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Probability Theory

Probability theory has been developed to analyze random events. Historically it has been motivated by the treatment of *games of chance* by the italian Renaissance mathematician Gerolama Cardano (1501-1576), famous for his contributions to algebra, and, later, by the mathematicians Pierre de Fermat (1601 or 1607/8 - 1665) and Blaise Pascal (1623-1662) in the sevententh century. The modern formulation of probability theory goes by to the Russian mathematician A.I. Kolmogorov (1903-1987), who also made fundamental contributions to classical mechanics and to the theory of fluid turbulence.

Probability theory is intimately related with the theory of *stochastic processes*. The treatment of stochastic processes has been initiated by Bachelier (1870-1946) (Theorie de la speculation, Dissertation 1900) for economic processes and by A. Einstein in his treatment of Brownian motion in the year 1905.

1.1 Random Events

The subject of probability theory are random events. Random events are the fundamental ingredients of games of chance. A random event can not be predicted with certainty.

1.1.1 Random Events and Deterministic Chaos

Quite frequently, random events are generated by processes governed by deterministic evolution laws, whose outcomes depend sensitively on choosen initial conditions of the process. The outcome of coin tossing depends sensitively on initial position, orientation, initial momentum, and angular momentum, although the motion of the coin is strictly determined.

A further example is the Galton board.

Sensitivity with respect to initial conditions is a signature of chaotic motion.

1.1.2 Random Events and Hidden Processes

An event can appear to be random in the case where there is incomplete knowledge on the process generating the outcome.

1.1.3 Bernoulli Sequences

A Bernoulli trial ncan be visualized as the flipping of a (fair) coin. A Bernoulli sequence is a process composed of a collection of independent Bernoulli trials. It can be generated by the Bernoulli map

$$z_{N+1} = 2z_N - 2[z_N] \tag{1.1}$$

1.1.4 Sample space

The sample space of a random event is the set of all possible outcomes of trials. The sample space can be discrete, i.e. consisting of an enumerable number of events, or continuous.

Discrete Random Events

As examples of discrete random events we mention coin tossing and throwing dice. The elementary events of coin tossing are the outcomes 0, 1 and for throwing dice the events 1,...,6.

Continuous Random Events

As examples of continuous random events we mention the case of a falling needle and a velocity component of a gas molecule. For continuous random variables it only makes sense to talk about the outcome as finding the variable in a certain interval.

For the case of a falling needle one can talk about finding the needle in a sector of angular width $d\varphi$. In case of the velocity of gas molecule a measurement yields a velocity in the interval dv close to v.

The distinction between discrete and continuous random variables is important for the definition of probabilities for random events.

1.2 Discrete Set of Random Variables

The intuitive definition of the probability for the random event ω_i is based on the notion of relative frequency: We perform trials generating a set of N random outcomes. In N_i cases the event ω_i is measured. Provided the outcomes of the trials are mutually independent it is straightforward to define the probability as the relative frequency

$$p_i = lim_{N\to\infty} \frac{N_i}{N} \tag{1.2}$$

The basic assumption here is that for large numbers of trials the probability approaches a limit.

An immediate consequence of this definition is the normalization of the probability. Due to the fact that $sum_i N_i = N$ we obtain the condition

$$\sum_{\omega_i} p_i = 1 \tag{1.3}$$

For a Bernoulli sequence with equal probability we obtain

$$p(0) = \frac{1}{2} \qquad , \qquad p(1) = \frac{1}{2} \tag{1.4}$$

For a fair dice, one obtains

$$p(1) = p(2) = p(3) = p(4) = p(5) = p(6) = \frac{1}{6} \tag{1.5}$$

1.2.1 Expectations, Characteristic Functions, Moments and Cumulants

The probabilities p_i of an event ω_i of the sample space Ω can be used to calculate expectations of functions $m_i = F(\omega_i)$ assigned to the random event ω_i via the mean value

$$\langle m \rangle = lim_{N\to\infty} \frac{1}{N} \sum_i N_i F(\omega_i) = \sum_i p_i m_i \tag{1.6}$$

Furthermore, we can define the second moment

$$\langle m^2 \rangle = \sum_i m_i^2 p_i \tag{1.7}$$

as well as the higher order moments

$$\langle m^n \rangle = \sum_i m_i^n p_i \tag{1.8}$$

An important expectation value is the variance,

$$\sigma^2 = \langle m^2 \rangle - \langle m \rangle^2 = \langle (m - \langle m \rangle)^2 \rangle \tag{1.9}$$

which is related to the so-called root mean square

$$\sigma = \sqrt{\langle (m - \langle m \rangle)^2 \rangle} \tag{1.10}$$

An important expectation value is the so-called characteristic function

$$Z(\alpha) = \sum_j p_j e^{im_j\alpha} = \langle e^{im_j\alpha} \rangle \tag{1.11}$$

which is a function of the variable α. A Taylor expansion of the characteristic function with respect to α yields

$$Z(\alpha) = \sum_{k=0} \frac{(i\alpha)^k}{k!} \sum_j (m_j)^k p_j = \sum_{k=0} \frac{(i\alpha)^k}{k!} \langle m \rangle^k \tag{1.12}$$

This equation demonstrates that $Z(\alpha)$ is the *moment generating function*: The n-th order moment can be obtain by repeated differentiation with respect to α according to

$$< m^n >= \{ \left(\frac{1}{i} \frac{d}{d\alpha} \right)^n Z(\alpha) \}_{\alpha=0} \tag{1.13}$$

A quantity, which is related to the characteristic function, is the so-called cumulant generating function, $W(\alpha)$, defined as the logarithm of $Z(\alpha)$:

$$W(\alpha) = lnZ(\alpha) \tag{1.14}$$

The cumulants are obtained due to

$$C_n = \{ \left(\frac{1}{i} \frac{d}{d\alpha} \right)^n W(\alpha) \}_{\alpha=0} \tag{1.15}$$

One obtains

$$C_1 = \langle m \rangle \qquad , \qquad C_2 = \langle m^2 \rangle - \langle m \rangle^2 \tag{1.16}$$

and similar expressions for higher order terms.

1.2.2 Examples of Discrete Probability Sets

Binomial Distribution

We consider a word of N letters formed by two symbols A, B

$$AA..BA...BBB...BA \tag{1.17}$$

The occurence of the letter A is given by the probability p, the letter B occurs with probability q, respectively:

$$p + q = 1 \tag{1.18}$$

We can ask for the probability to find a word which contains n_0 letters A and, consequently, $n_1 = N - n_0$ letters B

$$P_N(n_1) = \frac{N!}{(N - n_1)!n_1!} p^{n_1} q^{N-n_1} \tag{1.19}$$

This probability is normalized since by the binomial formula:

$$\sum_{n_1}^{N} P_N(n_i) = \sum_{n_1=0}^{N} \frac{N!}{(N-n_1)!n_1!} p^{n_1} q^{N-n_1} = (p+q)^N = 1 \tag{1.20}$$

Let us consider another application of the binomial distribution and consider N radioactive atoms. The probability for the decay of a single atom within a time interval T is given by, where $1/\mu$ is the radioactive decay time:

$$p = 1 - e^{-\mu T} \tag{1.21}$$

Let us determine the probability that, within a time interval T, k atoms have decayed. The probability is just

$$P_N(k) = \frac{N!}{(N-k)!k!}(1 - e^{-\mu T})^k \left(e^{-\mu T}\right)^{N-k} \tag{1.22}$$

Poisson Distribution

The Poisson distribution is obtained in the limiting case $N \to \infty$ under the assumption that

$$p = \frac{a}{N} \tag{1.23}$$

This yields

$$\begin{aligned} P_N(k) &= \frac{N!}{(N-k)!k!}(1 - \frac{a}{N})^{N-k} \left(\frac{a}{N}\right)^k \\ &= \frac{N!}{(N-k)!k!}(1 - \frac{a}{N})^{N} (1 - \frac{a}{N})^{-k} \left(\frac{a}{N}\right)^k \\ &= \frac{N!}{(N-k)!k!}(1 - \frac{a}{N})^{N} a^k (1 - \frac{a}{N})^{-k} \left(\frac{1}{N}\right)^k \end{aligned} \tag{1.24}$$

We use the approximations, which become exact in the limit $N \to \infty$

$$\begin{aligned} (1 - \frac{a}{N})^N &\approx e^{-a} \\ (1 - \frac{a}{N})^{-k} &\approx 1 \\ \frac{N!}{(N-k)!n^k} &\approx 1 \end{aligned} \tag{1.25}$$

Thus, we obtain the Poisson distribution

$$P(n) = \frac{a^n}{n!} e^{-a} \tag{1.26}$$

It is straightforward to see that the probability is normalized

$$\sum_{n=0} P(n) = \sum_{n=0} \frac{a^n}{n!} e^{-a} = e^{-a} \sum_{n=0} \frac{a^n}{n!} = 1 \tag{1.27}$$

The mean value $\langle n \rangle$ is calculated according to

$$\langle a \rangle = \sum_{n=0} n \frac{a^n}{n!} e^{-a} = a \sum_{n=1} \frac{a^{n-1}}{(n-1)!} e^{-a} = a \tag{1.28}$$

1.3 Continuous Set of Random Events, Probability Density

We consider now random variables which can take continuous values, denoted by q.

A realization of such a process could be the angle, which is formed by a needle which falls down and a given direction. This is surely a random variable, which is defined in the interval $0 \leq \varphi \leq 2\pi$. It is clear that the probability to obtain a specific value of this angle is zero. However, one may talk about the probability to find the needle in an angular sector of width $d\varphi$.

This example shows that it only makes sense to talk about the probability to find the continous random variable within a certain interval, denoted by Δq_i, located at the value q_i. This suggests the following procedure for the definition of the probability for a continous set of random events. We divide the space of the continous variable into a discrete set of intervals, so-called bins, of width Δq. For each bin characterized by its location q_i and its width Δq_i we operationally determine the probability as the relative frequency

$$p(q_i, \Delta q_i) = lim_{N \to \infty} \frac{N_i}{N} \tag{1.29}$$

Now, we assume that by a refinement of the bin size the number N_i is proportional to the bin size Δq_i as well as the number of trials N

$$lim_{N \to \infty} N_i = N f(q_i) \Delta q_i \tag{1.30}$$

The probability to find a random variable in a bin of size Δq_i is then given by

$$p(q_i, \Delta q_i) = lim_{N \to \infty} \frac{N_i}{N} = f(q_i) \Delta q_i \tag{1.31}$$

The basic assumption on the statistics of the continuous random variable q is that this density exists.

The probability to find the random variable in the finite interval $q_0, q_0 + Dq_0$ can be calculated by the integral

$$p(q_0, q_0 + Dq_0) = \int_{q_0}^{q_0 + Dq_0} dq f(q) \tag{1.32}$$

1.3.1 Mean Value, Moments

Again, we can define mean values and moments by the limiting procedure

$$< q >= \frac{1}{N} \sum_i N_i q_i = \sum_i p(q_i) q_i = \sum_i f(q_i) q_i \Delta q_i \tag{1.33}$$

The limit leads us to the integral

$$\langle q \rangle = \int dq f(q) q \tag{1.34}$$

Similarly, n-the order moments are obtained

$$\langle q^n \rangle = \int dq q^n f(q) \tag{1.35}$$

The variance and the root mean square of the distribution are defined as follows:

$$\sigma^2 =< q^2 > - < q >^2 = \int dq (q- < q >)^2 f(q) \tag{1.36}$$

Expectation values of functions $H(q)$ are defined accordingly:

$$\langle H(q) \rangle = \int dq H(q) f(q) \tag{1.37}$$

1.3.2 Characteristic Function

A special case is the so-called characteristic function $Z(\alpha)$:

$$Z(\alpha) =< e^{i\alpha q} >= \int dq e^{iq\alpha} f(q) \tag{1.38}$$

It is the Fourier transform of the probability density $f(q)$ and, hence, contains the similar information on the statistics of the random variable q.

The characteristic function is the *moment generating function*. Expanding the exponential function we obtain

$$Z(\alpha) = \sum_{k=0} \frac{(i\alpha)^k}{k!} < q^n > \tag{1.39}$$

This respresentation shows that we can determine the n-th moment by differentiation of the characteristic function

$$< q^n >= \left(\frac{1}{i} \frac{\partial}{\partial \alpha} \right)^n Z(\alpha) \tag{1.40}$$

1.3.3 Cumulant Generating Functions, Cumulants

We can define the so-called *cumulant generating function* as the logarithm of the characteristic function

$$W(\alpha) = lnZ(\alpha) \tag{1.41}$$

Taylor expansion of this function yields the so-called cumulants

$$W(\alpha) = \sum_k \frac{(i\alpha)^k}{k!} C_k \tag{1.42}$$

$$C_n = (\frac{1}{i}\frac{d}{d\alpha})^n Z(\alpha)|_{\alpha=0} \tag{1.43}$$

The first two cumulants are related to the moments:

$$\begin{aligned} C_1 &= \langle q \rangle \\ C_2 &= \langle q^2 \rangle - \langle q \rangle^2 \end{aligned} \tag{1.44}$$

1.3.4 Example: Gaussian Distribution

The Gaussian distribution is defined as

$$f(q) = \frac{1}{\sqrt{2\pi Q}} exp[-\frac{q^2}{2Q}] \tag{1.45}$$

As is well-known, the Fourier transform of a Gaussian is again a Gaussian function. Hence, the characteristic function of a Gaussian distribution is a Gaussian function:

$$Z(\alpha) = \int d\alpha e^{i\alpha q} f(q) = exp[-\frac{Q}{2}\alpha^2] \tag{1.46}$$

The cumulant generating function is a polynomial

$$W(\alpha) = -\frac{Q}{2}\alpha^2 \tag{1.47}$$

Moments of a Gaussian:

$$< q^{2k+1} >= 0 \tag{1.48}$$

$$\begin{aligned} < q^{2k} > &= \int dq \frac{1}{\sqrt{2\pi Q}} exp[-\frac{q^2}{2Q}] q^{2k} \\ &= Q^k \int \frac{1}{\sqrt{2\pi}} d\xi e^{-\frac{\xi^2}{2}} \xi^{2k} \end{aligned} \tag{1.49}$$

Normalization of the Gaussian distribution

We shall evaluate the integral

$$I = \int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2Q}} \tag{1.50}$$

To this end we determine I^2

$$I^2 = \left[\int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2Q}} \right]^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-\frac{x^2+y^2}{2Q}} \tag{1.51}$$

This integral can be calculated in cylindrical coordinates

$$I^2 = \int_0^{\infty} \int d\varphi dr r e^{-\frac{r^2}{2Q}} = 2\pi Q \tag{1.52}$$

As a consequence, we obtain

$$I = \int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2Q}} = \sqrt{2\pi Q} \tag{1.53}$$

Moments of the Gaussin Distribution

It is straightforward to calculate the even moments of the Gaussian distribution. They are defined according to

$$\langle x^{2k} \rangle = \int dx x^{2k} \frac{e^{-\frac{x^2}{2Q}}}{\sqrt{2\pi Q}} \tag{1.54}$$

and can be determined via the characteristic function. They read

$$\langle x^{2k} \rangle = \frac{(2k)!}{k! 2^k} Q^k \tag{1.55}$$

Cumulants of the Gaussian Distribution

A Gaussian distribution is completely specified by the two cumulants $C_1 = \langle q \rangle$ and $C_2 = \langle q^2 \rangle - \langle q \rangle^2$.

Perturbative evaluation of expectation values

We consider the approximative evaluation of expectations of functions $G(q)$ with respect to a Gaussian distribution, To this end we explicitly have to evaluate the integral

$$
\begin{aligned}
< G > &= \int \frac{1}{\sqrt{2\pi Q}} exp[-\frac{q^2}{2Q}] G(q) \\
&= \int \frac{1}{\sqrt{2\pi Q}} exp[-\frac{q^2}{2Q}] \sum_l \frac{g_l}{l!} q^l
\end{aligned}
\tag{1.56}
$$

The evaluation can be determined using the general expressions for the moments

$$
< G >= \sum_{2k} g_{2k} Q^k \frac{1}{k! 2^k} \tag{1.57}
$$

Usually, convergence of the sum is a problem.

1.3.5 Example: Cauchy distribution

$$
Z(\alpha) = e^{ika-|k|\gamma} \tag{1.58}
$$

1.3.6 Functions of Continuous Random Variables

We can consider functions $x(q)$ of a random variable q and investigate the probability distribution $F(x)$. The question is, how the distributions $F(x)$ and $f(q)$ are related. To this end we recall that

$$
F(x)dx = f(q)dq \tag{1.59}
$$

where x and q are related via the transformation $x(q)$, and the infinitesimal intervals are related by

$$
dx = |\frac{dx(q)}{dq}| dq \tag{1.60}
$$

Explicitly, this means

$$
f(q) = F(x(q)) |\frac{dx(q)}{dq}| \tag{1.61}
$$

If the function $x(q)$ has a unique inverse, $q = Q(x)$ we obtain the inverse formula

$$
F(x) = f(Q(x)) |\frac{dQ(x)}{dx}| \tag{1.62}
$$

Formally, we can express the relation between the two distributions by the relation

$$F(x) = \int dq \delta(x - x(q)) f(q) \tag{1.63}$$

This relationship allows us to calculate the distribution $F(x)$ also in case where the equation $x - x(q) = 0$ has several solutions, denoted by $Q_i(x)$. The property

$$\delta(x - x(q)) = \sum_i \delta(q - Q_i(x)) \frac{1}{|\frac{dQ_i(x(q))}{dq}|_{q=Q_i(x)}} \tag{1.64}$$

yields the general relation

$$F(x) = \sum_i f(Q_i(x)) \frac{1}{|\frac{dQ_i(x(q))}{dq}|_{q=Q_i(x)}} \tag{1.65}$$

1.4 Combinatorics and Probabilities

Example: A person has N different key's in his pocket. The probability to find the key for the car is just

$$p = \frac{1}{N} \tag{1.66}$$

How big is the probability to find the key after at a certain k trial k? We assume the trials to be independent. Answer: There are (N-1)! possibilities to arrange N keys in a line with the key of the car at the position k. Thus, the probability is

$$p_K = \frac{(N-1)!}{N!} = \frac{1}{N} \tag{1.67}$$

Example: We randomly distribute n (different) things into N boxes. We ask the question, how probable it is to find k thinks in one of the N boxes.

