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Statistical Physics (046242) - Lecture Notes

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Technion
Preface

to be written...
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1. Entropy

In this chapter the entropy of a given discrete probability distribution is defined, its relation to Shannon’s coding theory is demonstrated, and its connection to uncertainty is discussed.

1.1 Coding

The probability that a given discrete random variable \( X \) takes the value \( x_m \) is denoted by \( P \{ X = x_m \} = p_m \), where \( m \in \{ 1, 2, \ldots, N \} \). The normalization condition reads

\[
\sum_{m=1}^{N} p_m = 1 .
\]  

(1.1)

A communication channel is employed for transmitting the outcome of a measurement of \( X \). The channel allows transmitting binary sequences of 0’s and 1’s. A binary code denoted by \( B_m \) is sent when the outcome of the measurement is \( x_m \). Let \( l_m \) be the length (i.e. number of binary digits 0’s and 1’s) of the code \( B_m \).

The binary codes are sent one after the other without adding extra binary digits. Consequently, the code \( B_{m'} \) of any given outcome \( x_{m'} \) cannot be an extension of a code \( B_{m''} \) of any other outcome \( x_{m''} \), where \( m' \neq m'' \). For example, if a code '01' is employed for a given outcome, the code '011' cannot be used for any other outcome.

**Claim.** The following holds

\[
\sum_{m=1}^{N} \left( \frac{1}{2} \right)^{l_m} \leq 1 .
\]  

(1.2)

**Proof.** Let \( M_s \) be the number of codes having length \( s \). Since code extensions are not allowed, the following holds

\[
M_s \leq 2^s - M_{s-1}2^1 - M_{s-2}2^2 - \cdots - M_22^{(s-2)} - M_12^{(s-1)} ,
\]  

(1.3)

or (dividing by \( 2^s \))
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\[ \frac{M_s}{2^s} \leq 1 - \frac{M_{s-1}}{2^{s-1}} - \frac{M_{s-2}}{2^{s-2}} - \cdots - \frac{M_2}{2^2} - \frac{M_1}{2^1}, \]  \hspace{1cm} (1.4)

hence

\[ \sum_s M_s \left( \frac{1}{2} \right)^s = \sum_{m=1}^N \left( \frac{1}{2} \right)^{l_m} \leq 1. \]  \hspace{1cm} (1.5)

The expectation value \( \langle l \rangle \) of the message length \( l \) is given by

\[ \langle l \rangle = \sum_{m=1}^N p_m l_m. \]  \hspace{1cm} (1.6)

**Theorem 1.1.1 (Shannon’s noiseless coding theorem).** The following holds

\[ \langle l \rangle \geq \frac{1}{\log 2} \sigma(X), \]  \hspace{1cm} (1.7)

where \( \sigma(X) \), which is defined by

\[ \sigma(X) = \left\langle \frac{1}{\log p} \right\rangle = - \sum_{m=1}^N p_m \log p_m, \]  \hspace{1cm} (1.8)

is the entropy of the probability distribution \( \{p_m\} \), and \( \log p_m \) is the natural logarithm of \( p_m \).

**Proof.** Consider the function \( f(x) = x - 1 - \log x \). The following holds \( f(1) = 0 \), \( f' \equiv df/dx = 1 - 1/x \), and \( f'(1) = 0 \), hence for \( x > 0 \)

\[ x - 1 - \log x \geq 0. \]  \hspace{1cm} (1.9)

For the case where \( x \) is chosen to be

\[ x = \frac{s_m}{p_m}, \]  \hspace{1cm} (1.10)

where \( s_m \) is defined by

\[ s_m = \frac{\left( \frac{1}{2} \right)^{l_m}}{\sum_{m'=1}^N \left( \frac{1}{2} \right)^{l_{m'}}}, \]  \hspace{1cm} (1.11)

the inequality (1.9) yields

\[ s_m - p_m \log \frac{s_m}{p_m} \geq 0, \]  \hspace{1cm} (1.12)
1.2. Example - two-state system

For a two-state system with probabilities $p$ and $1-p$, where $0 \leq p \leq 1$, the entropy $\sigma$ (1.8) is given by (see Fig. 1.1)

$$\sigma = -p \log p - (1-p) \log (1-p).$$  \hspace{1cm} (1.15)

For this case the entropy $\sigma$ vanishes at $p = 0$ and $p = 1$, and peaks at the point $p = 0.5$, for which $\sigma = \log 2$. As will be shown below, this behavior demonstrates that generally the entropy $\sigma$ (1.8) measures the uncertainty associated with a given probability distribution.
1.3 Smallest and largest entropy

It is shown below that the uncertainty associated with a given probability distribution is minimized (maximized) when the entropy obtains its smallest (largest) value.

1.3.1 Smallest value

The term $-p \log p$ in the range $0 \leq p \leq 1$ is plotted in Fig. 1.2. Note that the value of $-p \log p$ in the limit $p \to 0$ can be calculated using L’Hospital’s rule

$$
\lim_{p \to 0} (-p \log p) = \lim_{p \to 0} \left( -\frac{d \log p}{dp} \right) = 0.
$$

(1.16)

As can be seen from Fig. 1.2, $-p \log p \geq 0$ in the range $0 \leq p \leq 1$, and $-p \log p = 0$ if and only if (iff) $p = 0$ or $p = 1$. Thus, $\sigma \geq 0$ [see Eq. (1.8)], and the smallest value of $\sigma = 0$ is obtained when

$$
p_m = \begin{cases} 
1 & m = m_0 \\
0 & m \neq m_0 
\end{cases}
$$

where $m_0 \in \{1, 2, \cdots, N\}$ [see Eq. (1.1)]. In this case there is no uncertainty associated with the probability distribution, since there is only one possible outcome having probability 1.
1.3.2 Largest value

We seek a maximum point of the entropy $\sigma$ with respect to all probability distributions $\{p_m\}$ which satisfy the normalization condition. This constrain, which is given by Eq. (1.1), is expressed as

$$0 = g_0(\vec{p}) = \sum_m p_m - 1,$$  

(1.17)

where $\vec{p}$ denotes the vector of probabilities

$$\vec{p} = (p_1, p_2, \cdots).$$  

(1.18)

A small change in $\sigma$ (denoted as $\delta\sigma$) due to a small change in $\vec{p}$ (denoted as $\delta\vec{p} = (\delta p_1, \delta p_2, \cdots)$) can be expressed as

$$\delta\sigma = \sum_m \frac{\partial \sigma}{\partial p_m} \delta p_m,$$  

(1.19)

or in terms of the gradient of $\sigma$ (denoted as $\vec{\nabla} \sigma$) as

$$\delta\sigma = \vec{\nabla} \sigma \cdot \delta\vec{p}.$$  

(1.20)

In addition the variables $(p_1, p_2, \cdots)$ are subjected to the constrain (1.17). Similarly to Eq. (1.20) we have

$$\delta g_0 = \vec{\nabla} g_0 \cdot \delta\vec{p}.$$  

(1.21)

Both vectors $\vec{\nabla} \sigma$ and $\delta\vec{p}$ can be decomposed as

$$\vec{\nabla} \sigma = (\vec{\nabla} \sigma)_\parallel + (\vec{\nabla} \sigma)_\perp,$$  

(1.22)

$$\delta\vec{p} = (\delta\vec{p})_\parallel + (\delta\vec{p})_\perp,$$  

(1.23)

where both $(\vec{\nabla} \sigma)_\parallel$ and $(\delta\vec{p})_\parallel$ are parallel to $\vec{\nabla} g_0$, and where both $(\vec{\nabla} \sigma)_\perp$ and $(\delta\vec{p})_\perp$ are orthogonal to $\vec{\nabla} g_0$. Using this notation Eq. (1.20) can be expressed as

$$\delta\sigma = (\vec{\nabla} \sigma)_\parallel \cdot (\delta\vec{p})_\parallel + (\vec{\nabla} \sigma)_\perp \cdot (\delta\vec{p})_\perp.$$  

(1.24)

Given that the constrain $g_0(\vec{p}) = 0$ is satisfied at a given point $\vec{p}$, one has $g_0(\vec{p} + \delta\vec{p}) = 0$ to first order in $\delta\vec{p}$ provided that $\delta\vec{p}$ is orthogonal to $\vec{\nabla} g_0$, namely, provided that $(\delta\vec{p})_\parallel = 0$. Thus, a stationary (maximum or minimum or saddle point) point of $\sigma$ occurs iff for every small change $\delta\vec{p}$, which is orthogonal to $\vec{\nabla} g_0$ (namely, $\delta\vec{p} \cdot \vec{\nabla} g_0 = 0$) one has $0 = \delta\sigma = \vec{\nabla} \sigma \cdot \delta\vec{p}$. As can be seen from Eq. (1.24), this condition is fulfilled only when $(\vec{\nabla} \sigma)_\perp = 0$, namely only when the vectors $\vec{\nabla} \sigma$ and $\vec{\nabla} g_0$ are parallel to each other. In other words, only when
where $\xi_0$ is a constant. This constant is called Lagrange multiplier. Using Eqs. (1.8) and (1.17) the condition (1.25) is expressed as

$$\log p_m + 1 = \xi_0 .$$

Let $M$ be the number of available states. From Eq. (1.26) we find that all probabilities are equal. Thus using Eq. (1.17), one finds that

$$p_1 = p_2 = \cdots = \frac{1}{M} .$$

After finding this stationary point it is necessary to determine whether it is a maximum or minimum or saddle point. To do this we expand $\sigma$ to second order in $\delta \bar{\sigma}$

$$\sigma (\bar{\sigma} + \delta \bar{\sigma}) = \exp \left( \delta \bar{\sigma} \cdot \nabla \right) \sigma (\bar{\sigma})$$

$$= \left( 1 + \delta \bar{\sigma} \cdot \nabla + \frac{\left( \delta \bar{\sigma} \cdot \nabla \right)^2}{2!} + \cdots \right) \sigma (\bar{\sigma})$$

$$= \sigma (\bar{\sigma}) + \delta \bar{\sigma} \cdot \nabla \sigma + \frac{\left( \delta \bar{\sigma} \cdot \nabla \right)^2}{2!} \sigma + \cdots$$

$$= \sigma (\bar{\sigma}) + \sum_m \frac{\partial \sigma}{\partial p_m} \delta p_m + \frac{1}{2} \sum_{m,m'} \delta p_m \delta p_{m'} \frac{\partial^2 \sigma}{\partial p_m \partial p_{m'}} + \cdots$$

Using Eq. (1.8) one finds that

$$\frac{\partial^2 \sigma}{\partial p_m \partial p_{m'}} = -\frac{1}{p_m} \delta_{m,m'} .$$

Since the probabilities $p_m$ are non-negative one concludes that any stationary point of $\sigma$ is a local maximum point. Moreover, since only a single stationary point was found, one concludes that the entropy $\sigma$ obtains its largest value, which is denoted as $\Lambda (M)$, and which is given by

$$\Lambda (M) = \sigma \left( \frac{1}{M}, \frac{1}{M}, \cdots, \frac{1}{M} \right) = \log M ,$$

for the probability distribution given by Eq. (1.27). For this probability distribution that maximizes $\sigma$, as expected, the state which is occupied by the system is most uncertain.

### 1.4 The composition property

Let $X$ and $Y$ be two discrete random variables. The probability that $X = x_{m'}$ $(Y = y_{m''})$ is denoted by $P \{ X = x_{m'} \} \ (P \{ Y = y_{m''} \})$. The entropy
associated with the joint probability distribution of $X$ and $Y$ is denoted by $\sigma(X,Y)$, the entropy associated with the probability distribution of $X$ is denoted by $\sigma(X)$, and the entropy associated with the conditional probability distribution of $Y$ given that $X = x_{m'}$ is denoted by $\sigma(Y|X = x_{m'})$.

**Claim (entropy composition).** The entropy $\sigma(X,Y)$ can be decomposed as

$$\sigma(X,Y) = \sigma(X) + \sigma_X(Y) \quad (1.31)$$

where

$$\sigma_X(Y) = \sum_{m'} P\{X = x_{m'}\} \sigma(Y|X = x_{m'}) \quad (1.32)$$

**Proof.** The following holds

$$P\{X = x_{m'}, Y = y_{m''}\} = P\{X = x_{m'}\} P\{Y = y_{m''}|X = x_{m'}\}
= P\{Y = y_{m''}\} P\{X = x_{m'}|Y = y_{m''}\} \quad (1.33)$$

hence [see Eq. (1.8)]

$$\sigma(X,Y) = -\sum_{m'} \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\} \log P\{X = x_{m'}, Y = y_{m''}\}
= -\sum_{m'} \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\} \log (P\{X = x_{m'}\} P\{Y = y_{m''}|X = x_{m'}\})
= -\sum_{m'} \left( \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\} \right) \log P\{X = x_{m'}\}
= \sigma_X(Y)
= \sigma_X(Y) \quad (1.34)$$

hence Eq. (1.31) holds.

The claim below (1.35) together with Eq. (1.31) imply that $\sigma(X,Y) \leq \sigma(X) + \sigma(Y)$.

**Claim.** The following holds

$$\sigma_X(Y) \leq \sigma(Y) \quad (1.35)$$

and equality holds iff $X$ and $Y$ are independent.
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Proof. With the help of Eqs. (1.33) and (1.32) one finds that
\[
\sigma_X(Y) - \sigma(Y) = - \sum_{m'} P\{X = x_{m'}\} \sum_{m''} P\{Y = y_{m''} | X = x_{m'}\} \log P\{Y = y_{m''} | X = x_{m'}\}
\]
\[
+ \sum_{m''} P\{Y = y_{m''}\} \log P\{Y = y_{m''}\}
\]
\[
= \sum_{m'} \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\} \left( \log \frac{P\{Y = y_{m''}\}}{P\{Y = y_{m''} | X = x_{m'}\}} \right),
\]
(1.36)
thus \(\sigma_X(Y) = \sigma(Y)\) if \(X\) and \(Y\) are independent. For the general case [see inequality (1.9) and Eqs. (1.33) and (1.36)]
\[
\sigma_X(Y) - \sigma(Y) \leq \sum_{m'} \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\} \left( \frac{P\{Y = y_{m''}\}}{P\{Y = y_{m''} | X = x_{m'}\}} - 1 \right)
\]
\[
= \sum_{m'} \sum_{m''} (P\{X = x_{m'}\} P\{Y = y_{m''}\} - P\{X = x_{m'}, Y = y_{m''}\})
\]
\[
= \sum_{m'} P\{X = x_{m'}\} \sum_{m''} P\{Y = y_{m''}\} - \sum_{m'} \sum_{m''} P\{X = x_{m'}, Y = y_{m''}\}
\]
\[
= 0,
\]
(1.37)
hence inequality (1.35) holds.

1.5 Alternative definition of entropy

Following Shannon [1, 2], the entropy function \(\sigma(p_1, p_2, \cdots, p_N)\) can be alternatively defined as follows:

1. \(\sigma(p_1, p_2, \cdots, p_N)\) is a continuous function of its arguments \(p_1, p_2, \cdots, p_N\).
2. If all probabilities are equal, namely if \(p_1 = p_2 = \cdots = p_N = 1/N\), then the quantity \(A(N) = \sigma(1/N, 1/N, \cdots, 1/N)\) is a monotonic increasing function of \(N\).
3. The function \(\sigma(p_1, p_2, \cdots, p_N)\) satisfies the composition property given by Eq. (1.31).

Exercise 1.5.1. Show that the above definition leads to the entropy given by Eq. (1.8) up to multiplication by a positive constant.
1.5. Alternative definition of entropy

Solution 1.5.1. The first property allows approximating the probabilities $p_1, p_2, \cdots, p_N$ using rational numbers, namely $p_1 = M_1/M_0$, $p_2 = M_2/M_0$, etc., where $M_1, M_2, \cdots$ are integers and $M_0 = M_1 + M_2 + \cdots + M_N$. Let $X$ be a random variable taking the values $(1, 2, \cdots, N)$ with probabilities $(p_1, p_2, \cdots, p_N)$, and let $Y$ be a random variable taking the values $(1, 2, \cdots, M_0)$ with equal probabilities $(1/M_0, 1/M_0, \cdots)$. The composition property (1.31) for this case implies that

$$A(M_0) = \sigma(p_1, p_2, \cdots, p_N) + p_1A(M_1) + p_2A(M_2) + \cdots$$

(1.38)

In particular, consider the case were $M_1 = M_2 = \cdots = M_N = K$. For this case one finds that

$$A(NK) = A(N) + A(K).$$

(1.39)

Taking $K = N = 1$ yields

$$A(1) = 0,$$

(1.40)

taking $N = 1 + x$ yields

$$\frac{A(K + Kx) - A(K)}{Kx} = \frac{1}{K} \frac{A(1 + x)}{x},$$

(1.41)

and taking the limit $x \to 0$ yields

$$\frac{dA}{dK} = \frac{C}{K},$$

(1.42)

where

$$C = \lim_{x \to 0} \frac{A(1 + x)}{x}.$$  

(1.43)

Integrating Eq. (1.42) and using the initial condition (1.40) yields

$$A(K) = C \log K.$$  

(1.44)

Moreover, the second property requires that $C > 0$. Choosing $C = 1$ and using Eq. (1.38) yields

$$\sigma(p_1, p_2, \cdots, p_N) = A(M_0) - p_1A(M_1) - p_2A(M_2) - \cdots$$

$$= -p_1 \log \frac{M_1}{M_0} - p_2 \log \frac{M_2}{M_0} - \cdots - p_M \log \frac{M_N}{M_0}$$

$$= -p_1 \log p_1 - p_2 \log p_2 - \cdots - p_N \log p_N,$$

(1.45)

in agreement with the definition (1.8).
1.6 Largest uncertainty estimator

The possible states of a given system are denoted as \( e_m \), where \( m = 1, 2, 3, \ldots \), and the probability that state \( e_m \) is occupied is denoted by \( p_m \). Let \( X_l \) \( (l = 1, 2, \cdots, L) \) be a set of variables characterizing the system (e.g., energy, number of particles, etc.). Let \( X_l (m) \) be the value which the variable \( X_l \) takes when the system is in state \( e_m \). Consider the case where the expectation values of the variables \( X_l \) are given

\[
\langle X_l \rangle = \sum_m p_m X_l (m),
\]

where \( l = 1, 2, \cdots, L \). However, the probability distribution \( \{p_m\} \) is not given.

Clearly, in the general case the knowledge of \( \langle X_1 \rangle, \langle X_2 \rangle, \cdots, \langle X_L \rangle \) is not sufficient to obtain the probability distribution because there are in general many different possibilities for choosing a probability distribution which is consistent with the contrarians (1.46) and the normalization condition (1.1). For each such probability distribution the entropy can be calculated according to the definition (1.8). The probability distribution \( \{p_m\} \), which is consistent with these conditions, and has the largest possible entropy is called the largest uncertainty estimator (LUE).

The LUE is found by seeking a stationary point of the entropy \( \sigma \) with respect to all probability distributions \( \{p_m\} \) which satisfy the normalization constrain (1.17) in addition to the constrains (1.46), which can be expressed as

\[
0 = g_l (\bar{p}) = \sum_m p_m X_l (m) - \langle X_l \rangle,
\]

where \( l = 1, 2, \cdots, L \). To first order one has

\[
\delta \sigma = \bar{\nabla} \sigma \cdot \delta \bar{p},
\]

\[
\delta g_l = \bar{\nabla} g_l \cdot \delta \bar{p},
\]

where \( l = 0, 1, 2, \cdots, L \). A stationary point of \( \sigma \) occurs iff for every small change \( \delta \bar{p} \), which is orthogonal to all vectors \( \bar{\nabla} g_0, \bar{\nabla} g_1, \bar{\nabla} g_2, \cdots, \bar{\nabla} g_L \) one has

\[
0 = \delta \sigma = \bar{\nabla} \sigma \cdot \delta \bar{p}.
\]

This condition is fulfilled only when the vector \( \bar{\nabla} \sigma \) belongs to the subspace spanned by the vectors \( \{ \bar{\nabla} g_0, \bar{\nabla} g_1, \bar{\nabla} g_2, \cdots, \bar{\nabla} g_L \} \) [see also the discussion below Eq. (1.24) above]. In other words, only when

\[
\bar{\nabla} \sigma = \xi_0 \bar{\nabla} g_0 + \xi_1 \bar{\nabla} g_1 + \xi_2 \bar{\nabla} g_2 + \cdots + \xi_L \bar{\nabla} g_L,
\]

where the numbers \( \xi_0, \xi_1, \cdots, \xi_L \), which are called Lagrange multipliers, are constants. Using Eqs. (1.8), (1.17) and (1.47) the condition (1.50) can be expressed as
\[-\log p_m - 1 = \xi_0 + \sum_{l=1}^{L} \xi_l X_l (m) \tag{1.51}\]

From Eq. (1.51) one obtains

\[p_m = \exp (-1 - \xi_0) \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right) \tag{1.52}\]

The Lagrange multipliers \(\xi_0, \xi_1, \cdots, \xi_L\) can be determined from Eqs. (1.17) and (1.47)

\[1 = \sum_m p_m = \exp (-1 - \xi_0) \sum_m \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right) \tag{1.53}\]

\[
\langle X_l \rangle = \sum_m p_m X_l (m)
= \exp (-1 - \xi_0) \sum_m \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right) X_l (m).
\tag{1.54}
\]

Using Eqs. (1.52) and (1.53) one finds

\[p_m = \frac{\exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right)}{\sum_m \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right)} \tag{1.55}\]

In terms of the partition function \(Z\), which is defined as

\[Z = \sum_m \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right), \tag{1.56}\]

one finds

\[p_m = \frac{1}{Z} \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right) \tag{1.57}\]

The entropy obtains its largest value for the stationary point associated with the probability distribution given by Eq. (1.57) [see Eq. (1.28)].

Example 1.6.1 (prime number theorem). Let \(N\) be a positive integer having \(\tau (N)\) distinct divisors [e.g. \(\tau (6) = 4\)]. The averaged number of divisors \(\langle \tau (N) \rangle\) can be roughly estimated to be given by
\\( \langle \tau (N) \rangle \simeq 1 + \frac{1}{2} + \frac{1}{3} + \cdots + \frac{1}{N} \simeq \int_1^N \frac{dx}{x} = \log N. \)  
\text{(1.58)}

Roughly estimate the probability \( p_N \) that a randomly chosen integer \( N \) is a prime. Note that for a prime number \( p \) the number of divisors is \( \tau (p) = 2 \).

