.3}$$

The collision integral in an isotropic medium for elastic collisions can be represented by a simple formula

$$I(f) = -\frac{f_1}{\tau}, \tag{11.4}$$

where $f_1 = f - f_0$ is a nonequilibrium counterpart of a distribution function and τ is an average life time of quasiparticles or an average scattering time, that is an average time between two consecutive collisions of a quasiparticle. τ is a natural time-scale in a system, we cannot consider particles existing longer than τ. Applied to a momentum, or rather a quasimomentum, time chage this statement shows that a quasiparticle acceleration cannot last longer than τ. When a defect or impurity scattering potential is isotropic, that is, it does not depend on any particular direction and its magnitude $w(\theta)$ depends solely on a deflection angle θ we obtain

$$\frac{1}{\tau} = \int W(\theta)(1 - \cos\theta)\frac{\mathrm{d}\Omega}{4\pi} \tag{11.5}$$

and we can write the kinetic equation in a form

$$\frac{\partial f}{\partial t} + \boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{r}} + e\boldsymbol{E}\frac{\partial f}{\partial \boldsymbol{p}} = -\frac{f - f_0}{\tau} \tag{11.6}$$

11.2 Electrical conductivity

In the presence of a stationary and uniform electric field the kinetic equation (11.6) reduces to

$$e\boldsymbol{E}\frac{\partial f}{\partial \boldsymbol{p}} = -\frac{f - f_0}{\tau} \tag{11.7}$$

Assuming a weak electric field we look for a linear in the electric field nonequilibrium correction f_1 to the distribution function $f = f_0 + f_1$, where $f_1 \ll f_0$ and $f_1 \sim E$. Therefore, keeping up to the linear terms in E we get

$$e\boldsymbol{E}\frac{f_0}{\partial \boldsymbol{p}} = -\frac{f_1}{\tau} \tag{11.8}$$

Since the Fermi-Dirac distribution is energy dependent we can straightforwardly evaluate its momentum derivative

$$\frac{\partial f_0}{\partial \boldsymbol{p}} = \frac{\partial f_0}{\partial \mathcal{E}}\frac{\partial \mathcal{E}}{\partial \boldsymbol{p}} = \boldsymbol{v}\frac{\partial f_0}{\partial \mathcal{E}} \tag{11.9}$$

and obtain

$$f_1 = -e\boldsymbol{E}\boldsymbol{v}\tau\frac{\partial f_0}{\partial \mathcal{E}} \tag{11.10}$$

We are now in a position to calculate an electric current density

$$\begin{aligned} \boldsymbol{j} = 2e\int \boldsymbol{v} f\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} &= 2e\int \boldsymbol{v}(f_0 + f_1)\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} = \\ &= 2e\int \boldsymbol{v} f_0\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} + 2e\int \boldsymbol{v} f_1\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} = 2e\int \boldsymbol{v} f_1\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} \end{aligned} \tag{11.11}$$

where we have used the property that f_0 is an even and $\boldsymbol{v}$ is an odd momentum function. Substituting the nonequilibrium distribution function formula we get

$$\boldsymbol{j} = -2e^2\int \boldsymbol{v}(\boldsymbol{v}\boldsymbol{E})\tau\frac{\partial f_0}{\partial \mathcal{E}}\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} = -\mathrm{e}^2\int \boldsymbol{v}(\boldsymbol{v}\boldsymbol{E})\tau\frac{\partial f_0}{\partial \mathcal{E}}\nu(\mathcal{E})\mathrm{d}\mathcal{E}\frac{\mathrm{d}\Omega}{4\pi} \tag{11.12}$$

In the first approximation, neglecting a small correction of the order of magnitude of $(\frac{k_BT}{\mu})^2$, $\dfrac{\partial f_0}{\partial \mathcal{E}} \simeq -\delta(\mathcal{E} - \mu)$ and the energy integral reads

$$\boldsymbol{j} = e^2\int \boldsymbol{v}(\boldsymbol{v}\boldsymbol{E})\tau\nu(\mu)\frac{\mathrm{d}\Omega}{4\pi} = e^2\int \boldsymbol{v}\ vE\cos\theta\ \tau\ \nu(\mu)\frac{\mathrm{d}\Omega}{4\pi} \tag{11.13}$$

If we fix the z-axis of a coordinate system along the electric field, $\boldsymbol{E} = (0, 0, E)$, then

$$\begin{aligned} \boldsymbol{j} &= e^2 E v^2(\mu)\tau(\mu)\nu(\mu)\times \\ &\qquad \int_0^{2\pi} \frac{\mathrm{d}\phi}{4\pi} \int_0^{\pi} \mathrm{d}\theta \sin\theta(\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)\cos\theta \end{aligned} \tag{11.14}$$

therefore we obtain the Ohm's law

$$\boldsymbol{j} = \sigma \boldsymbol{E} \tag{11.15}$$

with the electrical conductivity σ given by the integral

$$\begin{aligned} \sigma &= e^2 \int v^2 \cos^2\theta \tau\nu(\mu)\frac{\mathrm{d}\Omega}{4\pi} = \\ &= e^2 v^2 \frac{\cos^3\theta}{3}\tau\nu(\mu)\frac{1}{2}\bigg|_{-1}^{1} = \frac{1}{3}e^2 v^2(\mu)\tau(\mu)\nu(\mu) \end{aligned} \tag{11.16}$$

Thus, we have obtained the electrical conductivity

$$\sigma = \frac{1}{3}e^2\left[v^2(\mu)\tau(\mu)\nu(\mu)\right] \tag{11.17}$$

which is determined by the values of the velocity, life time and density of states at the Fermi level.