We consider the number of ways, to select k distinct objects, which is given by

$$n(n-1)...(n-k+1) \tag{1.68}$$

Since we are interested in the sequence, we have to divide this number by the number of permutations $k!$

$$(\frac{n}{k}) = \frac{n(n-1)...(n-k+1)}{k!} \tag{1.69}$$

The remaining (n-k) objects can be distributed into (N-1) boxes. The probability distribution is given by

$$p(k,n,N) = (\frac{n}{k})(N-1)^{n-k}\frac{1}{N^n} = (\frac{n}{k})\frac{1}{N^k}(1 - \frac{1}{N})^{n-k} \tag{1.70}$$

1.5 Joint Probabilities

Joint probabilities arise naturally by considering two sets of random events, Ω_1, Ω_2. The joint set of events is formed by the direct product of the set of events $\Omega = \Omega_1 \times \Omega_2$

1.5.1 Discrete Events

Again, we can define probability distributions for each event, which, for the case of discrete random events, are characterized by two numbers m_1, m_2. Operationally, they are defined by the limit

$$p(m_1, m_2) = lim_{N \to \infty} \frac{N_{m_1,m_2}}{N} \tag{1.71}$$

where N is the number of trials and N_{m_1,m_2} is the number of trials with outcomes m_1 for the first random event and m_2 for the second random event. Evidently, the treatment can be extended to a number n of random events characterized by the numbers $\mathbf{m} = [m_1, .., m_2]$. The probability distribution $p^1(m_1)$ of the single random event characterized by m_1 is obtined accordint to

$$p^1(m_1) = \sum_{m_2} p(m_1, m_2) \tag{1.72}$$

Similarly, we obtain the distribution $\tilde{p}^1(m_2)$ for the variable m_2.

The joint probability distributions are normalized

$$\sum_{m_1,m_2} p(m_1, m_2) = 1 \tag{1.73}$$

1.5.2 Continuous Random Variables

Furthermore, we can consider joint probability densities of joint continuous random events, which we characterize by the continuous variables q_1, q_2. Denoting the probabilities for finding the first variable in the interval $q_1, q_1 + dq_1$ and the second variable in the interval $q_2, q_2 + dq_2$ we can defined the probability distribution

$$p(q_1, dq_1; q_2, dq_2) \tag{1.74}$$

and the joint probability density Verteilungsfunktion

$$p(q_1, dq_1; q_2, dq_2) = f(q_1, q_2) dq_1 dq_2 \tag{1.75}$$

The probability density $f^1(q_1)$ of the single random event is given by

$$f^1(q_1) = \int dq_2 f(q_1, q_2) \tag{1.76}$$

The generalization to a vector of random continous variables is straightforward. The joint probability density is denoted by

$$f(\mathbf{q}) \tag{1.77}$$

The definition of the joint probability density via the limiting procedure shows that the probability densities are normalized

$$\int f(\mathbf{q})d^nq = 1 \tag{1.78}$$

The case of a distribution of a random vector $\mathbf{x}$ which is obtained by the coordinate transformation

$$\mathbf{x} = \mathbf{X}(\mathbf{q}) \tag{1.79}$$

is obtained via the relationship

$$F(\mathbf{x})d^nx = f(\mathbf{q})d^nq \tag{1.80}$$

This relation leads us to

$$F(\mathbf{x}) = f(\mathbf{Q}(\mathbf{x})J \qquad , \qquad J = Det\left[\frac{\partial Q_i}{\partial x_j}\right] \tag{1.81}$$

1.5.3 Statistical Independency

Discrete random variables:

$$p(m_1, m_2) = p_1(m_1)p_2(m_2) \tag{1.82}$$

Continuous random variables:

$$f(q_1, q_2) = f_1(q_1)f_2(q_2) \tag{1.83}$$

1.5.4 Conditional Probabilities, Bayes Theorem

Conditional probabilities are introduced to characterize joint events, where the outcome of one event is fixed. The conditional probability of the event m_1 with sure outcomes for the variable m_2 is defined according to

$$p(m_1|m_2) = \frac{p(m_1, m_2)}{p_2(m_2)} \tag{1.84}$$

Here, $p_2(m_2)$ denotes the probability of the event m_2. It is possible to consider the conditional probability

$$p(m_2|m_1) = \frac{p(m_1, m_2)}{p_1(m_1)} \tag{1.85}$$

As a result, we obtain Bayes theorem

$$P(m_2|m_1) = p(m_1|m_2)\frac{p_1(m_1)}{p_2(m_2)} \tag{1.86}$$

It is clear that we can define conditional probability densities for the case of continuous random variables.

1.5.5 Example: Maxwell-Distribution

As an example we consider the distribution of velocities of particles in an ideal gas. They are given by the Maxwell distribution

$$f(v_x, v_y, v_z) = e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2} = f(v_x)f(v_y)f(v_z) \tag{1.87}$$

Let us now determine the probability density of the modulus of the velocity, defined by

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{1.88}$$

1.5.6 Example: Multivariate Gaussian distribution

$$f(\mathbf{q}) = \frac{1}{\sqrt{(2\pi)^n det\sigma}} exp[-\frac{1}{2}\mathbf{q} \cdot \sigma^{(-1)} \cdot \mathbf{q}] \tag{1.89}$$

The expression in the exponent is defined according to

$$\mathbf{q} \cdot \sigma^{(-1)} \cdot \mathbf{q} = \sum_{i,j} q_i [\sigma^{(-1)}]_{ij} q_j \tag{1.90}$$

Thereby, the matrix elements of the matrix $\sigma^{(-1)}$ are denoted by

$$[\sigma^{(-1)}]_{ij} \tag{1.91}$$

In general

$$[\sigma^{(-1)}]_{ij} \neq \frac{1}{\sigma_{ij}} \tag{1.92}$$

Diagonalization

Since $\sigma^{(-1)}$ is a symmetric matrix, we can find a unitary transformation U

$$\mathbf{w} = U\mathbf{q} \tag{1.93}$$

such that the matrix $\Sigma^{(-1)}$

$$U^{(-1)}\sigma^{(-1)}U = \Sigma^{(-1)} \tag{1.94}$$

is a diagonal matrix. Due to

$$\det U = 1 = Det \left[\frac{\partial w_i}{\partial q_j}\right] \tag{1.95}$$

We simply opbtain.

We can find the normalization factor

$$\begin{aligned} N^{-1} &= \int d\mathbf{q} e^{-\frac{1}{2}\mathbf{q}\cdot\sigma^{-1}\cdot\mathbf{q}} \\ &= \int d\mathbf{w} e^{-\frac{1}{2}\mathbf{w}\cdot\Sigma^{-1}\cdot\mathbf{w}} \\ &= \int \Pi_i dw_i e^{-\frac{1}{2}\sum_i \frac{w_i^2}{\Sigma_i}} = \sqrt{(2\pi)^n \Sigma_1..\Sigma_n} \end{aligned} \tag{1.96}$$

However, since we have the identity

$$Det U^{-1}\Sigma^{-1}U = Det\Sigma^{-1} = Det\sigma^{-1} \tag{1.97}$$

we simply obtain:

$$N = \frac{1}{\sqrt{(2\pi)^n Det\sigma}} \tag{1.98}$$

Moments:

$$< q_1 q_2 >=< U_{1j}^{-1} w_j U_{2k}^{-1} w_k >= U_{1j}^{-1} U_{2k}^{-1} \delta_{jk} = \sigma_{12} \tag{1.99}$$

$$< q_1 q_1 >=< U_{1j}^{-1} w_j U_{1k}^{-1} w_k >= U_{1j}^{-1} U_{1k}^{-1} \delta_{jk} = \sigma_{11} \tag{1.100}$$

$$< q_1 q_2 q_3 q_4 >= \sigma_{12}\sigma_{34} + \sigma_{13}\sigma_{24} + \sigma_{14}\sigma_{23} \tag{1.101}$$

Characteristic Function, Cumulant Generating Function

The characteristic function reads

$$Z(\alpha) = e^{-\frac{1}{2}\alpha\sigma\alpha} \tag{1.102}$$

and the cumulant generating function takes the form

$$W(\alpha) = -\frac{1}{2}\alpha\sigma\alpha \tag{1.103}$$

1.6 Central limit theorem

The central limit theorem explains why the *normal distribution*, i.e. the Gaussian distribution is frequently encountered in nature.

The central limit theorem makes a statement about the statistics of a variable X, which is additively obtained from the following superposition of random variables q_i:

$$X = \frac{1}{N}\sum_i q_i \tag{1.104}$$

The random variables q_i, thereby, have to have the following properties:

- The variables q_i are mutually statistically independent.
- The variables q_i are identically distributed.
- They have vanishing mean $< q_i >$.
- The second moment exists $\sigma =< q_i^2 >= Q$.

Let us now formulate these conditions in mathematical terms. Due to the assumption of statistical independency the joint probability distribution of the variables $q_1, ..q_N$ is given by the product of the distribution $F(q_i)$ of the single variable q_i. All variables possess the same distribution $F(q)$

$$f(q_1, ..., q_N) = F(q_1)F(q_2)...F(q_N) \tag{1.105}$$

The probability distribution $g(X)$ of the random variable X is obtained from the evaluation of the integral

$$g(X) = \int dq_1.. \int dq_N \delta(X - \frac{1}{\sqrt{N}} \sum_i q_i) f(q_1, ..., q_N) \tag{1.106}$$

The *central limit theorem* states that in the limit $N \to \infty$ the distribution $g(X)$ tends to a Gaussian with the variance

$$Q = \sigma \tag{1.107}$$

The proof of the central limt theorem is as follows. We insert the representation of the δ-function

$$\delta(X - \frac{1}{\sqrt{N}} \sum_i q_i) = \frac{1}{2\pi} \int d\alpha e^{i\alpha(X - \frac{1}{\sqrt{N}} \sum_i q_i)} \tag{1.108}$$

into the basic relation (1.106):

$$\begin{aligned} g(X) &= \int dq_1..dq_N \frac{1}{2\pi} \int d\alpha e^{i\alpha X} F(q_1)...F(q_N) e^{-i\frac{\alpha}{\sqrt{N}} \sum_{i=1}^N q_i} \\ &= \frac{1}{2\pi} \int d\alpha e^{i\alpha X} \{ \int dq F(q) e^{-i\frac{\alpha}{\sqrt{N}} q} \}^N \end{aligned} \tag{1.109}$$

The integral with respect to q can be expressed by the characteristic function of the distribution $F(q)$,

$$Z(\alpha) = \int dq F(q) e^{i\alpha q} \tag{1.110}$$

Furthermore, we introduce the representation of the characteristic function in terms of the cumulant generating function $W(\alpha)$:

$$Z(\alpha) = e^{W(\alpha)} = e^{\sum_{k=2} \frac{C_k}{k!} (i\alpha)^k} \tag{1.111}$$

Due to the assumption, that the mean value of the distribution $F(q)$ vanishes the Taylor expansion of the cumulant generating function $W(\alpha)$ starts with the term α^2.

We are now in the position to perform the limit $N \to \infty$.

Therefore, we have to consider the quantity

$$\{Z(-\frac{\alpha}{\sqrt{N}})\}^N = e^{N\ W(\frac{-\alpha}{\sqrt{N}})} = e^{N \sum_{l=2} \frac{C_l}{l!}\left(-\frac{\alpha}{\sqrt{N}} i\right)^l} = e^{-\frac{C_2}{2}(\alpha)^2} \tag{1.112}$$

We have to identify the cumulant C_2 with the second moment, $C_2 = Q$.

The distribution $g(X)$ now takes the following form:

$$g(X) = \frac{1}{2\pi} \int d\alpha e^{i\alpha X} e^{-\frac{C_2}{2}\alpha^2} \tag{1.113}$$

This is the Fourier representation of the Gaussian distribution with variance $C_2 = Q$.

1.6.1 Example

It is instructive to perform the calculations leading to the central limit theorem for a specific example. To this end we consider variables q_i which are equally distributed in the range $-1 \leq q \leq 1$. The characteristic function reads

$$Z(\alpha) = \int dq f(q) e^{i\alpha q} = \frac{1}{2} \int_{-1}^{1} dq e^{i\alpha q} = \frac{1}{\alpha} sin\alpha \tag{1.114}$$

The cumulant generating function is

$$W(\alpha) = ln \frac{sin\alpha}{\alpha} \tag{1.115}$$

We have to consider the limit $N \to \infty$

$$N[W\left(-\frac{\alpha}{\sqrt{N}}\right)] = N ln \frac{sin \frac{-\alpha}{\sqrt{N}}}{\frac{-\alpha}{\sqrt{N}}} \tag{1.116}$$

1.7 Stable Distributions

1.7.1 The Definition of Stable Distributions

The Gaussian distribution belongs to the class of *stable distributions*. In order to define the class of stable distributions we generalize the treatment of the preceding section leading to the central limit theorem in several respects. Again we assume that the variables q_i $i = 1, .., N$ are independent identically distributed variables. However, we do not require the existence of the second moment. We consider the quantity X, which is obtained additively from the q_i with the coefficients C_N and γ_N, which are specified later:

$$X = \frac{1}{c_N}[\sum_{i=1}^{N} q_i - \gamma_N] \tag{1.117}$$

We determine the distribution of X, $g(X)$ according to

$$g(X) = \int dq_1..dq_N \delta(X - \frac{1}{c_N}[\sum_{i=1}^{N} q_i - \gamma_N])f(q_1)...f(q_N) \tag{1.118}$$

Like in the derivation of the central limit theorem we introduce the representation of the δ-function

$$\delta(X - \frac{1}{c_N}[\sum_{i=1}^{N} q_i - \gamma_N]) = \frac{1}{2\pi}\int d\Omega e^{i\Omega(X - \frac{1}{c_N}[\sum_{i=1}^{N} q_i - \gamma_N])} \tag{1.119}$$

and obtain the following representation of the distribution $g(X)$:

$$g(X) = \frac{1}{2\pi}\int d\Omega \left(Z(-\frac{\Omega}{c_N}) \right)^N e^{i\Omega X} e^{i\Omega\gamma_N/c_N} \tag{1.120}$$

We introduce the characteristic function $Z_g(\alpha)$ of the distribution $g(X)$. We can express this function in terms of the characteristic function of $f(q)$:

$$Z_g(\Omega) = Z(-\frac{\Omega}{c_N})^N e^{i\Omega\gamma_N} \tag{1.121}$$

Furthermore, we obtain for the corresponding cumulant generating functions

$$W_g(\Omega) = NW(-\frac{\Omega}{c_N}) + i\Omega\frac{\gamma_N}{c_N} \tag{1.122}$$

Definition: *A stable distribution is a distribution which fulfills the equation*

$$W(\Omega) = NW(-\frac{\Omega}{c_N}) + i\Omega\frac{\gamma_N}{c_N} \tag{1.123}$$

with suitably chosen variables c_N *and* γ_N.

As we shall show this equation has nontrivial solutions. A solution is the Gaussian distribution with

$$W(\Omega) = -\frac{Q}{2}\Omega^2 \tag{1.124}$$

where we have to chose $c_N = 1/\sqrt{N}$. We will see that there are further solutions, which define probability distributions.

1.7.2 Stable Distributions

To be completed

The defining equation (1.124) allows one to separate the linear terms in ω:

$$W(\Omega) = i\Omega < X > + \tilde{W}(\Omega) \tag{1.125}$$

This yields a first equation for the mean values:

$$\langle X \rangle = -\frac{N}{c_N} < X > + \frac{\gamma_N}{c_N} \tag{1.126}$$

For each value of c_N we can find a value γ_N such that this relation can be fulfilled:

$$\gamma_N = (c_N + N) < X > \tag{1.127}$$

As a consequence, we can now restrict our attention to solutions of the functional equation

$$W(\Omega) = NW(-\frac{\Omega}{c_N}) \tag{1.128}$$

$$W(\Omega) = lnZ(\Omega) = i\gamma\Omega - c|\Omega|^{\alpha}\{1 + i\beta\frac{\Omega}{|\Omega|}h(\Omega, \alpha)\} \tag{1.129}$$

α, β, γ, c sind Konstanten, sodass

$$\begin{aligned} 0 < \alpha &\leq 2 \\ -1 < \beta &< 1 \\ c &> 0 \\ h(\Omega, \alpha) = tan\frac{\pi\alpha}{2} \qquad \alpha &\neq 1 \\ h(\Omega, \alpha) = \frac{2}{\pi}ln|\Omega| \qquad \alpha &= 1 \end{aligned} \tag{1.130}$$

c: Skalierung
γ: Translation

Lévy Index α. $C_N = n^{1/\alpha}$

Symmetrische Verteilungen: $\beta = 0$

Lévy-Gnedenko central limit theorem:

- q_i: identisch verteilte, statistisch unabhängige Zufallszahlen
- $Q = \sum_i q_i$
- Bei geeigneter Normierung strebt im Grenzfall $N \to \infty$ die Verteilung von Q gegen eine stabile Verteilung. Ist die Varianz von Q endlich, dann ist die Verteilung die Gauss-Verteilung

Lévy-Verteilungen:

$$f_{\alpha,\beta}(q) = \frac{1}{\pi} \int_0^\infty exp[-i\Omega q - \Omega^\alpha e^{i\frac{\pi\beta}{2}}] \tag{1.131}$$

Asymptotisches Verhalten für $q \to \infty$:

$$f_{\alpha,\beta}(q) \approx \frac{A_{\alpha,\beta}}{|q|^{1+\alpha}} \qquad \alpha < 2 \tag{1.132}$$

$$f_{1,0}(q) = \frac{a}{\pi(a^2 + q^2)} \tag{1.133}$$

Für $\alpha \approx 0$ kann $f_{\alpha,1}$ durch eine Log-normal-Verteilung angenähert werden

$$f_{\alpha,1} = \frac{1}{q} e^{-\frac{\alpha^2}{2} ln^2 q} \tag{1.134}$$

1.8 Bedingte Verteilungen, Bayessches Theorem

$$p(m_1|m_2) = p(m_1, m_2)/p(m_2) \tag{1.135}$$

Bayessches Theorem

$$p(m_1|m_2) = p(m_2|m_1) \frac{p(m_1)}{p(m_2)} \tag{1.136}$$

1.9 Axiomatic Foundation of Probability

1.9.1 Elementary Events Ω, Sample Space

Elementary events: ω_i
Sample Space: Ω Set of elementary events

Example: Throwing Coins

Events: $\omega_1 = 0$, $\omega_2 = 1$
Sample space:

$$\Omega = \{0, 1\} \tag{1.137}$$

Example: Throwing Dices

$\omega_1 = 1$, $\omega_2 = 2$, ..., $\omega_6 = 6$
Sample space:

$$\Omega = \{1, 2, ...6\} \tag{1.138}$$

Example: Ideal gas

Events: Velocity of a gas particle
Sample space: real velocity axis R^1

1.9.2 Events

Events are subsects of the sample space Ω
A, B: Subsets of Ω , $A \in \Omega$, $B \in \Omega$

Sure Event: $A = \Omega$
Empty Set : $A = 0$

Events are constructed by union and intersection
1. Union $A \bigcup B$
2. Intersection $A \bigcap B$
3. Complement $\bar{A} = \Omega - A$

1.9.3 σ-Algebra

A σ-Algebra is a class B of subsets B_i of the sample space Ω with the properties :
1. $\Omega \in B$
2. $B_i \in B \rightarrow \Omega - B_i \in B$
3. $B_i \in B \rightarrow \bigcup_{i=1}^{N} B_i \in B$

The conditions 2, 3 imply:
$B_i \in B \rightarrow \bigcap_{i=1}^{N} B_i \in B$

The sample space Ω together with a σ-Algebra B form the measurable space $\{\Omega, B\}$.