**Solution 1.6.1.** The probability \( p_m \) that \( N \) has \( m \) distinct divisors is expressed in terms of the Lagrange multiplier \( \xi \) as [see Eq. (1.57)]

\[
p_m = \frac{1}{Z} e^{-m\xi},
\]
where the partition function is given by [see Eq. (1.56)]

\[
Z = \sum_m e^{-m\xi},
\]
where for \( N \gg 1 \)

\[
Z \simeq \sum_{m=2}^{\infty} e^{-m\xi} = \frac{e^{-2\xi}}{1 - e^{-\xi}}.
\]

By using the estimation (1.58) one finds that [see Eq. (1.65)]

\[
\langle \tau (N) \rangle = \log N = -\frac{\partial \log Z}{\partial \xi} = \frac{2 - e^{-\xi}}{1 - e^{-\xi}},
\]

hence

\[
\xi = \log \frac{\log N - 1}{\log N - 2},
\]

and thus the probability \( p_2 \) that \( N \) is prime [i.e. the probability that \( \tau (N) = 2 \)] is given by [see Eq. (1.59) and (1.63)]

\[
p_2 = \frac{e^{-2\xi}}{1 - e^{-\xi}} = 1 - e^{-\xi} = \frac{1}{\log N - 1} \simeq \frac{1}{\log N}.
\]

1.6.1 Useful Relations

The expectation value \( \langle X_l \rangle \) can be expressed as

\[
\langle X_l \rangle = \sum_m p_m X_l (m)
\]

\[
= \frac{1}{Z} \sum_m \exp \left( -\sum_{l=1}^L \xi_l X_l (m) \right) X_l (m)
\]

\[
= -\frac{1}{Z} \frac{\partial Z}{\partial \xi_l}
\]

\[
= -\frac{\partial \log Z}{\partial \xi_l}.
\]

\text{(1.65)}
Similarly, \( \langle X_i^2 \rangle \) can be expressed as
\[
\langle X_i^2 \rangle = \sum_m p_m X_i^2 (m)
= \frac{1}{Z} \sum_m \exp \left( - \sum_{l=1}^L \xi_l X_l (m) \right) X_i^2 (m)
= \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_i^2}.
\]

(1.66)

Using Eqs. (1.65) and (1.66) one finds that the variance of the variable \( X_i \) is given by
\[
\left\langle (\Delta X_i)^2 \right\rangle = \left\langle (X_i - \langle X_i \rangle)^2 \right\rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_i^2} = \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right)^2.
\]

(1.67)

With the help of the identity
\[
\frac{\partial^2 \log Z}{\partial \xi_i^2} = \frac{\partial}{\partial \xi_i} \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_i^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right)^2,
\]

(1.68)

Eq. (1.67) becomes
\[
\left\langle (\Delta X_i)^2 \right\rangle = \frac{\partial^2 \log Z}{\partial \xi_i^2}.
\]

(1.69)

Note that the above results Eqs. (1.65) and (1.69) are valid only when \( Z \) is expressed as a function of the the Lagrange multipliers, namely
\[
Z = Z (\xi_1, \xi_2, \cdots, \xi_L).
\]

(1.70)

Using the definition of entropy (1.8) and Eq. (1.57) one finds that
\[
\sigma = -\sum_m p_m \log p_m
= -\sum_m p_m \log \left( \frac{1}{Z} \exp \left( - \sum_{l=1}^L \xi_l X_l (m) \right) \right)
= \sum_m p_m \left( \log Z + \sum_{l=1}^L \xi_l X_l (m) \right)
= \log Z + \sum_{l=1}^L \xi_l \sum_m p_m X_l (m),
\]

(1.71)
thus
\[ \sigma = \log Z + \sum_{l=1}^{L} \xi_l \langle X_l \rangle . \] (1.72)

Using the above relations one can also evaluate the partial derivative of the entropy \( \sigma \) when it is expressed as a function of the expectation values, namely
\[ \sigma = \sigma (\langle X_1 \rangle, \langle X_2 \rangle, \cdots, \langle X_L \rangle) . \] (1.73)

Using Eq. (1.72) one has
\[
\frac{\partial \sigma}{\partial \langle X_l \rangle} = \frac{\partial \log Z}{\partial \langle X_l \rangle} + \sum_{l' = 1}^{L} \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \sum_{l' = 1}^{L} \xi_{l'} \frac{\partial \langle X_{l'} \rangle}{\partial \langle X_l \rangle} \\
= \frac{\partial \log Z}{\partial \langle X_l \rangle} + \sum_{l' = 1}^{L} \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \xi_l \\
= \sum_{l' = 1}^{L} \frac{\partial \log Z}{\partial \xi_{l'}} \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \sum_{l' = 1}^{L} \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \xi_l ,
\] (1.74)

thus using Eq. (1.65) one finds
\[
\frac{\partial \sigma}{\partial \langle X_l \rangle} = \xi_l . \] (1.75)

### 1.6.2 The Free Entropy

The free entropy \( \sigma_F \) is defined as the term \( \log Z \) in Eq. (1.71)
\[
\sigma_F = \log Z \\
= \sigma - \sum_{i=1}^{L} \xi_i \sum_{m} p_m X_i (m) \\
= -\sum_{m} p_m \log p_m - \sum_{l=1}^{L} \xi_l \sum_{m} p_m X_l (m) .
\] (1.76)

The free entropy is commonly expressed as a function of the Lagrange multipliers
\[ \sigma_F = \sigma_F (\xi_1, \xi_2, \cdots, \xi_L) . \] (1.77)

As was shown above, the LUE maximizes \( \sigma \) for given values of expectation values \( \langle X_1 \rangle, \langle X_2 \rangle, \cdots, \langle X_L \rangle \). A similar result can be obtained for the free energy \( \sigma_F \) with respect to given values of the Lagrange multipliers, as is shown by the claim below.
Claim. The LUE maximizes $\sigma_F$ for given values of the Lagrange multipliers $\xi_1, \xi_2, \ldots, \xi_L$.

Proof. As before, the normalization condition is expressed as

$$0 = g_0(\bar{p}) = \sum_m p_m - 1 . \tag{1.78}$$

At a stationary point of $\sigma_F$, as we have seen previously, the following holds

$$\nabla \sigma_F = \eta \nabla g_0 , \tag{1.79}$$

where $\eta$ is a Lagrange multiplier. Thus

$$-(\log p_m + 1) - \sum_{l=1}^{L} \xi_l X_l(m) = \eta , \tag{1.80}$$

or

$$p_m = \exp(-\eta - 1) \exp\left(-\sum_{l=1}^{L} \xi_l X_l(m)\right). \tag{1.81}$$

This result is the same as the one given by Eq. (1.52). Taking into account the normalization condition (1.78) one obtains the same expression for $p_m$ as the one given by Eq. (1.57). Namely, the stationary point of $\sigma_F$ corresponds to the LUE probability distribution. Since

$$\frac{\partial^2 \sigma_F}{\partial p_m \partial p_{m'}} = -\frac{1}{p_m} \delta_{m,m'} < 0 , \tag{1.82}$$

one concludes that this stationary point is a maximum point [see Eq. (1.28)].

1.7 Problems

1. Let $p$ be the probability of a coin coming up head. What is the mean number of coin flips $\langle N \rangle$ until the first time it comes up head?

2. Let $p$ be the probability of a coin coming up head. The coin is flipped $N$ times.
   a) Calculate the expectation values $\langle n_H \rangle$ and $\langle n_H^2 \rangle$, where $n_H$ is the number of times the coin came up head.
   b) Calculate the probability $p_n$ to get $n$ heads, where $0 \leq n \leq N$ is an integer, in the limit where $p \to 0$, $N \to \infty$, and $Np \to \lambda$, where $\lambda$ is positive. Calculate $\langle n_H \rangle$ and $\langle n_H^2 \rangle$ for this case.

3. A molecule in a gas moves equal distances $l$ between collisions with equal probability in any direction. After a total of $N$ such displacements, what is the mean square displacement $\langle R^2 \rangle$ of the molecule from its starting point?
4. Consider a system of $N$ spins. Each spin can be in one of two possible states: in state 'up' the magnetic moment of each spin is $+m$, and in state 'down' it is $-m$. Let $N_+$ ($N_-$) be the number of spins in state 'up' ('down'), where $N = N_+ + N_-$. The total magnetic moment of the system is given by

$$M = m (N_+ - N_-).$$ \hspace{1cm} (1.83)

Assume that the probability that the system occupies any of its $2^N$ possible states is equal. Moreover, assume that $N \gg 1$. Let $f(M)$ be the probability distribution of the random variable $M$ (that is, $M$ is considered in this approach as a continuous random variable). Use the Stirling's formula

$$N! = (2\pi N)^{1/2} N^N \exp \left( -N + \frac{1}{2N} + \cdots \right)$$ \hspace{1cm} (1.84)

to show that

$$f(M) = \frac{1}{m \sqrt{2\pi N}} \exp \left( -\frac{M^2}{2m^2 N} \right).$$ \hspace{1cm} (1.85)

Use this result to evaluate the expectation value and the variance of $M$.

5. Consider two objects traveling in the $xy$ plane. Object A starts from the point $(0,0)$ and object B starts from the point $(N,N)$, where $N$ is an integer. At each step both objects A and B simultaneously make a single move of length unity. Object A makes either a move to the right $(x,y) \rightarrow (x+1,y)$ with probability $1/2$ or an upward move $(x,y) \rightarrow (x,y+1)$ with probability $1/2$. On the other hand, object B makes either a move to the left $(x,y) \rightarrow (x-1,y)$ with probability $1/2$ or a downward move $(x,y) \rightarrow (x,y-1)$ with probability $1/2$. What is the probability that objects A and B meet along the way in the limit $N \rightarrow \infty$?

6. Consider A dice having 6 faces. All faces have equal probability of outcome. Initially, $n$ faces are colored white and $6-n$ faces are colored black, where $n \in \{0,1,2,\cdots,6\}$. Each time the outcome is white (black) one black (white) face is turned into a white (black) face before the next roll. The process continues until all faces have the same color. What is the probability $p_n$ that all faces will become white?

7. Alice, Bob and other $N-2$ people are randomly seated at a round table. What is the probability $p_C$ that Alice and Bob will be seated next to each other? What is the probability $p_R$ that Alice and Bob will be seated next to each other for the case where the group is randomly seated in a row.

8. Write a computer function returning the value 1 with probability $p$ and the value 0 with probability $1-p$ for any given $0 \leq p \leq 1$. The function can use another given function, which returns the value 1 with probability 1/2 and the value 0 with probability 1/2. Make sure the running time is finite.
9. A single coin is placed on the table. Every second afterwards, each coin on the table undergoes one of the following four possible events: (a) the coin disappears, (b) the coin is unchanged, (c) the coin replicates itself and an additional coin is added on the table, (d) the coin replicates itself twice and two additional coins are added on the table. The probability of all four possible events is $\frac{1}{4}$. What is the probability $p$ that the number of coins on the table will eventually become zero?

10. Consider a one-dimensional random walk. The probabilities of transiting to the right and left are $p$ and $q = 1 - p$ respectively. The step size for both cases is $a$.
   a) Show that the average displacement $\langle X \rangle$ after $N$ steps is given by
   \[ \langle X \rangle = aN (2p - 1) = aN (p - q) . \] (1.86)
   b) Show that the variance $\langle (X - \langle X \rangle)^2 \rangle$ is given by
   \[ \langle (X - \langle X \rangle)^2 \rangle = 4a^2 Npq . \] (1.87)

11. A classical harmonic oscillator of mass $m$, and spring constant $k$ oscillates with amplitude $a$. Show that the probability density function $f(x)$, where $f(x)dx$ is the probability that the mass would be found in the interval $dx$ at $x$, is given by
   \[ f(x) = \frac{1}{\pi \sqrt{a^2 - x^2}} . \] (1.88)

12. A coin having probability $p = 2/3$ of coming up heads is flipped 6 times. Show that the entropy of the outcome of this experiment is $\sigma = 3.8191$ (use log in natural base in the definition of the entropy).

13. A fair coin is flipped until the first head occurs. Let $X$ denote the number of flips required. Calculate the entropy $\sigma$ associated with the random variable $X$.

1.8 Solutions

1. The mean number $\langle N \rangle$ is given by
   \[ \langle N \rangle = \sum_{n=0}^{\infty} n (1 - p)^n p , \] (1.89)
   By using the identity
   \[ \sum_{n=0}^{\infty} nx^{n-1} = \frac{d}{dx} \sum_{n=0}^{\infty} x^n = \frac{d}{dx} \frac{1}{1 - x} = \frac{1}{(1 - x)^2} , \] (1.90)
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one finds that

\[ \langle N \rangle = p (1 - p) \sum_{n=0}^{\infty} n (1 - p)^{n-1} = \frac{1 - p}{p}. \quad (1.91) \]

2. The moment generating function \( \phi(t) \) for this case is given by

\[ \phi(t) = \langle e^{tn_H} \rangle = \sum_{m=0}^{\infty} \frac{t^m}{m!} \langle n_H^m \rangle, \quad (1.92) \]

and the following holds

\[ \langle n_H^m \rangle = \phi^{(m)} (t = 0), \quad (1.93) \]

where \( \phi^{(m)} \) is the \( m \)'th derivative of \( \phi(t) \).

a) Using the relation

\[ \phi(t) = \sum_{n=0}^{N} p_n e^{nt}, \quad (1.94) \]

where the probability \( p_n \) to get \( n \) heads is given by the binomial distribution

\[ p_n = \frac{N!}{n! (N - n)!} p^n (1 - p)^{N-n}, \quad (1.95) \]

one finds with the help of the binomial theorem that

\[ \phi(t) = \sum_{n=0}^{N} \frac{N!}{n! (N - n)!} p^n (1 - p)^{N-n} e^{nt} \]

\[ = (pe^t + 1 - p)^N, \quad (1.96) \]

and thus

\[ \langle n_H \rangle = Np, \quad (1.97) \]

\[ \langle n_H^2 \rangle = Np (Np + 1 - p), \quad (1.98) \]

and

\[ \langle n_H^2 \rangle - \langle n_H \rangle^2 = Np (1 - p). \quad (1.99) \]

b) The binomial moment generating function \( \phi(t) \) given by Eq.(1.96) can be expressed as

\[ \phi(t) = \left( 1 + \frac{\lambda (e^t - 1)}{N} \right)^N, \quad (1.100) \]

where \( \lambda = pN \). Using the identity
1.8. Solutions

\[
\lim_{N \to \infty} \left(1 + \frac{x}{N}\right)^N = e^x ,
\]  

(1.101)

one finds that in the limit \( N \to \infty \)

\[
\phi(t) = e^{\lambda(e^t-1)} .
\]  

(1.102)

The moment generating function (1.102) together with Eq. (1.94) yields the Poisson distribution

\[
p_n = \frac{\lambda^n e^{-\lambda}}{n!} .
\]  

(1.103)

Note that

\[
\sum_{n=0}^{\infty} p_n = e^{-\lambda} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} = 1 .
\]  

(1.104)

c) With the help of Eqs. (1.93) and (1.102) one finds that

\[
\langle n_H \rangle = \lambda ,
\]  

(1.105)

\[
\langle n_H^2 \rangle = \lambda (1 + \lambda) ,
\]  

(1.106)

and thus

\[
\langle n_H^2 \rangle - \langle n_H \rangle^2 = \lambda (1 + \lambda) - \lambda^2 = \lambda .
\]  

(1.107)

3. Let \( r_n \) be the \( n \)'th displacement vector of the molecule. The expectation value \( \langle R^2 \rangle \) is given by

\[
\langle R^2 \rangle = \left( \sum_{n=1}^{N} r_n \right)^2 = \sum_{n=1}^{N} \langle r_n^2 \rangle + \sum_{n \neq m} \langle r_n \cdot r_m \rangle = N l^2 .
\]  

(1.108)

4. Using

\[
N_+ + N_- = N ,
\]  

(1.109a)

\[
N_+ - N_- = \frac{M}{m} ,
\]  

(1.109b)

one has

\[
N_+ = \frac{N}{2} \left(1 + \frac{M}{mN}\right) ,
\]  

(1.110a)

\[
N_- = \frac{N}{2} \left(1 - \frac{M}{mN}\right) ,
\]  

(1.110b)

or

\[
N_+ = \frac{N}{2} (1 + x) ,
\]  

(1.111a)

\[
N_- = \frac{N}{2} (1 - x) ,
\]  

(1.111b)
where
\[ x = \frac{M}{mN}. \]  
(1.112)

The number of states having total magnetization \( M \) is given by
\[ \Omega(M) = \frac{N!}{N_N! N_{-N}!} = \frac{N!}{[\frac{N}{2} (1+x)]! [\frac{N}{2} (1-x)]!}. \]  
(1.113)

Since all states have equal probability one has
\[ f(M) = \frac{\Omega(M)}{2^N}. \]  
(1.114)

Taking the natural logarithm of Stirling’s formula one finds
\[ \log N! = N \log N - N + O \left( \frac{1}{N} \right), \]  
thus in the limit \( N \gg 1 \) one has
\[ \log f = -\log 2^N + N \log N - N \]
\[ - \left[ \frac{N}{2} (1+x) \right] \log \left[ \frac{N}{2} (1+x) \right] + \left[ \frac{N}{2} (1-x) \right] \log \left[ \frac{N}{2} (1-x) \right] \]
\[ = -N \log 2 + N \log N \]
\[ - \left[ \frac{N}{2} (1+x) \right] \log \left[ \frac{N}{2} (1+x) \right] - \left[ \frac{N}{2} (1-x) \right] \log \left[ \frac{N}{2} (1-x) \right] \]
\[ = \left( -\frac{N}{2} \right) \left( -2 \log \frac{N}{2} + (1+x) \log \left[ \frac{N}{2} (1+x) \right] + (1-x) \log \left[ \frac{N}{2} (1-x) \right] \right) \]
\[ = \left( -\frac{N}{2} \right) \left( -2 \log \frac{N}{2} + (1+x) \left( \log \frac{N}{2} + \log (1+x) \right) + (1-x) \left( \log \frac{N}{2} + \log (1-x) \right) \right) \]
\[ = \left( -\frac{N}{2} \right) \left( \log (1 - x^2) + x \log \frac{1+x}{1-x} \right). \]  
(1.116)

The function \( \log f(x) \) has a sharp peak near \( x = 0 \), thus we can approximate it by assuming \( x \ll 1 \). To lowest nonvanishing order
\[ \log (1 - x^2) + x \log \frac{1+x}{1-x} = x^2 + O(x^3), \]  
thus
\[ f(M) = A \exp \left( -\frac{M^2}{2m^2 N} \right), \]  
(1.118)
where $A$ is a normalization constant, which is determined by requiring that

$$
1 = \int_{-\infty}^{\infty} f(M) \, dM .
$$

(1.119)

Using the identity

$$
\int_{-\infty}^{\infty} \exp \left( -ay^2 \right) \, dy = \sqrt{\frac{\pi}{a}} ,
$$

(1.120)

one finds

$$
\frac{1}{A} = \int_{-\infty}^{\infty} \exp \left( -\frac{M^2}{2m^2N} \right) \, dM = m\sqrt{2\pi N} ,
$$

(1.121)

thus

$$
f(M) = \frac{1}{m\sqrt{2\pi N}} \exp \left( -\frac{M^2}{2m^2N} \right) ,
$$

(1.122)

The expectation value is giving by

$$
\langle M \rangle = \int_{-\infty}^{\infty} Mf(M) \, dM = 0
$$

(1.123)

and the variance is given by

$$
\left\langle (M - \langle M \rangle)^2 \right\rangle = \langle M^2 \rangle = \int_{-\infty}^{\infty} M^2f(M) \, dM = m^2N .
$$

(1.124)

5. Let $\sigma_{An} = 1$ ($\sigma_{Bn} = 1$) if object $A$ ($B$) makes a move to the right (left) at step $n$, and $\sigma_{An} = 0$ ($\sigma_{Bn} = 0$) if object $A$ ($B$) makes an upward (downward) move at step $n$. The location $(x_{Am}, y_{Am})$ of object $A$ and the location $(x_{Bm}, y_{Bm})$ of object $B$ after $m$ steps is given by

$$
(x_{Am}, y_{Am}) = (S_{Am}, m - S_{Am}) ,
$$

(1.125)

$$
(x_{Bm}, y_{Bm}) = (N - S_{Bm}, N - m + S_{Bm}) ,
$$

(1.126)

where

$$
S_{Am} = \sum_{n=1}^{m} \sigma_{An} ,
$$

(1.127)

$$
S_{Bm} = \sum_{n=1}^{m} \sigma_{Bn} .
$$

(1.128)
Chapter 1. Entropy

A meeting occurs if for some $m$

\begin{align*}
S_{Am} &= N - S_{Bm}, \\
m - S_{Am} &= N - m + S_{Bm},
\end{align*}

(1.129)

(1.130)

i.e. if

\begin{equation}
S_{Am} + S_{Bm} = N = 2m - N.
\end{equation}

(1.131)

Thus, a meeting is possible only after $m = N$ steps, and it occurs if $S_{Am} + S_{Bm} = N$. Therefore, the probability is given by

\begin{equation}
p_N = \frac{\binom{2N}{N}}{2^{2N}} = \frac{(2N)!}{(N!2^N)^2}.
\end{equation}

(1.132)

With the help of the Stirling’s formula (1.84) one finds that

\begin{equation}
\lim_{N \to \infty} p_N = \frac{1}{\sqrt{N\pi}}.
\end{equation}

(1.133)

6. The following holds

\begin{align*}
p_0 &= 0, \\
p_1 &= \frac{5}{6}p_0 + \frac{1}{6}p_2, \\
p_2 &= \frac{4}{6}p_1 + \frac{2}{6}p_3, \\
p_3 &= \frac{3}{6}p_2 + \frac{3}{6}p_4, \\
p_4 &= \frac{2}{6}p_3 + \frac{4}{6}p_5, \\
p_5 &= \frac{1}{6}p_4 + \frac{5}{6}p_6, \\
p_6 &= 1.
\end{align*}

(1.134)

and thus

\begin{align*}
p_1 &= \frac{1}{32}, \\
p_2 &= \frac{3}{16}, \\
p_3 &= \frac{1}{2}, \\
p_4 &= \frac{13}{16}, \\
p_5 &= \frac{31}{32}.
\end{align*}

(1.135)

7. For the case of a round table (and $N > 2$)

\begin{equation}
p_C = \frac{N \times 2 \times (N - 2)!}{N!} = \frac{2}{N - 1},
\end{equation}

(1.136)

and for the case of a row

\begin{equation}
p_R = \frac{(2 + (N - 2) \times 2) \times (N - 2)!}{N!} = \frac{2}{N}.
\end{equation}

(1.137)
8. Let the binary representation of $p$ be given by

$$p = \sum_{m=1}^{\infty} \sigma_m \left( \frac{1}{2} \right)^m,$$

where $\sigma_m \in \{0, 1\}$. Let $\Sigma_m$ be a sequence of random variables generated by the given computer function (i.e. $\Sigma_m = 1$ with probability 1/2 and $\Sigma_m = 0$ with probability 1/2). The proposed function has a while loop running over integer values of the variable $m$ starting from the value $m = 1$. At each iteration the random variable $\Sigma_m$ is generated and compared with $\sigma_m$. If $\sigma_m = \Sigma_m$ the value of $m$ is increased by 1, i.e. $m \rightarrow m + 1$, and the loop continues. If $\sigma_m \neq \Sigma_m$ the program stops and the value 1 is returned if $\sigma_m > \Sigma_m$ and the value 0 is returned if $\sigma_m < \Sigma_m$. Note that the probability that the program will never stop vanishes even when $p$ is irrational and/or the number of nonzero binary digits $\sigma_m$ is infinite.

9. The probability that the number of coins will never become zero given that there are $N$ coins on the table is $1 - p^N$, where the survival probability of a single coin is denoted by $1 - p$. The probability $p$ is found from solving

$$1 - p^1 = \frac{1 - p^1}{4} + \frac{1 - p^2}{4} + \frac{1 - p^3}{4},$$

which yields $p = \sqrt{2} - 1 \simeq 0.41421$.