11.3 Thermal conductivity

In a nonuniformly heated system the kinetic equation (11.6) reduces to

$$\boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{r}} = -\frac{f - f_0}{\tau} \tag{11.18}$$

We consider a small temperature gradient and look for a nonequilibrium correction $f_1 \sim \boldsymbol{\nabla} T$ to the Fermi-Dirac distribution, $f = f_0 + f_1$. A partial derivative on the left hand side of the equation above in the linear approximation with respect to ∇T

$$\boldsymbol{v}\frac{\partial f}{\partial \boldsymbol{r}} = \frac{\partial f}{\partial T}\boldsymbol{\nabla} T\boldsymbol{v} = \frac{\partial f_0}{\partial T}\boldsymbol{\nabla} T\boldsymbol{v} + \frac{\partial f_1}{\partial T}\boldsymbol{\nabla} T\boldsymbol{v} \simeq$$

$$\frac{\partial f_0}{\partial T}(\boldsymbol{v}\boldsymbol{\nabla}T) = -\frac{\zeta}{T}\frac{\partial f_0}{\partial \mathcal{E}}(\boldsymbol{v}\boldsymbol{\nabla}T) \quad (11.19)$$

where $\zeta = \mathcal{E}(\boldsymbol{p}) - \mu$ is a quasiparticle energy. Therefore the nonequilibrium correction to the equilibrium Fermi-Dirac distribution is determined by the kinetic equation

$$-\frac{\partial f_0}{\partial \mathcal{E}}\frac{\zeta}{T}(\boldsymbol{v}\boldsymbol{\nabla}T) = -\frac{f_1}{\tau} \quad (11.20)$$

and reads

$$f_1 = (\boldsymbol{v}\boldsymbol{\nabla}T)\tau\frac{\zeta}{T}\frac{\partial f_0}{\partial \mathcal{E}} \quad (11.21)$$

We calculate now a kinetic energy flux

$$\boldsymbol{q} = 2\int \zeta\boldsymbol{v}f\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} \quad (11.22)$$

which again is determined by f_1, as $\zeta\boldsymbol{v}f_0$ is an odd momentum function

$$\boldsymbol{q} = 2\int \zeta\boldsymbol{v}f_1\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} \quad (11.23)$$

After using an explicit f_1 formula we come to an integral

$$\boldsymbol{q} = 2\int \zeta^2\frac{\tau}{T}\frac{\partial f_0}{\partial \mathcal{E}}\boldsymbol{v}(\boldsymbol{v}\boldsymbol{\nabla}T)\frac{\mathrm{d}^3p}{(2\pi\hbar)^3} = \int \boldsymbol{v}(\boldsymbol{v}\boldsymbol{\nabla}T)\tau\nu(\mathcal{E})\frac{\zeta^2}{T}\frac{\partial f_0}{\partial \mathcal{E}}\frac{\mathrm{d}\Omega}{4\pi}\mathrm{d}\mathcal{E} \quad (11.24)$$

which after the energy integration turns into an angle integral over the Fermi surface

$$\boldsymbol{q} = -\frac{\pi^2 k_B^2 T}{3}\int \boldsymbol{v}(\boldsymbol{v}\boldsymbol{\nabla}T)\tau(\mu)\nu(\mu)\frac{\mathrm{d}\Omega}{4\pi} \quad (11.25)$$

and similarly to the electric current flow gives the thermal flux determined by the Fourier law

$$\boldsymbol{q} = -\kappa\boldsymbol{\nabla}T \quad (11.26)$$

where κ is the thermal conductivity given by the following integral

$$\kappa = \frac{\pi^2 k_B^2 T}{3}\int \boldsymbol{v}^2(\mu)\tau(\mu)\nu(\mu)\frac{\mathrm{d}\Omega}{4\pi} = \frac{1}{9}\pi^2 k_B^2 T v^2(\mu)\tau(\mu)\nu(\mu) \quad (11.27)$$

Therefore, we have obtained the thermal conductivity

$$\kappa = \frac{1}{9}\pi^2 k_B^2 T v^2(\mu)\tau(\mu)\nu(\mu) \quad (11.28)$$

determined by values at the Fermi level of the same quantities which determine the electrical conductivity. A comparison of these two coefficients leads to the Wiedemann-Franz law of a universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3e^2} \tag{11.29}$$

given by the Lorentz constant $\frac{\pi^2}{3e^2}$. In conclusion, it is important to note that crucial for this law to hold is the assumption of elastic scattering.

11.4 Free electron gas

Although not applicable to real metals, the free electron gas model gives useful estimations of both electrical and thermal conductivities. For a dispersion $\mathcal{E} = p^2/2m$ the chemical potential $\mu = p_0^2/2m$, and the velocity at the Fermi surface $v(\mu) = p_0/m$. As we have shown

$$\nu(\mu) = \frac{mp_0}{\pi^2 \hbar^3} = \frac{3}{2}\frac{n}{\mu} \tag{11.30}$$

The electrical conductivity formula gives

$$\sigma = \frac{1}{3}e^2 v^2(\mu)\tau(\mu)\nu(\mu) = \frac{2}{3}e^2\frac{1}{m}\mu\tau(\mu)\nu(\mu) = \frac{2}{3}\frac{e^2}{m}\tau(\mu)\frac{3}{2}\frac{n}{\mu}\mu \tag{11.31}$$

that is

$$\sigma = \frac{ne^2\tau(\mu)}{m} \tag{11.32}$$

and the Wiedemann-Franz law gives the thermal conductivity

$$\kappa = \frac{\pi^2}{3e^2}\sigma T = \frac{\pi^2}{3}\frac{n\tau}{m}T \tag{11.33}$$

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