Coins

$\Omega = \{0, 1\}$

trivial σ-algebra: $B_1 = 0$, $B_2 = \Omega$

A nontrivial σ-algebra is generated by the sets: $\Omega = \{0, 1\}$, 0, $\{0\}$, $\{1\}$

Motion along a line $\boldsymbol{\Omega : R}$

σ-Algebra

R
interval [a,b)
complement to [a,b)

The sample space Ω together with the σ-Algebra B consisting of all intervals $[a, b)$ and its complements forms the measurable space $\{\Omega, B\}$.

1.9.4 Probability space $\{\boldsymbol{\Omega, B, P}\}$

A measurable space becomes a probability space, if we assign to each element of the σ-algebra a function P such that

- $P(B_i) \geq 0$
- $P(\Omega) = 1$
- $P(\bigcup_{i=1}^{N} B_i) = \sum_i^N P(B_i)$, falls $A_i \wedge A_j = 0$, für alle i,j

These conditions infer $P(0) = 0$

Interpretation:
$P(B_i)$ is the probability that an elementary event ω is contained in the subset B_i. The intuitiv definition of $P(B_i)$ is:

$$P(B_i) = lim_{N\to\infty} \frac{\mathrm{e}rfolgreicheVersuche}{N} \tag{1.139}$$

The axioms have the following meaning::

1. Probabilities are ≥ 0
2. The probability of the sure event is $P(\Omega) = 1$
3. If $B_1 \bigcap B_2 = 0$, then no event is simultaneously contained in the set B_1 and B_2. It is intuitive that the probability is additive, $P(B_1 \bigcap B_2) = P(B_1) + P(B_2)$.

The notion of a probability space gives the intuitive definition of probability an axiomatic basis.

2

Information and Entropy

2.1 Stirling's Formula

In the following we shall make use of an approximate formula for the quantity $N!$. To this end we consider

$$lnN! = ln1 + ln\ 2 + .. + lnN = \sum_{i=1}^{N} ln\ i \tag{2.1}$$

For large values of N we can approximate the discrete sum by an integral:

$$\sum_{i=1}^{N} lni = \int_1^N dxlnx = [xln\ x - x]_1^N = N[ln\ N - 1] + 1 \tag{2.2}$$

As a consequence we obtain

$$N! \approx e^{Nln\ N - N + 1} \approx e^{N(ln\ N-1)} \tag{2.3}$$

2.2 Information and Entropy

The probabilities of random events are determined by trials. Observation of the outcome of a trial yields some information, which clearly depends on the detailed form of the distribution p_i. It is clear, that a deterministic event yields no information, since the outcome of the trial is determined and can be predicted with certainty. The information is maximal for the case where the probabilities p_i of the random event ω_i are equal. In this case the outcome of the trials are maximally undetermined and, performing the trial, the outcome yields maximal information.

In the following we shall formalize this subjective meaning of information by introducing the information $S(p)$ as a functional of the probability p_i. We restrict our treatment to the case of discrete random variables.

2.2.1 Number of Realizations

We consider the random process of throwing a coin n-times. Each realization can be represented by a sequence of zero's and one's:

$$0, 0, 1, 0, ...1 \tag{2.4}$$

We can now count the number of all possible words or sequences, which can be formed by this process. We obtain

$$R = 2^n \tag{2.5}$$

realizations R.

2.2.2 Measure of Information

It is evident that the information I, which is gained after the observation of a single trial, is a function of the number R of realizations of a random process.

$$I = I(R) \tag{2.6}$$

The functional form of the information is fixed by the requirement that the information is additive for joint events, which are statistically independent.

Let us consider the simple example: We perform N trials, where we simultaneously through a dice and a coin. The number of different outcomes is

$$R = (2 \times 6)^N = 2^N \times 6^N = R_1 \times R_2 \tag{2.7}$$

It is quite natural to postulate that the information $I(R)$ factors if the number of realizations factorizes:

$$R = R_1 R_2 \tag{2.8}$$

$$I(R_1 R_2) = I(R_1) + I(R_2) \tag{2.9}$$

This is a functional equation which defines the information up to a constant K as the logarithm of the number of realizations

$$I = KlnR \tag{2.10}$$

This relation frequently is denoted as Hartley's formula.

The information of a Bernoulli sequence of length N is just

$$I = NKln2 \tag{2.11}$$

The constant K can be choosen in order to fix the unit of I. In information theory one sets

$$K = \frac{1}{ln2}[Bit] \tag{2.12}$$

2.2.3 Information of Two-Letter Words

In contrast to the preceding subsection we consider now two-letter words with a prescibed number N_1 of zero's and number N_2 of one's. The information is obtained from the number of realizations

$$R = \frac{N!}{N_1!N_2!} \tag{2.13}$$

From the number R we can determine the information which can be transported by a word with N_1 zero's and N_2 one's. We obtain

$$I = KlnR = K[lnN! - lnN_1! - lnN_2!] \tag{2.14}$$

The use of Stirling's formula for $lnN!$, which is already good for $N > 100$,

$$lnN! \approx N(lnN - 1) \tag{2.15}$$

yields

$$I = K[NlnN - N_1lnN_1 - N_2lnN_2] = K[(N_1 + N_2)lnN - N_1lnN_1 - N_2lnN_2] \tag{2.16}$$

where we have considered that $N = N_1 + N_2$. Now we can determine the information per symbol

$$i = \frac{I}{N} = -K[\frac{N_1}{N}ln\frac{N_1}{N} + \frac{N_2}{N}ln\frac{N_2}{N}] \tag{2.17}$$

2.2.4 Information of n-Letter Words

We can easily generalize this to the case of Words with n symbols.

$$i = -K\sum_{i=1}^{n}\frac{N_i}{N}ln\frac{N_i}{N} \tag{2.18}$$

This formula defines the so-called *Shannon information*

2.2.5 Information and Probability

We can interpret the numbers

$$p_i = \frac{N_i}{N} \qquad i = 1, ..., n \tag{2.19}$$

for large values of N as the probabilities of random events ω_i.

As a consequence, we can define the information, or information entropy of random events with probability p_i by

$$i = -K \sum_{i=1}^{n} p_i ln p_i \tag{2.20}$$

This quantity is a functional which can be assigned to each probability p_i.

We denote the quantity i information-entropy

$$S = -K \sum_{i} p_i ln p_i \tag{2.21}$$

2.3 Jaynes Principle

A probability distribution can be measured performing large numbers of trials. However, one may also make guesses on distributions.

2.3.1 Equal a Priori Estimates

We can pose the question:

What probability distribution p_i maximizes the information $I(p_1, ...p_n)$?

We have to take into account that the probability is normalized:

$$\sum_{i=1}^{n} p_i = 1 \tag{2.22}$$

In order to answer the above question we have to find the maximum of the information

$$S = -K \sum_{i=1}^{n} p_i ln p_i \tag{2.23}$$

under the constraint (2.22).

To this end we introduce a Lagrange parameter λ and consider the problem:

$$Max_{p_i}\{S + \lambda[\sum_i p_i - 1]\} = Max_{p_i}\{-K \sum_i p_i ln p_i + \lambda[\sum_i p_i - 1]\} \tag{2.24}$$

We solve this problem by the method of variation. We consider

$$p_i = P_i + \delta p_i \tag{2.25}$$

and determine the value of $I + \lambda(\sum_i p_i - 1)]$ up to the order δp_i:

$$\begin{aligned} &- K \sum_i P_i ln P_i + \lambda[\sum_i P_i - 1] \\ &- K \sum_i \delta p_i - K \sum_i \delta p_i ln P_i + \lambda \sum_i \delta p_i \end{aligned} \tag{2.26}$$

Since we want to determine the extremum of this expression we have to conclude that the terms with δp_i vanish identically. This yields

$$-K - KlnP_i + \lambda = 0 \tag{2.27}$$

This yields the solution

$$P_i = e^{\lambda/K-1} \tag{2.28}$$

We are now able to determine the Lagrange parameter λ in order to fulfill the constraint

$$\sum P_i = 1 \qquad \to e^{\lambda/K-1} = \frac{1}{n} \tag{2.29}$$

The answer to the above question is therefore:
The probability P_i which maximizes information is the distribution

$$p_i = \frac{1}{n} \tag{2.30}$$

This means all states have the same probability. The information entropy can be easily calculated:

$$S = Klnn \tag{2.31}$$

Constraints

We extend the question of the previous subsection by taking into account the fact that more is known about the probability distribution except that it should be normalized.

We assume that the mean values of functions f_i^α $\alpha = 1, ..k$ are known,

$$\sum_i p_i f_i^\alpha = F^\alpha \qquad \alpha = 0, 1, .., k \tag{2.32}$$

where we have included for $\alpha = 0$ the case $f^0 = 1$. Now we pose the question: *How can we choose a probability distribution p_i, which is compatible with the constraints (2.32).*

The question can be solved by invoking the maximum entropy principle by Jaynes. He suggests to use the probability distribution which maximizes the information

$$S = -K \sum_i p_i ln p_i \tag{2.33}$$

where the probability p_i is choosen in accordance with the constraints (2.32).

In order to solve the problem we introduce (k+1) Lagrange parameters λ^α and consider the variational problem

$$Max\{S/K - \sum_{\alpha=0}^{k} \lambda^\alpha [\sum_i p_i f_i^\alpha - F^\alpha]\} = 0 \tag{2.34}$$

The variation leads us to

$$[-\sum_i P_i lnP_i - \sum_i [\delta p_i lnP_i + \delta p_i] - \sum_{\alpha=0}^{k} \lambda^\alpha \sum_i f_i^\alpha \delta p_i] = 0 \tag{2.35}$$

The extremum is obtained for

$$lnP_i + 1 = -\sum_{\alpha=0}^{k} \lambda^\alpha f_i^\alpha \tag{2.36}$$

The solution is then given by

$$P_i = e^{-\sum_{\alpha=0}^{k} \lambda^\alpha f_i^\alpha} = e^{\lambda_0 - 1 - \sum_{\alpha=1}^{k} \lambda^\alpha f_i^\alpha} \tag{2.37}$$

We can exploit the normalization condition

$$\sum_i P_i = 1 = e^{\lambda_0 - 1} \sum_i e^{-\sum_{\alpha=1}^{k} \lambda^\alpha f_i^\alpha} \tag{2.38}$$

in terms of the Lagrange parameters. Now, we define the quantity

$$Z = \sum_i e^{-\sum_{\alpha=1}^{k} \lambda^\alpha f_i^\alpha} \tag{2.39}$$

Then we can rewrite the probability distribution

$$P_i = Z^{-1} e^{-\sum_{\alpha=1}^{k} \lambda^\alpha f_i^\alpha} \tag{2.40}$$

The next step is to eliminate the Lagrange parameters by the constraints (2.22).

2.3.2 Evaluation of the Information-Entropy

It is interesting to calculate the information-entropy S for the probability distribution P_i, which maximizes this quantity under the constraints (2.22). A straightforward calculation yields

$$\begin{aligned} S/K &= lnZ + \sum_i P_i \sum_{\alpha=1}^{k} \lambda^\alpha f_i^\alpha \\ &= lnZ + \sum_{\alpha}^{k} \lambda^\alpha \sum_i P_i f_i^\alpha = lnZ + \sum_\alpha \lambda^\alpha F^\alpha \end{aligned} \tag{2.41}$$

and the final relationship yields an expression of the information entropy in terms of the constraints and the Lagrangian parameters:

$$S = KlnZ + K \sum_{\alpha=1}^{k} \lambda^\alpha F^\alpha \tag{2.42}$$

2.4 Maximum Information Principle: Continous States

We consider now the case of continous random variable. We introduce

$$p_i = h(q_i)dq_i \tag{2.43}$$

The entropy reads

$$S = -K\sum_i h(q_i)dq_i ln\left[h(q_i)dq_i\right] = -\sum_i h(q_i)lnh(q_i)dq_i - \sum_i h(q_i)dq_i lndq_i \tag{2.44}$$

We take $dq_i = \epsilon$ small but finite, the we obtain

$$S = -K\int dqh(q)lnh(q) - Kln\ \epsilon \tag{2.45}$$

The probability density can be estimated again by the maximum information principle

$$Max\{-\frac{1}{K}\int dqh(q)lnh(q) - \sum_{\alpha=0}^{k}\lambda^{(\alpha)}\left[\int dqh(q)f(q)^{\alpha} - F^{\alpha}\right]\} \tag{2.46}$$

The result is a straightforward generalization of the discrete case:

$$h(q) = Z^{-1}(\lambda^1 ... \lambda^k)e^{-\sum_{\alpha=1}^{k}\lambda^{(\alpha)}f^{\alpha}(q)} \tag{2.47}$$

The extension to the multidimensional case again is evident:

$$h(\mathbf{q}) = Z^{-1}(\lambda^1 ... \lambda^k)e^{-\sum_{\alpha=1}^{k}\lambda^{(\alpha)}f^{\alpha}(\mathbf{q})} \tag{2.48}$$

3

Maximum Entropy Principle and Thermodynamics

In this section we shall apply the maximum entropy principle to estimate the probability distributions of thermodynamic systems under various constraints. This will allow us to introduce the various ensembles of statistical physics of equilibrium.

3.1 Microcanonical Distribution

We consider a system like a gas consisting of N particles contained in a volume V. We assume the system to be isolized. As a consequence, it can be characterized by the total energy U. In thermodynamics, this energy has to be identified with the internal energy U. Then, the entropy is given in terms of the number N of states with the total energy U.

$$S = k_B ln N(U, V, N) \tag{3.1}$$

This is the famous formula of L. Boltzmann, who gave the thermodynamic entropy a statistical interpretation. The entropy is proportional to the logarithm of the number of microscopic realizations of a macrostate.

3.2 Canonical Distribution

We consider now a system, which is in contact with its surrounding. In thermodynamic equlibrium it has the same temperature as the surrounding, which is then called a *heat bath*. In order to maintain this temperature there has to exchange energy with the heat bath. Thus, the energy of the system under consideration fluctuates.

Now, we make the following assumption. The system has states which are characterized by the energies E_i. We estimate the probability for p_i for these states. The maximum entropy principle yields

$$p_i = Z^{-1}(\beta)e^{-\beta E_i} \tag{3.2}$$

where we have denoted the Lagrange parameter by β. The partition function is a function of β and given by the expression

$$Z(\beta) = \sum_i e^{-\beta E_i} \tag{3.3}$$

3.2.1 Lagrange Parameter β

We have to consider the meaning of the Lagrange parameter β. To this end we calculate the entropy S, where we identify the quantity K with the Boltzmann constant k_B:

$$S = -k_B \sum_k p_k ln p_k \tag{3.4}$$

to obtain explicitly

$$S = -k_B \sum_k \frac{e^{-\beta E_k}}{Z}(-\beta E_k - lnZ) \tag{3.5}$$

It is evident that we have to identify the quantity

$$U = \sum_k E_k p_k = \sum_k \frac{e^{-\beta E_k}}{Z} E_k \tag{3.6}$$

with the free energy U and we obtain the relation

$$S = k_B(\beta U + lnZ) \tag{3.7}$$

In order to give a meaning to the Lagrangian parameter β we consider the change of the entropy

$$dS = k_B(d\beta U + \beta dU + \frac{dZ}{Z}) \tag{3.8}$$

under the condition that the energies E_i do not change. From the point of view of thermodynamics, this amounts to keep the volume fixed. We explicitly obtain

$$dZ = -(d\beta)\sum_k E_k e^{-\beta E_k} = -UZd\beta \tag{3.9}$$

which immediately leads us to the relation

$$dS = k_b \beta dU = \frac{dU}{T} \tag{3.10}$$

From this relation we obtain the meaning of the Lagrange parameter β. It is proportional to the inverse temperature

$$\beta = \frac{1}{k_B T} \tag{3.11}$$

3.2.2 Free Energy

It is interesting to determine the thermodynamic potential free energy. It is defined by the Legendre transformation

$$F = U - TS = -k_B T ln Z \tag{3.12}$$

Due to

$$S = \frac{U}{T} + k_B ln Z \tag{3.13}$$

we see that the free energy is directly connected with the partition function Z. The change of the free energy is obtained from

$$dF = -pdV - SdT \tag{3.14}$$

which inferes

$$\begin{aligned} S &= -(\frac{\partial F}{\partial T})_V = k_B \frac{\partial}{\partial T}(T ln Z)_V \\ p &= -(\frac{\partial F}{\partial V})_T = k_B \frac{\partial}{\partial V}(T ln Z)_T \end{aligned} \tag{3.15}$$

The energy values E_i remain unchanged if the volume of a system is kept constant.

Formula (3.15) explicitly shows that the partition function Z plays a central role in statistical physics. One can obtain the pressure and the entropy by differentiating Z with respect to T (with constant V) and with respect to V (with constant T).

3.2.3 Gibbs Free Energy

A further Legendre transform yields the Gibbs free energy

$$G = U + pV = F - UT + pV \tag{3.16}$$

This yields

$$dG = V dp + T dS \tag{3.17}$$

3.3 Grand Canonical Ensemble

We consider a system of particles, which can exchange energy as well as particles with its surroundings. The probability distribution depends on two indices, the index i corresponding to the energy E_i and the index n corresponding to the number of particles.

Then we have two constraints

$$\sum_i \sum_N p_{in} E_i^n = U$$

$$\sum_i \sum_N n p_{in} = N \tag{3.18}$$

The maximum entropy principle yields the probability distribution p_{in} in the form

$$p_{in} = Z(\lambda, \beta)^{-1} e^{-\lambda n - \beta E_i^n} \tag{3.19}$$

where we have defined the *grand canonical partition function*

$$Z(\mu, \beta) = \sum_{i,n} e^{-\lambda n - \beta E_i^n} \tag{3.20}$$

The fundamental termodynamic relation of a system in contact with a heat bath and a particle reservoir is

$$dU = TdS - pdV + \mu dN \tag{3.21}$$

Here, μ denotes the chemical potential.

We calculate the entropy with the grandcanonical distribution to obtain

$$S/k_B = -\sum_{in} Z(\lambda, \beta)^{-1} e^{-\lambda n - \beta E_i^n} [-\lambda n - \beta E_i^n - lnZ] \tag{3.22}$$

Evaluation of the expectations yield

$$S/k_b = \lambda N + \beta U + lnz \tag{3.23}$$

and we obtain the fundamental relationship

$$TS = KTlnZ + KT\lambda N + U] \tag{3.24}$$

Now, we identify

$$kT\lambda = -\mu \tag{3.25}$$

with the chemical potential μ and obtain

$$U = TS + F + \mu N \tag{3.26}$$

The grand canonical distribution function reads

$$p_{i,n} = \frac{1}{Z(\beta, \mu)} e^{-\beta(E_i - \mu n} \tag{3.27}$$

where we have to identify β with $1/k_B T$ and μ with the chemical potential.

4

Statistics of Classical Many-Particle Systems

In this chapter we discuss the equilibrium statistics of classical many particle systems. Classical systems are described by Hamilton's mechanics. The Hamilton function of a many particle system takes the form

$$H(\mathbf{p}_i, \mathbf{q}_i) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_1 ... \mathbf{q}_N) \tag{4.1}$$

$U(\mathbf{q}_1 ... \mathbf{q}_N)$ denotes the potential energy, which contains the two particle interactions as well as the influence of an external force field. The Hamilton function is a constant of motion and equals the energy of the system.