10. The probability to have $n$ steps to the right is given by

$$W(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}.$$

a) The expectation value $\langle n \rangle$ is given by

$$\langle n \rangle = \sum_{n=0}^{N} \frac{N! n}{n!(N-n)!} p^n q^{N-n}$$

$$= p \frac{\partial}{\partial p} \sum_{n=0}^{N} \frac{N! n}{n!(N-n)!} p^n q^{N-n}$$

$$= p \frac{\partial}{\partial p} (p + q)^N = pN (p + q)^{N-1} = pN ,$$

and

$$X = aN - a(N - n) = a(2n - N) ,$$

thus

$$\langle X \rangle = aN (2p - 1) = aN (p - q) .$$
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b) The expectation value \( \langle n^2 \rangle \) is given by

\[
\langle n^2 \rangle = \sum_{n=0}^{N} \frac{N!n^2}{n!(N-n)!} p^n q^{N-n}
\]

\[
= \sum_{n=0}^{N} \frac{N!n}{n!(N-n)!} p^n q^{N-n} + \sum_{n=0}^{N} \frac{N!n}{n!(N-n)!} p^n q^{N-n}
\]

\[
= p^2 \frac{\partial^2}{\partial p^2} \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n q^{N-n} + \langle n \rangle
\]

\[
= p^2 \frac{\partial^2}{\partial p^2} (p+q)^N + \langle n \rangle = p^2 N (N-1) + pN ,
\]

thus

\[
\langle (n - \langle n \rangle)^2 \rangle = p^2 N (N-1) + pN - p^2 N^2 = Npq ,
\]

and

\[
\langle (X - \langle X \rangle)^2 \rangle = 4a^2 Npq .
\]

11. The total energy is given by

\[
E = \frac{kx^2}{2} + \frac{m\dot{x}^2}{2} = \frac{ka^2}{2} ,
\]

where \( a \) is the amplitude of oscillations. The time period \( T \) is given by

\[
T = 2 \int_{-a}^{a} \frac{dx}{\dot{x}} = 2 \sqrt{\frac{m}{k}} \int_{-a}^{a} \frac{dx}{\sqrt{a^2 - x^2}} = 2 \pi \sqrt{\frac{m}{k}} ,
\]

thus

\[
f(x) = \frac{2}{T|\dot{x}|} = \frac{1}{\pi \sqrt{a^2 - x^2}} .
\]

12. The six experiments are independent, thus

\[
\sigma = 6 \times \left( -\frac{2}{3} \ln \frac{2}{3} - \frac{1}{3} \ln \frac{1}{3} \right) = 3.8191 .
\]

13. The random variable \( X \) obtains the value \( n \) with probability \( p_n = q^n \)

where \( n = 1, 2, 3, \cdots \), and \( q = 1/2 \), hence the entropy is given by [see Eq. (1.90)]

\[
\sigma = -\sum_{n=1}^{\infty} p_n \log p_n = -\sum_{n=1}^{\infty} q^n \log q^n = 2 \log 2 .
\]
In quantum mechanics the state of a physical system is described by a state vector $|\alpha\rangle$, which is a vector in a vector space $\mathcal{F}$, namely

$$|\alpha\rangle \in \mathcal{F}.$$  

(2.1)

2.1 Quantum Measurement

Consider a measurement of a physical variable denoted as $A^{(c)}$ performed on a quantum system. The physical variable $A^{(c)}$ is represented in quantum mechanics by an observable, namely by a Hermitian operator, which is denoted as $A = A^\dagger$. Quantum theory predicts that:

1. The possible results of the measurement are the eigenvalues $\{a_n\}$ of the operator $A$.
2. The average result, namely the expectation value, is given by $\langle A \rangle = \langle \alpha | A | \alpha \rangle$, where $\langle \alpha | A | \alpha \rangle$ is the inner product of the vectors $A |\alpha\rangle$ and $|\alpha\rangle$. Alternatively, the expectation value $\langle A \rangle$ can be expressed as

$$\langle A \rangle = \text{Tr} (\rho_\alpha A),$$  

(2.2)

where the operator $\rho_\alpha$ is expressed as an outer product of $|\alpha\rangle$ with itself

$$\rho_\alpha = |\alpha\rangle \langle \alpha |.$$  

(2.3)

The trace of a given operator is defined by

$$\text{Tr} (X) = \sum_n \langle a_n | X | a_n \rangle,$$  

(2.4)

where $\{|a_n\rangle\}$ is an orthonormal and complete basis of the vector space. The trace is basis independent, and for any operators $X$ and $Y$ the following holds

$$\text{Tr} (XY) = \text{Tr} (YX).$$  

(2.5)
2.2 Time evolution

The time evolution of a state vector $|\alpha\rangle$ is governed by the Schrödinger equation

$$i\hbar \frac{d|\alpha\rangle}{dt} = \mathcal{H} |\alpha\rangle,$$

(2.6)

where the Hermitian operator $\mathcal{H} = \mathcal{H}^\dagger$ is the Hamiltonian of the system, and where $\hbar$ is Planck’s h-bar constant. The time evolution operator $u(t,t_0)$ relates the state vector at time $|\alpha(t_0)\rangle$ with its value $|\alpha(t)\rangle$ at time $t$:

$$|\alpha(t)\rangle = u(t,t_0)|\alpha(t_0)\rangle.$$

(2.7)

2.3 Position representation

The position wavefunction $\psi_{\alpha}(r')$ at spatial point $r'$ of a given state vector $|\alpha\rangle$ is defined as

$$\psi_{\alpha}(r') = \langle r' | \alpha \rangle,$$

(2.8)

where $|r'\rangle$ is an eigenvector of the position operator. Consider a particle having mass $m$ that moves in three dimension under the influence of the potential $V(r')$. Eigenvectors of the Hamiltonian operator $\mathcal{H}$ are found by solving the time-independent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(r')\right) \psi(r') = E \psi(r').$$

(2.9)

where $E$ represents an energy eigenvalue.

2.4 Density operator

The relation (2.2) can be generalized for cases where the state vector $|\alpha\rangle$ is not known in advance. Consider an ensemble of $N$ identical copies of a quantum system. The ensemble can be divided into subsets, where all systems belonging to the same subset have the same state vector. Let $Nw_i$ be the number of systems having state vector $|\alpha^{(i)}\rangle$, where

$$0 \leq w_i \leq 1,$$

(2.10)

and where

$$\sum_i w_i = 1.$$
The state vectors $|\alpha^{(i)}\rangle$ are all assumed to be normalized

$$\langle \alpha^{(i)} | \alpha^{(i)} \rangle = 1.$$  \hfill (2.12)

The expectation value $\langle A \rangle$ (i.e. the averaged measured value) can be expressed as

$$\langle A \rangle = \text{Tr}(\rho A),$$  \hfill (2.13)

where the so-called density operator $\rho$ is given by

$$\rho = \sum_i w_i |\alpha^{(i)}\rangle \langle \alpha^{(i)}|.$$  \hfill (2.14)

**Exercise 2.4.1.** Show that

$$\text{Tr}(\rho) = 1.$$ \hfill (2.15)

**Solution 2.4.1.** With the help of the normalization conditions (2.11) and (2.12) one obtains

$$\text{Tr}(\rho) = \sum_i w_i \text{Tr} \left( |\alpha^{(i)}\rangle \langle \alpha^{(i)}| \right) = \sum_i w_i \langle \alpha^{(i)} | \alpha^{(i)} \rangle = 1.$$  \hfill (2.16)

An ensemble is said to be pure if its density operator can be expressed as

$$\rho = |\alpha\rangle \langle \alpha|.$$ \hfill (2.17)

In general $\text{Tr}(\rho^2) \leq 1$. Equality holds, i.e. $\text{Tr}(\rho^2) = 1$ iff $\rho$ represents a pure ensemble.

With the help of Eq. (2.7) one finds that $\rho$ evolves in time according to

$$\rho(t) = u(t, t_0) \rho(t_0) u^\dagger(t, t_0).$$ \hfill (2.18)

As can be seen from the definition (2.14), the density operator is Hermitian, i.e.

$$\rho^\dagger = \rho.$$ \hfill (2.19)

This guarantees the existence of a complete orthonormal basis $\{|p_m\rangle\}$ of eigenvectors of $\rho$, which satisfies

$$\langle p_{m'} | p_m \rangle = \delta_{mm'},$$ \hfill (2.20)

$$\sum_m |p_m\rangle \langle p_m| = 1,$$ \hfill (2.21)

and

$$\rho |p_m\rangle = p_m |p_m\rangle,$$ \hfill (2.22)

where the eigenvalues $p_m$ are real.
Claim. The following holds

\[ 0 \leq p_m \leq 1. \quad (2.23) \]

Proof. With the help of Eqs. (2.14) and (2.22) one finds that

\[ p_m = \langle p_m | \rho | p_m \rangle = \sum_i w_i \left| \left\langle p_m | \alpha^{(i)} \right\rangle \right|^2, \quad (2.24) \]

hence inequality (2.23) holds [recall the Schwartz inequality and see Eqs. (2.10), (2.12) and (2.20)].

2.5 Entropy

The entropy \( \sigma \) associated with a given density operator \( \rho \) is defined by

\[ \sigma (\rho) = - \text{Tr} (\rho \log \rho). \quad (2.25) \]

In terms of the real eigenvalues \( p_m \) of \( \rho \) [see Eqs. (2.22) and (2.23), and compare with Eq. (1.8)]

\[ \sigma (\rho) = - \sum_m p_m \log p_m. \quad (2.26) \]
3. The principle of largest uncertainty in statistical physics

Let \( \{ |e_m\rangle \} \) be the set of energy eigenvectors of a given physical system, and let 
\[ U(m) = \langle e_m | \mathcal{H} | e_m \rangle \] and 
\[ N(m) = \langle e_m | \mathcal{N} | e_m \rangle \] be, respectively, the energy and number of particles of state \( |e_m\rangle \), where \( \mathcal{H} \) is the Hamiltonian operator, and where \( \mathcal{N} \) is the number of particles operator. The probability that state \( e_m \) is occupied is denoted as \( p_m \) [see Eq. (2.26)]. Three cases are considered below (see table 3.1). In the first one (microcanonical distribution), the system is isolated and its total energy \( U \) and number of particles \( N \) are constrained, that is for all accessible states \( U(m) = U \) and \( N(m) = N \). In the second case (canonical distribution), the system is allowed to exchange energy with its environment, and it is assumed that its average energy \( \langle U \rangle \), which is related to the density operator \( \rho \) by \( \langle U \rangle = \text{Tr}(\rho \mathcal{H}) = \langle \mathcal{H} \rangle \) [see Eq. (2.13)], is given. However, its number of particles is constrained, that is \( N(m) = N \). In the third case (grandcanonical distribution), the system is allowed to exchange both energy and particles with its environment, and it is assumed that both the average energy \( \langle U \rangle \) and the average number of particles \( \langle N \rangle = \text{Tr}(\rho \mathcal{N}) = \langle \mathcal{N} \rangle \), are given. However, in all cases, the probability distribution \( \{ p_m \} \) is not given.

According to the principle of largest uncertainty in statistical mechanics [1, 2, 3], the LUE (see section 1.6) is employed to estimate the probability distribution \( \{ p_m \} \). A probability distribution will be derived below, which is consistent with the normalization condition (1.1) and with the given expectation values (energy, in the second case, and both energy and number of particles, in the third case), which maximizes the entropy.

| Table 3.1. The microcanonical, canonical and grandcanonical distributions. |
|-------------------------------|-------------------------------|
| energy                        | number of particles           |
| microcanonical distribution   | constrained \( U(m) = U \)   |
| canonical distribution        | constrained \( N(m) = N \)   |
| grandcanonical distribution   | average is given \( \langle U \rangle \) |
|                              | constrained \( N(m) = N \)   |

The principle of largest uncertainty is then employed to estimate the probability distribution \( \{ p_m \} \).
3.1 Functionals of $\rho$

Consider a general functional $g(\rho)$ of the density operator having the form

$$g(\rho) = \text{Tr} (f(\rho)),$$  \hspace{1cm} (3.1)

where the function $f(\rho)$ can be Taylor expanded as a power series

$$f(\rho) = \sum_{k=0}^{\infty} a_k \rho^k,$$  \hspace{1cm} (3.2)

and where $a_k$ are complex constants. For the general case, $g(\rho)$ maps the density operator $\rho$ to a complex number, i.e. $g(\rho) \in \mathbb{C}$. For the example of the entropy given by Eq. (2.25), $\sigma(\rho)$ is a mapping of $\rho$ to a nonnegative real number.

Consider an infinitesimal change in the density operator $\rho \rightarrow \rho + d\rho$. To first order in $d\rho$ the corresponding change $dg$ in the functional $g(\rho)$ can be expressed as

$$dg = g(\rho + d\rho) - g(\rho)$$

$$= \text{Tr} \left( \sum_{k=0}^{\infty} a_k \left[ (\rho + d\rho)^k - \rho^k \right] \right)$$

$$= \text{Tr} \left[ \sum_{k=0}^{\infty} a_k \left( \rho^{k-1} d\rho + \rho^{k-2} (d\rho) \rho + \rho^{k-3} (d\rho)^2 \rho^2 + \cdots \right) \right] + O \left((d\rho)^2\right).$$  \hspace{1cm} (3.3)

By exploiting the general identity (2.5 the above result can be simplified (note that generally $\rho$ needs not to commute with $d\rho$)

$$dg = \text{Tr} \left[ \sum_{k=0}^{\infty} a_k k \rho^{k-1} d\rho \right] + O \left((d\rho)^2\right),$$  \hspace{1cm} (3.4)

thus to first order in $d\rho$ the following holds

$$dg = \text{Tr} \left( \frac{df}{d\rho} d\rho \right).$$  \hspace{1cm} (3.5)

In the above expression the term $df/d\rho$ is calculated by simply taking the derivative of the function $f(x)$ (where $x$ is considered to be a number) and substituting $x = \rho$.

Alternatively, the change $dg$ can be expressed in terms of the infinitesimal change $d\rho_{nm}$ in the matrix elements $\rho_{nm}$ of $\rho$. To first order in the infinitesimal variables $d\rho_{nm}$ one has
3.2 Distributions

\[ dg = \sum_{n,m} \frac{\partial g}{\partial \rho_{nm}} d\rho_{nm} . \]  
(3.6)

It is convenient to rewrite the above expression as

\[ dg = \nabla g \cdot \overrightarrow{d\rho} , \]  
(3.7)

where the vector elements of the nabla operator \( \nabla \) and of \( \overrightarrow{d\rho} \) are given by

\[ (\nabla)_{n,m} = \frac{\partial}{\partial \rho_{nm}} , \]  
(3.8)

and

\[ (\overrightarrow{d\rho})_{n,m} = d\rho_{nm} . \]  
(3.9)

3.2 Distributions

Consider the case where the density matrix is assumed to satisfy a set of contrarians, which are expressed as

\[ g_l (\rho) = 0 , \]  
(3.10)

where \( l = 0, 1, \cdots, L \), and where \( g_l (\rho) \) are functionals of \( \rho \). The constrain \( l = 0 \) is the requirement that \( \text{Tr} (\rho) = 1 \) [see Eq. (2.15)], i.e. \( g_0 (\rho) \) can be taken to be given by

\[ g_0 (\rho) = \text{Tr} (\rho) - 1 = 0 . \]  
(3.11)

The other constrains \( l = 1, \cdots, L \) are the requirements that the expectation values of the Hermitian operators \( X_1, X_2, \cdots, X_L \) are the following real numbers \( X_1, X_2, \cdots, X_L \) respectively, i.e. \( g_l (\rho) \) for \( l \geq 1 \) can be taken to be given by

\[ g_l (\rho) = \text{Tr} (\rho X_l) - X_l = 0 . \]  
(3.12)

To first order one has [see Eq. (3.7)]

\[ d\sigma = \nabla \sigma \cdot \overrightarrow{d\rho} , \]  
(3.13)

and

\[ dg_l = \nabla g_l \cdot \overrightarrow{d\rho} , \]  
(3.14)

where \( l = 0, 1, 2, \cdots, L \).

Below a LUE is derived, for which the entropy \( \sigma \) obtains a stationary point (maximum, minimum or a saddle point), and all the constrains (3.10)
Chapter 3. The principle of largest uncertainty in statistical physics

all satisfied. The technique of Lagrange multipliers is very useful for finding stationary points of a function, when constrains are applied (see section 1.6). A stationary point of $\sigma$ occurs iff for every small change $d\rho$ [see Eq. (3.9)], which is orthogonal to all vectors $\nabla g_0, \nabla g_1, \nabla g_2, \ldots, \nabla g_L$ (i.e. a change which does not violate the constrains) one has

$$0 = d\sigma = \nabla \sigma \cdot d\rho.$$  (3.15)

This condition is fulfilled only when the vector $\nabla \sigma$ belongs to the subspace spanned by the vectors $\{\nabla g_0, \nabla g_1, \nabla g_2, \ldots, \nabla g_L\}$. In other words, only when [compare with Eq. (1.50)]

$$\nabla \sigma = \xi_0 \nabla g_0 + \xi_1 \nabla g_1 + \xi_2 \nabla g_2 + \ldots + \xi_L \nabla g_L,$$  (3.16)

where the numbers $\xi_0, \xi_1, \ldots, \xi_L$, which are called Lagrange multipliers, are constants. By multiplying by $d\rho$ the last result becomes [see Eq. (3.7)]

$$d\sigma = \xi_0 d g_0 + \xi_1 d g_1 + \xi_2 d g_2 + \ldots + \xi_L d g_L.$$  (3.17)

Using Eqs. (2.25), (3.5), (3.11) and (3.12) one finds that

$$d\sigma = - \text{Tr}((1 + \log \rho) d\rho),$$  (3.18)

$$d g_0 = \text{Tr}(d\rho),$$  (3.19)

$$d g_l = \text{Tr}(X_l d\rho),$$  (3.20)

thus

$$0 = \text{Tr} \left[ \left(1 + \log \rho + \xi_0 + \sum_{l=1}^{L} \xi_l X_l \right) d\rho \right].$$  (3.21)

The requirement that the last identity holds for any $d\rho$ implies that

$$1 + \log \rho + \xi_0 + \sum_{l=1}^{L} \xi_l X_l = 0,$$  (3.22)

thus

$$\rho = e^{-1-\xi_0} \exp \left(- \sum_{l=1}^{L} \xi_l X_l \right).$$  (3.23)

The Lagrange multipliers $\xi_0, \xi_1, \ldots, \xi_L$ can be determined from Eqs. (3.11) and (3.12). The first constrains (3.11) is satisfied by replacing the factor $e^{-1-\xi_0}$ by the inverse of the partition function $Z$ [compare with Eq. (1.57)]

$$\rho = \frac{1}{Z} \exp \left(- \sum_{l=1}^{L} \xi_l X_l \right).$$  (3.24)
3.2. Distributions

where [compare with Eq. (1.56)]

\[ Z = \text{Tr} \left( - \sum_{l=1}^{L} \xi_l X_l \right). \] (3.25)

As can be seen from the above expression for \( Z \), the following holds [compare with Eq. (1.65)]

\[ \langle X_l \rangle = \frac{\partial \log Z}{\partial \xi_l}. \] (3.26)

The entropy \( \sigma = - \text{Tr} (\rho \log \rho) = - \langle \log \rho \rangle \) [see Eq. (2.25)] is related to \( Z \) by [see Eqs. (3.24) and (3.25), and compare with Eq. (1.72)]

\[ \sigma = \log Z + \sum_{l=1}^{L} \xi_l \langle X_l \rangle. \] (3.27)

3.2.1 Microcanonical distribution

For this case the only required constrain is (3.11), hence Eq. (3.24) yields \( \rho = 1/Z \), i.e. the density operator \( \rho \) of a microcanonical distribution is proportional to the identity operator. The corresponding probability distribution is \( p_1 = p_2 = \cdots = 1/M \), where \( M \) is the number of accessible states of the system [see also Eq. (1.30)], and the entropy for this case is given by [see Eq. (2.26)]

\[ \sigma = \log M. \] (3.28)

3.2.2 Canonical distribution

For a canonical ensemble, in addition to the normalization constrain is (3.11), the expectation value of the Hamiltonian \( \langle \mathcal{H} \rangle \) is required to have a given value \( \langle U \rangle \). For this case Eq. (3.24) yields

\[ \rho_c = \frac{1}{Z_c} e^{-\beta \mathcal{H}}, \] (3.29)

where the canonical partition function \( Z_c \) is given by

\[ Z_c = \text{Tr} \left( e^{-\beta \mathcal{H}} \right), \] (3.30)

and where \( \beta \) labels the Lagrange multiplier associated with the given expectation value \( \langle \mathcal{H} \rangle = \langle U \rangle \). By solving Eq. (3.12), which for this case is given by [see Eq. (3.26), and compare with Eq. (1.65)]

\[ \langle U \rangle = \frac{1}{Z_c} \text{Tr} \left( \mathcal{H} e^{-\beta \mathcal{H}} \right) = - \frac{\partial \log Z_c}{\partial \beta}. \] (3.31)
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The following holds [see Eq. (1.69)]
\[
\left\langle (\Delta U)^2 \right\rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2},
\tag{3.32}
\]
and [see Eq. (1.72)]
\[
\sigma = \log Z_c + \beta \left\langle U \right\rangle.
\tag{3.33}
\]

Using Eq. (1.75) one can expressed the Lagrange multiplier \( \beta \) as
\[
\beta = \frac{\partial \sigma}{\partial U}.
\tag{3.34a}
\]

The dimensionless temperature \( \tau \) is defined by
\[
\tau = \frac{1}{\beta}.
\tag{3.35}
\]

The probability \( p_m \) to occupy the state \( |e_m \rangle \) is related to its energy \( U(m) \) by [see Eq. (1.57)]
\[
p_m = \frac{1}{Z_c} \exp \left( -\beta U(m) \right),
\tag{3.36}
\]
and the partition function (3.30) can be expressed as
\[
Z_c = \sum_m \exp \left( -\beta U(m) \right).
\tag{3.37}
\]

The term \( \exp \left( -\beta U(m) \right) \) is called the Boltzmann factor.

**Exercise 3.2.1.** Consider a system that can be in one of two states having energies \( \pm \varepsilon/2 \). Calculate the average energy \( \left\langle U \right\rangle \) and the variance \( \left\langle (\Delta U)^2 \right\rangle \) in thermal equilibrium at temperature \( \tau \).

**Solution 3.2.1.** The partition function is given by Eq. (3.37)
\[
Z_c = \exp \left( \frac{\beta \varepsilon}{2} \right) + \exp \left( -\frac{\beta \varepsilon}{2} \right) = 2 \cosh \frac{\beta \varepsilon}{2},
\tag{3.38}
\]
thus [see Eq. (3.31)]
\[
\left\langle U \right\rangle = -\frac{\varepsilon}{2} \tanh \frac{\beta \varepsilon}{2},
\tag{3.39}
\]
and [see Eq. (3.32)]
\[
\left\langle (\Delta U)^2 \right\rangle = \left( \frac{\varepsilon}{2} \right)^2 \frac{1}{\cosh^2 \frac{\beta \varepsilon}{2}},
\tag{3.40}
\]
where \( \beta = 1/\tau \).
3.2.3 Grandcanonical distribution

For a grandcanonical ensemble, in addition to the normalization constrain is (3.11), the expectation value of the Hamiltonian \( \langle H \rangle \) is required to have a given value \( \langle U \rangle \), and the expectation value of the number of particles operator \( \langle N \rangle \) is required to have a given value \( \langle N \rangle \). For this case Eq. (3.24) yields

\[
\rho_{gc} = \frac{1}{Z_{gc}} e^{-\beta H - \eta N},
\]

where the grandcanonical partition function \( Z_{gc} \) is given by

\[
Z_{gc} = \text{Tr} \left( e^{-\beta H - \eta N} \right),
\]

and where \( \eta \) labels the Lagrange multiplier associated with the given expectation value \( \langle N \rangle = \langle N \rangle \).