For the probabilistic description of the equilibrium states of such systems we can use the maximum entropy principle to guess the probability distribution

$$f(\mathbf{p}_1 ... \mathbf{p}_N, \mathbf{q}_1 .... \mathbf{q}_N) \tag{4.2}$$

Since momenta and coordinates are continous variables $f(p_1 ... p_N, q_1 .... q_N)$ is a probability density.

We have to consider the normalization and the calculation of expectation values of function $G(\mathbf{p}_1 ... \mathbf{p}_1, \mathbf{q}_1 ... \mathbf{q}_N)$. To this end we have to define the infinitesimal volume element $d\mathit{\Gamma}$ in the *phase space* spanned by the coordinates and momenta. A suitable definition, which is in accordance with quantum statistics is:

$$d\mathit{\Gamma} = \frac{1}{N!} \frac{\mathit{\Pi}_{i=1}^{N} d\mathbf{q}_i d\mathbf{p}_i}{h^{3N}} \tag{4.3}$$

Thereby, h denotes Planck's constant. The volume element is dimensionless, since the product $d\mathbf{q}_i d\mathbf{p}_i$ has the dimension of the $[action]^3$. The factor $1/N!$ also is of quantum mechanical origin.

Normalization of the probability density is

$$\int d\mathit{\Gamma} f(\mathbf{p}_1 ... \mathbf{p}_N, \mathbf{q}_1 .... \mathbf{q}_N) = 1 \tag{4.4}$$

Expectation values are calculated according to

$$\int d\Gamma f(\mathbf{p}_1...\mathbf{p}_N,\mathbf{q}_1....\mathbf{q}_N)G(\mathbf{p}_1...\mathbf{p}_N,\mathbf{q}_1....\mathbf{q}_N) =< G(\mathbf{p}_1...\mathbf{p}_N,\mathbf{q}_1....\mathbf{q}_N) > \tag{4.5}$$

4.1 Microcanonical Distribution

We consider a closed system with fixed energy E and fixed number of particles N

$$E = \sum_i \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_1...\mathbf{q}_N) = H(\mathbf{p}_i,\mathbf{q}_i) \tag{4.6}$$

Since E is conserved, the motion is restricted to the hypersurface (4.6).

Due to the maximum information principle, all states of this hypersurface are equally probable. We can now consider the entropy which is given by

$$S(E,V,N) = kln\Omega(E,V,N) \tag{4.7}$$

where $\Omega(E,V,N)$, in the case of a discrete set of states, would be the total number of these states. In the continuous case it is proportional to the area of the hypersurface, which can be calculated according to

$$\Omega(E,V,N) = \int \frac{\Pi_{i=1}^N d\mathbf{p}_i \int d\mathbf{q}_i}{N!h^{3N}} \delta\left[E - H(\mathbf{q}_j,\mathbf{p}_j)\right] \tag{4.8}$$

The probability distribution is given by

$$f(\mathbf{q}_j,\mathbf{p}_j) = \frac{1}{\Omega(E,V,N)} \delta\left[E - H(\mathbf{q}_j,\mathbf{p}_j)\right] \tag{4.9}$$

We can determine the equation of state for the system as follows: We start from the fundamental thermodynamic relation

$$dU = TdS - pdV + \mu dN \tag{4.10}$$

We obtain the relation

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \tag{4.11}$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \tag{4.12}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S} \tag{4.13}$$

$$0 = \frac{\partial S}{\partial U}\frac{\partial U}{\partial V} + \frac{\partial S}{\partial V} \tag{4.14}$$

This yields:

$$p = \frac{\frac{\partial S}{\partial V}}{\frac{\partial S}{\partial U}} \tag{4.15}$$

$$1 = \frac{\partial S}{\partial U}\frac{\partial U}{\partial S} \tag{4.16}$$

This yields

$$T = \frac{1}{\frac{\partial S}{\partial U}} \tag{4.17}$$

$$0 = \frac{\partial S}{\partial U}\frac{\partial U}{\partial N} + \frac{\partial S}{\partial N} \tag{4.18}$$

This yields:

$$\mu = -\frac{\frac{\partial S}{\partial N}}{\frac{\partial S}{\partial U}} \tag{4.19}$$

4.2 Canonical Distribution

We consider a system of N particles in contact with a heat bath. The constraint is

$$U = \int \frac{\Pi_{i=1}^{N} d\mathbf{p}_i d\mathbf{q}_i}{N! h^{3N}} H(\mathbf{p}_i, \mathbf{q}_i) f(\mathbf{p}_i, \mathbf{q}_i) \tag{4.20}$$

The probability distribution is given by

$$f(\mathbf{p}_i, \mathbf{q}_i) = Z^{-1}(\beta, N, V) e^{-\beta H(\mathbf{p}_i, \mathbf{q}_i)} \tag{4.21}$$

where we have defined the canonical partition function

$$Z(\beta, N, V) = \int \frac{\Pi_{i=1}^{N} d\mathbf{p}_i d\mathbf{q}_i}{N! h^{3N}} e^{-\beta H(\mathbf{p}_i, \mathbf{q}_i)} \tag{4.22}$$

4.3 Grand Canonical Distribution

We consider systems in contact with a heat bath and a particle reservoir. The probability distribution depends on the number N of particles considered:

$$f(\mathbf{q}_j, \mathbf{p}_j, N) \tag{4.23}$$

Normalization requires

$$\sum_N \int \frac{\Pi_{i=1}^{N} d\mathbf{p}_i d\mathbf{q}_i}{N! h^{3N}} f(\mathbf{q}_j, \mathbf{p}_j, N) = 1 \tag{4.24}$$

As a consequence we have two constraints, one for the mean number of particles $< N >$,

$$\sum_n \int \frac{\Pi_{i=1}^n d\mathbf{p}_i d\mathbf{q}_i}{n! h^{3n}} n f(\mathbf{q}_j, \mathbf{p}_j, n) = N \tag{4.25}$$

the other for the mean energy U

$$\sum_n \int \frac{\Pi_{i=1}^n d\mathbf{p}_i d\mathbf{q}_i}{n! h^{3n}} H^n(\mathbf{q}_j, \mathbf{p}_j) f(\mathbf{q}_j, \mathbf{p}_j, n) = U \tag{4.26}$$

The central quantity is the grand partition function

$$Z(\beta, \mu, V) = \sum_{n=0} \int \frac{\Pi_{i=1}^n d\mathbf{p}_i d\mathbf{q}_i}{n! h^{3n}} e^{-\beta[H^n(\mathbf{q}_j, \mathbf{p}_j) - \mu n]} \tag{4.27}$$

We obtain for the entropy

$$S = K[lnZ(\beta, \mu, V) + \beta U - \beta \mu N] \tag{4.28}$$

$$U - TS - \mu N = -\frac{1}{\beta} lnZ(\beta, \mu, V) \tag{4.29}$$

As a consequence, the grand partition function is related to the free energy

$$F = U - TS - \mu N = -\frac{1}{\beta} lnZ(\beta, \mu, V) \tag{4.30}$$

4.4 Example: Ideal Gas

The ideal gas consists of N identical particles in a finite box of volume V. The energy is purely kinetic

$$E = \sum_{i=1}^N \frac{m}{2} \mathbf{u}_i^2 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \tag{4.31}$$

4.4.1 Microcanonical Distribution

In order to determine the entropy we have to calculate the quantity

$$\begin{aligned} \Omega(E, V, N) &= \int \frac{\Pi_{i=1}^N d\mathbf{p}_i d\mathbf{q}_i}{N! h^{3N}} \delta\left(E - \sum_i^N \frac{\mathbf{p}_i^2}{2m}\right) \\ &= \frac{V^N}{N! h^{3N}} \int \Pi_{i=1}^N d\mathbf{p}_i \delta\left(E - \sum_i^N \frac{\mathbf{p}_i^2}{2m}\right) \end{aligned} \tag{4.32}$$

The integral can be assessed using the relation

$$\frac{d}{dE}\Theta(E-H)=\delta(E-H) \tag{4.33}$$

Here, the function $\Theta(x)$ denotes the Heaviside function.

This leads us to consider the quantity

$$\Omega(E,V,N)=\frac{V^N}{N!h^{3N}}\frac{d}{dE}\int d\mathbf{p}_i\Theta\left(E-\sum_i^N\frac{\mathbf{p}_i^2}{2m}\right) \tag{4.34}$$

However, the integral is just the volume of a 3N dimensional sphere with radius $\sqrt{2mE}$ and, hence, is proportional to $\sqrt{2mE}^{3N}$.

The exact expression for the volume of a N-dimensional sphere with radius R is given by

$$V_R=C_NR^N=R^N\frac{2\pi^{N/2}}{\Gamma(N/2)} \tag{4.35}$$

As a consequence, we obtain

$$\Omega(E,V,N)=\frac{V^N}{N!h^{3N}}\frac{d}{dE}C_N(2mE)^{3N/2} \tag{4.36}$$

The constant C_N thereby, is given by

$$C_N=\frac{2\pi^{(3N)/2}}{\Gamma(3N/2)} \tag{4.37}$$

This yields

$$\Omega(E,V,N)=2\pi mV^N(2\pi mE)^{3N/2-1}\frac{1}{h^{3N}N!(3N/2-1)!} \tag{4.38}$$

Using Stirling's approximation

$$\Gamma(3N/2)=(3N/2-1)!=e^{(3N/2-1)(ln(3N/2-1)-1)} \tag{4.39}$$

we obtain the final result

$$\Omega(E,V,N)=\left(\frac{V}{N}\right)^N(\frac{4\pi mEe}{3h^2N})^{3N/2}e^{5N/2}\frac{1}{E}\frac{3N}{2} \tag{4.40}$$

In the next step we can determine the entropy

$$S(E,V,N)=Kln\Omega(E,V,N)=\frac{5NK}{2}+NKln\left[\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right] \tag{4.41}$$

This expression is denoted as *Sackur-Tetrode entropy.*

Internal Energy

We now determine the internal energy U as a function of S, V, N. From we obtain

$$U(S,V,N) = \left(\frac{N}{V}\right)^{2/3} \frac{3h^2N}{4\pi m} e^{\frac{3}{2NK}(S-\frac{5}{2}Nk)} \tag{4.42}$$

The thermodynamic relation

$$dU = -pdV + TdS + \mu dN \tag{4.43}$$

allows us to determine pressure, temperature, and chemical potential.

Temperature

We can obtain the temperature via the relation

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{2}{3Nk}U \tag{4.44}$$

Ideal Gas Law

We determine the ideal gas law. To this end we have to differentiate with respect to V:

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{2}{3}\frac{U}{V} \tag{4.45}$$

This yields

$$pV = \frac{2}{3}U \tag{4.46}$$

Using the relation for the temperature, (4.44), we obtain the well-known *ideal gas law*

$$pV = \frac{2}{3}U = NkT \tag{4.47}$$

Chemical Potential

The chemical potential μ of the ideal gas can be determined from

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S} \tag{4.48}$$

4.4.2 Canonical Distribution

We shall now discuss the ideal gas based on the canonical distribution.

The central quantity is the canonical partition function

$$Z(\beta) = \int \frac{\Pi_i d\mathbf{q}_i d\mathbf{p}_i}{N! h^{3N}} e^{-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}} \tag{4.49}$$

Again integration with respect to the coordinates is trivial and the integral with respect to momentum factorizes:

$$Z = \frac{V^N}{N! h^{3N}} \left[\int d^3\mathbf{p} e^{-\beta \frac{\mathbf{p}^2}{2m}} \right]^N \tag{4.50}$$

Thus, we have to perform the Gaussian integral

$$\int d^3\mathbf{p} e^{-\beta \frac{\mathbf{p}^2}{2m}} = 4\pi \int_0^\infty dp p^2 e^{-\frac{\beta}{2m} p^2} = \pi^{3/2} (\frac{2m}{\beta})^{3/2} \tag{4.51}$$

The canonical partition function reads:

$$Z = \frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \tag{4.52}$$

It is straightforward to determine thermodynamic quantities from this partition function. First of all we determine the internal energie

$$U = -\frac{\partial}{\partial \beta} ln Z = \frac{\partial}{\partial \beta} \frac{3N}{2} ln \beta m = \frac{3N}{2} \frac{1}{\beta} = \frac{3}{2} RT = C_v T \tag{4.53}$$

The free energy is given by

$$F = -\frac{1}{\beta} ln Z = \tag{4.54}$$

$$R = N k_b, \qquad , \qquad C_v = \frac{3}{2} R \tag{4.55}$$

4.5 Real Gases: Classical Treatment: Canonical Distribution

4.5.1 Interaction between Gas Molecules

Lendard Jones Potential

$$U(q) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \tag{4.56}$$

Exp-6 -Potential

$$U(q) = 4\epsilon \left[e^{\frac{a-r}{\sigma_1}} - \left(\frac{\sigma}{r} \right)^6 \right] \tag{4.57}$$

The forces contain a repulsive part at short distances and an attractive part at large distances.

4.5.2 Virial Expansion, Van der Waals Equation

The van der Waals equation is an equation of state for a real gas, which generalizes the ideal gas law:

$$[p + \frac{a}{V^2}][V - b] = NkT \tag{4.58}$$

The physical interpretation is as follows: The interaction between gas molecules can, at a first glance, be viewed replacing a gas molecule by a hard sphere. This has the consequence that the volume has to be replaced by the effective volume $V - b$. The attractive interaction between gas molecules leads to an enhanced pressure

We can rewrite this equation in the form

$$p = \frac{NkT}{V-b} - \frac{a}{V^2} = \frac{NkT}{V} + \frac{NkT}{V} \sum_{k=1} \left(\frac{b}{V} \right)^k - \frac{a}{V^2} \tag{4.59}$$

This representation suggests a general expansion of the real gas law in powers of V^{-1} of the form

$$pV = NkT[1 + \sum_{k=2} \frac{B_k}{V^{k-1}}] \tag{4.60}$$

This representation is denoted as the virial expansion, the coefficients B_k are denoted as k-th order virial coefficient. The second virial coefficient for the Van der Waals Gas then reads

$$B_2 = b - \frac{a}{kT} \tag{4.61}$$

There exist several other closed equations, which give a good representation of the state equation of certain real gases. We mention the Dieterici law

$$p(V - b) = NkTe^{-\frac{a}{NkTV}} \tag{4.62}$$

In the following subsection, we shall show that an expansion of the form eq. (**??**) is indeed possible.

4.5.3 Canonical Partition Function for Real Gases

We shall adress the statistical description of real gases, i.e. gases interacting via the potential

$$U = \frac{1}{2} \sum_{i=1,j=1}^{N,N} U(q_i - q_j) \tag{4.63}$$

We consider the canonical distribution and calculate the canonical partition function

$$Z(\beta) = \int \frac{\mathit{\Pi}_{i=1}^{N} d\mathbf{q}_i d\mathbf{p}_i}{N! h^{3N}} e^{-\beta[\sum_i^N \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2}\sum_{i,j} U(q_i - q_j)]} \tag{4.64}$$

The integral with respect to the coordinates and the momenta factorizes. We obtain the product

$$Z(\beta, V, N) = Z_P(\beta, V, N) Z_Q(\beta, V, N) \tag{4.65}$$

where the quantities $Z_P(\beta, V, N)$ and $Z_Q(\beta, V, N)$ are defined according to

$$\begin{aligned} Z_P(\beta, V, N) &= \frac{V^N}{N! h^{3N}} \int \mathit{\Pi}_{i=1}^{N} d\mathbf{p}_i e^{-\sum_i^N \frac{\mathbf{p}_i^2}{2m}} = \frac{V^N}{N! h^{3N}} \{ \int d\mathbf{p} e^{-\beta \frac{\mathbf{p}^2}{2m}} \}^N \\ &= \frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \end{aligned} \tag{4.66}$$

We remind the reader that $Z_P(\beta, V, N)$ is nothing else but the canonical partition function of the ideal gas.

The function $Z_U(\beta, V, N)$ equals one for the ideal gas case and, hence, contains the effects related with intermolecular interactions:

$$\begin{aligned} Z_U(\beta, V, N) &= \frac{1}{V^N} \int \mathit{\Pi}_{i=1}^{N} d\mathbf{q}_i e^{-\frac{1}{2}\beta \sum_{i,j} U(|q_i - q_j|)} \\ &= \frac{1}{V^N} \int \mathit{\Pi}_{i=1}^{N} d\mathbf{q}_i \mathit{\Pi}_{i,j,j<i} e^{-\beta U_{ij}} \end{aligned} \tag{4.67}$$

Thereby, the product has to be performed with respect to all indices i, j where $j < i$ ($U_{ij} = U(|\mathbf{q}_i - \mathbf{q}_j|)$. This term yields contributions to the equation of states for nonideal gases.

We can easily determine the free energy according to

$$F = -kT lnZ = -kT[lnZ_P + lnZ_u] \tag{4.68}$$

Since Z_P is the partition function of an ideal gas, we obtain

$$F = F_{ideal} + F_{nonideal} \tag{4.69}$$

where the first part is the free energy of the ideal gas.

Virial Expansion

Now we can make contact with the vrial expansion, which we rewrite in the form

$$pV = NkT[1 + B(V,T)] \tag{4.70}$$

Since

$$p = -\frac{\partial F}{\partial V} = kT\frac{\partial}{\partial V}lnZ = kT[\frac{1}{Z_P}\frac{\partial}{\partial V}Z_P + \frac{1}{Z_U}\frac{\partial}{\partial V}Z_U] \tag{4.71}$$

we are able to identify the virial function $B(V,T)$ with

$$B(V,T) = \frac{V}{N}\frac{1}{Z_U}\frac{\partial}{\partial V}Z_U \tag{4.72}$$

Now, the function Z_U takes the form

$$Z_u = 1 + z \tag{4.73}$$

and we obtain for the virial function

$$B(V,T) = \frac{V}{N}\frac{\partial}{\partial V}z_u \tag{4.74}$$

Expansion

In order to perform an approximative calculation of Z_V, it is convenient to introduce the function

$$\Phi(|q_i - q_j|) = e^{-\beta U(|q_i - q_j|)} - 1 \tag{4.75}$$

The consideration of this function can be motivated as follows: For large distances $|q_i - q_j|)$ the function Φ approaches zero. For small distances we obtain $\Phi(0) = -1$.

In the limiting case of a hard sphere gas we obtain

$$\Phi(|q|) = \begin{pmatrix} -1 & |q| \leq 2r_0 \\ -\beta U(|q|) & |q| > 2r_0 \end{pmatrix} \tag{4.76}$$

where r_0 denotes the radius of the hard sphere atom.