The probability \( p_m \) to occupy the state \( |e_m\rangle \) is related to its energy \( U(m) \) and number of particles \( N(m) \) by [see Eq. (1.57)]

\[
p_m = \frac{1}{Z_{gc}} \exp \left( -\beta U(m) - \eta N(m) \right),
\]

and the partition function \( Z_{gc} \) (3.42) can be expressed as

\[
Z_{gc} = \sum_m \exp \left( -\beta U(m) - \eta N(m) \right).
\]

The term \( \exp \left( -\beta U(m) - \eta N(m) \right) \) is called the Gibbs factor. The following holds [see Eq. (1.65)]

\[
\langle U \rangle = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta,
\]

\[
\langle N \rangle = - \left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta,
\]

and [see Eq. (1.69)]

\[
\left\langle (\Delta U)^2 \right\rangle = \left( \frac{\partial^2 \log Z_{gc}}{\partial \beta^2} \right)_\eta,
\]

\[
\left\langle (\Delta N)^2 \right\rangle = \left( \frac{\partial^2 \log Z_{gc}}{\partial \eta^2} \right)_\beta,
\]

and [see Eq. (1.72)]

\[
\sigma = \log Z_{gc} + \beta \langle U \rangle + \eta \langle N \rangle.
\]
### 3.2.4 Temperature and Chemical Potential

Probability distributions in statistical mechanics of macroscopic parameters are typically extremely sharp and narrow. Consequently, in many cases no distinction is made between a parameter and its expectation value. That is, the expression for the entropy in Eq. (3.33) can be rewritten as

\[ \sigma = \log Z_c + \beta U , \]  

(3.50)

and the one in Eq. (3.49) as

\[ \sigma = \log Z_{gc} + \beta U + \eta N . \]  

(3.51)

Using Eq. (1.75) one can express the Lagrange multipliers \( \beta \) and \( \eta \) as

\[ \beta = \left( \frac{\partial \sigma}{\partial U} \right)_N , \]  

(3.52)

\[ \eta = \left( \frac{\partial \sigma}{\partial N} \right)_U . \]  

(3.53)

The chemical potential \( \mu \) is defined as

\[ \mu = -\tau \eta . \]  

(3.54)

In the definition (1.8) the entropy \( \sigma \) is dimensionless. Historically, the entropy was defined as

\[ S = k_B \sigma , \]  

(3.55)

where

\[ k_B = 1.38 \times 10^{-23} \text{ JK}^{-1} \]  

(3.56)

is the Boltzmann constant. Moreover, the historical definition of the temperature is

\[ T = \frac{\tau}{k_B} . \]  

(3.57)

The following holds [see Eqs. (3.41) and (3.54)]

\[ \langle U \rangle = \text{Tr} (\mathcal{H} \rho_{gc}) \]
\[ = \frac{\text{Tr} (\mathcal{H} e^{-\beta (\mathcal{H} - \mu N)})}{\text{Tr} (e^{-\beta (\mathcal{H} - \mu N)})} \]
\[ = - \frac{\text{Tr} \left( - (\mathcal{H} - \mu N) e^{-\beta (\mathcal{H} - \mu N)}) \right)}{\text{Tr} (e^{-\beta (\mathcal{H} - \mu N)})} + \frac{\mu}{\beta} \frac{\text{Tr} \left( N e^{-\beta (\mathcal{H} + \beta \mu N)} \right)}{\text{Tr} (e^{-\beta H + \beta \mu N})} , \]
and
\[
\langle N \rangle = \text{Tr} ( N \rho_{gc} ) = \frac{\text{Tr} ( N e^{-\beta H + \beta_N} )}{\text{Tr} ( e^{-\beta H + \beta_N} )},
\]  
(3.58)

hence, when the grandcanonical partition function \( Z_{gc} \) is expressed in terms of \( \beta \) and \( \mu \) (instead of in terms of \( \beta \) and \( \eta \)), the following holds [see Eqs. (3.45) and (3.46)]

\[
\langle U \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu + \tau \mu \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta ,
\]  
(3.59)

\[
\langle N \rangle = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda},
\]  
(3.60)

where \( \lambda \), which is defined by
\[
\lambda = \exp ( \beta \mu ) = e^{-\eta} ,
\]  
(3.61)
is the fugacity.

**Exercise 3.2.2.** In general the notation
\[
\left( \frac{\partial z}{\partial x} \right)_y
\]  

is used to denote the partial derivative of \( z \) with respect to \( x \), where the variable \( y \) is kept constant. To correctly calculate this derivative the variable \( z \) has to be expressed as a function of \( x \) and \( y \), namely, \( z = z ( x, y ) \). Show that
\[
\left( \frac{\partial z}{\partial x} \right)_y = -\left( \frac{\partial y}{\partial x} \right)_z \left( \frac{\partial z}{\partial y} \right)_x,
\]  
(3.62)

and
\[
\left( \frac{\partial z}{\partial x} \right)_w = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_w.
\]  
(3.63)

**Solution 3.2.2.** Consider an infinitesimal change in the variable \( z = z ( x, y ) \)
\[
\delta z = \left( \frac{\partial z}{\partial x} \right)_y \delta x + \left( \frac{\partial z}{\partial y} \right)_x \delta y .
\]  
(3.64)

For a process for which \( z \) is a constant \( \delta z = 0 \), thus
\[
0 = \left( \frac{\partial z}{\partial x} \right)_y (\delta x)_z + \left( \frac{\partial z}{\partial y} \right)_x (\delta y)_z .
\]  
(3.65)
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Dividing by \((\delta x)_z\) yields

\[
\left( \frac{\partial z}{\partial x} \right)_y = - \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\delta y}{\delta x} \right)_z = - \left( \frac{\partial y}{\partial x} \right)_z = - \left( \frac{\partial y}{\partial x} \right)_z, \tag{3.66}
\]

hence Eq. (3.62) holds. Consider a process for which the variable \(w\) is kept constant. An infinitesimal change in the variable \(z = z(x, y)\) is expressed as

\[
(\delta z)_w = \left( \frac{\partial z}{\partial x} \right)_y (\delta x)_w + \left( \frac{\partial z}{\partial y} \right)_x (\delta y)_w. \tag{3.67}
\]

Dividing by \((\delta x)_w\) yields

\[
\frac{(\delta z)_w}{(\delta x)_w} = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \frac{\delta y}{\delta x}. \tag{3.68}
\]

hence Eq. (3.63) holds.

**Exercise 3.2.3.** Employ the identity (3.63) to show that Eq. (3.59) holds.

**Solution 3.2.3.** Using the identity (3.63) one obtains

\[
\langle U \rangle = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu - \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta \left( \frac{\partial \mu}{\partial \beta} \right)_\eta = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu - \frac{\eta}{\beta^2} \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta, \tag{3.69}
\]

thus Eq. (3.59) holds.

### 3.3 Entropy time evolution

Consider a perturbation giving rise to transitions between states. Let \(\Gamma_{rs}\) denotes the rate of transition from state \(r\) to state \(s\). The probability that state \(s\) is occupied is denoted as \(p_s\).
3.3. Entropy time evolution

**Theorem 3.3.1 (H theorem).** If for every pair of states \( r \) and \( s \)

\[
\Gamma_{rs} = \Gamma_{sr} ,
\]  

(3.70)

then

\[
\frac{d\sigma}{dt} \geq 0 .
\]  

(3.71)

Moreover, equality holds iff \( p_s = p_r \) for all pairs of states for which \( \Gamma_{sr} \neq 0 \).

**Proof.** The rate of change in the probability \( p_s \) is given by

\[
\frac{dp_r}{dt} = \sum_s p_s \Gamma_{sr} - \sum_s p_r \Gamma_{rs} .
\]  

(3.72)

The first term on the right hand side of Eq. (3.72) represents the transitions to state \( r \), whereas the second one represents transitions from state \( r \). Using property (3.70) one finds that

\[
\frac{dp_r}{dt} = \sum_s \Gamma_{sr} (p_s - p_r) .
\]  

(3.73)

The last result and the entropy definition (1.8) allows calculating the rate of change of entropy

\[
\frac{d\sigma}{dt} = -\frac{d}{dt} \sum_r p_r \log p_r
\]  

\[
= -\sum_r \frac{dp_r}{dt} \left( \log p_r + 1 \right)
\]  

\[
= -\sum_r \sum_s \Gamma_{sr} (p_s - p_r) \left( \log p_r + 1 \right) .
\]  

(3.74)

Exchanging the summation indices allows rewriting the last result as [see Eq. (3.70)]

\[
\frac{d\sigma}{dt} = \sum_r \sum_s \Gamma_{sr} (p_s - p_r) \left( \log p_s + 1 \right) .
\]  

(3.75)

Both expressions (3.74) and (3.75) yield

\[
\frac{d\sigma}{dt} = \frac{1}{2} \sum_r \sum_s \Gamma_{sr} (p_s - p_r) \left( \log p_s - \log p_r \right) .
\]  

(3.76)

In general, since \( \log x \) is a monotonic increasing function.
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\[(p_s - p_r) (\log p_s - \log p_r) \geq 0, \quad (3.77)\]

and equality holds iff \(p_s = p_r\). Thus, in general

\[\frac{d\sigma}{dt} \geq 0, \quad (3.78)\]

and equality holds iff \(p_s = p_r\) holds for all pairs of states satisfying \(I_{sr} \neq 0\). When \(\sigma\) becomes time independent the system is said to be in thermal equilibrium.

3.4 Thermal Equilibrium

Consider two isolated systems denoted as \(S_1\) and \(S_2\). Let \(\sigma_1 = \sigma_1(U_1, N_1)\) and \(\sigma_2 = \sigma_2(U_2, N_2)\) be the entropy of the first and second system respectively and let \(\sigma = \sigma_1 + \sigma_2\) be the total entropy. The systems are brought to contact and now both energy and particles can be exchanged between the systems. Let \(\delta U\) be an infinitesimal energy, and let \(\delta N\) be an infinitesimal number of particles, which are transferred from system 1 to system 2. The corresponding change in the total entropy is given by [see Eqs. (3.52), (3.53) and (3.54)]

\[\delta \sigma = -\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} \delta U + \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2} \delta U - \left(\frac{\partial \sigma_1}{\partial N_1}\right)_{U_1} \delta N + \left(\frac{\partial \sigma_2}{\partial N_2}\right)_{U_2} \delta N
= \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2}\right) \delta U - \left(-\frac{\mu_1}{\tau_1} + \frac{\mu_2}{\tau_2}\right) \delta N. \quad (3.79)\]

The change \(\delta \sigma\) in the total entropy is obtained by removing a constrain. Thus, at the end of this process more states become accessible, and therefore, according to the principle of largest uncertainty it is expected that

\[\delta \sigma \geq 0. \quad (3.80)\]

For the case where no particles can be exchanged \(\delta N = 0\) this implies that energy flows from the system of higher temperature to the system of lower temperature. Another important case is the case where \(\tau_1 = \tau_2\), for which we conclude that particles flow from the system of higher chemical potential to the system of lower chemical potential.

In thermal equilibrium the entropy of the total system obtains its largest possible value. This occurs when

\[\tau_1 = \tau_2 \quad (3.81)\]

and

\[\mu_1 = \mu_2. \quad (3.82)\]
3.4.1 Externally Applied Potential Energy

In the presence of externally applied potential energy $\mu_{\text{ex}}$, the total chemical potential $\mu_{\text{tot}}$ is given by

$$\mu_{\text{tot}} = \mu_{\text{int}} + \mu_{\text{ex}},$$

(3.83)

where $\mu_{\text{int}}$ is the internal chemical potential. For example, for particles having charge $q$ in the presence of electric potential $V$ one has

$$\mu_{\text{ex}} = qV,$$

(3.84)

whereas, for particles having mass $m$ in a constant gravitational field $g$ one has

$$\mu_{\text{ex}} = mgz,$$

(3.85)

where $z$ is the height. The thermal equilibrium relation (3.82) is generalized in the presence of externally applied potential energy as

$$\mu_{\text{tot},1} = \mu_{\text{tot},2}.$$  

(3.86)

3.5 Free entropy and free energies

The free entropy [see Eq. (1.76)] for the canonical distribution is given by [see Eq. (3.50)]

$$\sigma_{F,c} = \sigma - \beta U,$$

(3.87)

whereas for the grandcanonical case it is given by [see Eq. (3.51)]

$$\sigma_{F,gc} = \sigma - \beta U - \eta N.$$  

(3.88)

Multiplication of Eq. (3.87) by $-\tau$ yields the canonical free energy (known also as the Helmholtz free energy) [see Eq. (3.50)]

$$F = -\tau \sigma_{F,c} = U - \tau \sigma = -\tau \log Z_c,$$

(3.89)

whereas multiplication of Eq. (3.88) by $-\tau$ yields the grandcanonical free energy [see Eq. (3.51)]

$$G = -\tau \sigma_{F,gc} = U - \tau \sigma + \tau \eta N = -\tau \log Z_{gc}.$$  

(3.90)

In section 1.6.2 above it was shown that the LUE maximizes $\sigma_F$ for given values of the Lagrange multipliers $\xi_1, \xi_2, \cdots, \xi_L$. This principle can be implemented to show that:

- In equilibrium at a given temperature $\tau$ the Helmholtz free energy obtains its smallest possible value.
- In equilibrium at a given temperature $\tau$ and chemical potential $\mu$ the grandcanonical free energy obtains its smallest possible value.

Our main results are summarized in table 3.2 below
### Table 3.2. Summary of main results.

<table>
<thead>
<tr>
<th></th>
<th>general</th>
<th>micro</th>
<th>canonical</th>
<th>grandcanonical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\langle X_1 \rangle$ where $l = 1, 2, ..., L$</td>
<td></td>
<td>$\langle U \rangle$</td>
<td>$\langle U \rangle, \langle N \rangle$</td>
</tr>
<tr>
<td>partition function</td>
<td>$Z = \sum_m e^{-\frac{1}{L} \xi_l X_l(m)}$</td>
<td>$Z_c = \sum_m e^{-\beta U(m)}$</td>
<td>$Z_{gc} = \sum_m e^{-\beta U(m) - \eta N(m)}$</td>
<td></td>
</tr>
<tr>
<td>$p_m$</td>
<td>$p_m = \frac{1}{Z_c} e^{-\beta U(m)}$</td>
<td>$p_m = \frac{1}{Z_{gc}} e^{-\beta U(m) - \eta N(m)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\langle X_1 \rangle$</td>
<td>$\langle X_1 \rangle = -\frac{\partial \log Z}{\partial \xi_1}$</td>
<td>$\langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta}$</td>
<td>$\langle U \rangle = -\frac{\partial \log Z_{gc}}{\partial \beta}$</td>
<td></td>
</tr>
<tr>
<td>$\langle (\Delta X)^2 \rangle$</td>
<td>$\langle (\Delta X)^2 \rangle = \frac{\partial^2 \log Z}{\partial \xi_1^2}$</td>
<td>$\langle (\Delta U)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2}$</td>
<td>$\langle (\Delta U)^2 \rangle = \frac{\partial^2 \log Z_{gc}}{\partial \beta^2}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$\sigma = \log Z + \sum_l \xi_l \langle X_l \rangle$</td>
<td>$\sigma = \log Z_c + \beta \langle U \rangle$</td>
<td>$\sigma = \log Z_{gc} + \beta \langle U \rangle + \eta \langle N \rangle$</td>
<td></td>
</tr>
<tr>
<td>Lagrange multipliers</td>
<td>$\xi_l = \left( \frac{\partial F}{\partial \langle X_l \rangle} \right)<em>{\langle X_n \rangle</em>{n \neq l}}$</td>
<td>$\beta = \frac{\partial F}{\partial \langle U \rangle}$</td>
<td>$\beta = \left( \frac{\partial G}{\partial \langle U \rangle} \right)_{\langle \mu \rangle}$</td>
<td></td>
</tr>
<tr>
<td>min / max principle</td>
<td>$\max \sigma F (\xi_1, \xi_2, ..., \xi_L)$</td>
<td>$\max \sigma F = \sigma - \sum_l \xi_l \langle X_l \rangle$</td>
<td>$\min F (\tau) = U - \tau \sigma$</td>
<td>$\min G (\tau, \mu) = U - \tau \sigma - \mu N$</td>
</tr>
</tbody>
</table>

### 3.6 Mean field approximation

In this section, the Helmholtz free energy is evaluated for a system of coupled spins using an approximation called mean field. Consider an array of $N$ spins. Each spin can be in one of two states having energies $\pm \varepsilon/2$, where $\varepsilon$ is the Larmor energy, which is proportional to an externally applied magnetic field. Each spin in the array interacts with its nearest neighbors. The number nearest neighbors of each spin is denoted by $l$. The system energy $U$ is assumed to be given by

$$
U = \frac{\varepsilon}{2} \sum_n \sigma_n - J \sum_{n', n''} \sigma_n' \sigma_{n''},
$$

(3.91)
where $\sigma_n \in \{-1, 1\}$, $J$ is the coupling coefficient between spins, and the symbol $\sum'_{n',n''}$ denotes sum over nearest neighbors.

In the mean field approximation it is assumed that $\langle \sigma_n \rangle = m$, where $\langle \sigma_n \rangle$ is the expectation value of $\sigma_n$, and $m$, which called the mean field magnetization, is independent of $n$. Moreover, it is assumed that $|\delta_n| \ll 1$, where $\delta_n = \sigma_n - \langle \sigma_n \rangle$ is the deviation of $\sigma_n$ from its expectation value $\langle \sigma_n \rangle = m$. To first order in $\delta_n$ one finds that (the term $\delta_n \delta_{n''}$ is disregarded in the mean field approximation)

$$
\sigma_n \sigma_{n''} = m^2 + m (\delta_{n'} + \delta_{n''}) = -m^2 + m (\sigma_{n'} + \sigma_{n''}) ,
$$

hence for this approximation [see Eq. (3.91)]

$$
U = \frac{\varepsilon_{\text{eff}}}{2} \sum_n \sigma_n + \frac{NJm^2}{2} ,
$$

where $\varepsilon_{\text{eff}}$ is given by

$$
\varepsilon_{\text{eff}} = \varepsilon - 2Jm .
$$

The canonical partition function $Z_c$ is given by [see Eq. (3.37), and compare with Eq. (3.38)]

$$
Z_c = \exp \left( -\frac{\beta N J m^2}{2} \right) (2 \cosh \frac{\beta \varepsilon_{\text{eff}}}{2})^N ,
$$

where $\tau = \beta^{-1}$ is the temperature, hence the Helmholtz free energy $F$ is given by [see Eqs. (3.89) and (3.93)]

$$
F = -\tau \log Z_c = NJ \left( \frac{m^2}{2} - \frac{1}{\beta l J} \log \left( 2 \cosh \left( \frac{\varepsilon_{\text{eff}}}{2l J} - m \right) \right) \right) ,
$$

or in a dimensionless form

$$
\frac{F}{NJ} = f \left( m, \frac{1}{\beta l J}, \frac{\varepsilon}{2l J} \right) ,
$$

where the function $f$ is given by

$$
f (m, \theta, u) = \frac{m^2}{2} - \theta \log \left( 2 \cosh \frac{u - m}{\theta} \right) .
$$

The following holds

$$
\frac{df}{dm} = m - \frac{u}{\theta} .
$$

In equilibrium the Helmholtz free energy obtains its smallest possible value. The condition $df/dm = 0$ yields
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Fig. 3.1. The function $f(m, \theta, u)$ (3.98).

$$m = \tanh \frac{m - u}{\theta}.$$  \hspace{1cm} (3.100)

Note that in the limit $J \to 0$ the relation (3.100) becomes

$$m = -\tanh \frac{\beta \varepsilon}{2},$$  \hspace{1cm} (3.101)

in agreement with Eq. (3.39). Plots of $f(m, \theta, u)$ [see Eq. (3.98)] as a function of $m$ for various values of $\theta$ and $u$ are shown in Fig. 3.1.

3.7 Problems

1. Consider an array on $N$ distinguishable two-level (binary) systems. The two-level energies of each system are $\pm \varepsilon/2$. Show that the temperature $\tau$ of the system is given by

$$\tau = \frac{\varepsilon}{2 \tanh^{-1} \left( -\frac{2 \langle U \rangle}{N \varepsilon} \right)},$$  \hspace{1cm} (3.102)

where $\langle U \rangle$ is the average total energy of the array.

2. Consider an array of $N$ distinguishable quantum harmonic oscillators in thermal equilibrium at temperature $\tau$. The resonance frequency of all oscillators is $\omega$. The quantum energy levels of each quantum oscillator is given by

$$\varepsilon_n = \hbar \omega \left( n + \frac{1}{2} \right),$$  \hspace{1cm} (3.103)

where $n = 0, 1, 2, \cdots$ is integer.
3.7. Problems

a) Show that the average energy of the system is given by

\[ \langle U \rangle = \frac{Nh\omega}{2} \coth \frac{\beta h\omega}{2}, \]

where \(\beta = 1/\tau\).

b) Show that the variance of the energy of the system is given by

\[ \langle (\Delta U)^2 \rangle = \frac{N}{\sinh^2 \frac{2h\omega}{2}}. \]

3. Consider a lattice containing \(N\) non-interacting atoms. Each atom has 3 non-degenerate energy levels \(E_1 = -\varepsilon, E_2 = 0, E_3 = \varepsilon\). The system is at thermal equilibrium at temperature \(\tau\).

a) Show that the average energy of the system is

\[ \langle U \rangle = -\frac{2N\varepsilon \sinh (\beta\varepsilon)}{1 + 2 \cosh \beta\varepsilon}, \]

where \(\beta = 1/\tau\).

b) Show that the variance of the energy of the system is given by

\[ \langle (U - \langle U \rangle)^2 \rangle = 2N\varepsilon^2 \frac{\cosh (\beta\varepsilon) + 2}{[1 + 2 \cosh (\beta\varepsilon)]^2}. \]

4. Consider a one dimensional chain containing \(N \gg 1\) sections. Each section can be in one of two possible states. In the first one the section contributes a length \(a\) to the total length of the chain, whereas in the other state the section has no contribution to the total length of the chain. The total length of the chain is \(Na\), and the tension applied to the end points of the chain is \(F\). The system is in thermal equilibrium at temperature \(\tau\).

a) Show that \(\alpha\) is given by

\[ \alpha = a \left[ 1 + \tanh \left( \frac{Fa}{2\tau} \right) \right]. \]

b) Show that in the limit of high temperature the spring constant is given approximately by

\[ k \simeq \frac{4\tau}{Na^2}. \]

5. A long elastic molecule can be modelled as a linear chain of \(N\) links. The state of each link is characterized by two quantum numbers \(l\) and \(n\). The length of a link is either \(l = a\) or \(l = b\). The vibrational state of a link is modelled as a harmonic oscillator whose angular frequency is \(\omega_a\) for a
link of length $a$ and $\omega_b$ for a link of length $b$. Thus, the energy of a link is

$$E_{n,l} = \begin{cases} \hbar \omega_a \left(n + \frac{1}{2}\right) & \text{for } l = a \\ \hbar \omega_b \left(n + \frac{1}{2}\right) & \text{for } l = b \end{cases},$$

where $n = 0, 1, 2, \cdots$. The chain is held under a tension $F$. Show that the mean length $\langle L \rangle$ of the chain in the limit of high temperature $T$ is given by

$$\langle L \rangle = Na\omega_b + \frac{b\omega_a}{\omega_b + \omega_a} - \frac{F\omega_b\omega_a(a - b)}{(\omega_b + \omega_a)^2}\beta + O(\beta^2),$$

(3.111)

where $\beta = 1/\tau$.