With this definition the function Z_V has to be calculated

$$Z_U(\beta,V,N) = \frac{1}{V^N}\int \Pi_{i=1}^N d\mathbf{q}_i \Pi_{i,j,j\leq i}(1 + \Phi(|q_i - q_j|) \tag{4.77}$$

The product takes the form

$$\begin{aligned}(1+f_{12})(1+f_{13}).....(1+f_{23})(1+f_{24})...(1+f_{N-1,N}) = \\ 1 + f_{12} + f13 + .. + f_{N-1,N} + f_{12}f_{13}....\end{aligned} \tag{4.78}$$

We can now neglect the higher order products $f_{ij}f_{kl}..$ and obtain

$$Z_U(\beta, V, N) = \frac{1}{V^N} \int \Pi_{i=1}^{N} d\mathbf{q}_i \left[1 + \sum_i \sum_{j<i} \Phi(|q_i - q_j|) + O(\Phi^2)... \right]$$
$$= 1 + \frac{1}{V^2} \frac{N(N-1)}{2} \int d\mathbf{q}_1 d\mathbf{q}_2 \Phi(|\mathbf{q}_1 - \mathbf{q}_2|) \qquad (4.79)$$

For the derivation of this expression, we have taken into account that the integrals not involving $\Phi(|\mathbf{q}_i - \mathbf{q}_j|)$ can be performed trivially leading to the factor V^{N-1}.

The latter integral can be evaluated for the above model, (4.76). We obtain two contributions

$$\int d\mathbf{q}_1 d\mathbf{q}_2 \Phi(|\mathbf{q}_1 - \mathbf{q}_2|) = V \int d\mathbf{q} \Phi(|\mathbf{q}|) \qquad (4.80)$$

The latter integral can be evaluated for the case of hard spheres. In this case,

$$\int d\mathbf{q} \Phi(|\mathbf{q}|) = -\frac{4\pi}{3} 8 r_0^3 - \beta \int_{2r_0}^{\infty} U(q) = -8v_0 + \beta A \qquad (4.81)$$

We ca now summarize

$$Z_U = [1 + \frac{N(N-1)}{2V}(-8v_0 + \beta b)] \qquad (4.82)$$

Now, we can determine using Taylor expansion of $ln(1+x) \approx x$

$$lnZ_U = \frac{N(N-1)}{2V}(-8v_0 + \beta A) \qquad (4.83)$$

The Virial function B is determined according to

$$B = \frac{V}{N} \frac{\partial}{\partial V} lnZ_u = \frac{N}{V}(\beta A - 8v_0) \qquad (4.84)$$

and we obtain the equation of state

$$pV = NkT[1 + \frac{1}{V}(\frac{A}{kT} - 8V_0) \qquad (4.85)$$

which we compare with the virial expansion of the van der Waals equation

$$pV = NKT[1 + \frac{b}{V} - \frac{a}{kTV} + .. \qquad (4.86)$$

This comparision yields

$$b = 8V_0 = 8Nv_0 \qquad (4.87)$$

and

$$a = A \qquad (4.88)$$

4.6 Maxwell's Distribution of Momenta

The probability distribution of the N-particle gas is given by

$$\begin{aligned} f(\mathbf{p}_i, \mathbf{q}_i) &= Z(\beta, V, N)^{-1} e^{-\beta H(\mathbf{p}_i, \mathbf{q}_i)} \\ &= \frac{1}{Z_P(\beta, V, N) Z_U(\beta, V, N)} e^{-\beta \sum_i \frac{\mathbf{p}_i}{2m}} e^{-\beta \frac{1}{2} \sum_{ij} U(|\mathbf{q}_i - \mathbf{q}_j|)} \end{aligned} \tag{4.89}$$

We have defined the partition functions Z_U, Z_P above. We can now determine the distribution $h(\mathbf{p}_i$ of the momenta by integrating with respect to the coordinates

$$\begin{aligned} h(\mathbf{p}_i) &= \frac{1}{V^N} \int \Pi_{i=1}^N d\mathbf{q}_i f(\mathbf{p}_i, \mathbf{q}_i) \\ &= \frac{1}{Z_P(\beta, V, N)} e^{-\beta \sum_i \frac{\mathbf{p}_i}{2m}} \end{aligned} \tag{4.90}$$

This formula shows that irrespective of the interaction potential U, the momenta of the particles are statistically independent in thermodynamic equilibrium, since the probability distributions factorize.

As a consequence, the probability distribution of momentum of a single particle is given by

$$h(\mathbf{p}) = z^{-1} e^{-\frac{\mathbf{p}^2}{2mkT}} \tag{4.91}$$

and the distribution of the velocity is given by

$$h(\mathbf{v}) = \tilde{z}^{-1} e^{-\frac{m\mathbf{v}^2}{2kT}} \tag{4.92}$$

As a consequence, we obtain the general statement: The mean kinetic energy of a particle of an interacting gas in thermodynamic equilibrium is

$$\langle \frac{\mathbf{mv^2}}{2} \rangle = \frac{3}{2} kT \tag{4.93}$$

The velocities are gaussian distributed.

4.7 Equipartition Theorem

We consider now a Hamilton function, which has a quadratic contribution with respect to the coordinates:

$$H(\mathbf{p}_i, \mathbf{q}_i) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \frac{m\omega^2 \mathbf{q}_i^2}{2} \tag{4.94}$$

We calculate the canonical partition function

$$Z = \int d\Gamma e^{-\beta\{\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{m\omega^2 \mathbf{q}_i^2}{2}\}} \tag{4.95}$$

The integral factorizes and we obtain

$$\begin{aligned} Z &= \left[\int d\mathbf{p} d\mathbf{q} e^{-\beta\{\frac{\mathbf{p}^2}{2m} + \frac{m\omega^2 \mathbf{q}^2}{2}\}}\right]^N \\ &= \left[\int d\mathbf{p} e^{-\beta\frac{\mathbf{p}^2}{2m}}\right]^N \left[\int d\mathbf{q} e^{-\beta\frac{m\omega^2 \mathbf{q}^2}{2}}\right]^N \end{aligned} \tag{4.96}$$

We are left with the determination of the Gaussian integrals

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \tag{4.97}$$

$$\int d\mathbf{q} e^{-\beta\frac{m\omega^2 \mathbf{q}^2}{2}} = \sqrt{\frac{2\pi}{m\omega^2\beta}} \tag{4.98}$$

$$\int d\mathbf{q} e^{-\beta\frac{\mathbf{p}^2}{2m}} = \sqrt{\frac{2\pi m}{\beta}} \tag{4.99}$$

As a result, we obtain the canonical partition function

$$Z(\beta, V, N) = \frac{1}{N! h^{3N}} \left(\frac{4\pi m}{\beta}\right)^{3N/2} \left(\frac{4\pi}{m\omega^2\beta}\right)^{3N/2} \tag{4.100}$$

Now it is straightforward to determine the free energy

$$F(\beta, V, N) = -\frac{1}{\beta} ln \frac{1}{N! h^{3N}} \left(\frac{4\pi m}{\beta}\right)^{3N/2} \left(\frac{4\pi}{m\omega^2\beta}\right)^{3N/2} \tag{4.101}$$

as well as the internal energy U:

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta} lnZ \\ &= -\frac{\partial}{\partial\beta}[-3N ln\beta + Const] = 3NkT \end{aligned} \tag{4.102}$$

This is the famous equipartition theorem. We have 3N degrees of freedom. The contribution to the mean kinetic energy is $3NkT/2$ and the contirbution to the mean potential energy is also $3NkT/2$.

We can generalize this result further. We lump the momenta and coordinates into a state vector x_α, where $\alpha = 1, ..6N$. We assume that we have the canonical partition function

$$Z(\beta) = \int \Pi_\alpha dx_\alpha e^{-\frac{1}{2}\sum_{\alpha=1}^{f}\sum_{\alpha=1}^{f} x_\alpha [A^{-1}]_{\alpha\beta} x_\beta} \tag{4.103}$$

where $A_{\alpha\beta}$ is a matrix with $DetA \neq 0$. Since A^{-1} is a symmetric matrix, it can be diagonalized by a unitary transformation

$$\tilde{A}^{-1} = U^{-1}A^{-1}U \tag{4.104}$$

$$Z(\beta) = \int \Pi_\alpha dx_\alpha e^{-\frac{1}{2}\sum_\alpha^f \sum_\beta^f x_\alpha [U\tilde{A}^{-1}U^{-1}]_{\alpha\beta} x_\beta} \tag{4.105}$$

The introduction of the new coordinates

$$y_\alpha = \sum_\beta U_{\alpha\beta}^{-1} x_\beta \tag{4.106}$$

leads to the Gaussian integrals

$$\begin{aligned} Z(\beta) &= \int \Pi_\alpha dy_\alpha e^{-\frac{1}{2}\sum_\alpha^f -\beta y_\alpha^2 \lambda_\alpha} \\ &= \Pi_\alpha^f [\sqrt{\frac{2\pi}{\lambda_\alpha}}] \frac{1}{\beta^f} \end{aligned} \tag{4.107}$$

We can again determine the internal energy

$$U = -\frac{\partial}{\partial \beta} Z = fkT \tag{4.108}$$

This is the contents of the equipartition theorem, which is a rather strong statement for equilibrium thermodynamics: For each quadratic form

$$H = \frac{1}{2}\sum_{i=1}^f \sum_{j=1}^f x_i A_{ij}^{-1} x_j \tag{4.109}$$

with $DetA = 0$ and positive eigenvalues a_i the internal energy in thermodynamic equilibrium is given by

$$U = \frac{f}{2} kT \tag{4.110}$$

4.8 Gases with Structured Particles:

We now consider a gas consisting of molecules which have internal degrees of freedom. As an example, we mention rotational motion of the molecules or vibrational motion. All these internal motions contribute to the internal energy of the gas. Let us consider this external degrees of freedom explicitly. Besides the coordinates and momenta $\mathbf{q}_i$ and $\mathbf{p}_i$ of the center of mass of the molecules we have to consider the relative motion by additional coordinates $\mathbf{Q}_{i\alpha}$ and momenta $\mathbf{P}_{i\alpha}$. The Hamilton function is composed of the part for the center of mass coordinates and momenta and the internal degrees of freedom

$$H = H(\mathbf{p}_i, \mathbf{q}_i) + K(\mathbf{P}_{i\alpha}, \mathbf{Q}_{i\alpha}) \tag{4.111}$$

We determine the canonical partition function according to

$$Z(\beta, V, N) = \int d\Gamma e^{-H(\mathbf{p}_i,\mathbf{q}_i)} e^{-K(\mathbf{P}_{i,\alpha},\mathbf{Q}_{i,\alpha})} \tag{4.112}$$

Integration again factorizes and we obtain

$$Z(\beta, V, N) = Z_{CM}(\beta, V, N) Z_{IF}(\beta, V, N) \tag{4.113}$$

Here the canonical partition functions are defined as

$$Z_{CM}(\beta, V, N) = \int \frac{\Pi_{i=1}^N d\mathbf{q}_i d\mathbf{p}_i}{N!(h^{3N}} e^{-H\beta(\mathbf{p}_i,\mathbf{q}_i)} \tag{4.114}$$

$$Z_{IF}(\beta, V, N) = \int \frac{\Pi_{i=1}^N d\mathbf{Q}_{i,\alpha} d\mathbf{P}_{i,\alpha}}{(h^{3Nk}} e^{-\beta K(\mathbf{P}_{i,\alpha},\mathbf{Q}_{i,\alpha})} \tag{4.115}$$

As a consequence, the free energy $F(\beta, V, N)$ is composed additively

$$F(\beta, V, N) = -\frac{1}{\beta} ln Z_{CM}(\beta, V, N) - \frac{1}{\beta} ln Z_{IF}(\beta, V, N) \tag{4.116}$$

4.8.1 Diatomic Molecules

We consider a molecul which consists of two identical atoms which are coupled by a harmonic force, i.e. there is an equilibrium position for the distance, around which the atomes perform harmonic oscillations. The molecule can perform rotations about two rotation axis. This gives a contribution of

$$H = \frac{1}{2} \omega \Theta \omega \tag{4.117}$$

and an oscillation along its axis, whose contribution is

$$H = \frac{P^2}{2\mu} + \frac{\mu\omega^2}{2m} Q^2 \tag{4.118}$$

Each motion contirbutes to the internal energy U. Due to the equipartition theorem rotation contributes with

$$U = 2 \times \frac{N}{2} kT \tag{4.119}$$

whereas the oscillation contributes with

$$U = NkT \tag{4.120}$$

because of the contribution of the

If we consider an ideal gas consisting of such diatomic molecules, we obtain the total internal energy

$$U = \frac{3}{2} NkT + 2NkT = \frac{7}{2} NkT \tag{4.121}$$

This behaviour is observed at high temperature. As we shall see the low temperature internal energy is changed by quantum mechanical effects.

4.8.2 General Molecules: Equipartition for Internal Degrees of Freedom

Let us now consider the dynamics of the internal degrees of freedom for general molecules. If the molecule consists of F atoms, we have 3 translational degress of freedom, each contributing with $\frac{1}{2}kT$ to the internal energy U. Furthermore, in general we have rotations about three axis each contributing with $\frac{1}{2}kT$. Then we have $3F-6$ oscillations, each contributing with kT.

The total internal energy, therefore, is given by

$$U=\frac{3}{2}NkT+\frac{3}{2}NkT+(3F-6)NkT=(3F-3)NkT \tag{4.122}$$

We remind the reader that the shape of the molecule plays a role. For instance if we have three atoms aligned in a line, we only have two rotations left. Instead, we have 2 oscillations leading us to

$$U=\frac{3}{2}NkT+\frac{2}{2}NkT+4NkT=\frac{13}{2}NkT \tag{4.123}$$

We remind the reader that this fact only applies at high temperatures. For low temperatures we have to take into account quantum effects. For $T=0$ the above formula predicts $U=0$. This contradicts Heisenberg's uncertainty principle.

5

Quantum Statistics

Quantum theory contains a probabilistic interpretation of the wave function from the beginning. For quantum systems consisting of a huge number of quantum particles an additional statistical treatment has to be performed in order to compensate the restricted knowledge on then many-particle wave function.

5.1 Quantum Mechanics: A Reminder

5.1.1 Evolution, Expectation Values

The state of a quantum mechanical system is described in terms of the N-particle wave function $|\psi(\mathbf{q}_1, ..., \mathbf{q}_N, t) >$. Its temporal evolution is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi >= H|\psi > \tag{5.1}$$

The state vectors are elements of a Hilbert space. The corresponding scalar product is denoted by

$$< u|v >= \tag{5.2}$$

The Hilbert space is spanned by a complete set of orthogonal vectors $|a_i >$, $i = 1, ...$. The completeness relation and the orthogonality properties read

$$\begin{aligned} \sum_j |a_j >< a_j| &= I \\ < a_i|a_j > &= \delta_{ij} \end{aligned} \tag{5.3}$$

Physical observables are related to operators defined in this Hilbert space. The expectation value of an operator A is determined by then scalar product

$$< A(t) >=< \psi(t)|A|\psi(t) > \tag{5.4}$$

We expand the wave function into a superposition of eigenstates $|a_i>$.

$$A|a_i>= A_i|a_i> \tag{5.5}$$

The eigenstates fulfill the orthonormal condition

$$\begin{aligned} &\sum_i |a_i>< a_i| = I \\ &< a_i|a_j>= \delta_{ij} \end{aligned} \tag{5.6}$$

The expectation value is determined according to

$$< A >= \sum_j |c_j|^2 A_j \tag{5.7}$$

where $|c_j|^2$ denotes the probability to find the quantum mechanical system in the state $|a_j>$. The expectation can be calculated via the expansion

$$|\psi(t)\rangle = \sum_j c_j |a_j\rangle \tag{5.8}$$

The expectation value of the operator A can also be calculated with respect to a complete set of vectors $b_i>$, which are not eigenvectors of A. Using the decomposition

$$|\psi(t)\rangle = \sum_j d_j |b_j\rangle \tag{5.9}$$

we obtain

$$< A >= \sum_i \sum_j \tilde{c}_i^* c_j < b_i|A|b_j > \tag{5.10}$$

In the following we shall introduce the trace of an operator A and the density matrix ρ. This will allow us to rewrite the expectation value of the operator in a way, which allows us to introduce ensemble of states in a straightforward manner.

5.1.2 The Trace of an Operator

We introduce the following definition of the trace of an operator A. We consider a complete basis $b_i>$ of the Hilbert space. We introduce the matrix elements

$$A_{ij} =< b_i|A|b_j > \tag{5.11}$$

The trace of the operator A is defined as the sum of all diagonal elements

$$tr\ A = \sum_i A_{ii} \tag{5.12}$$

The introduction of the trace makes only sense, if the definition of this quantity is independent on the selected basis $|b_i>$.

In fact, one can proof the relationship

$$trBA = trAB \tag{5.13}$$

In detail, we obtain

$$trBA = \sum_i < b_i|BA|b_i > \tag{5.14}$$

In order to proof this relationship we insert unity in the form of

$$E = \sum_j |b_j >< b_j| \tag{5.15}$$

which leads to

$$trBA = \sum_i \sum_j \sum_k B_{ij} A_{ji} = trAB \tag{5.16}$$

Now, we can show the independence of the trace on the chosen basis $|b_i>$. We can define a new basis by an unitary transformation

$$|a_i >= U|b_i > \tag{5.17}$$

with the relation

$$U^\dagger = U^{-1} \tag{5.18}$$

The cyclic commutability demonstrates independency of the trace on the chosen basis:

$$trU^\dagger AU = trA \tag{5.19}$$

5.1.3 The Density Matrix

We can express the expectation value of an observable A in a rather concise form as the trace of the product ρA. Thereby, we have introduced the density matrix ρ according to

$$\rho = |\psi(t) >< \psi(t)| \tag{5.20}$$

In fact,

$$< A >= tr(\rho A) = \sum_i < a_i|\psi >< \psi|A|a_i >= \sum_i |c_i|^2 A_i \tag{5.21}$$

Thereby, we have defined the density matrix

$$\rho = \sum_{ij} \rho_{ij} |a_i >< a_j| \tag{5.22}$$

It is obvious that the elements of the density matrix are determined by

$$\rho_{ij}(t) = c_i^*(t) c_j(t) \tag{5.23}$$

For a general basis, we obtain

$$< A(t) >=< \psi(t)|A|\psi(t) >= tr\rho A = \sum_{ij} c_i^*(t) c_j(t) A_{ij} \tag{5.24}$$

5.1.4 Von Neumann Equation

The evolution equation for the density matrix is the Von Neumann equation. It can be obtained from the definiton

$$\rho = |\psi(t) >< \psi(t)| \tag{5.25}$$

The time derivative reads

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}\rho(t) &= i\hbar \left[|\dot{\psi}(t) >< \psi(t)| + |\psi(t) < \dot{\psi}(t)| \right] \\ &= H\psi(t) >< \psi(t)| - |\psi(t) >< \psi(t)|H = [H, \rho] \end{aligned} \tag{5.26}$$

We shall return to this equation when we discuss the ergodic theory.

5.1.5 Functions of Operators

In the following it will be important to consider functions of operators

$$F(A) \tag{5.27}$$

We can define these operators through their spectral representation. Each hermitian operator has a spectral representation

$$A = \sum_i A_i |a_i >< a_i| \tag{5.28}$$

It is obvious to define the opertor $F(A)$ by its spectral representation

$$f(A) = \sum_i f(A_i) |a_i >< a_i| \tag{5.29}$$

5.2 Quantum Statistics

Besides the probabilistic description which is inherent to quantum mechanics we have to consider a secondary statistics, which is best introduced by considering an ensemble of identical quantum systems, which are described by the wave functions $\psi_\alpha(t) >$. For each system, quantum mechanical expectation values are calculated with the density matrix

$$\rho_\alpha(t) = |\psi_\alpha(t) >< \psi_\alpha(t)| \tag{5.30}$$

This yields the expectation value

$$< A_\alpha >= tr\rho(t)A \tag{5.31}$$

Now, we can assign a probability p_α finding a system of the ensemble with the expectation value A_α

$$p_\alpha \tag{5.32}$$

An ensemble average yields

$$< A >= \sum_\alpha p_\alpha tr[\rho_\alpha A] = tr[\rho A] \tag{5.33}$$

Here, we have introduced the ensemble density matrix

$$\rho = \sum_\alpha \rho_\alpha \tag{5.34}$$

The question arises how the probabilities p_α are obtained. As in the classical case we can use the maximum information principle in order to determine density matrix. To this end we define the entropy according to

$$S = -ktr\rho ln\rho \tag{5.35}$$

Since ρ is a Hermitian operator, we obtain the classical expression for the entropy

$$S = -k \sum_\alpha \rho_\alpha ln \rho_\alpha \tag{5.36}$$

where ρ_α are the eigenvalues of the operator ρ.

5.3 Microcanonical Distribution

We consider a quantum system, which can take the energy states E_i with eigenfunctions $\varphi_i >$. We consider now an ensemble of systems, where each system has the energy E.

5.4 Canonical Distribution

Now, we consider systems, which have to fullfill the constraints

$$\begin{aligned} tr\rho &= 1 \\ tr\rho H &= U \end{aligned} \tag{5.37}$$

We assume that the density matrix commutes with the Hamilton operator H:

$$[H, \rho] = 0 \tag{5.38}$$

We can represent the density matrix ρ in the form

$$\rho = \sum_i p_i |\varphi_i >< \varphi_i| \tag{5.39}$$

where $|\varphi_i>$ are the eigenstates of the Hamilton operator H with energy eigenvalues E_i

$$H|\varphi_i>= E_i|\varphi_i> \tag{5.40}$$

The constraints and the entropy explictly read

$$\begin{aligned} tr\rho &= \sum_i p_i = 1 \\ tr\rho H &= \sum_i p_i E_i = U \\ S &= -\sum_i p_i ln p_i \end{aligned} \tag{5.41}$$

Applying the maximum information principle leads to estimate the probabilities p_i according to

$$p_i = Z^{-1} e^{-\beta E_i} \tag{5.42}$$

The density matrix then takes the form

$$\rho = \sum_i Z^{-1} e^{-\beta E_i} |\varphi_i >< \varphi_i| = Z^{-1} e^{-\beta H} \tag{5.43}$$

The canonical partition function is defined as the trace

$$Z(\beta, V) = tr e^{-\beta H} \tag{5.44}$$

Distribution	ρ	$f(p_i, q_i)$
Expectation	$< A >= tr\rho A$	$< A >= \int d\Gamma A(p_i, q_i) f(p_i, q_i)$
Constraint	$1 = tr\rho$	$1 = \int d\Gamma f(p_i, q_i)$
Constraint	$U = tr\rho H$	$U = \int d\Gamma H(p_i, q_i) f(p_i, q_i)$
Entropy	$S = -ktr\rho ln\rho$	$S = -k \int d\Gamma f(p_i, q_i) ln f(p_i, q_i)$
Canonical Distribution	$\rho = Z^{-1} e^{-\beta H}$	$f(p_i, q_i) = Z^{-1} e^{-\beta H(p_i, q_i)}$
Canonical Partition Function	$Z = tr e^{-\beta H}$	$Z = \int d\Gamma e^{-\beta H(p_i, q_i)}$

The canonical partition function is the starting point for the calculation of thermodynamic properties like free energies, equation of state, etc. in the canonical ensemble due to the relationship

$$F(T,V) = -kTlnZ(\beta,V) \tag{5.45}$$

between the free energy and the partition function.

The equation of state is obtained via the relationship

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\frac{\frac{\partial Z}{\partial V}}{\partial V} \tag{5.46}$$

5.5 Grand Canonical Distribution

In case of the grand canonical distribution we consider systems, for which also the number of particles is a fluctuating quantity. The constraints are then

$$tr\rho = 1 \tag{5.47}$$

and

$$tr\rho H = U \tag{5.48}$$

and

$$tr\rho N =< N > \tag{5.49}$$

The Hamilton operator and the number operator N commute,

$$[H,N] = 0 \tag{5.50}$$

and, therefore possess the same eigenvectors. The grand canonical distribution takes the form

$$\rho = [J]^{-1}e^{-\beta(H-\mu N)} \tag{5.51}$$

where J denotes the grand canonical partition function

$$J = tre^{-\beta(H-\mu N)} \tag{5.52}$$

6

Photons and the Planck's Formula

6.1 The Electromagnetic Field

In this section we review the quantization of the free electromagnetic field. In the classical description the field is determined by Maxwell's Equations:

$$
\begin{aligned}
\nabla \cdot \mathbf{E} &= 0 \\
\nabla \times \mathbf{E} &= -\frac{\partial}{\partial t}\mathbf{B} \\
\nabla \cdot \mathbf{B} &= 0 \\
\nabla \times \mathbf{B} &= \frac{1}{c^2}\frac{\partial}{\partial t}\mathbf{E}
\end{aligned}
\tag{6.1}
$$

The energy density takes the form

$$
h = \frac{\epsilon_0}{2}[\mathbf{E}^2 + c^2\mathbf{B}^2] \tag{6.2}
$$

As is well-known, it is convenient to introduce the electromagnetic potentials $\mathbf{A}$, Φ:

$$
\begin{aligned}
\mathbf{B} &= \nabla \times \mathbf{A} \\
\mathbf{E} &= -\nabla\Phi - \dot{\mathbf{A}}
\end{aligned}
\tag{6.3}
$$

It is convenient to use the *radiation gauge* $\Phi = 0$. In this case the electromagnetic energy density takes the form

$$
h = \frac{\epsilon_0}{2}\{(\dot{\mathbf{A}})^2 + c^2[\nabla \times \mathbf{A}]^2\} \tag{6.4}
$$

6.1.1 Periodic Boundaries: Cavity

We investigate the free electromagnetic field in a cavity of volume V. for the sake of simplicty we consider a cube of length L. We postulate periodic boundary conditions. In that case we can represent the vector potential as Fourier series

$$\mathbf{A}(\mathbf{x},t) = \frac{N}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{i=1}^{2} \mathbf{e}_i \{ b_{\mathbf{k},i} e^{i\mathbf{k}\cdot\mathbf{x}} + b^*_{\mathbf{k},i} e^{-i\mathbf{k}\cdot\mathbf{x}} \} \tag{6.5}$$

Periodic boundary conditions require

$$\mathbf{k} = \frac{2\pi}{L}[l_x, l_y, l_z] \qquad , \qquad l_i = -\infty, ..., -1, 0, 1, .. + \infty \tag{6.6}$$

As a consequence the electric field and the magnetic induction also are represented as Fourier series:

$$\mathbf{E}(\mathbf{x},t) = -\frac{N}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{i=1}^{2} \{ \mathbf{e}_i \dot{b}_{\mathbf{k},i} e^{i\mathbf{k}\cdot\mathbf{x}} + \mathbf{e}_i \dot{b}^*_{\mathbf{k},i} e^{-i\mathbf{k}\cdot\mathbf{x}} \} \tag{6.7}$$

$$\mathbf{B}(\mathbf{x},t) = \frac{N}{\sqrt{V}} \sum_{\mathbf{k}} \sum_{i=1}^{2} i[\mathbf{k} \times \mathbf{e}_i] \{ b_{\mathbf{k},i} e^{i\mathbf{k}\cdot\mathbf{x}} - b^*_{\mathbf{k},i} e^{-i\mathbf{k}\cdot\mathbf{x}} \} \tag{6.8}$$

$$\begin{aligned} \int_V d^3\mathbf{x}\mathbf{E}^2(\mathbf{x},t) = N^2 \sum_{\mathbf{k}} \sum_{i=1}^{2} \{ & \dot{b}_{\mathbf{k},i} \dot{b}_{-\mathbf{k},i} + \dot{b}_{\mathbf{k},i} \dot{b}^*_{\mathbf{k},i} \\ & + \dot{b}^*_{\mathbf{k},i} \dot{b}_{\mathbf{k},i} + \dot{b}^*_{\mathbf{k},i} \dot{b}^*_{-\mathbf{k},i} \} \end{aligned} \tag{6.9}$$

$$\begin{aligned} \int_V d^3\mathbf{x}\mathbf{B}^2(\mathbf{x},t) = N^2 \sum_{\mathbf{k}} \sum_{i=1}^{2} (-\mathbf{k}^2 \{ & b_{\mathbf{k},i} b_{-\mathbf{k},i} + b_{\mathbf{k},i} b^*_{\mathbf{k},i} \\ & + b^*_{\mathbf{k},i} b_{\mathbf{k},i} + b^*_{\mathbf{k},i} b^*_{-\mathbf{k},i} \} \end{aligned} \tag{6.10}$$

Electromagnetic Energy:

$$H = \frac{1}{2} \sum_{\mathbf{k}} \sum_{i=1}^{2} \hbar\omega_{\mathbf{k}} \left[b_{\mathbf{k},i} b^*_{\mathbf{k}-,i} + b^*_{\mathbf{k},i} b_{\mathbf{k},i} \right] \tag{6.11}$$

6.2 Failure of Classical Physics: The Ultraviolet Catastrophy

The derivation is as follows. The electron magnetic field is composed of hramonic oscillators, each oscillating with frequency $\omega_{\mathbf{k}}$. Due to the equipartition theorem, each oscillator contributes kT to the internal energy. Furthermore, we have to take into account that light is polarized leading to a factor of two in the internal energy

$$U = 2\sum_{\mathbf{k}} k_B T = \frac{V}{8\pi^3} 4\pi \int k^2 dk kT = \int d\nu kT \frac{8\pi\nu^2}{c^3} \tag{6.12}$$

thereby, we made the replacement

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \sum_{\mathbf{k}} d^3\mathbf{k} \tag{6.13}$$

The failure of this classical treatment becomes evident from the fact that this integral does not converge in the limit of large frequencies.

6.3 Quantization of the Electromagnetic Field

The quantization of the electromagnetic field is achieved by postulating the existence of the following comuutation rules for the creation and annihilation operators $b^\dagger_{\mathbf{k},i}$, $b_{\mathbf{k},i}$:

$$\begin{aligned} [b_{\mathbf{k},i}, b^\dagger_{\mathbf{k}',j}] &= \delta_{\mathbf{k},\mathbf{k}'}\delta_{ij} \\ [b_{\mathbf{k},i}, b_{\mathbf{k}',j}] &= 0 \\ \left[b^\dagger_{\mathbf{k},i}, b^\dagger_{\mathbf{k}',j}\right] &= 0 \end{aligned} \tag{6.14}$$

Hamiltonian

$$H = \sum_{\mathbf{k}} \sum_i \hbar\omega_{\mathbf{k}} [b^\dagger_{\mathbf{k},i} b_{\mathbf{k},i} + \frac{1}{2}] \tag{6.15}$$

In the following it will be convenient to neglect the energy of the vacuum,

$$H = \sum_{\mathbf{k}} \sum_i \hbar\omega_{\mathbf{k}} \frac{1}{2} \tag{6.16}$$

The basis of the Hilbert Space is spanned by the vectors

$$|...n^i_{\mathbf{k}}....n'^j_{\mathbf{k}'}... >= .... \frac{1}{\sqrt{n^i_{\mathbf{k}}!}} (b^\dagger_{\mathbf{k},i})^{n^i_{\mathbf{k}}} .... \frac{1}{\sqrt{n^j_{\mathbf{k}'}}} (b^\dagger_{\mathbf{k}',j})^{n^j_{\mathbf{k}'}} |0 > \tag{6.17}$$

Here, $n^i_{\mathbf{k}}$ denotes the occupation number of the states with wave vector $\mathbf{k}$ and the polarization $i = 1, 2$.

6.4 Photon Statistics: Canonical Distribution

We calculate the canonical partion sum for photons in a cavity with periodic boundary conditions. The Hamilton operator reads

$$H = \sum_{\mathbf{k}} \sum_{i=1}^{2} \hbar \omega_{\mathbf{k}} n_{\mathbf{k},i} \tag{6.18}$$

with the occumation number operator

$$n_{\mathbf{k},i} = b^{\dagger}_{\mathbf{k},i} b_{\mathbf{k},i} \tag{6.19}$$

The angular frequency is related to the wave number k via the speed of light c:

$$\omega_{\mathbf{k}} = c|\mathbf{k}| \tag{6.20}$$

The Hilbert space is spanned by the states

$$|.., n^i(\mathbf{k}), ..., n^{i'}(\mathbf{k}'), .. > \tag{6.21}$$

6.4.1 Evaluation of the Partition Function

We have to evaluate the canonical partition function

$$\begin{aligned} Z(\beta, V) &= tre^{-\beta H} \\ &= \sum_{...n^i(\mathbf{k}),....} < ..., n^i(\mathbf{k}), ...|e^{-\beta \sum_{\mathbf{k}_j} \sum_i \hbar \omega_{\mathbf{k}_j} b^{\dagger}_{\mathbf{k},i} b_{\mathbf{k},i}} ||..., n^i(\mathbf{k}), > \end{aligned} \tag{6.22}$$

Simple Example

At first glance, this seems to be a rather difficult task. Therefore, we consider, as a simple example, the case of two modes with frequencies ω_1 and ω_2. The Hamilton operator reads

$$H = \hbar b_1^{\dagger} b_1 + \hbar b_2^{\dagger} b_2 \tag{6.23}$$

The basis is

$$|n_1, n_2 > \tag{6.24}$$

with

$$\begin{aligned} b_1^{\dagger} b_1 |n_1, n_2 > &= n_1 |n_1, n_2 > \\ b_2^{\dagger} b_2 |n_1, n_2 > &= n_2 |n_1, n_2 > \end{aligned} \tag{6.25}$$

Furthermore, we have

$$e^{-\beta H} |n_1, n_2 >= e^{-\beta[\hbar \omega_1 n_1 + \omega_2 n_2]} |n_1, n_2 > \tag{6.26}$$

As a consequence the partition sum reads

$$\begin{aligned} Spe^{-\beta H} &= \sum_{n_1,n_2} < n_1, n_2 | e^{-\beta H} | n_1, n_2 > \\ &= \sum_{n_1,n_2} e^{-\beta[\hbar\omega_1 n_1 + \omega_2 n_2]} \\ &= \sum_{n_1=0}^{\infty} e^{-\beta[\hbar\omega_1 n_1]} \times \sum_{n_2=0}^{\infty} e^{-\beta[\hbar\omega_2 n_2]} \end{aligned} \tag{6.27}$$

The sums can be easily evaluated:

$$\sum_{n=0}^{\infty} e^{-\hbar\omega n} = \frac{1}{1 - e^{-\hbar\omega}} \tag{6.28}$$

We obtain our final result

$$Spe^{-\beta H} = \frac{1}{1 - e^{-\hbar\omega_1}} \frac{1}{1 - e^{-\hbar\omega_2}} \tag{6.29}$$

General Case

We return to the evaluation of the canonical partition function. A similar procedure leads to

$$Z(\beta, V) = \Pi_{\mathbf{k}} [\sum_{n(\mathbf{k})} e^{-\beta \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} n_{\mathbf{k}}}]^2 \tag{6.30}$$

The square is due to the fact that we have two contributions to each wave vector **k**, due to the two different polarizations.

The sum again can be easily evaluated:

$$Z(\beta, V) = \Pi_{\mathbf{k}} \left(\frac{1}{1 - e^{-\beta\hbar\omega_{\mathbf{k}}}} \right)^2 \tag{6.31}$$

This is the canonical partition sum for a gas of noninteracting photons.

6.4.2 Free Energy

We are now able to determine the free energy of the photon gas

$$F(\beta, V) = -\frac{1}{\beta} ln Z(\beta, V) = -2kT \sum_{\mathbf{k}} ln \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_{\mathbf{k}} n} \tag{6.32}$$

With the help of

$$\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_{\mathbf{k}} n} = \frac{1}{1 - e^{-\beta\hbar\omega_{\mathbf{k}}}} \tag{6.33}$$

we obtain the free energy of the photon gas

$$F(\beta, V) = 2kT \sum_{\mathbf{k}} ln(1 - e^{-\beta\hbar\omega_{\mathbf{k}}}) \tag{6.34}$$

In order to evaluate the sum over all wave vectors **k** we approximate the discrete sum by an integral with respect to $|\mathbf{k}|$. To this end we note that

$$\sum_{\mathbf{k}} ... \to \int d\mathbf{k} \frac{L^3}{(2\pi)^3} .. \tag{6.35}$$

Since , due to isotropy, the integrand depends only on $|\mathbf{k}|$, we can use spherical coordinates and obtain

$$F(T, V) = 2kT \frac{V}{2\pi^2} \int k^2 dkln(1 - e^{-\beta\hbar|\mathbf{k}|c}) \tag{6.36}$$

The factor 2 is due to the two polarizations. The frequency dependence is linear in $|\mathbf{k}|$,

$$\omega_{\mathbf{k}} = c|\mathbf{k}| \tag{6.37}$$

and we obtain with the help of

$$\nu = \frac{c}{2\pi}|\mathbf{k}| \tag{6.38}$$

$$F(T, V) = 8\pi kT \frac{V}{c^3} \int \nu^2 d\nu ln(1 - e^{-\beta h\nu}) \tag{6.39}$$

The further transformation

$$x = \beta h\nu \tag{6.40}$$

yields

$$F(T, V) = 8\pi V \frac{(kT)^4}{(hc)^3} \int_0^\infty x^2 dxln(1 - e^{-x}) \tag{6.41}$$

The result of the integration is

$$F(T, V) = -8\pi V \frac{(kT)^4}{(hc)^3} \frac{1}{45} \tag{6.42}$$

We can calculate the entropy

$$S = -\frac{\partial F}{\partial T} = 4 \times 8\pi V \frac{k^4 T^3}{45(hc)^3} \tag{6.43}$$

The internal energy is given by

$$U = F + TS = 8\pi V \frac{(kT)^4}{15(\hbar c)^3} \tag{6.44}$$

6.4.3 Equation of State of the Photon Gas

The photon gas has an equation of state comparable to an ideal gas. We obtain this equation of state by calculating the pressure

$$p = -\frac{\partial F}{\partial V} = \frac{U}{3V} \tag{6.45}$$

Explicitly we obtain

$$p = (kT)^4 \frac{8\pi}{(hc)^3} \frac{1}{45} \tag{6.46}$$

This relations has to be compared with the one of the ideal classical gas:

$$p = -\frac{\partial F}{\partial V} = \frac{2U}{3V} \tag{6.47}$$

6.4.4 Internal Energy

We can now calculate the internal energy according to the relation

$$U = -\frac{\partial}{\partial \beta} lnZ(\beta, V) \tag{6.48}$$

which yields

$$U = 2 \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1} \tag{6.49}$$

This representation of the internal energy U of the photon gas can be interpreted as follows: The energy of a photon is just $\hbar\omega_{\mathbf{k}}$. In thermodynamic equilibrium there are

$$\bar{n}(\omega_{\mathbf{k}}) = \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1} \tag{6.50}$$

numbers of photons with wave vector $\mathbf{k}$. The function $\bar{n}(\omega_{\mathbf{k}}$ is the distribution function of the photon gas.