6. Consider a system which has two single particle states both of the same energy. When both states are unoccupied, the energy of the system is zero; when one state or the other is occupied by one particle, the energy is $\varepsilon$. Assume that the energy of the system is much higher (infinitely higher) when both states are occupied. Show that in thermal equilibrium at temperature $\tau$ the average number of particles in the level is

$$\langle N \rangle = \frac{2}{2 + \exp[\beta(\varepsilon - \mu)]},$$

(3.112)

where $\mu$ is the chemical potential and $\beta = 1/\tau$.

7. Consider an array of $N$ two-level particles. Each one can be in one of two states, having energy $E_1$ and $E_2$ respectively. The numbers of particles in states 1 and 2 are $n_1$ and $n_2$ respectively, where $N = n_1 + n_2$ (assume that $n_1 \gg 1$ and $n_2 \gg 1$). Consider an energy exchange with a reservoir at temperature $\tau$ leading to population changes $n_2 \rightarrow n_2 - 1$ and $n_1 \rightarrow n_1 + 1$.

a) Calculate the entropy change of the two-level system, $\Delta \sigma_{2LS}$.

b) Calculate the entropy change of the reservoir, $\Delta \sigma_R$.

c) What can be said about the relation between $\Delta \sigma_{2LS}$ and $\Delta \sigma_R$ in thermal equilibrium? Use your answer to express the ration $n_2/n_1$ as a function of $E_1, E_2$ and $\tau$.

8. Consider a lattice containing $N$ sites of one type, which is denoted as A, and the same number of sites of another type, which is denoted as B. The lattice is occupied by $N$ atoms. The number of atoms occupying sites of type A is denoted as $N_A$, whereas the number of atoms occupying atoms of type B is denoted as $N_B$, where $N_A + N_B = N$. Let $\varepsilon$ be the energy necessary to remove an atom from a lattice site of type A to a lattice site of type B. The system is in thermal equilibrium at temperature $\tau$. Assume that $N, N_A, N_B \gg 1$.

a) Calculate the entropy $\sigma$.

b) Calculate the average number $\langle N_B \rangle$ of atoms occupying sites of type B.
9. Consider a *microcanonical* ensemble of $N$ quantum harmonic oscillators in thermal equilibrium at temperature $\tau$. The resonance frequency of all oscillators is $\omega$. The quantum energy levels of each quantum oscillator is given by

$$\varepsilon_n = \hbar \omega \left( n + \frac{1}{2} \right),$$

(3.113)

where $n = 0, 1, 2, \ldots$. The total energy $E$ of the system is given by

$$E = \hbar \omega \left( m + \frac{N}{2} \right),$$

(3.114)

where

$$m = \sum_{l=1}^{N} n_l,$$

(3.115)

and $n_l$ is state number of oscillator $l$.

a) Calculate the number of states $g(N, m)$ of the system with total energy $\hbar \omega (m + N/2)$.

b) Use this result to calculate the entropy $\sigma$ of the system with total energy $\hbar \omega (m + N/2)$. Approximate the result by assuming that $N \gg 1$ and $m \gg 1$.

c) Use this result to calculate (in the same limit of $N \gg 1$ and $m \gg 1$) the average energy of the system $U$ as a function of the temperature $\tau$.

3.8 Solutions

1. The canonical partition function is given by

$$Z_c = Z_1^N,$$

(3.116)

where [see Eq. (3.37)]

$$Z_1 = \exp \left( \frac{\beta \varepsilon}{2} \right) + \exp \left( -\frac{\beta \varepsilon}{2} \right) = 2 \cosh \left( \frac{\beta \varepsilon}{2} \right).$$

(3.117)

Thus [see Eq. (3.31)]

$$\langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} = -N \frac{\partial \log Z_1}{\partial \beta} = -\frac{N \varepsilon}{2} \tanh \frac{\beta \varepsilon}{2},$$

(3.118)

and
\[ \tau = \frac{\varepsilon}{2 \tanh^{-1} \left( -\frac{2\langle U \rangle}{N\varepsilon} \right)} . \]  
\hspace{1cm} (3.119)

Note that the temperature can become negative if \( \langle U \rangle > 0 \). The negative temperature originates from the unphysical assumption that the energy of a single magnet has an upper bound.

2. The canonical partition function is given by

\[ Z_c = Z_1^N, \]  
\hspace{1cm} (3.120)

where [see Eq. (3.37)]

\[ Z_1 = \exp \left( -\frac{\beta \hbar \omega}{2} \right) \sum_{n=0}^{\infty} \exp (-\beta \hbar \omega n) \]  
\hspace{1cm} (3.121)

\[ = \frac{\exp \left( -\frac{\beta \hbar \omega}{2} \right)}{1 - \exp (-\beta \hbar \omega)} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}}. \]

a) The average energy \( \langle U \rangle \) is given by [see Eq. (3.31)]

\[ \langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} = -N \frac{\partial \log Z_1}{\partial \beta} = \frac{N \hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2}. \]  
\hspace{1cm} (3.122)

b) The variance \( \langle (\Delta U)^2 \rangle \) given by [see Eq. (3.32)]

\[ \langle (\Delta U)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2} = N \frac{\partial^2 \log Z_1}{\partial \beta^2} = \frac{N \left( \frac{\hbar \omega}{2} \right)^2}{\sinh \frac{3 \beta \hbar \omega}{2}}. \]  
\hspace{1cm} (3.123)

3. The canonical partition function is given by [see Eq. (3.37)]

\[ Z_c = [\exp (\beta \varepsilon) + 1 + \exp (-\beta \varepsilon)]^N = [1 + 2 \cosh (\beta \varepsilon)]^N, \]  
\hspace{1cm} (3.124)

where \( \beta = 1/\tau \).

a) Thus the average energy \( \langle U \rangle \) is given by [see Eq. (3.31)]

\[ \langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} = -\frac{2N \varepsilon \sinh (\beta \varepsilon)}{1 + 2 \cosh (\beta \varepsilon)}, \]  
\hspace{1cm} (3.125)

b) and the variance \( \langle (U - \langle U \rangle)^2 \rangle \) is given by [see Eq. (3.32)]

\[ \langle (U - \langle U \rangle)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2} = \frac{\partial \langle U \rangle}{\partial \beta} = 2N \varepsilon^2 \frac{\cosh (\beta \varepsilon) + 2}{[1 + 2 \cosh (\beta \varepsilon)]^2}. \]  
\hspace{1cm} (3.126)

4. Each section can be in one of two possible states with corresponding energies \( 0 \) and \( -F_a \).
a) By definition, $\alpha$ is the mean length of each segment, which is given by

$$\alpha = \frac{a \exp(Fa\beta)}{1 + \exp(Fa\beta)} = \frac{a}{2} \left[ 1 + \tanh \left( \frac{Fa\beta}{2} \right) \right], \quad (3.127)$$

where $\beta = 1/\tau$.

b) At high temperature $Fa\beta \ll 1$ the length of the chain $L = N\alpha$ is given by

$$L = \frac{Na}{2} \left[ 1 + \tanh \left( \frac{Fa\beta}{2} \right) \right] \approx \frac{Na}{2} \left( 1 + \frac{Fa\beta}{2} \right), \quad (3.128)$$

or

$$F = k \left( L - \frac{Na}{2} \right), \quad (3.129)$$

where the spring constant $k$ is given by

$$k = \frac{4\tau}{Na^2}. \quad (3.130)$$

5. The average length of a single link is given by

$$\langle l \rangle = \frac{a \exp(\beta Fa) \sum_{n=0}^{\infty} \exp \left[ -\beta \hbar \omega_a \left( n + \frac{1}{2} \right) \right] + b \exp(\beta Fb) \sum_{n=0}^{\infty} \exp \left[ -\beta \hbar \omega_b \left( n + \frac{1}{2} \right) \right]}{\exp(\beta Fa) \sum_{n=0}^{\infty} \exp \left[ -\beta \hbar \omega_a \left( n + \frac{1}{2} \right) \right] + \exp(\beta Fb) \sum_{n=0}^{\infty} \exp \left[ -\beta \hbar \omega_b \left( n + \frac{1}{2} \right) \right]}$$

$$= \frac{a \exp(\beta Fa)}{2 \sinh \frac{m \omega_a}{2}} + \frac{b \exp(\beta Fb)}{2 \sinh \frac{m \omega_b}{2}} \cdot \frac{\exp(\beta Fa)}{2 \sinh \frac{m \omega_a}{2}} + \frac{\exp(\beta Fb)}{2 \sinh \frac{m \omega_b}{2}}. \quad (3.131)$$

To first order in $\beta$

$$\langle l \rangle = \frac{a\omega_b + b\omega_a}{\omega_b + \omega_a} + \frac{F\omega_b\omega_a(a-b)^2}{(\omega_b + \omega_a)^2} - \beta + O(\beta^2). \quad (3.132)$$

The average total length is $\langle L \rangle = n \langle l \rangle$.

6. The grand partition function $Z_{gc}$ is given by [see Eq. (3.44)]

$$Z_{gc} = 1 + 2 \exp \left[ \beta (\mu - \bar{\varepsilon}) \right], \quad (3.133)$$

thus

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \log Z_{gc}}{\partial \mu} = \frac{2}{2 + \exp \left[ \beta (\varepsilon - \mu) \right]} \cdot \quad (3.134)$$
Chapter 3. The principle of largest uncertainty in statistical physics

7. The entropy of the two-level system $\sigma_{2LS}$ is given by [see Eq. (3.28)]

$$\sigma_{2LS} = \log \frac{N!}{n_2! n_1!}.$$  (3.135)

a) The change $(\Delta \sigma)_{2LS}$ is given by

$$(\Delta \sigma)_{2LS} = \log \frac{N!}{(n_2 - 1)! (n_1 + 1)!} - \log \frac{N!}{n_2! n_1!}$$

$$= \log \frac{n_2}{n_1 + 1} \simeq \log \frac{n_2}{n_1}.$$  (3.136)

b) The change $(\Delta \sigma)_R$ is given by

$$(\Delta \sigma)_R = \frac{E_2 - E_1}{\tau}.$$  (3.137)

c) For a small change near thermal equilibrium one expects $(\Delta \sigma)_{2LS} + (\Delta \sigma)_R = 0$, thus

$$\frac{n_2}{n_1} = \exp \left( - \frac{E_2 - E_1}{\tau} \right).$$  (3.138)

8. The number of ways to select $N_B$ occupied sites out of $N$ sites is $N!/ (N_B! (N - N_B)!)$.

a) The entropy $\sigma$ is given by

$$\sigma = \log \left( \frac{N!}{N_B! (N - N_B)!} \right)^2 \simeq 2 \left[ N \log N - N_B \log N_B - (N - N_B) \log (N - N_B) \right].$$  (3.139)

b) The energy of the system is given by $U = N_B \varepsilon$, thus, the Helmholtz free energy is given by

$$F = U - \tau \sigma = U - 2\tau \left[ N \log N - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} - \left( N - \frac{U}{\varepsilon} \right) \log \left( N - \frac{U}{\varepsilon} \right) \right].$$  (3.140)

At thermal equilibrium $(\partial F/\partial U)_\tau = 0$, thus

$$0 = \left( \frac{\partial F}{\partial U} \right)_\tau = 1 + \frac{2\tau}{\varepsilon} \left[ \log \frac{U}{\varepsilon} - \log \left( N - \frac{U}{\varepsilon} \right) \right],$$  (3.141)

or

$$\frac{N - N_B}{N_B} = \exp \left( \frac{\varepsilon}{2\tau} \right).$$  (3.142)
therefore
\[ \langle N_B \rangle = \frac{N}{1 + \exp \left( \frac{\varepsilon}{\tau} \right)} . \]

Alternatively, one can calculate the chemical potential from the requirement
\[ 1 = \frac{N_A}{N} + \frac{N_B}{N} , \]

where
\[ \frac{N_A}{N} = \frac{\exp (\beta \mu)}{1 + \exp (\beta \mu)} , \]
\[ \frac{N_B}{N} = \frac{\exp (\beta \mu - \beta \varepsilon)}{1 + \exp (\beta \mu - \beta \varepsilon)} , \]

which is satisfied when
\[ \mu = \frac{\varepsilon}{2} , \]

thus
\[ \langle N_B \rangle = \frac{N}{1 + \exp \left( \frac{\varepsilon}{\tau} \right)} . \]

9. In general,
\[ g(N, m) = \{ \text{# os ways to distribute } m \text{ identical balls in } N \text{ boxes} \} \]

Moreover (see Fig. 3.2)
\[ \{ \text{# os ways to distribute } m \text{ identical balls in } N \text{ boxes} \} = \{ \text{# os ways to arrange } m \text{ identical balls and } N - 1 \text{ identical partitions in a line} \} \]

a) Therefore
\[ g(N, m) = \frac{(N - 1 + m)!}{(N - 1)!m!} . \]

b) The entropy is given by
\[ \sigma = \log \frac{(N - 1 + m)!}{(N - 1)!m!} \approx (N + m) \log (N + m) - N \log N - m \log m , \]
or in terms of the total energy $E = \hbar \omega (m + N/2)$

$$\sigma = \left[ N + \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \right] \log \left[ N + \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \right]$$

$$- N \log N - \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \log \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right).$$

(3.149)

c) The temperature $\tau$ is given by

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial E}$$

$$= \frac{1}{\hbar \omega} \ln \frac{2E + Nh\omega}{2E - Nh\omega} + \frac{\ln \frac{2E + Nh\omega}{2E - Nh\omega} - 1}{\hbar \omega}$$

$$= \frac{1}{\hbar \omega} \ln \left( \frac{2E + Nh\omega}{2E - Nh\omega} \right).$$

(3.150)

In the thermodynamical limit ($N \gg 1$, $m \gg 1$) the energy $E$ and its average value $U$ are indistinguishable, thus

$$\exp \left( \frac{\hbar \omega}{\tau} \right) = \frac{2U + Nh\omega}{2U - Nh\omega},$$

(3.151)

or

$$U = \frac{Nh\omega}{2} \coth \frac{\hbar \omega}{2\tau}.$$

(3.152)
4. Ideal Gas

This chapter is devoted to some basic properties of ensembles of non-interacting identical particles (ideal gases). The indistinguishability postulate for identical particles is introduced, and the statistical properties of Fermions and Bosons are described. The last part of this chapter discusses an heat engine based on an ideal gas (Carnot heat engine). It is shown that the efficiency of such a heat engine, which employs a reversible process, obtains the largest possible value that is allowed by the second law of thermodynamics.

4.1 A Particle in a Box

Consider a particle having mass $M$ in a box. For simplicity the box is assumed to have a cube shape with a volume $V = L^3$. The corresponding potential energy is given by

$$V(x, y, z) = \begin{cases} 
0 & 0 \leq x, y, z \leq L \\
\infty & \text{else}
\end{cases}. \quad (4.1)$$

The quantum eigenstates and eigenenergies are determined by requiring that the wavefunction $\psi(x, y, z)$ satisfies the Schrödinger equation [see Eq. (2.9)]

$$-\frac{\hbar^2}{2M} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi. \quad (4.2)$$

In addition, the wavefunction $\psi$ is required to vanishes on the surfaces of the box. The normalized solutions are given by

$$\psi_{n_x, n_y, n_z}(x, y, z) = \left( \frac{2}{L} \right)^{3/2} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}, \quad (4.3)$$

where

$$n_x, n_y, n_z = 1, 2, 3, \ldots. \quad (4.4)$$

The corresponding eigenenergies are given by

$$\varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{2M} \left( \frac{\pi}{L} \right)^2 \left( n_x^2 + n_y^2 + n_z^2 \right). \quad (4.5)$$
For simplicity, internal degree of freedom (such as spin) are first disregarded. Later this simplifying assumption will be released, and the results will be generalized for particles having internal degrees of freedom.

The single particle partition function $Z_1$ is given by

$$Z_1 = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp\left(-\frac{\varepsilon_{n_x,n_y,n_z}}{\tau}\right)$$

$$= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp\left(-\alpha^2 \left(n_x^2 + n_y^2 + n_z^2\right)\right),$$  

(4.6)

where

$$\alpha^2 = \frac{\hbar^2 \pi^2}{2ML^2 \tau}.\quad (4.7)$$

The following relation can be employed to estimate the dimensionless parameter $\alpha$

$$\alpha^2 = \frac{7.9 \times 10^{-17}}{\frac{M}{m_p} \left(\frac{1}{\text{cm}}\right)^2 \frac{\pi}{300 \text{K}}},$$  

(4.8)

where $m_p$ is the proton mass. As can be seen from the last result, it is often the case that $\alpha^2 \ll 1$. In this limit the sum can be approximated by an integral

$$\sum_{n_x=1}^{\infty} \exp\left(-\alpha^2 n_x^2\right) \simeq \int_0^{\infty} \exp\left(-\alpha^2 n_x^2\right) \, dn_x.\quad (4.9)$$

By changing the integration variable $x = \alpha n_x$ one finds that

$$\int_0^{\infty} \exp\left(-\alpha^2 n_x^2\right) \, dn_x = \frac{1}{\alpha} \int_0^{\infty} \exp\left(-x^2\right) \, dx = \frac{\sqrt{\pi}}{2\alpha},$$  

(4.10)

thus

$$Z_1 = \left(\frac{\sqrt{\pi}}{2\alpha}\right)^3 = \left(\frac{ML^2 \tau}{2\pi \hbar^2}\right)^{3/2} = n_Q V,$$  

(4.11)

where $n_Q$, which is given by

$$n_Q = \left(\frac{M \pi}{2\pi \hbar^2}\right)^{3/2},$$  

(4.12)

is the quantum density.
4.2 Gibbs Paradox

The single particle partition function (4.11) together with Eq. (3.31) allow evaluating the average energy (recall that $\beta = 1/\tau$)

$$\langle \varepsilon \rangle = -\frac{\partial \log Z_1}{\partial \beta}$$

$$= -\frac{\partial \log \left( \frac{ML^2}{2\hbar \beta} \right)^{3/2}}{\partial \beta}$$

$$= -\frac{\partial \log \beta^{-3/2}}{\partial \beta}$$

$$= \frac{3}{2} \frac{\partial \log \beta}{\partial \beta}$$

$$= \frac{3}{2} \tau^2.$$  

(4.13)

This result can be written as

$$\langle \varepsilon \rangle = d \frac{\tau}{2},$$  

(4.14)

where $d = 3$ is the number of degrees of freedom of the particle. As we will see later, this is an example of the equipartition theorem of statistical mechanics. Similarly, the energy variance can be evaluated using Eq. (3.32)

$$\left\langle (\Delta \varepsilon)^2 \right\rangle = \frac{\partial^2 \log Z_1}{\partial \beta^2}$$

$$= -\frac{\partial \langle \varepsilon \rangle}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta} \frac{3}{2} \frac{\partial \log \beta}{\partial \beta}$$

$$= \frac{3}{2} \beta^2$$

$$= \frac{3}{2} \tau^2.$$  

(4.15)

By using Eq. (4.13) one finds that the standard deviation is given by

$$\sqrt{\left\langle (\Delta \varepsilon)^2 \right\rangle} = \sqrt{\frac{2}{3}} \langle \varepsilon \rangle.$$  

(4.16)

4.2 Gibbs Paradox

Consider the case where the box is occupied by $N$ particles of the same type. For simplicity, it is assumed that the density $n = N/V$ is sufficiently small to
Chapter 4. Ideal Gas

safely allow disregarding any interaction between the particles. In this case the gas is said to be ideal.

What is the partition function of the ideal gas? Recall that for the single particle case, the partition function was found to be given by [see Eq. (4.6)]

\[ Z_1 = \sum_n \exp \left( -\beta \varepsilon_n \right) . \] (4.17)

In this expression \( Z_1 \) is obtained by summing over all single particle orbital states, which are denoted by the vector of quantum numbers \( \mathbf{n} = (n_x, n_y, n_z) \). These states are called orbitals.

For treating the case where the total number of particles \( N \) is constrained, the canonical partition function \( Z_c \) is calculated below. For the case of distinguishable particles one may argue that the canonical partition function \( Z_c \) is related to the single particle partition function \( Z_1 \) by

\[ Z_c \equiv Z_1^N = \left( \sum_n \exp \left( -\beta \varepsilon_n \right) \right)^N . \] (4.18)

However, as was demonstrated by Gibbs, Eq. (4.18) yields a paradox. To see this, we employ Eqs. (3.33) and (4.11) and assume that the partition function is given by Eq. (4.18). For this case one finds that

\[ \sigma - \beta U \equiv \log Z_c \equiv \log Z_1^N = N \log (n_Q V) , \] (4.19)

or

\[ \sigma - \beta U \equiv N \log \left( N \frac{n_Q}{n} \right) , \] (4.20)

where \( \sigma \) is the entropy, \( U \) is the energy, and \( n = N/V \) is the density. What is wrong with this result? It suggests that the quantity \( \sigma - \beta U \) is not simply proportional to the size of the system. In other words, for a given \( n \) and a given \( n_Q \), \( \sigma - \beta U \) is not proportional to \( N \). As is shown below, such a behavior may lead to a violation of the second law of thermodynamics. To see this consider a box containing \( N \) identical particles having volume \( V \). What happens when the box is divided into two sections by introducing a partition? Let the number of particles in the first (second) section be \( N_1 \) \( (N_2) \) whereas the volume in the first (second) section be \( V_1 \) \( (V_2) \). The following hold

\[ N = N_1 + N_2 , \] (4.21)
\[ V = V_1 + V_2 . \] (4.22)

The density in each section is expected to be the same as the density in the box before the partition was introduced

\[ n = \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2} . \] (4.23)
4.3 Fermions and Bosons

With the help of Eq. (4.20) one finds that the change in entropy $\Delta \sigma$ due to the process of dividing the box is given by

$$\Delta \sigma = \sigma_{\text{tot}} - \sigma_1 - \sigma_2$$

$$\approx N \log \left( \frac{N Q n}{n} \right) - N_1 \log \left( \frac{N_1 Q n}{n} \right) - N_2 \log \left( \frac{N_2 Q n}{n} \right)$$

$$= N \log N - N_1 \log N_1 - N_2 \log N_2 .$$

(4.24)

By using the Stirling’s formula (1.115)

$$\log N! \approx N \log N - N ,$$

(4.25)

one finds that

$$\Delta \sigma \approx \log \frac{N!}{N_1!N_2!} > 0 .$$

(4.26)

Thus, the process of dividing the box leads to a reduction in the total entropy! This paradoxical result violates the second law of thermodynamics. According to this law we expect no change in the entropy, since the process of dividing the box is a reversible one, and no energy is required to add (or to remove) the partition.