Spectral Energy Density

From the internal energy we can deduce Planck's formula for the spectral energy density of the photon gas.

$$U = 2\frac{V}{8\pi^3} 4\pi \int_0^\infty k^2 dk \frac{\hbar ck}{e^{\beta\hbar ck} - 1} \tag{6.51}$$

Using $\hbar ck = h\nu$ and $k = 2\pi\nu/c$ we obtain the representation

$$U = \int_0^\infty d\nu u(\nu, T) = \frac{8\pi V}{c^3} \int \nu^2 d\nu \frac{h\nu}{e^{\beta h\nu} - 1} \tag{6.52}$$

The spectral energy density $u(\nu)$ is given by

$$u(\nu) = \frac{8\pi V}{c^3} \nu^2 \frac{h\nu}{e^{\beta h\nu} - 1} \tag{6.53}$$

Rayleigh-Jeans Law

We can immediately make contact with the Rayleigh-Jeans law. To this end we consider the approximation

$$e^{\beta h\nu} - 1 \approx \beta h\nu \tag{6.54}$$

and are led to the spectral density in terms of the *Rayleigh-Jeans formula*

$$u(\nu)d\nu = kT\frac{8\pi}{c^3}\nu^2 d\nu \tag{6.55}$$

The total internal energy is given by

$$U = V\int_0^\infty d\nu u(\nu) \tag{6.56}$$

and, as we have discussed above, does not converge. As mentioned above, Lord Rayleigh obtained this result using the equipartition theorem within classical statistics.

Wien's Formula

For large values of the frequency one obtains *Wien's formula.* Performing the approximation

$$\frac{h\nu}{kT} >> 1 \tag{6.57}$$

Wien's law reads

$$u(\nu)d\nu = \frac{8\pi}{c^3}h\nu^3 e^{-\beta h\nu} d\nu \tag{6.58}$$

Stefan-Boltzmann's Law

It is straightforward to derive the Stefan-Boltzmann law.

$$U = V\int d\nu u(\nu) == V\frac{8\pi}{c^3}\int \frac{h\nu^3}{e^{\beta h\nu} - 1}d\nu \tag{6.59}$$

Introducing the integration variable

$$x = \beta h\nu \tag{6.60}$$

one derives

$$U = V\frac{8\pi}{(hc)^3}k^4T^4\int_0^\infty dx\frac{x^3}{e^x - 1} \tag{6.61}$$

As a consequence the Stefan- Boltzmann reads

$$U = V\sigma T^4 \tag{6.62}$$

By comparison we obtain the constant

$$\sigma = \frac{8\pi}{(hc)^3}k^4\int_0^\infty dx\frac{x^3}{e^x - 1} \tag{6.63}$$

Specific Heat of the Photon Gas

Using the internal energy $U = V\sigma T^4$ we can determine the specific heat at constant volume of the photon gas

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 4\sigma V T^3 \tag{6.64}$$

7

Phonons in a Solid

8

Ideal Quantum Gases

In this chapter we shall present the statistics of a system of quantum mechanical particles contained in a box of volume V. We consider periodic boundary conditions for the single particle wave function. These wave functions are then plane waves

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}} \tag{8.1}$$

where the energy of the single particle is given by

$$E_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{\hbar^2}{2m}(2\pi)^2 \left[\frac{l_x^2}{L^2} + \frac{l_y^2}{L^2} + \frac{l_z^2}{L^2}\right] \tag{8.2}$$

Thereby, the numbers $l_i = -\infty, .., 0, 1..\infty$.

For the following it is interesting to note that

$$E_{\mathbf{k}_i} = \frac{1}{V^{2/3}} \frac{\hbar^2}{2m}(2\pi)^2 \left[l_x^2 + l_y^2 + l_z^2\right] \tag{8.3}$$

This leads us to the relation

$$\frac{E(\mathbf{k}_i)}{\partial V} = -\frac{2}{3}\frac{1}{V} E(\mathbf{k}_i) \tag{8.4}$$

However, we may also consider different energy spectra, i.e. energies which are a result, e.g. of a Hartree-Fock calculation. The gas particles are then considered as quasiparticles. Quasiparticles incorporate besides the bare particles also effective multi-particle interactions.

8.1 Fermions and Bosons

The impossibility to distinguish quantum particles, which is a direct consequence of Heisenberg's uncertainty relationship, requires that the wave function $\psi(\mathbf{x}_1, \sigma_1; ...\mathbf{x}_N, \sigma_N; t)$ has to be either an even or an odd function with respect to permutations of two coordinates in the wave function

$$\psi(\mathbf{x}_1,\sigma_1;...\mathbf{x}_i,\sigma_i;..\mathbf{x}_j,\sigma_j..\mathbf{x}_N,\sigma_N;t) = \begin{pmatrix} +\ \psi(\mathbf{x}_1,\sigma_1;...\mathbf{x}_j,\sigma_j;..\mathbf{x}_i,\sigma_i;..\mathbf{x}_N,\sigma_N;t) \\ -\ \psi(\mathbf{x}_1,\sigma_1;...\mathbf{x}_j,\sigma_j;..\mathbf{x}_i,\sigma_i;..\mathbf{x}_N,\sigma_N;t) \end{pmatrix} \tag{8.5}$$

There are two types of quantum particles: Bosons, whose wave function is completely symmetric with respect to permutations, and Fermions, whose wave function is completely antisymmetric with respect to permutations.

8.1.1 Wave Functions for noninteracting Fermions and Bosons

The Schrödinger equation for noninteracting quantum particles allows one to represent the N-particle wave functions in terms of the product basis of single particle wave functions

$$\psi_{\mathbf{k},\sigma}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}} \chi(\sigma) \tag{8.6}$$

A product basis of the N-particle Hilbert space is then

$$\psi_{\mathbf{k}_1,\sigma_1;...\mathbf{k}_N,\sigma_N}(\mathbf{x}_1,...\mathbf{x}_2) = \psi_{\mathbf{k},\sigma_1}(\mathbf{x}_1)...\psi_{\mathbf{k}_N,\sigma_N}(\mathbf{x}_N) \tag{8.7}$$

However, the states $\psi_{\mathbf{k}_1...\mathbf{k}_N}(\mathbf{x}_1,...\mathbf{x}_2)$ due not fulfill the symmetry properties under permutation.

A basis which fulfills these requirements can be built from a linear combination of the vectors (8.7).

Bosons:

For Bosons, we consider the completely symmetric functions

$$\Psi_{\mathbf{k}_1,\sigma_1...\mathbf{k}_N,\sigma_N}(\mathbf{x}_1,\sigma_1...\mathbf{x}_N,\sigma_N) = \frac{1}{N!} \sum_P \psi_{\mathbf{k}_1,\sigma_1}(\mathbf{x}_1)...\psi_{\mathbf{k}_N,\sigma_N}(\mathbf{x}_N) \tag{8.8}$$

In the case of two particles we obtain

$$\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{V}} e^{i\mathbf{k}_1\cdot\mathbf{x}_1} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_2\cdot\mathbf{x}_2} \chi_1(\sigma_1)\chi_2(\sigma_2) + \frac{1}{\sqrt{V}} e^{i\mathbf{k}_1\cdot\mathbf{x}_2} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_2\cdot\mathbf{x}_1} \chi_1(\sigma_2)\chi_2(\sigma_1) \right] \tag{8.9}$$

Fermions:

For Fermions we take the completely antisymmetric functions

$$\Psi_{\mathbf{k}_1,\sigma_1...\mathbf{k}_N,\sigma_N}(\mathbf{x}_1,...\mathbf{x}_2) = \frac{1}{N!} \sum_P (-1)^p \psi_{\mathbf{k}_1,\sigma_1}(\mathbf{x}_1)...\psi_{\mathbf{k}_N,\sigma_N}(\mathbf{x}_N) \tag{8.10}$$

The multiparticle wave function for Fermions can be represented in terms of a Slater determinant.

In the case of two Fermions we obtain

$$\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{V}} e^{i\mathbf{k}_1\cdot\mathbf{x}_1} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_2\cdot\mathbf{x}_2} \chi_1(\sigma_1)\chi_2(\sigma_2) - \frac{1}{\sqrt{V}} e^{i\mathbf{k}_1\cdot\mathbf{x}_2} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_2\cdot\mathbf{x}_1} \chi_1(\sigma_2)\chi_2(\sigma_1) \right] \tag{8.11}$$

We explicitly see that the eigenstates with $\mathbf{k}_1 = \mathbf{k}_2$ are zero.

The symmetric and antisymmetric wave functions are eigenstates of the Hamiltonian H:

$$H\Psi_{\mathbf{k}_1,\sigma_1\ldots\mathbf{k}_N,\sigma_N}(\mathbf{x}_1, \ldots\mathbf{x}_N) = \sum_{i=1}^{N} E(\mathbf{k}_i)\Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N}(\mathbf{x}_1, \ldots\mathbf{x}_N) \tag{8.12}$$

We can rewrite this equation as

$$H\Psi_{\mathbf{k}_1,\sigma_1\ldots\mathbf{k}_N,\sigma_N}(\mathbf{x}_1, \ldots\mathbf{x}_N) = \sum_{\mathbf{k},\sigma} \left[n_{\mathbf{k},\sigma}E(\mathbf{k})\right] \Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N}(\mathbf{x}_1, \ldots\mathbf{x}_N) \tag{8.13}$$

Here, $n_{\mathbf{k}_i,\sigma_i}$ denotes the *number of particles* with energy $E(\mathbf{k}_i)$ and spin σ_i.

For Fermions, these numbers can take only the values

$$n(\mathbf{k}, \sigma) = 0, 1 \tag{8.14}$$

For Bosons, however, these numbers can take the values

$$n(\mathbf{k}, \sigma) = 0, 1, \ldots\infty \tag{8.15}$$

The numbers $n(\mathbf{k}, \sigma)$ are denoted as occupation numbers. They count the number of particles with spin σ and wave vector $\mathbf{k}$, i.e. the number of particles having the energy $E(\mathbf{k}$. The occupation numbers for systems with N particles are subjected to the following constraints

$$\sum_{\mathbf{k},\sigma} n(\mathbf{k}, \sigma) = N \tag{8.16}$$

8.1.2 Fock-Space

The *Fock space* is a Hilbert space for many particle systems, where the number N of particles is variable. The introduction of such a space facilitates the treatment of many particle systems based on the occupation numbers, since now the constraints (8.16) do not have to be taken into account. Furthermore, when dealing with statistical treatment of many particle systems, the use of the grand canonical description requires to consider states with variable numbers N of particles.

The Fock space is the direct sum of Hilbert spaces with $0, 1, .., \infty$ number of particles:

$$H = H_0 + H_1 + H_2 + \ldots H_\infty \tag{8.17}$$

A basis of each Hilbert space H_i are the symmetrized (Bosons) or antiysmmetrized (Fermions) wave functions, (8.8) and (8.10).

8.2 Grand-Canonical Distribution

The grand canonical partition function for free quantum particles takes the following form

$$\sum_{N=0}^{\infty}\sum_{\mathbf{k_1}}\ldots\sum_{\mathbf{k_N}} < \Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N}|e^{-\beta(H-\mu N)}|\Psi\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N >= \tag{8.18}$$

where

$$|\Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N} >= \frac{1}{\sqrt{N!}}\sum_P \frac{1}{\sqrt{V}}e^{i\mathbf{k}_1\cdot\mathbf{x}_1}\ldots\frac{1}{\sqrt{V}}e^{i\mathbf{k}_N\cdot\mathbf{x}_N} \tag{8.19}$$

for Bosons. For Fermions, we obtain

$$|\Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N} >= \frac{1}{\sqrt{N!}}\sum_P (-1)^P\frac{1}{\sqrt{V}}e^{i\mathbf{k}_1\cdot\mathbf{x}_1}\ldots\frac{1}{\sqrt{V}}e^{i\mathbf{k}_N\cdot\mathbf{x}_N} \tag{8.20}$$

In order to calculate the canonical partition function, we should evaluate

$$\begin{gathered} Z(\beta,V,N) = \\ \sum_{\mathbf{k}_1,\sigma_1;..\mathbf{k}_N,\sigma_N} < \Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N}|e^{-\beta H}|\Psi\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N >= \\ \sum_{\ldots n(\mathbf{k}',\sigma');..n(\mathbf{k}'',\sigma'')\ldots} e^{-\beta\sum_{\mathbf{k}} n(\mathbf{k},\sigma)E(\mathbf{k})} \end{gathered} \tag{8.21}$$

Here, the summation has to be performed in such a way that

$$N = \sum_{\mathbf{k},\sigma} n(\mathbf{k},\sigma) \tag{8.22}$$

This constraint renders the evaluation of the partition function rather difficult. This is the reason to evaluate the thermodynamic quantities for ideal quantum gases using the grand canonical partition function. This partition function is given by

$$\begin{gathered} Z(\beta,V,N) = \\ \sum_{N=0}^{\infty}\sum_{\mathbf{k}_1,\sigma_1;..\mathbf{k}_N,\sigma_N} < \Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N}|e^{-\beta(H-\mu N)}|\Psi_{\mathbf{k}_1,\sigma_1;\ldots\mathbf{k}_N,\sigma_N} >= \\ \sum_{N=0}^{\infty}\sum_{..n(\mathbf{k}',\sigma');..n(\mathbf{k}'',\sigma'')} e^{-\beta\sum_{\mathbf{k},\sigma} n(\mathbf{k},\sigma)E(\mathbf{k})-\mu)} \end{gathered} \tag{8.23}$$

Thereby, we have used the occupation numbers

$$n(\mathbf{k},\sigma) \tag{8.24}$$

Consequently, the grand partition function is calculated according to

$$Z(\beta, V, N) = \sum_{N=0}^{\infty} \{ \sum_{..n(\mathbf{k}',\sigma')} .. \sum_{n(\mathbf{k}'',\sigma'')} \}_{\sum_{\mathbf{k},\sigma} n(\mathbf{k},\sigma)=N} e^{-\beta \sum_{\mathbf{k},\sigma} n(\mathbf{k},\sigma)(E(\mathbf{k})-\mu)} \tag{8.25}$$

However, a rearrangement of the terms shows that

$$Z(\beta, V, N) = \{.. \sum_{n(\mathbf{k}',\sigma')} .. \sum_{n(\mathbf{k}'',\sigma'')} ..e^{-\beta \sum_{\mathbf{k},\sigma} n(\mathbf{k},\sigma)(E(\mathbf{k})-\mu)} \tag{8.26}$$

We explicitly see that now, there is no restriction on the sums with respect to the occupation numbers $n(\mathbf{k}, \sigma)$.

8.2.1 From the Grand Canonical Partition to Thermodynamics

In order to obtain the equation of state and related thermodynamic quantities from the grand canonical partition function, we note that the grand potential $J(\beta, V, \mu)$ is obtained from the grand partition function according to

$$\begin{aligned} J(\beta, \mu, V) &= -\frac{1}{\beta} lnZ(\beta, \mu, V) \\ &= -\frac{1}{\beta} \sum_{\mathbf{k}_i} ln(1 + e^{-\beta(E(\mathbf{k}_i)-\mu)}) \end{aligned} \tag{8.27}$$

This can be seen from the fundamental relation

$$S = -ktr\rho ln\rho = k\beta U - k\beta\mu N + klnZ \tag{8.28}$$

$$U = TS + \mu N - kTlnZ \tag{8.29}$$

We define the *grand free energy* by the Legendre transform of the inner energy

$$J(\beta, V, \mu) = U - TS - \mu N = -\frac{1}{\beta} lnZ \tag{8.30}$$

We obtain the following relations, which are important for the derivation of thermodynamic quantities.

$$p = -\left(\frac{\partial J}{\partial V}\right)_{\mu,T} \tag{8.31}$$

$$S = -\left(\frac{\partial J}{\partial T}\right)_{\mu,V} \tag{8.32}$$

$$N = -\left(\frac{\partial J}{\partial \mu}\right)_{\mu,V} \tag{8.33}$$

Let us briefly show how these relations arise. We have the fundamental thermodynamic relation

$$dU = TdS - pdV + \mu dN \tag{8.34}$$

Therefore,

$$dJ(T, V, \mu) = -SdT - pdV - Nd\mu \tag{8.35}$$

8.2.2 Evaluation of the Grand Canonical Partition Function

The grand canonical partition function is denoted by

$$\begin{aligned} Z(\beta, V, \mu) &= \sum_{N=0}^{\infty} \{ \sum_{n(\mathbf{k}_1,\sigma_1)} .. \sum_{n(\mathbf{k}_N,\sigma_N)} \}_{\sum n(\mathbf{k},\sigma)=N} e^{-\beta \sum_{\mathbf{k}} (E(\mathbf{k}-\mu) n(\mathbf{k},\sigma))} \\ &= \{ \sum_{n(\mathbf{k}_1,\sigma_1)} .. \sum_{n(\mathbf{k}_N,\sigma_N)} \}_{\sum n(\mathbf{k},\sigma)=N} e^{-\beta \sum_{\mathbf{k}} (E(\mathbf{k}-\mu) n(\mathbf{k},\sigma))} \end{aligned} \tag{8.36}$$

Now, the occupation numbers of the states $E(\mathbf{k}_i)$ are free. In contrast to the canonical partition function, they are not subjected to the restriction $\sum n(\mathbf{k}_i) = N$.

The grand canonical partition function has to be evaluated for Fermions and Bosons separately. For Bosons, the occupation numbers are in the range

$$0 \leq n(\mathbf{k}, \sigma) \leq \infty \tag{8.37}$$

whereas for Fermions

$$n(\mathbf{k}, \sigma) = 0, 1 \tag{8.38}$$

This yields fundamental differences in the evaluation of the partition function.

8.3 Fermions, Fermi-Distribution

For *Fermions* the grand partition function is easily evaluated considering that only terms with $n(\mathbf{k}) = 0, 1$ contribute, due to the Pauli exclusion principle. As a result we obtain the grand partition function

$$Z(\beta, \mu, V) = \Pi_{\mathbf{k}} (1 + e^{-\beta(E(\mathbf{k}) - \mu)})^g \tag{8.39}$$

We take into account the fact that electrons have a spin. Therefore, we include the factor g. g=2 for spin 1/2 particles.

In order to obtain the equation of state we note that the grand potential $J(\beta, V, \mu)$ is obtained from the grand partition function according to

$$\begin{aligned} J(\beta,\mu,V) &= -\frac{1}{\beta} lnZ(\beta,\mu,V) \\ &= -\frac{1}{\beta} g \sum_{\mathbf{k}} ln(1+e^{-\beta(E(\mathbf{k})-\mu)}) \end{aligned} \tag{8.40}$$

We derive the mean particle number

$$N = -\frac{\partial}{\partial\mu} J(\beta,\mu,V) = g\sum(\mathbf{k}\frac{e^{-\beta(E(\mathbf{k})-\mu)}}{1+e^{-\beta(E(\mathbf{k})-\mu)}} \tag{8.41}$$

and calculate the mean occupation number

$$N(\mathbf{k}) = g\frac{1}{e^{\beta(E(\mathbf{k})-\mu)}+1} \tag{8.42}$$

This is the Fermi distribution.

We can now derive the pressure according to

$$p = -\left(\frac{\partial}{\partial V} J(\beta,\mu,V)\right)_{\beta,\mu} \tag{8.43}$$

This leads us to

$$p = \frac{\partial}{\partial V}\frac{1}{\beta}\sum_{\mathbf{k}_i} ln(1+e^{-\beta(E(\mathbf{k}_i)-\mu)}) \tag{8.44}$$

The only quantities which depend on V when μ and β is fixed are the energies $E(\mathbf{k}_i)$. Therefore,

$$p = -\sum_{\mathbf{k}_i}\frac{e^{-\beta(E(\mathbf{k}_i)-\mu)}}{1+e^{-\beta(E(\mathbf{k}_i)-\mu)}}\frac{\partial E(\mathbf{k}_i)}{\partial V} \tag{8.45}$$

Considering the relation (**??**) we immediately obtain

$$pV = \frac{2}{3}U \tag{8.46}$$

Thereby, we have considered that the inner energy is determined by the sum

$$U = g\sum_{\mathbf{k}}\frac{E(\mathbf{k})}{e^{\beta(E(\mathbf{k}_i)-\mu)}+1} \tag{8.47}$$

$$U = \sum_{\mathbf{k}_i} N_{Fermi}(\mathbf{E}_{\mathbf{k}_i})\mathbf{E}(\mathbf{k}_i) \tag{8.48}$$

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3}4\pi\int dkk^2 \tag{8.49}$$

Now, we introduce

$$\epsilon = \frac{\hbar^2 k^2}{2m} \tag{8.50}$$

and obtain

$$dkk^2 = \frac{1}{2}\sqrt{\frac{2m\epsilon}{\hbar^2}}^3 \epsilon^{1/2} d\epsilon \tag{8.51}$$

$$\sum_{\mathbf{k}} .... \rightarrow V 2\pi \int \sqrt{\frac{2m}{h^2}}^3 \epsilon^{1/2} d\epsilon .... \tag{8.52}$$

We can now summarize:

$$J(\beta, V, \mu) = -\frac{1}{\beta} g 2\pi \sqrt{\frac{2m}{h^2}}^3 \int \epsilon^{1/2} d\epsilon ln(1 + e^{-\beta(\epsilon - \mu)} \tag{8.53}$$

The mean particle number takes the form

$$N = g 2\pi \sqrt{\frac{2m}{h^2}}^3 \int \epsilon^{1/2} d\epsilon \frac{1}{(e^{\beta(\epsilon-\mu)} + 1} \tag{8.54}$$

Fermi-Energy

For Fermi-Distributions we can consider the case $T \rightarrow 0$. In this case, $\beta \rightarrow \infty$ and the Fermi distribution takes the form

$$N(\mathbf{k}) = \{ \begin{matrix} 0 & \text{for} E(\mathbf{k} > \mu \\ 1 & \text{for} E(\mathbf{k} < \mu \end{matrix} \tag{8.55}$$

Relation

$$\bar{N} = \sum_{\mathbf{E(k)} < \mu} \tag{8.56}$$

defines the Fermi-Energy

$$E_F \tag{8.57}$$

Explicitly, we obtain the definition of the Fermi energy

$$\begin{aligned} \bar{N} &= \frac{V}{2\pi^2} (\frac{2m}{\hbar^2})^{3/2} \int_0^{E_F} d\epsilon \epsilon^{1/2} \\ &= \frac{V}{\pi^2} (\frac{2m}{\hbar^2})^{3/2} \frac{1}{3} E_f^{3/2} = V g (\frac{2m}{h^2})^{3/2} 8\pi \frac{1}{3} E_f^{3/2} \end{aligned} \tag{8.58}$$

This yields the Fermi energy

$$E_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3} \tag{8.59}$$

Internal Energy and Specific Heat of an Ideal Fermi Gas

We calculate the internal energy

$$U = g\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m}\frac{1}{e^{\beta(E(\mathbf{k}-\mu)}+1} \tag{8.60}$$

Passing to an integral, we obtain

$$U = g2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)}+1} \tag{8.61}$$

For $\beta \to 0$ we obtain

$$U = g2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^{E_f} d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)}+1} \tag{8.62}$$

$$U = \frac{3}{5}\bar{N}E_F[1+\frac{5}{12}\left(\frac{kT}{E_F}\right)^2+.. \tag{8.63}$$

Specific heat

$$C_v \approx T \tag{8.64}$$

The calculation of the various integrals is discussed in the next subsection.

Calculation of Integrals

We have to calculate integrals of the Form

$$I = \int_0^\infty d\epsilon \frac{F(\epsilon)}{e^{\beta(\epsilon-\mu)}+1} \tag{8.65}$$

To this end we perform the substitution

$$z = \beta(\epsilon-\mu) \tag{8.66}$$

$$I = kT\int_{-\beta\mu} d\epsilon \frac{F(\mu+kTz)}{e^z+1} \tag{8.67}$$

Now, we can split this integral in

$$I = kT\{\int_0^{\beta\mu} dz\frac{F(\mu-kTz)}{e^{-z}+1} + \int_0^\infty dz\frac{F(\mu+kTz)}{e^z+1} \tag{8.68}$$

We rewrite

$$\frac{1}{e^{-z}+1} = 1-\frac{1}{e^z+1} \tag{8.69}$$

and obtain

$$I = \int_0^{\mu} F(\epsilon) d\epsilon + kT \int_0^{\infty} dz \frac{F(\mu + kTz) - F(\mu - kTz)}{e^z + 1} \tag{8.70}$$

Expansion in a Taylor series leads to

$$\begin{aligned} I = &\int_0^{\mu} F(\epsilon) d\epsilon + 2(kT)^2 F''(\mu) \int_0^{\infty} dz \frac{z}{e^z + 1} \\ &+ \frac{1}{3}(kT)^4 F'''(\mu) \int_0^{\infty} dz \frac{z^3}{e^z + 1} + ... \end{aligned} \tag{8.71}$$

8.3.1 Relativistic Fermi Gas

We consider a gas of relativistic Fermi particles. The energy is given by

$$E(\mathbf{k}) = cp = c\hbar k \tag{8.72}$$

Now, we have the correspondence

$$\sum_{\mathbf{k}} \rightarrow g 4\pi \frac{V}{(2\pi)^3} \int dk k^2 = g 4\pi \frac{V}{(hc)^3} \int d\epsilon \epsilon^2 \tag{8.73}$$

The fermi energy is

$$\bar{N} = g 4\pi \frac{V}{(hc)^3} \frac{1}{3} E_f^3 \tag{8.74}$$

This yields

$$E_F = \left(n \frac{3}{4\pi g} \right)^{1/3} hc \tag{8.75}$$

The grand partition function is

$$J = -\frac{1}{\beta} g 4\pi \frac{V}{(hc)^3} \int d\epsilon \epsilon^2 ln(1 + e^{-\beta(\epsilon - \mu)}) \tag{8.76}$$

Partial integration yields

$$J = -\frac{1}{3\beta} g 4\pi \frac{V}{(hc)^3} \int d\epsilon \frac{\epsilon^3}{e^{\beta(\epsilon - \mu)} + 1} = -\frac{U}{3} \tag{8.77}$$

8.4 Bosons

As a first step we calculate the grand partition function Z for Bosons noting that

$$\sum_{n=0}^{\infty} e^{-\beta E(\mathbf{k}_i - \mu) n} = \frac{1}{1 - e^{-\beta E(\mathbf{k}_i - \mu) n}} \tag{8.78}$$

This leads us to the grand partition function

$$Z(\beta,\mu,V) = \Pi_{\mathbf{k}_i} \frac{1}{1 - e^{-\beta(E(\mathbf{k}_i)-\mu)}} \tag{8.79}$$

The grand potential is given by the relation

$$J = -\frac{1}{\beta} lnZ(\beta,\mu,V) = \frac{1}{\beta} \sum_{\mathbf{k}_i} ln1 - e^{-\beta(E(\mathbf{k}_i)-\mu)} \tag{8.80}$$

We derive the mean particle number

$$\bar{N} = -\frac{\partial}{\partial\mu} J(\beta,\mu,V) = \sum_{\mathbf{k}} \frac{e^{-\beta(E(\mathbf{k})-\mu)}}{1 + e^{-\beta(E(\mathbf{k})-\mu)}} \tag{8.81}$$

As a consequence we obtain the mean occupation number of the state with energy $E(\mathbf{k})$:

$$N(\mathbf{k}) = \frac{1}{e^{\beta(E(\mathbf{k})-\mu)} - 1} \tag{8.82}$$

This defines the Bose-Einstein distribution.

The chemical potential is again defined implicitly by the relationship

$$\bar{N} = \sum_{\mathbf{k}} N(\mathbf{k}) \tag{8.83}$$

We note that the Bose-Einstein distribution depends on the chemical potential μ. The above relation defines μ as a function of the mean particle number $\bar{N}$.

The pressure can be calculated via the relationship

$$p = -\frac{\partial J}{\partial V} \tag{8.84}$$

leading to

$$p = -\sum_{\mathbf{k}_i} \frac{e^{-\beta(E(\mathbf{k}_i)-\mu)}}{1 - e^{-\beta(E(\mathbf{k}_i)-\mu)}} \frac{\partial E(\mathbf{k}_i)}{\partial V} \tag{8.85}$$

Again, using

$$\frac{\partial E(\mathbf{k}_i)}{\partial V} = -\frac{2}{3}\frac{1}{V} E(\mathbf{k}_i) \tag{8.86}$$

we end up with the relation

$$pV = \frac{2}{3} U \tag{8.87}$$

The inner energy takes the form

$$U = \sum_{\mathbf{k}_i} \frac{e^{-\beta(E(\mathbf{k}_i)-\mu)}}{1 - e^{-\beta(E(\mathbf{k}_i)-\mu)}} E(\mathbf{k}_i) \tag{8.88}$$

$$N_{Bose}(\mathbf{E}_{\mathbf{k}_i}) = \frac{1}{e^{\beta(E(\mathbf{k}_i)-\mu)} - 1} \tag{8.89}$$

in the form

$$U = \sum_{\mathbf{k}_i} N_{Bose}(\mathbf{E}_{\mathbf{k}_i}) \mathbf{E}(\mathbf{k}_i) \tag{8.90}$$

8.4.1 Bose-Einstein-Condensation

The mean number of Bosons is determined by the relation

$$\bar{N} = \sum_{\mathbf{k}_i} \frac{1}{e^{\beta(E(\mathbf{k}_i)-\mu)} - 1} \tag{8.91}$$

This sum can be split up into two constributions. There is a contribution due to the ground state $E = 0$ and contributions due to higher levels.

$$\bar{N} = \frac{1}{e^{-\beta\mu} - 1} + \sum_{\mathbf{k}_i} \frac{1}{e^{\beta(E(\mathbf{k}_i)-\mu)} - 1} \tag{8.92}$$

The quantity z is the fugacity

$$z = e^{\beta\mu} \tag{8.93}$$

In contrast to the Fermi gas, for which at temperature $T = 0$ all energy levels up to the Fermi level are occupied, Bosons can occupy the lowest energy state. Therefore, we expect that

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} \tag{8.94}$$

tends to $\bar{N}$ for $\beta \to 0$. That means that the fugazity z should tend to one.

We approximate the second sum by an integral:

$$\sum_{\mathbf{k}} \to 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int d\epsilon \sqrt{\epsilon} \tag{8.95}$$

and obtain

$$\tilde{N} = N_0 + 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int d\epsilon \sqrt{\epsilon} \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \tag{8.96}$$

A further transformation

$$\beta\epsilon \to \tilde{\epsilon} \tag{8.97}$$

yields

$$\tilde{N} = N_0 + 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \int d\epsilon \sqrt{\epsilon} \frac{1}{e^{\epsilon-\beta\mu} - 1} \tag{8.98}$$

We can now express the fugacity z by N_0

$$z^{-1} = 1 + \frac{1}{N_0} \tag{8.99}$$

Our relation then reads

$$\bar{N} = N_0 + 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \int_0^\infty \frac{d\epsilon \epsilon^{1/2}}{e^{\epsilon}(1 + 1/N_0) - 1} \tag{8.100}$$

If $N_0 >> 1$, i.e. if the ground state is macroscopically occupied, we can approximate this relation by

$$\bar{N} = N_0 + 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \int_0^\infty \frac{d\epsilon \epsilon^{1/2}}{e^\epsilon - 1} \tag{8.101}$$

The integral can be evaluated using the Riemann zeta function

$$\zeta(3/2) = \int_0^\infty \frac{d\epsilon \epsilon^{1/2}}{e^\epsilon - 1} \tag{8.102}$$

We can define a temperatue T_B by the relation

$$\bar{N} = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} (kT_B)^{3/2} \int_0^\infty \frac{d\epsilon \epsilon^{1/2}}{e^\epsilon - 1} \tag{8.103}$$

This defines a temperature T_B, at which the transition to the Bose-Einstein condensate takes place.

Then, if $N_0 >> 1$ we can derive the relationship

$$\bar{N} = N_0 + \bar{N} \left(\frac{T}{T_0}\right)^{3/2} \tag{8.104}$$

This leads us to the number of particles N_0 in the ground state, or in the Bose-Einstein condensate

$$N_0 = N[1 - \left(\frac{T}{T_0}\right)^{3/2}] \tag{8.105}$$

More Refined treatment

We can rewrite

$$N = \frac{Z}{1-z} + \frac{V}{\lambda^3} G(z) \tag{8.106}$$

Here, we have defined the thermal de'Broglie wave length

$$\lambda = \sqrt{\frac{h^2}{2\pi 2m} \frac{1}{kT}} \tag{8.107}$$

$$G(z) = \frac{2}{\pi} \int_0^\infty dx \frac{x^{1/2}}{z^{-1} e^x - 1} \tag{8.108}$$

Furthermore,

$$G(z) = \zeta(3/2) \tag{8.109}$$

to be done...

Condition for the Occurence of the Bose-Einstein Condensate

The condition for the occurence of Bose-Einstein condensation can be read of from eq. (**??**):

$$\bar{N} = V 2\pi \left(\frac{2m}{h^2} kT\right)^{3/2} \zeta(3/2) \tag{8.110}$$

This condition can be met by either lowering the temperature at fixed density, or, by increasing density at fixed temperature.

Condensed Phase

We can now calculate the mean energy in the condensed phase, i.e. for $T < T_B$. the calculations are based on the approximation $zby(kT)^{3/2}z = 1$.

We notice that only Bosons in the excited state contribute,

$$U = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{5/2} \int d\epsilon \sqrt{\epsilon} \frac{z}{e^{\epsilon} - 1} \tag{8.111}$$

This yields

$$U = akT \left(\frac{T}{T_0}\right)^{3/2} \tag{8.112}$$

The specific heat is obtained by

$$C_V = \frac{5}{2} \frac{U}{T} \tag{8.113}$$

Above the Consensed Phase

8.5 Calculation of Integrals

We consider the evaluation of integrals of the form

$$\int_0^{\infty} dz \frac{z^{x-1}}{e^z + 1} \tag{8.114}$$

To this end we expand into a Taylor series

$$\int_0^{\infty} dz \frac{z^{x-1}}{e^z + 1} = \int_0^{\infty} dz z^{x-1} e^{-z} \sum_{n=0}^{\infty} (-1)^n e^{-nz} \tag{8.115}$$

The Gamma function is defines as

$$\Gamma(x) = \int_0^{\infty} dz z^{x-1} e^{-z} \tag{8.116}$$

We obtain

$$\int_0^\infty dz z^{x-1} e^{-nz} = \frac{1}{n^x} \int_0^\infty dz' z'^{x-1} e^{-z'} = \frac{1}{n^x} \Gamma(x) \tag{8.117}$$

This leads us to the representation

$$\int_0^\infty dz \frac{z^{x-1}}{e^z + 1} = (1 - 2^{1-x}) \Gamma(x) \zeta(x) \tag{8.118}$$

Here, we have defined Riemann's zeta function

$$\zeta(x) = \sum_{n=1}^{\infty} \frac{1}{n^x} \tag{8.119}$$

$$\int_0^\infty dx \frac{x}{e^x + 1} = \frac{\pi^2}{12} \tag{8.120}$$

$$\int_0^\infty dx \frac{x^2}{e^x + 1} = \frac{3}{2} \zeta(3) \tag{8.121}$$

$$\int_0^\infty dx \frac{x^3}{e^x + 1} = \frac{7\pi^4}{120} \tag{8.122}$$

$$\int_0^\infty dx \frac{x}{e^x - 1} = \frac{\pi^2}{6} \tag{8.123}$$

$$\int_0^\infty dx \frac{x^2}{e^x - 1} = 2\zeta(3) \tag{8.124}$$

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \tag{8.125}$$

8.6 Bose, Fermi Distributions, Summary

	Fermions	Bosons
Grand partition function $Z(\beta, \mu, V)$	$\Pi_{\mathbf{k}} (1 + e^{-\beta(E(\mathbf{k}) - \mu)})$	$\Pi_{\mathbf{k}} \frac{1}{(1 - e^{-\beta(E(\mathbf{k}_i) - \mu)})}$
Grand potential $J(\beta, \mu, V)$	$\sum_{\mathbf{k}} ln \left(1 + e^{-\beta(E(\mathbf{k}) - \mu)}\right)$	$-\sum_{\mathbf{k}} ln(1 - e^{-\beta(E(\mathbf{k}) - \mu)})$
Mean particle number $\bar{N}$	$\bar{N} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(E(\mathbf{k}) - \mu)} + 1}$	$\bar{N} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(E(\mathbf{k}) - \mu)} - 1}$
Equation of state	$pV = \frac{2}{3} U$	$pV = \frac{2}{3} U$
Distribution	$\frac{1}{e^{\beta(E(\mathbf{k}) - \mu)} + 1}$	$\frac{1}{e^{\beta(E(\mathbf{k}) - \mu)} - 1}$

The quantities can be calculated according to

grand partition function	$Z(\beta, V, \mu)$
grand potential	$J = -\frac{1}{\beta} ln Z(\beta, V, \mu)$
mean particle number	$J = -\left(\frac{\partial J}{\partial \mu}\right)_{V,\beta}$
pressure	$p = -\left(\frac{\partial J}{\partial V}\right)_{\mu,\beta}$
entropy	$S = -\left(\frac{\partial J}{\partial T}\right)_{\mu,V}$