What is wrong with the partition function $Z_c$ given by Eq. (4.18)? Expanding this partition function yields a sum of terms, each having the form

$$\exp \left( -\beta \sum_n N_n \varepsilon_n \right) ,$$

where $N_n$ is the number of particles occupying orbital $n$.

Let $g(N_1, N_2, \cdots)$ be the number of terms in such an expansion associated with a given set of occupation numbers $\{N_1, N_2, \cdots\}$. Since the partition function (4.18) treats the particles as being distinguishable, $g(N_1, N_2, \cdots)$ may in general be larger than unity

$$g(N_1, N_2, \cdots) = \frac{N!}{N_1!N_2! \times \cdots} .$$

(4.27)

For example, consider the state that is schematically represented by the sketch shown in Fig. 4.1 below for a gas containing $N = 3$ particles. The expansion (4.18) contains $3!/1!/2! = 3$ terms having the same occupation numbers ($N_n = 1$ if $n = 1$, $N_n = 2$ if $n = 2$, and $N_n = 0$ for all other values of $n$). However, for identical particles these 3 states are indistinguishable. Therefore, only a single term in the partition function should represent such a configuration. In general, the partition function should include a single term only for each given set of occupation numbers $\{N_1, N_2, \cdots\}$.

4.3 Fermions and Bosons

As was shown in the previous section, the canonical partition function given by Eq. (4.18) is incorrect. For indistinguishable particles, each set of orbital
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Fig. 4.1. The sketch represents an example term in the expansion (4.18) for a gas containing $N = 3$ identical particles.

occupation numbers $\{N_1, N_2, \cdots\}$ should be counted only once. In this section we take another approach and instead of evaluating the canonical partition function of the system we consider the grandcanonical partition function. This is done by considering each orbital as a subsystem and by evaluating its grandcanonical partition function, which we denote below as $\zeta$. To do this correctly, however, it is important to take into account the exclusion rules imposed by quantum mechanics upon the possible values of the occupation numbers $N_n$.

The elementary particles in nature are divided into two type: Fermions and Bosons. While Fermions have half integer spin, Bosons have integer spin. According to quantum mechanics the orbital occupation numbers $N_n$ can take the following values:

- For Fermions: $N_n = 0$ or $1$.
- For Bosons: $N_n$ can be any non-negative integer.

These rules are employed below to evaluate the grandcanonical partition function of an orbital.

4.3.1 Fermi-Dirac Distribution

In this case the occupation number can take only two possible values: 0 or 1. Thus, the grandcanonical partition function of an orbital having energy is $\varepsilon$ is given by [see Eq. (3.44)]

$$\zeta = 1 + \lambda \exp (-\beta \varepsilon) ,$$

(4.28)

where

$$\lambda = \exp (\beta \mu) ,$$

(4.29)

is the fugacity [see Eq. (3.61)]. The average occupation of the orbital, which is denoted by $f_{FD} (\varepsilon) = \langle N (\varepsilon) \rangle$, is found using Eq. (3.60)
4.3. Fermions and Bosons

\[ f_{FD}(\varepsilon) = \lambda \frac{\partial \log \zeta}{\partial \lambda} = \frac{\lambda \exp(-\beta \varepsilon)}{1 + \lambda \exp(-\beta \varepsilon)} = \frac{1}{\exp[\beta (\varepsilon - \mu)] + 1}. \]  

(4.30)

The function \( f_{FD}(\varepsilon) \) is called the Fermi-Dirac function.

4.3.2 Bose-Einstein Distribution

In this case the occupation number can take any integer value. Thus, the grandcanonical partition function of an orbital having energy \( \varepsilon \) is given by [see Eq. (3.44)]

\[ \zeta = \sum_{N=0}^{\infty} \lambda^N \exp(-N\beta \varepsilon) = \sum_{N=0}^{\infty} [\lambda \exp(-\beta \varepsilon)]^N = \frac{1}{1 - \lambda \exp(-\beta \varepsilon)}. \]  

(4.31)

The average occupation of the orbital, which is denoted by \( f_{BE}(\varepsilon) = \langle N(\varepsilon) \rangle \), is found using Eq. (3.60)

\[ f_{BE}(\varepsilon) = \lambda \frac{\partial \log \zeta}{\partial \lambda} = \frac{\exp(-\beta \varepsilon)}{1 - \lambda \exp(-\beta \varepsilon)} = \frac{1}{\exp[\beta (\varepsilon - \mu)] - 1}. \]  

(4.32)

The function \( f_{BE}(\varepsilon) \) is called the Bose-Einstein function.

4.3.3 Classical Limit

The classical limit occurs when

\[ \exp[\beta (\varepsilon - \mu)] \gg 1. \]  

(4.33)

As can be seen from Eqs. (4.30) and (4.32) the following holds
Table 4.1. Fermi-Dirac, Bose-Einstein and classical distributions.

<table>
<thead>
<tr>
<th>orbital partition function</th>
<th>average occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermions</td>
<td>$1 + \lambda \exp(-\beta \varepsilon)$</td>
</tr>
<tr>
<td>Bosons</td>
<td>$\frac{1}{1 - \lambda \exp(-\beta \varepsilon)}$</td>
</tr>
<tr>
<td>classical limit</td>
<td>$1 + \lambda \exp(-\beta \varepsilon)$</td>
</tr>
</tbody>
</table>

Thus the classical limit corresponds to the case where the averaged occupation of an orbital is close to zero, namely the orbital is nearly empty. The main results of the above discussed cases (Fermi-Dirac distribution, Bose-Einstein distribution and the classical limit) are summarized in table 4.1 below.

4.4 Ideal Gas in the Classical Limit

The rest of this chapter is devoted to the classical limit. The grandcanonical partition function $\zeta_n$ of orbital $n$ having energy $\varepsilon_n$ is given by Eq. (4.35) above. The grandcanonical partition function of the entire system $Z_{gc}$ is found by multiplying $\zeta_n$ of all orbitals

$$Z_{gc} = \prod_n (1 + \lambda \exp(-\beta \varepsilon_n)) .$$

Each term in the expansion of the above expression represents a set of orbital occupation numbers, where each occupation number can take one of the possible values: 0 or 1. We exploit the fact that in the classical limit

$$\lambda \exp(-\beta \varepsilon) \ll 1$$

and employ the first order expansion

$$\log(1 + x) = x + O(x^2)$$

to obtain

$$\log Z_{gc} = \sum_n \log (1 + \lambda \exp(-\beta \varepsilon_n))$$

$$\simeq \lambda \sum_n \exp(-\beta \varepsilon_n)$$

$$= \lambda Z_1 ,$$

4.34 and 4.35

and

$$\zeta \simeq 1 + \lambda \exp(-\beta \varepsilon) .$$

Thus the classical limit corresponds to the case where the averaged occupation of an orbital is close to zero, namely the orbital is nearly empty. The main results of the above discussed cases (Fermi-Dirac distribution, Bose-Einstein distribution and the classical limit) are summarized in table 4.1 below.
4.4. Ideal Gas in the Classical Limit

where

\[ Z_1 = V \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2}, \quad (4.40) \]

[see Eq. (4.11)] is the single particle partition function. In terms of the Lagrange multipliers \( \eta = -\mu/\tau \) and \( \beta = 1/\tau \) the last result can be rewritten as

\[ \log Z_{gc} = e^{-\eta V} \left( \frac{M}{2 \pi \hbar^2 \beta} \right)^{3/2}. \quad (4.41) \]

The average energy and average number of particle are calculated using Eqs. (3.45) and (3.46) respectively

\[ \langle U \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_{\eta} = \frac{3}{2\beta} \log Z_{gc}, \quad (4.42) \]

\[ \langle N \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_{\beta} = \log Z_{gc}. \quad (4.43) \]

In what follows, to simplify the notation, the diagonal brackets are removed, and the notations \( \langle U \rangle \) and \( \langle N \rangle \) are replaced by \( U \) and \( N \), respectively. As was already pointed out earlier, probability distributions in statistical mechanics of macroscopic parameters are typically extremely sharp and narrow. Consequently, in many cases no distinction is made between a parameter and its expectation value. By using this simplified notation, and by employing Eqs. (4.42) and (4.43), one finds that

\[ U = \frac{3N \tau}{2}, \quad (4.44) \]

thus, the total energy is \( N \langle \varepsilon \rangle \), where \( \langle \varepsilon \rangle \) is the average single particle energy that is given by Eq. (4.13).

The entropy is evaluate using Eq. (3.51)

\[ \sigma = \log Z_{gc} + \beta U + \eta N \]
\[ = N \left( 1 + \frac{3}{2} - \frac{\mu}{\tau} \right) \]
\[ = N \left( \frac{5}{2} - \mu \beta \right). \quad (4.45) \]

Furthermore, using Eqs. (4.39), (4.43), (4.11) and (3.61) one finds that

\[ \mu \beta = \log \frac{n}{n_Q}, \quad (4.46) \]

where \( n = N/V \) is the density. This allows expressing the entropy as

\[ Eyal Buks Statistical Physics 61 \]
4.4.1 Pressure

The pressure $p$ is defined by

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N}.$$  \hfill (4.49)

Using Eq. (4.48) and keeping in mind that $n = N/V$ one finds that

$$p = \frac{N\tau}{V}. \hfill (4.50)$$

The pressure represents the force per unit area acting on the walls of the box containing the gas due to collisions between the particles and the walls. To see that this is indeed the case, consider a gas of $N$ particles contained in a box having cube shape and volume $V = L^3$. One of the walls is chosen to lie on the $x = 0$ plane. Consider an elastic collision between this wall and a particle having momentum $\mathbf{p} = (p_x, p_y, p_z)$. After the collision $p_y$ and $p_z$ remain unchanged, however, $p_x$ becomes $-p_x$. Thus each collision results in transferring $2|p_x|$ momentum in the $x$ direction from the particle to the wall. The rate at which a particle collides with the wall $x = 0$ is $|p_x|/2mL$. Thus the pressure acting on the wall due to a single particle is

$$\{\text{pressure}\} = \frac{\{\text{force}\}}{\{\text{area}\}} = \frac{\{\text{rate of momentum change}\}}{\{\text{area}\}} = \frac{2|p_x|}{L^2} \times \frac{p_x}{4mL} = \frac{p_x^2}{mV}. \hfill (4.51)$$

The average energy of a particle is given by Eq. (4.13)

$$\frac{3\tau}{2} = \langle \varepsilon \rangle = \frac{\langle p_x^2 + p_y^2 + p_z^2 \rangle}{2m}, \hfill (4.52)$$
thus one finds that
\[ \langle p_x^2 \rangle_m = \tau . \] (4.53)

Using this result and Eq. (4.51) one finds that the pressure due to a single particle is \( p = \tau / V \), thus the total pressure is
\[ p = \frac{N \tau}{V} , \] (4.54)
in agreement with Eq. (4.50).

4.4.2 Useful Relations

In this section we derive some useful relations between thermodynamical quantities.

\textbf{Claim.} The following holds
\[ p = - \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} . \]

\textbf{Proof.} Using the definition (4.49) and recalling that \( F = U - \tau \sigma \) one finds
\[ -p = \left( \frac{\partial F}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\tau,N} - \left( \frac{\partial (\tau \sigma)}{\partial V} \right)_{\tau,N} . \] (4.55)

Using identity (3.63), which is given by
\[ \left( \frac{\partial z}{\partial x} \right)_w = \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial y}{\partial x} \right)_w , \] (4.56)
one finds
\[ \left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \left( \frac{\partial U}{\partial \sigma} \right)_{\tau,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} , \] (4.57)
thus
\[ -p = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} - \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} . \] (4.58)

In a similar way the following relations can be obtained
\[ p = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{U,N} = - \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} = - \left( \frac{\partial F}{\partial V} \right)_{\tau,N} , \] (4.59)
\[ \mu = -\tau \left( \frac{\partial \sigma}{\partial N} \right)_{U,V} = \left( \frac{\partial U}{\partial N} \right)_{\sigma,V} = \left( \frac{\partial F}{\partial N} \right)_{\tau,V} . \] (4.60)
4.4.3 Heat Capacity

The heat capacity at constant volume is defined by
\[ c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V, \]  
(4.61)

whereas the heat capacity at constant pressure is defined by
\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p. \]  
(4.62)

Using Eq. (4.61) one finds that (recall that \( n Q \propto \tau^{3/2} \))
\[ c_V = \frac{3N}{2\tau} = \frac{3N}{2}. \]  
(4.63)

4.4.4 Internal Degrees of Freedom

In this section, internal degrees of freedom, which were previously disregarded, are taken into account. This is done by expressing the grandcanonical partition function of a given orbital having orbital energy \( \varepsilon_n \), as \( \zeta_{FD,n} \) for the case of Fermions, and as \( \zeta_{BE,n} \) for the case of Bosons, where
\[ \zeta_{FD,n} = \Pi l \left( \sum_{m=0}^{1} \lambda^m \exp(\beta m \varepsilon_n) \exp(-\beta m E_l) \right), \]  
(4.64)
\[ \zeta_{BE,n} = \Pi l \left( \sum_{m=0}^{\infty} \lambda^m \exp(\beta m \varepsilon_n) \exp(-\beta m E_l) \right), \]  
(4.65)

\( \{ E_l \} \) are the eigenenergies associated with the internal degrees of freedom, \( \lambda = \exp(\beta \mu) \) and \( \beta = 1/\tau \). As is required by the Pauli exclusion principle, no more than one Fermion can occupy a given internal eigenstate [see Eq. (4.64)], whereas for the Bosonic case, each state can be occupied by any integer number of particles [see Eq. (4.65)].

In the classical limit the average occupation of an orbital is close to zero. In this limit, namely when
\[ \lambda \exp(-\beta \varepsilon_n) \ll 1, \]  
(4.66)
[see Eq. (4.33)] the following holds
\[ \zeta_{FD,n} \simeq \zeta_{BE,n} \simeq \zeta_n, \]  
(4.67)
where
\[ \zeta_n = 1 + \lambda \exp(-\beta \varepsilon_n) Z_{\text{int}}, \]  
(4.68)
and where
\[ Z_{\text{int}} = \sum_l \exp(-\beta E_l) , \]  
(4.69)
is the internal partition function.

Using Eq. (3.60) one finds that the average occupation of the orbital \( f_n \) in the classical limit is given by
\[ f_n = \lambda \frac{\partial \log \zeta_n}{\partial \lambda} = \frac{\lambda Z_{\text{int}} \exp(-\beta \varepsilon_n)}{1 + \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n)} \approx \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n) . \]  
(4.70)
The total grandcanonical partition function is given by
\[ Z_{\text{gc}} = \prod_n \zeta_n , \]  
(4.71)
thus (recall that in the classical limit \( \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n) \ll 1 \))
\[ \log Z_{\text{gc}} = \sum_n \log \zeta_n 
= \sum_n \log [1 + \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n)] 
\approx \lambda Z_{\text{int}} \sum_n \exp(-\beta \varepsilon_n) 
= \lambda Z_{\text{int}} Z_1 . \]  
(4.72)
Furthermore, using Eq. (4.11) one finds that (recall that \( \eta = -\mu/\tau \))
\[ \log Z_{\text{gc}} = e^{-\eta} Z_{\text{int}} V \left( \frac{M}{2\pi \hbar^2 \beta} \right)^{3/2} . \]  
(4.73)
This result together with Eqs. (3.45) and (3.46) yield
\[ \langle U \rangle = -\left( \frac{\partial \log Z_{\text{gc}}}{\partial \beta} \right)_{\eta} = \frac{3}{2\beta} \log Z_{\text{gc}} + \langle E_l \rangle \log Z_{\text{gc}} , \]  
(4.74)
\[ \langle N \rangle = -\left( \frac{\partial \log Z_{\text{gc}}}{\partial \eta} \right)_{\beta} = \log Z_{\text{gc}} , \]  
(4.75)
where
\[ \langle E_l \rangle = \frac{\sum_l E_l \exp(-\beta E_l)}{\sum_l \exp(-\beta E_l)} = -\frac{\partial \log Z_{\text{int}}}{\partial \beta} . \]  
(4.76)
4.5 Processes in Ideal Gas

The state of an ideal gas is characterized by extensive parameters (by definition, parameters that are proportional to the system size) such as $U$, $V$, $N$ and $\sigma$ and by intensive parameters (parameters that are independent on the system size) such as $\tau$, $\mu$ and $p$. In this section we discuss some examples of processes that occur by externally changing some of these parameters. We will use these processes in the next section to demonstrate how one can construct a heat engine based on an ideal gas.

In general, the entropy is commonly expressed as a function of the energy, volume and number of particles $\sigma = \sigma(U,V,N)$. A small change in $\sigma$ is expressed in terms of the partial derivatives

$$d\sigma = \left(\frac{\partial\sigma}{\partial U}\right)_{V,N} dU + \left(\frac{\partial\sigma}{\partial V}\right)_{U,N} dV + \left(\frac{\partial\sigma}{\partial N}\right)_{U,V} dN.$$  \hspace{1cm} (4.77)

Using Eqs. (3.52), (4.59) and (4.60) one finds that

$$d\sigma = \frac{1}{\tau}dU + \frac{p}{\tau}dV - \frac{\mu}{\tau}dN,$$  \hspace{1cm} (4.78)

or

$$dU = \tau d\sigma - pdV + \mu dN.$$  \hspace{1cm} (4.79)

This relation expresses the change in the energy of the system $dU$ in terms of

- $dQ = \tau d\sigma$ heat added to the system
- $dW = pdV$ work done by the system
- $\mu dN$ energy change due to added particles

For processes that keep the number of particles unchanged $dN = 0$, one has

$$dU = dQ - dW.$$  \hspace{1cm} (4.80)

Integrating this relation for the general case (not necessarily an infinitesimal process) yields

$$\Delta U = Q - W.$$  \hspace{1cm} (4.81)

We discuss below some specific examples for processes for which $dN = 0$. The initial values of the pressure, volume and temperature are denoted as $p_1$, $V_1$ and $\tau_1$ respectively, whereas the final values are denoted as $p_2$, $V_2$ and $\tau_2$ respectively. In all these processes we assume that the gas remains in
thermal equilibrium throughout the entire process. This can be achieved by varying the external parameters at a rate that is sufficiently slow to allow the system to remain very close to thermal equilibrium at any moment during the process. The four example to be analyzed below are (see fig. 4.2):

- Isothermal process - temperature is constant
- Isobaric process - pressure is constant
- Isochoric process - volume is constant
- Isentropic process - entropy is constant

Note that in general, using the definition of the heat capacity at constant volume given by Eq. (4.61) together with Eq. (3.52), one finds that

\[ c_V = \left( \frac{\partial U}{\partial \tau} \right)_{N,V}. \] (4.82)

Furthermore, as can be seen from Eq. (4.119), the energy \( U \) of an ideal gas in the classical limit is independent on the volume \( V \) (it can be expressed as a function of \( \tau \) and \( N \) only). Thus, one concludes that, for processes for which \( dN = 0 \), the change in energy \( dU \) can be expressed as

\[ dU = c_V d\tau. \] (4.83)
4.5.1 Isothermal Process

Since $\tau$ is constant one finds using Eq. (4.83) that $\Delta U = 0$. Integrating the relation $dW = pdV$ and using Eq. (4.50) yield

$$Q = W = \int_{V_1}^{V_2} p\,dV$$

$$= N\tau \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= N\tau \log \frac{V_2}{V_1}.$$  \hspace{1cm} (4.84)

4.5.2 Isobaric Process

Integrating the relation $dW = pdV$ for this case where the pressure is constant yields

$$W = \int_{V_1}^{V_2} pdV = p (V_2 - V_1).$$  \hspace{1cm} (4.85)

The change in energy $\Delta U$ can be found by integrating Eq. (4.83)

$$\Delta U = \int_{\tau_1}^{\tau_2} c_V d\tau.$$  \hspace{1cm} (4.86)

The heat added to the system $Q$ can be found using Eq. (4.81)

$$Q = W + \Delta U$$

$$= p (V_2 - V_1) + \int_{\tau_1}^{\tau_2} c_V d\tau.$$  \hspace{1cm} (4.87)

Note that if the temperature dependence of $c_V$ can be ignored to a good approximation one has

$$\Delta U = c_V (\tau_2 - \tau_1).$$  \hspace{1cm} (4.88)
4.5.3 Isochoric Process

In this case the volume is constant, thus $W = 0$. By integrating Eq. (4.83) one finds that

$$Q = \Delta U = \int_{\tau_1}^{\tau_2} c_V d\tau .$$  

(4.89)

Also in this case, if the temperature dependence of $c_V$ can be ignored to a good approximation one has

$$Q = \Delta U = c_V (\tau_2 - \tau_1) .$$

4.5.4 Isentropic Process

In this case the entropy is constant, thus $dQ = \tau d\sigma = 0$, and therefore $dU = -dW$, thus by using the relation $dW = p dV$ and Eq. (4.83) one finds that

$$c_V d\tau = -p dV ,$$  

(4.90)

or [see Eq. (4.50)]

$$c_V \frac{d\tau}{\tau} = -N \frac{dV}{V} .$$  

(4.91)

This relation can be rewritten using Eq. (4.123) as

$$\frac{d\tau}{\tau} = (1 - \gamma) \frac{dV}{V} ,$$  

(4.92)

where

$$\gamma = \frac{c_p}{c_V} .$$  

(4.93)

The last result can be easily integrated if the temperature dependence of the factor $\gamma$ can be ignored to a good approximation. For that case one has

$$\log \frac{\tau_2}{\tau_1} = \log \left( \frac{V_2}{V_1} \right)^{1-\gamma} .$$  

(4.94)

Thus

$$\tau_1 V_1^{\gamma-1} = \tau_2 V_2^{\gamma-1} ,$$  

(4.95)

or [see Eq. (4.50)]

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma} .$$  

(4.96)
In other words, both quantities $\tau V^{\gamma-1}$ and $pV^\gamma$ remain unchanged during this process. Using the last result allows integrating the relation $dW = p\,dV$

$$-\Delta U = W = \int_{V_i}^{V_2} p\,dV = p_1 V_1^\gamma \int_{V_i}^{V_2} V^{-\gamma} dV = p_1 V_1^\gamma \frac{(V_1^{1-\gamma+1} - V_2^{1-\gamma+1})}{\gamma - 1}$$

$$= \frac{p_2 V_2 - p_1 V_1}{1 - \gamma} = \frac{N}{1 - \gamma} (\tau_2 - \tau_1) = -c_V (\tau_2 - \tau_1).$$

(4.97)

### 4.6 Carnot Heat Engine

In this section we discuss an example of a heat engine proposed by Carnot that is based on an ideal classical gas. Each cycle is made of four steps (see Figs. 4.3 and 4.4)

1. Isothermal expansion at temperature $\tau_h$ ($a \rightarrow b$)
2. Isentropic expansion from temperature $\tau_h$ to $\tau_l$ ($b \rightarrow c$)
3. Isothermal compression at temperature $\tau_l$ ($c \rightarrow d$)
4. Isentropic compression from temperature $\tau_l$ to $\tau_h$ ($d \rightarrow a$)

All four steps are assumed to be sufficiently slow to maintain the gas in thermal equilibrium throughout the entire cycle. The engine exchanges heat with the environment during both isothermal processes. Using Eq. (4.84) one finds that the heat extracted from the hot reservoir $Q_h$ at temperature $\tau_h$ during step 1 ($a \rightarrow b$) is given by

$$Q_h = N\tau_h \log \frac{V_b}{V_a},$$

(4.98)

and the heat extracted from the cold thermal reservoir $Q_l$ at temperature $\tau_l$ during step 3 ($c \rightarrow d$) is given by

$$Q_l = N\tau_l \log \frac{V_d}{V_c}.$$

(4.99)
where $V_n$ is the volume at point $n \in \{a, b, c, d\}$. Note that $Q_h > 0$ since the system undergoes expansion in step 1 whereas $Q_l < 0$ since the system undergoes compression during step 3. Both thermal reservoirs are assumed to be very large systems that can exchange heat with the engine without changing their temperature. No heat is exchanged during the isentropic steps 2 and 4 (since $dQ = \tau d\sigma$).

The total work done by the system per cycle is given by
\[ W = W_{ab} + W_{cd} + W_{bc} + W_{da} \]
\[ = N \tau_h \log \frac{V_b}{V_a} + N \tau_l \log \frac{V_d}{V_c} + \]
\[ \frac{N (\tau_l - \tau_h)}{1 - \gamma} + \frac{N (\tau_h - \tau_l)}{1 - \gamma} \]
\[ = N \left( \tau_h \log \frac{V_b}{V_a} + \tau_l \log \frac{V_d}{V_c} \right), \]  
\[ (4.100) \]

where the work in both isothermal processes \(W_{ab}\) and \(W_{cd}\) is calculated using Eq. (4.84), whereas the work in both isentropic processes \(W_{bc}\) and \(W_{da}\) is calculated using Eq. (4.97). Note that the following holds

\[ W = Q_h + Q_l. \]  
\[ (4.101) \]

This is expected in view of Eq. (4.81) since the gas returns after a full cycle to its initial state and therefore the total energy change vanishes.

The efficiency of the heat engine is defined as the ratio between the work done by the system and the heat extracted from the hot reservoir per cycle

\[ \eta = \frac{W}{Q_h} = 1 + \frac{Q_l}{Q_h}. \]  
\[ (4.102) \]

Using Eqs. (4.98) and (4.100) one finds that

\[ \eta = 1 + \frac{\tau_l \log \frac{V_b}{V_a}}{\tau_h \log \frac{V_d}{V_c}}. \]  
\[ (4.103) \]

Employing Eq. (4.95) for both isentropic processes yields

\[ \tau_h V_b^{\gamma - 1} = \tau_l V_c^{\gamma - 1}, \]  
\[ (4.104) \]
\[ \tau_h V_a^{\gamma - 1} = \tau_l V_d^{\gamma - 1}, \]  
\[ (4.105) \]

thus by dividing these equations one finds that

\[ \frac{V_b^{\gamma - 1}}{V_a^{\gamma - 1}} = \frac{V_c^{\gamma - 1}}{V_d^{\gamma - 1}}, \]  
\[ (4.106) \]

or

\[ \frac{V_b}{V_a} = \frac{V_c}{V_d}. \]  
\[ (4.107) \]

Using this result one finds that the efficiency of the Carnot heat engine \(\eta_C\) is given by

\[ \eta_C = 1 - \frac{\tau_l}{\tau_h}. \]  
\[ (4.108) \]
Is it possible to construct a heat engine that operates between the same heat reservoirs at temperatures $\tau_h$ and $\tau_l$ that will have efficiency larger than the value given by Eq. (4.108)? As will shown below, the answer is no. This conclusion is obtained by noticing that the total entropy remains unchanged in each of the four steps that constructs the Carnot’s cycle. Consequently, the entire process is reversible, namely, by varying the external parameters in the opposite direction, the process can be reversed.

We consider below a general model of a heat engine. In a continuous operation the heat engine repeats a basic cycle one after another. The following is assumed:

- At the end of each cycle the heat engine returns to the same macroscopic state that it was in initially (otherwise, continuous operation is impossible).
- The work $W$ done per cycle by the heat engine does not change the entropy of the environment (this is the case when, for example, the work is used to lift a weight - a process that only changes the center of mass of the weight, and therefore causes no entropy change).

Figure (4.5) shows an ideal heat engine that fully transforms the heat $Q$ extracted from a thermal reservoir into work $W$, namely $Q = W$. Such an idle engine has a unity efficiency $\eta = 1$. Is it possible to realized such an idle engine? Such a process does not violate the law of energy conservation (first law of thermodynamics). However, as will be shown below, it violates the second law of thermodynamics. Note also that the opposite process, namely a process that transforms work into heat without losses is possible, as can be seen from the example seen in Fig. (4.6). In this system the weigh normally goes down, and consequently the blender rotates and heats the liquid in the container. In principle, the opposite process at which the weigh goes up and the liquid cools down doesn’t violate the law of energy conservation, however, it violates the second law (Perpetuum Mobile of the second kind), as will be shown below.

To show that the idle heat engine shown in Fig. (4.5) cannot be realized we employ the second law and require that the total change in entropy $\Delta \sigma$ per cycle is non-negative

$$\Delta \sigma \geq 0.$$  \hspace{1cm} (4.109)

The only change in entropy per cycle is due to the heat that is subtracted from the heat bath

$$\Delta \sigma = -\frac{Q}{\tau},$$  \hspace{1cm} (4.110)

thus since $Q = W$ (energy conservation) we find that
Fig. 4.5. An idle heat engine (*Perpetuum Mobile* of the second kind).

![Diagram of an idle heat engine](image1.png)

Fig. 4.6. Transforming work into heat.

![Diagram of work transformation](image2.png)

\[
\frac{W}{\tau} \leq 0 . \tag{4.111}
\]

Namely, the work done by the heat engine is non-positive \( W \leq 0 \). This result is known as Kelvin’s principle.

**Kelvin’s principle:** In a cycle process, it is impossible to extract heat from a heat reservoir and fully convert it into work.

As we will be shown below, Kelvin’s principle is equivalent to Clausius’s principle that states:
Clausius’s principle: It is impossible that at the end of a cycle process, heat has been transferred from a colder to a hotter thermal reservoirs without applying any work in the process.

A refrigerator and an air conditioner (in cooling mode) are examples of systems that transfer heat from a colder to a hotter thermal reservoirs. According to Clausius’s principle such systems require that work is consumed for their operation.

**Theorem 4.7.1.** Kelvin’s principle is equivalent to Clausius’s principle.

**Proof.** Assume that Clausius’s principle does not hold. Thus the system shown in Fig. 4.7(a) that transfers heat \(Q_0 > 0\) from a cold thermal reservoir at temperature \(\tau_l\) to a hotter one at temperature \(\tau_h > \tau_l\) is possible. In Fig. 4.7(b) a heat engine is added that extracts heat \(Q > Q_0\) from the hot thermal reservoir, delivers heat \(Q_0\) to the cold one, and performs work \(W = Q - Q_0\). The combination of both systems extracts heat \(Q - Q_0\) from the hot thermal reservoir and converts it all into work, in contradiction with Kelvin’s principle. Assume that Kelvin’s principle does not hold. Thus the system shown in Fig. 4.8(a) that extracts heat \(Q_0\) from a thermal reservoir at temperature \(\tau_h\) and converts it all into work is possible. In Fig. 4.8(b) a refrigerator is added that employs the work \(W = Q_0\) to remove heat \(Q\) from a colder thermal reservoir at temperature \(\tau_l < \tau_h\) and to deliver heat \(Q_0 + Q\) to the hot thermal reservoir. The combination of both systems transfers heat \(Q\) from a colder to a hotter thermal reservoirs without consuming any work in the process, in contradiction with Clausius’s principle.

As was shown above, unity efficiency is impossible. What is the largest possible efficiency of an heat engine?

**Theorem 4.7.2.** The efficiency \(\eta\) of a heat engine operating between a hotter and colder heat reservoirs at temperature \(\tau_h\) and \(\tau_l\) respectively can not exceed the value

\[
\eta_C = 1 - \frac{\tau_l}{\tau_h}.
\]  

(4.112)

**Proof.** A heat engine (labeled as ’I’) is seen in Fig. 4.9. A Carnot heat engine operated in the reverse direction (labeled as ’C’) is added. Here we exploit the fact the Carnot’s cycle is reversible. The efficiency \(\eta\) of the heat engine ’I’ is given by

\[
\eta_I = \frac{W}{Q_h},
\]  

(4.113)

whereas the efficiency of the reversed Carnot heat engine ’C’ is given by Eq. (4.108)

\[
\eta_C = \frac{W}{Q_h} = 1 - \frac{\tau_l}{\tau_h}.
\]  

(4.114)
Fig. 4.7. The assumption that Clausius’s principle does not hold.

For the combined system, the Clausius’s principle requires that
\[ Q'_h - Q_h > 0, \quad (4.115) \]
thus
\[ \eta_I \leq \eta_C = 1 - \frac{\tau_l}{\tau_h}. \]

The same argument that was employed in the proof above can be used to deduce the following corollary:

**Corollary 4.7.1.** All reversible heat engines operating between a hotter heat reservoir and a colder one at temperatures \( \tau_h \) and \( \tau_l \) respectively have the same efficiency.
4.8 Problems

1. The heat capacity at constant pressure is defined as

\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p \]  

(4.116)

Calculate \( c_p \) of an classical ideal gas having no internal degrees of freedom.

2. Show that
Fig. 4.9. Limit imposed upon engine efficiency.

\[
\left( \frac{\partial \sigma}{\partial V} \right)_T = \left( \frac{\partial p}{\partial \tau} \right)_V \tag{4.117}
\]

where \( \sigma \) is entropy, \( V \) is volume, and \( p \) is pressure.

3. Consider a classical ideal gas having internal partition function \( Z_{\text{int}} \).
   a) Show that the chemical potential \( \mu \) is given by

\[
\mu = \tau \left( \log \frac{n}{n_Q} - \log Z_{\text{int}} \right) \tag{4.118}
\]

where \( \tau \) is the temperature, \( n = N/V \), \( V \) is the volume, and \( n_Q \) is the quantum density.

b) Show that the energy \( U \) is related to the number of particles \( N \) by

\[
U = N \left( \frac{3\tau}{2} - \frac{\partial \log Z_{\text{int}}}{\partial \beta} \right) \tag{4.119}
\]

where \( \beta = 1/\tau \).

c) Show that the Helmholtz free energy \( F \) is given by

\[
F = N \tau \left( \log \frac{n}{n_Q} - \log Z_{\text{int}} - 1 \right) \tag{4.120}
\]

d) Show that the entropy \( \sigma \) is given by

\[
\sigma = N \left( \frac{5}{2} + \log \frac{n_Q}{n} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right) \tag{4.121}
\]
4.8. Problems

e) Show that the heat capacity at constant volume $c_V$ is given by

$$c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} \right), \quad (4.122)$$

f) Show that the heat capacity at constant pressure $c_p$ is given by

$$c_p = c_V + N. \quad (4.123)$$

4. The heat capacity $c$ of a body having entropy $\sigma$ is given by

$$c = \tau \frac{\partial \sigma}{\partial \tau}, \quad (4.124)$$

where $\tau$ is the temperature. Show that

$$c = \frac{\langle (\Delta U)^2 \rangle}{\tau^2}, \quad (4.125)$$

where $U$ is the energy of the body and where $\Delta U = U - \langle U \rangle$.

5. Consider an ideal classical gas made of diatomic molecules. The internal vibrational degree of freedom is described using a model of a one-dimensional harmonic oscillator with angular frequency $\omega$. That is, the eigen energies associated with the internal degree of freedom are given by

$$\varepsilon_n = \left( n + \frac{1}{2} \right) \hbar \omega, \quad (4.126)$$

where $n = 0, 1, 2, \ldots$. The system is in thermal equilibrium at temperature $\tau$, which is assumed to be much larger than $\hbar \omega$. Calculate the heat capacities $c_V$ and $c_p$.

6. A thermally isolated container is divided into two chambers, the first containing $N_A$ particles of classical ideal gas of type $A$, and the second one contains $N_B$ particles of classical ideal gas of type $B$. Both gases have no internal degrees of freedom. The volume of first chamber is $V_A$, and the volume of the second one is $V_B$. Both gases are initially in thermal equilibrium at temperature $\tau$. An opening is made in the wall separating the two chambers, allowing thus mixing of the two gases. Calculate the change in entropy during the process of mixing.

7. Consider an ideal gas of $N$ molecules in a vessel of volume $V$. Show that the probability $p_n$ to find $n$ molecules in a small volume $v$ (namely, $v \ll V$) contained in the vessel is given by

$$p_n = \frac{\lambda^n}{n!} e^{-\lambda}, \quad (4.127)$$

where $\lambda = Nv/V$. 
8. A lattice contains \( N \) sites, each occupied by a single atom. The set of eigenstates of each atom, when a magnetic field \( H \) is applied, contains 2 states having energies \( \varepsilon_- = -\mu_0 H \) and \( \varepsilon_+ = \mu_0 H \), where the magnetic moment \( \mu_0 \) is a constant. The system is in thermal equilibrium at temperature \( \tau \).

a) Calculate the magnetization of the system, which is defined by

\[
M = -\left( \frac{\partial F}{\partial H} \right)\tau,
\]

where \( F \) is the Helmholtz free energy.

b) Calculate the heat capacity

\[
C = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_H,
\]

where \( \sigma \) is the entropy of the system.

c) Consider the case where initially the magnetic field is \( H_1 \) and the temperature is \( \tau_1 \). The magnetic field is then varied slowly in an isentropic process from \( H_1 \) to \( H_2 \). Calculate the final temperature of the system \( \tau_2 \).

9. A lattice contains \( N \) sites, each occupied by a single atom. The set of eigenstates of each atom, when a magnetic field \( H \) is applied, contains 3 states with energies

\[
\varepsilon_{-1} = -\Delta - \mu_0 H, \\
\varepsilon_0 = 0, \\
\varepsilon_1 = -\Delta + \mu_0 H,
\]

where the magnetic moment \( \mu_0 \) is a constant. The system is in thermal equilibrium at temperature \( \tau \). Calculate the magnetic susceptibility

\[
\chi = \lim_{H \to 0} \frac{M}{H},
\]

where

\[
M = -\left( \frac{\partial F}{\partial H} \right)\tau,
\]

is the magnetization of the system, and where \( F \) is the Helmholtz free energy.

10. A lattice contains \( N \) sites, each occupied by a single atom. The set of eigenstates of each atom, when a magnetic field \( H \) is applied, contains \( 2J + 1 \) states with energies \( \varepsilon_m = -m\mu H \), where \( J \) is integer, \( m = -J, -J + 1, \ldots, J - 1, J \), and the magnetic moment \( \mu \) is a constant. The system is in thermal equilibrium at temperature \( \tau \).
4.8. Problems

a) Calculate the free energy $F$ of the system.

b) Show that the average magnetization, which is defined as

$$M = -\left(\frac{\partial F}{\partial H}\right)_\tau,$$

is given by

$$M = \frac{N\mu}{2}\left\{(2J + 1) \coth \left[\frac{(2J + 1)\mu H}{2\tau}\right] - \coth \left(\frac{\mu H}{2\tau}\right)\right\}. \quad (4.133)$$

11. Consider a system made of two localized spin 1/2 particles whose energy is given by

$$\varepsilon_{\sigma_1, \sigma_2} = -\mu_0 H (\sigma_1 + \sigma_2) + J\sigma_1\sigma_2,$$

where both $\sigma_1$ and $\sigma_2$ can take one of two possible values $\sigma_n = \pm 1 \ (n \in \{1, 2\})$. While $H$ is the externally applied magnetic field, $J$ is the coupling constant between both spins. The system is in thermal equilibrium at temperature $\tau$. Calculate the magnetic susceptibility

$$\chi = \lim_{H \to 0} \frac{\partial M}{\partial H}, \quad (4.135)$$

where

$$M = -\left(\frac{\partial F}{\partial H}\right)_\tau$$

is the magnetization of the system, and where $F$ is the Helmholtz free energy.

12. Assume the earth’s atmosphere is pure nitrogen in thermodynamic equilibrium at a temperature of 300 K. Calculate the height above sea level at which the density of the atmosphere is one-half its sea-level value (answer: 12.6 km).

13. Consider a box containing an ideal classical gas made of atoms of mass $M$ having no internal degrees of freedom at pressure $p$ and temperature $\tau$. The walls of the box have $N_0$ absorbing sites, each of which can absorb 0, 1, or 2 atoms of the gas. The energy of an unoccupied site and the energy of a site occupying one atom is zero. The energy of a site occupying two atoms is $\varepsilon$. Show that the mean number of absorbed atoms is given by

$$\langle N_a \rangle = N_0 \frac{\lambda + 2\lambda^2 e^{-\beta \varepsilon}}{1 + \lambda + \lambda^2 e^{-\beta \varepsilon}},$$

where $\beta = 1/\tau$ and

$$\lambda = \left(\frac{M}{2\pi \hbar^2}\right)^{-3/2} \tau^{-5/2} p.$$

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14. An ideal gas containing $N$ atoms is in equilibrium at temperature $\tau$. The internal degrees of freedom have two energy levels, the first one has energy zero and degeneracy $g_1$, and the second one energy $\varepsilon$ and degeneracy $g_2$. Show that the heat capacities at constant volume and at constant pressure are given by

$$c_V = N \left\{ \frac{3}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{\left[ g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right) \right]^2} \right\} ,$$  \hspace{1cm} (4.139) \\
$$c_p = N \left\{ \frac{5}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{\left[ g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right) \right]^2} \right\} .$$  \hspace{1cm} (4.140)

15. A classical gas is described by the following equation of state

$$p (V - b) = N \tau ,$$  \hspace{1cm} (4.141)

where $p$ is the pressure, $V$ is the volume, $\tau$ is the temperature, $N$ is the number of particles and $b$ is a constant.

a) Calculate the difference $c_p - c_V$ between the heat capacities at constant pressure and at constant volume.

b) Consider an isentropic expansion of the gas from volume $V_1$ and temperature $\tau_1$ to volume $V_2$ and temperature $\tau_2$. The number of particles $N$ is kept constant. Assume that $c_V$ is independent on temperature. Calculate the work $W$ done by the gas during this process.

16. A classical gas is described by the following equation of state

$$\left( p + \frac{a}{V^2} \right) (V - b) = N \tau ,$$  \hspace{1cm} (4.142)

where $p$ is the pressure, $V$ is the volume, $\tau$ is the temperature, and $a$ and $b$ are constants. Calculate the difference $c_p - c_V$ between the heat capacities at constant pressure and at constant volume.

17. A classical gas is described by the equation of state (4.142). The gas undergoes a reversible isothermal expansion at a fixed temperature $\tau_0$ from volume $V_1$ to volume $V_2$. Show that the work $W$ done by the gas in this process, and the heat $Q$ which is supplied to the gas during this process are given by

$$W = N \tau_0 \log \frac{V_2 - b}{V_1 - b} - a \frac{V_2 - V_1}{V_2 V_1} ,$$  \hspace{1cm} (4.143) \\
$$Q = \Delta U + W = N \tau_0 \log \frac{V_2 - b}{V_1 - b} .$$  \hspace{1cm} (4.144)

18. The energy of a classical ideal gas having no internal degrees of freedom is denoted as $E$, the deviation from the average value $U = \langle E \rangle$ as $\Delta E = E - U$. The gas, which contains $N$ particles and has volume is $V$, is in thermal equilibrium at temperature $\tau$. 

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Fig. 4.10. Engine cycle.

a) Calculate \( (\Delta E)^3 \).

b) Calculate \( (\Delta E)^3 \).

19. A body having a constant heat capacity \( C \) and a temperature \( \tau_a \) is put into contact with a thermal bath at temperature \( \tau_b \). Show that the total change in entropy after equilibrium is established is given by

\[
\Delta \sigma = C \left( \frac{\tau_a}{\tau_b} - 1 - \log \frac{\tau_a}{\tau_b} \right). \tag{4.145}
\]

Use this result to show that \( \Delta \sigma \geq 0 \).

20. Consider an engine based on the ideal gas cycle shown in Fig 4.10. In the first step \( a \rightarrow b \) the volume is kept constant at a value \( V_2 \). The second step \( b \rightarrow c \) is an isentropic process, and in the third one the pressure is kept constant at a value \( p_2 \). Assume that the heat capacities \( c_V \) and \( c_p \) are temperature independent. Show that the efficiency of this engine is given by

\[
\eta = 1 - \frac{\gamma p_2 (V_1 - V_2)}{V_2 (p_1 - p_2)}, \tag{4.146}
\]

where \( \gamma = c_p / c_V \).

21. Consider a refrigerator consuming work \( W \) per cycle to extract heat from a cold thermal bath at temperature \( \tau_l \) to another thermal bath at higher temperature \( \tau_h \). Let \( Q_l \) be the heat extracted from the cold bath per cycle and \( -Q_h \) the heat delivered to the hot one per cycle. The coefficient of refrigerator performance is defined as

\[
\gamma = \frac{Q_l}{W}. \tag{4.147}
\]
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Show that the second law of thermodynamics imposes an upper bound on $\gamma$

$$\gamma \leq \frac{\tau_l}{\tau_h - \tau_l}.$$  \hspace{1cm} (4.148)

22. A room air conditioner operates as a Carnot cycle refrigerator between an outside temperature $\tau_h$ and a room at a lower temperature $\tau_l$. The room gains heat from the outdoors at a rate $A(\tau_h - \tau_l)$; this heat is removed by the air conditioner. The power supplied to the cooling unit is $P$. Calculate the steady state temperature of the room.

23. The state equation of a given matter is

$$p = \frac{A\tau^3}{V},$$  \hspace{1cm} (4.149)

where $p$, $V$ and $\tau$ are the pressure, volume and temperature, respectively, $A$ is a constant. The internal energy of the matter is written as

$$U = B\tau^n \log \frac{V}{V_0} + f(\tau),$$  \hspace{1cm} (4.150)

where $B$ and $V_0$ are constants, $f(\tau)$ only depends on the temperature. Find $B$ and $n$.

24. The state equation of a given matter is

$$p = \frac{A\tau^n}{V},$$  \hspace{1cm} (4.151)

where $p$, $V$ and $\tau$ are the pressure, volume and temperature, respectively, and $A$ and $n$ are both constants. Calculate the difference $c_p - c_V$ between the heat capacities at constant pressure and at constant volume.

25. An ideal classical gas is made of $N$ identical molecules each having mass $M$. The volume of the gas is $V$ and the temperature is $\tau$. The energy spectrum due to internal degrees of freedom of each molecule has a ground state, which is nondegenerate state (singlet state), and a first excited energy state, which has degeneracy 3 (triplet state). The energy gap between the ground state and the first excited state is $\Delta$ and all other states have a much higher energy. Calculate:
a) the heat capacity at constant volume $c_V$.
b) the heat capacity at constant pressure $c_p$.

26. Two identical bodies have internal energy $U = C\tau$, with a constant heat capacity $C$. The initial temperature of the first body is $\tau_1$ and that of the second one is $\tau_2$. The two bodies are used to produce work by connecting them to a reversible heat engine and bringing them to a common final temperature $\tau_f$.
a) Calculate $\tau_f$. 

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Fig. 4.11. Engine reversible cycle.

b) Calculate the total work $W$, which is delivered by the process.

27. An ideal classical gas having no internal degrees of freedom is contained in a vessel having two parts separated by a partition. Each part contains the same number of molecules, however, while the pressure in the first one is $p_1$, the pressure in the second one is $p_2$. The system is initially in thermal equilibrium at temperature $\tau$. Calculate the change of entropy caused by a fast removal of the partition.

28. Consider a mixture of two classical ideal gases, consisting of $N_A$ particles of type A and $N_B$ particles of type B. The heat capacities $c_{p,A}$ and $c_{V,A}$ ($c_{p,B}$ and $c_{V,B}$) at constant pressure and at constant volume respectively of gas A (B) are assumed to be temperature independent. The volume of the mixture is initially $V_1$ and the pressure is initially $p_1$. The mixture undergoes an adiabatic (slow) and isentropic (at a constant entropy) process leading to a final volume $V_2$. Calculate the final pressure $p_2$.

29. A classical ideal gas contains $N$ particles having mass $M$ and no internal degrees of freedom is in a vessel of volume $V$ at temperature $\tau$. Express the canonical partition function $Z_c$ as a function of $N$, $M$, $V$ and $\tau$.

30. Consider an engine working in a reversible cycle and using an ideal classical gas as the working substance. The cycle consists of two processes at constant pressure ($a \rightarrow b$ and $c \rightarrow d$), joined by two isentropic processes ($b \rightarrow c$ and $d \rightarrow a$), as show in Fig. 4.11. Assume that the heat capacities $c_V$ and $c_p$ are temperature independent. Calculate the efficiency of this engine.

31. Consider an engine working in a cycle and using an ideal classical gas as the working substance. The cycle consists of two isochoric processes (constant volume) $a \rightarrow b$ at volume $V_1$ and $c \rightarrow d$ at volume $V_2$, joined by two isentropic processes (constant entropy) $b \rightarrow c$ and $d \rightarrow a$, as shown in Fig. 4.12. Assume that the heat capacities $c_V$ and $c_p$ are temperature independent. Calculate the efficiency $\eta$ of this engine.
32. Consider two vessels A and B each containing ideal classical gas of particles having no internal degrees of freedom. The pressure and number of particles in both vessels are $p$ and $N$ respectively, and the temperature is $\tau_A$ in vessel A and $\tau_B$ in vessel B. The two vessels are brought into thermal contact. No heat is exchanged with the environment during this process. Moreover, the pressure is kept constant at the value $p$ in both vessels during this process. Find the change in the total entropy $\Delta \sigma = \sigma_{\text{final}} - \sigma_{\text{initial}}$.

4.9 Solutions

1. The entropy is given by

$$\sigma = N \left\{ \log \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} \frac{V^3}{N} + \frac{5}{2} \right\},$$

or using $pV = N\tau$

$$\sigma = N \left\{ \log \left( \frac{M}{2\pi \hbar^2} \right)^{3/2} \frac{\tau^{5/2}}{p} + \frac{5}{2} \right\},$$

(4.152)  

(4.153)
thus
\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p = \frac{5}{2} N . \] (4.154)

2. Since
\[ \frac{\partial^2 F}{\partial V \partial \tau} = \frac{\partial^2 F}{\partial \tau \partial V} , \] (4.155)
where \( F \) is Helmholtz free energy, one has
\[ \left( \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial \tau} \right)_V \right)_\tau = \left( \frac{\partial}{\partial \tau} \left( \frac{\partial F}{\partial V} \right)_\tau \right)_V . \] (4.156)

By definition
\[ \left( \frac{\partial F}{\partial V} \right)_\tau = -p . \]

Moreover, using \( F = U - \tau \sigma \) one finds that
\[ \left( \frac{\partial F}{\partial \tau} \right)_V = \left( \frac{\partial U}{\partial \tau} \right)_V - \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V - \sigma \]
\[ = \left( \frac{\partial U}{\partial \tau} \right)_V - \left( \frac{\partial U}{\partial \sigma} \right)_V \left( \frac{\partial \sigma}{\partial \tau} \right)_V - \sigma \]
\[ = -\sigma , \] (4.157)

thus
\[ \left( \frac{\partial \sigma}{\partial V} \right)_\tau = \left( \frac{\partial p}{\partial \tau} \right)_V . \] (4.158)

3. Recall that
\[ n_Q = \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2} , \] (4.159)
\[ \eta = -\frac{\mu}{\tau} , \] (4.160)
\[ \log Z_{gc} = e^{-\eta Z_{int}} V n_Q , \] (4.161)
\[ U = \left( \frac{3\tau}{2} - \frac{\partial \log Z_{int}}{\partial \beta} \right) \log Z_{gc} , \] (4.162)
\[ N = \log Z_{gc} . \] (4.163)

a) Using Eqs. (4.161) and (4.163) one finds that
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\[ \log \frac{n}{nQ}Z_{\text{int}} = \frac{\mu}{\tau}, \]  

(4.164)

thus

\[ \mu = \tau \left( \log \frac{n}{nQ} - \log Z_{\text{int}} \right). \]  

(4.165)

b) Using Eqs. (4.162) and (4.163) one finds that

\[ U = N \left( \frac{3\tau}{2} - \frac{\partial \log Z_{\text{int}}}{\partial \beta} \right). \]  

(4.166)

c) Using the relations

\[ F = U - \tau \sigma, \]  

(4.167)

\[ \sigma = \log Z_{\text{gc}} + \beta U + \eta N, \]  

(4.168)

one obtains

\[ F = U - \tau \sigma \]
\[ = N\tau (-\eta - 1) \]  

(4.170)

\[ = N\tau \left( \frac{\mu}{\tau} - 1 \right) \]  

(4.171)

\[ = N\tau \left( \log \frac{n}{nQ} - \log Z_{\text{int}} - 1 \right). \]  

(4.172)

d) Using the relation

\[ \sigma = - \left( \frac{\partial F}{\partial \tau} \right)_V, \]  

(4.174)

one obtains

\[ \sigma = - \left( \frac{\partial F}{\partial \tau} \right)_V \]
\[ = N \left( - \left( \frac{\partial \left( \tau \log \frac{n}{nQ} \right)}{\partial \tau} \right)_V + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \right) \]
\[ = N \left( -\tau \left( \frac{\partial \left( \log \frac{n}{nQ} \right)}{\partial \tau} \right)_V - \log \frac{n}{nQ} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \right) \]
\[ = N \left( \frac{3}{2} - \log \frac{n}{nQ} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \right) \]
\[ = N \left( \frac{5}{2} + \log \frac{nQ}{n} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right) . \]  

(4.175)
4.9. Solutions

e) By definition
\[
c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{int})}{\partial \tau^2} \right) .
\]
(4.176)

f) The following holds
\[
c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V + \tau \left( \frac{\partial V}{\partial \tau} \right)_p
\]
\[= c_V + \tau \left( \frac{\partial V}{\partial \tau} \right)_p ,
\]
hence [recall that $V_p = N\tau$ and see Eq. (4.175)]
\[c_p = c_V + \tau \frac{N}{V} \frac{N}{p} = c_V + N .
\]
(4.178)

4. With the help of Eqs. (3.52), (3.31) and (3.32) together with the following relation
\[\frac{\partial}{\partial \tau} = - \frac{1}{\tau^2} \frac{\partial}{\partial \beta} ,
\]
(4.179)
one finds that
\[c = \tau \frac{\partial \sigma}{\partial \tau} = \frac{\partial U}{\partial \tau} = - \frac{1}{\tau^2} \frac{\partial U}{\partial \beta} = \frac{\langle (\Delta U)^2 \rangle}{\tau^2} .
\]
(4.180)

5. The internal partition function is given by
\[Z_{int} = \frac{1}{2 \sinh \frac{h \omega}{2\pi}} \approx \frac{\tau}{\hbar \omega} ,
\]
(4.181)
thus using Eqs. (4.176) and (4.178) one finds that
\[c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{int})}{\partial \tau^2} \right) = \frac{5N}{2} ,
\]
(4.182)
\[c_p = \frac{7N}{2} .
\]
(4.183)
6. Energy conservation requires that the temperature of the mixture will remain \( \tau \). The entropy of an ideal gas of density \( n \), which contains \( N \) particles, is given by

\[
\sigma (N, n) = N \left( \log \frac{nQ}{n} + \frac{5}{2} \right)
\]

thus the change in entropy is given by

\[
\Delta \sigma = \sigma_{\text{mix}} - \sigma_A - \sigma_B
\]

\[
= \sigma \left( N_A, \frac{N_A}{V_A + V_B} \right) + \sigma \left( N_B, \frac{N_B}{V_A + V_B} \right) - \sigma \left( N_A, \frac{N_A}{V_A} \right) - \sigma \left( N_B, \frac{N_B}{V_B} \right)
\]

\[
= N_A \log \frac{V_A + V_B}{V_A} + N_B \log \frac{V_A + V_B}{V_B}.
\]

(4.184)

7. The probability to find a molecule in the volume \( v \) is given by \( p = v/V \), thus, \( p_n \) is given by

\[
p_n = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}.
\]

(4.185)

In the macroscopic limit \( p_n \) becomes [see Eq. (1.103)]

\[
p_n = \frac{\lambda^n}{n!} e^{-\lambda},
\]

(4.186)

where \( \lambda = Nv/V \).

8. The partition function of a single atom is given by

\[
Z_1 = \exp (\mu_0 H \beta) + \exp (-\mu_0 H \beta) = 2 \cosh (\mu_0 H \beta),
\]

(4.187)

where \( \beta = 1/\tau \), thus the partition function of the entire system is

\[
Z = (2 \cosh (\mu_0 H \beta))^N.
\]

(4.188)

a) The free energy \( F \) is given by

\[
F = -\tau \log Z = -N \tau \log (2 \cosh (\mu_0 H \beta)),
\]

(4.189)

and the magnetization \( M \) is given by

\[
M = -\left( \frac{\partial F}{\partial H} \right)_{\tau} = N \mu_0 \tanh (\mu_0 H \beta).
\]

(4.190)

b) The energy \( U \) is given by

\[
U = -\frac{\partial \log Z}{\partial \beta} = -N \mu_0 H \tanh (\mu_0 H \beta),
\]

(4.191)
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thus
\[ C = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_H \]
\[ = \left( \frac{\partial U}{\partial \tau} \right)_H \]
\[ = -N\mu_0 H \left( \frac{\partial \tanh \frac{\mu_0 H}{\tau}}{\partial \tau} \right)_H \]
\[ = N \left( \frac{\mu_0 H}{\tau} \cosh \frac{\mu_0 H}{\tau} \right)^2. \]

\[ (4.192) \]

c) The entropy \( \sigma \), which is given by
\[ \sigma = \beta (U - F) \]
\[ = N \left[ \log \left( 2 \cosh \frac{\mu_0 H}{\tau} \right) - \frac{\mu_0 H}{\tau} \tanh \frac{\mu_0 H}{\tau} \right], \]
and which remains constant, is a function of the ratio \( H/\tau \), therefore
\[ \tau_2 = \tau_1 \frac{H_2}{H_1}. \]

\[ (4.193) \]

9. The partition function of a single atom is given by
\[ Z = \sum_{m=-1}^{1} \exp \left( -\beta \varepsilon_m \right) \]
\[ = 1 + 2 \exp (\beta \Delta) \cosh (\beta \mu_0 H), \]
\[ (4.195) \]

where \( \beta = 1/\tau \). The free energy is given by
\[ F = -N \tau \log Z, \]
\[ (4.196) \]

thus the magnetization is given by
\[ M = -\left( \frac{\partial F}{\partial H} \right)_\tau \]
\[ = \frac{2N\mu_0 \exp (\beta \Delta) \sinh (\beta \mu_0 H)}{1 + 2 \exp (\beta \Delta) \cosh (\beta \mu_0 H)}, \]
\[ (4.197) \]

and the magnetic susceptibility is given by
\[ \chi = \frac{N\mu_0^2}{\tau \left( 1 + \frac{1}{2} \exp (-\beta \Delta) \right)}. \]
\[ (4.198) \]
10. The partition function of a single atom is given by

\[ Z = \sum_{m=-J}^{J} \exp (m\mu H\beta) , \]  

(4.199)

where \( \beta = 1/\tau \). By multiplying by a factor \( \sinh (\mu H/2) \) one finds that

\[ \sinh \left( \frac{\mu H}{2} \right) Z = \frac{1}{2} \left[ \exp \left( \frac{\mu H}{2} \right) - \exp \left( -\frac{\mu H}{2} \right) \right] \sum_{m=-J}^{J} \exp (m\mu H\beta) \]

\[ = \frac{1}{2} \left[ \exp \left( (J + \frac{1}{2}) \mu H \beta \right) - \exp \left[ -(J + \frac{1}{2}) \mu H \beta \right] \right] , \]

(4.200)

thus

\[ Z = \frac{\sinh \left( (J + \frac{1}{2}) \mu H \beta \right)}{\sinh \left( \frac{\mu H}{2} \right)} . \]

(4.201)

a) The free energy is given by

\[ F = -N\tau \log Z = -N\tau \log \left[ \frac{\sinh \left( (J + \frac{1}{2}) \mu H \beta \right)}{\sinh \left( \frac{\mu H}{2} \right)} \right] . \]

(4.202)

b) The magnetization is given by

\[ M = -\left( \frac{\partial F}{\partial H} \right)_{\tau} = \frac{N\mu}{2} \left\{ (2J + 1) \coth \left( \frac{(2J + 1) \mu H}{2\tau} \right) - \coth \left( \frac{\mu H}{2\tau} \right) \right\} . \]

(4.203)

11. The partition function is given by

\[ Z = \sum_{\sigma_1, \sigma_2 = \pm 1} \exp (-\beta \varepsilon_{\sigma_1, \sigma_2}) \]

\[ = \exp (-\beta J) \left[ \exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H) \right] + 2 \exp (\beta J) , \]

(4.204)

where \( \beta = 1/\tau \). The free energy is given by

\[ F = -\tau \log Z , \]

(4.205)

thus the magnetization is given by

\[ M = -\left( \frac{\partial F}{\partial H} \right)_{\tau} \]

\[ = \frac{2\mu_0 \exp (-\beta J) \left[ -\exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H) \right]}{\exp (-\beta J) \left[ \exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H) \right] + 2 \exp (\beta J)} , \]

(4.206)
and the magnetic susceptibility is given by

$$\chi = \frac{4\beta \mu_0^2}{1 + e^{2\beta J}}. \quad (4.207)$$

Note that in the high temperature limit $\beta J \ll 1$

$$\chi \simeq \frac{2\mu_0^2}{\tau + J}. \quad (4.208)$$

12. The internal chemical potential $\mu_g$ is given by Eq. (4.118). In thermal equilibrium, the total chemical potential $\mu_{tot} = \mu_g + mgz$ is $z$ independent ($m$ is the mass of each diatomic molecule $N_2$, $g$ is the gravity acceleration constant, and $z$ is the height). Thus, the density $n(z)$ as a function of height above see level $z$ is given by

$$n(z) = n(0) \exp \left( \frac{mgz}{k_B T} \right). \quad (4.209)$$

The condition $n(z) = 0.5 \times n(0)$ yields

$$z = \frac{k_B T \ln 2}{mg} = \frac{1.3806568 \times 10^{-23} \text{JK}^{-1} \times 300 \text{K} \times \ln 2}{14 \times 1.6605402 \times 10^{-27} \text{kg} \times 9.8 \text{ms}^{-2}} = 12.6 \text{km}. \quad (4.210)$$

13. The Helmholtz free energy of an ideal gas of $N$ particles is given by

$$F = -\tau N \log \left[ \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} V \right] + \tau N \log N - \tau N, \quad (4.211)$$

thus the chemical potential is

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau,V} = -\tau \log \left( \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} V \right) + \tau \log N, \quad (4.212)$$

and the pressure is

$$p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,V} = \frac{N\tau}{V}. \quad (4.213)$$

Using these results the fugacity $\lambda = \exp(\beta \mu)$ can be expressed in terms of $p$ as

$$\lambda = e^{\beta \mu} = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{-3/2} \frac{N}{V} = \left( \frac{M}{2\pi \hbar^2} \right)^{-3/2} \tau^{-5/2} p. \quad (4.214)$$

At equilibrium the fugacity of the gas and that of the system of absorbing sites is the same. The grand canonical partition function of a single absorption site is given by
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\[ Z = 1 + e^{\beta \mu} + e^{\beta (2 \mu - \epsilon)} , \]  
\hspace{1cm} (4.215)

or in terms of the fugacity \( \lambda = \exp(\beta \mu) \)

\[ Z = 1 + \lambda + \lambda^2 e^{-\beta \epsilon} , \]  
\hspace{1cm} (4.216)

thus

\[ \langle N_a \rangle = N_0 \lambda \frac{\partial \log Z}{\partial \lambda} = N_0 \frac{\lambda + 2 \lambda^2 e^{-\beta \epsilon}}{1 + \lambda + \lambda^2 e^{-\beta \epsilon}} , \]  
\hspace{1cm} (4.217)

where \( \lambda \) is given by Eq. (4.214).

14. The internal partition function is given by

\[ Z_{\text{int}} = g_1 + g_2 \exp \left( -\frac{\epsilon}{\tau} \right) . \]  
\hspace{1cm} (4.218)

Using Eq. (4.122) one finds that

\[ c_V = \frac{3}{2} N + N \tau \left[ \frac{\partial^2}{\partial \tau^2} (\tau \log Z_{\text{int}}) \right]_V \]
\[ = N \left\{ \frac{3}{2} + \left( \frac{\epsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\epsilon}{\tau} \right)}{\left[ g_1 + g_2 \exp \left( -\frac{\epsilon}{\tau} \right) \right]^2} \right\} , \]  
\hspace{1cm} (4.219)

and using Eq. (4.123) one obtains

\[ c_p = N \left\{ \frac{5}{2} + \left( \frac{\epsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\epsilon}{\tau} \right)}{\left[ g_1 + g_2 \exp \left( -\frac{\epsilon}{\tau} \right) \right]^2} \right\} . \]  
\hspace{1cm} (4.220)

15. Using Maxwell’s relation

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N} , \]  
\hspace{1cm} (4.221)

and the equation of state one finds that

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \frac{N}{V - b} . \]  
\hspace{1cm} (4.222)

a) Using the definitions

\[ c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{V,N} , \]  
\hspace{1cm} (4.223)

\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{p,N} , \]  
\hspace{1cm} (4.224)
and the general identity

\[
\left( \frac{\partial z}{\partial x} \right)_\alpha = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_\alpha,
\]

one finds that

\[
c_p - c_V = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N},
\]

or [see Eqs. (4.141) and (4.222)]

\[
c_p - c_V = N \frac{N\tau}{p(V-b)} = N.
\]

b) Using the identity

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \left( \frac{\partial U}{\partial \sigma} \right)_{V,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N},
\]

together with Eq. (4.222) one finds that

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = -p + \frac{N\tau}{V-b} = 0.
\]

Thus, the energy \( U \) is independent on the volume \( V \) (it can be expressed as a function of \( \tau \) and \( N \) only), and therefore for processes for which \( dN = 0 \) the change in energy \( dU \) can be expressed as

\[
dU = c_V d\tau.
\]

For an isentropic process no heat is exchanged, and therefore \( dW = -dU \), thus since \( c_V \) is independent on temperature one has

\[
W = -\Delta U = -c_V (\tau_2 - \tau_1).
\]

16. Using the definitions

\[
c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{V,N},
\]

\[
c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{p,N},
\]

and the general identity

\[
\left( \frac{\partial z}{\partial x} \right)_\alpha = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_\alpha,
\]
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one finds that

\[ c_p - c_V = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N}. \quad (4.235) \]

Using Maxwell’s relation

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N}, \quad (4.236) \]

and the equation of state (4.142) one finds that

\[
c_p - c_V = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N}
= \frac{\tau}{N \left( V - b \right)} \left( \frac{-aV + 2ab + pV^3}{NV^3} \right)
= \frac{N}{1 + \frac{2aV + 2ab}{V^3 (b + \frac{a}{\tau})}}, \]

or

\[ c_p - c_V = \frac{N}{1 - \frac{2a(1 - \frac{b}{V})^2}{V^2 N \tau}}. \quad (4.238) \]

17. The work \( W \) is given by

\[ W = \int_{V_1}^{V_2} pdV. \quad (4.239) \]

Using the equation of state (4.142) one finds that

\[
W = \int_{V_1}^{V_2} \left( \frac{N\tau_0}{V - b} - \frac{a}{V^2} \right) dV = N\tau_0 \log \frac{V_2 - b}{V_1 - b} - \frac{aV_2 - V_1}{V_2 V_1}. \quad (4.240)
\]

Using the identity

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial \sigma} \right)_{\sigma,N} + \left( \frac{\partial U}{\partial \sigma} \right)_{V,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = -p + \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N}, \quad (4.241)
\]

and Maxwell’s relation

\[
\left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N}, \quad (4.242)
\]
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one finds that

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} - p. \tag{4.243}
\]

For the present case

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \frac{N \tau}{V - b} - p = \frac{a}{V^2}, \tag{4.244}
\]

thus

\[
\Delta U = \int_{V_1}^{V_2} \left( \frac{\partial U}{\partial V} \right)_{\tau,N} dV = a \int_{V_1}^{V_2} \frac{dV}{V^2} = a \frac{V_2 - V_1}{V_2 V_1}, \tag{4.245}
\]

hence

\[
Q = \Delta U + W = N \tau_0 \log \frac{V_2 - b}{V_1 - b}. \tag{4.246}
\]

18. In general the following holds

\[
\langle E^n \rangle = \frac{1}{Z_{gc}} \left( - \frac{\partial^n Z_{gc}}{\partial \beta^n} \right)_\eta, \tag{4.247}
\]

and

\[
U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta. \tag{4.248}
\]

Thus the variance is given by

\[
\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2
\]

\[
= \frac{1}{Z_{gc}} \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_\eta - \frac{1}{Z_{gc}^2} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta^2
\]

\[
= \left( \frac{\partial^2 \log Z_{gc}}{\partial \beta^2} \right)_\eta. \tag{4.249}
\]

Furthermore, the following holds:
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\[ \langle (\Delta E)^3 \rangle = \langle E^3 - 3E^2U + 3EU^2 - U^3 \rangle \]
\[ = \langle E^3 \rangle - 3U \langle E^2 \rangle + 2U^3 \]
\[ = - \left[ \frac{1}{Z_{gc}} \left( \frac{\partial^3 Z_{gc}}{\partial \beta^3} \right)_\eta - \frac{3}{Z_{gc}^2} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_\eta + \frac{2}{Z_{gc}^3} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta \right]^3 \]
\[ = - \frac{\partial}{\partial \beta} \left[ \frac{1}{Z_{gc}} \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_\eta - \frac{1}{Z_{gc}^2} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta^2 \right] \]
\[ = - \left( \frac{\partial^3 \log Z_{gc}}{\partial \beta^3} \right)_\eta. \]
(4.250)

For classical gas having no internal degrees of freedom one has

\[ N = \log Z_{gc} = e^{-\eta}V \left( \frac{M}{2\pi \hbar^2 \beta} \right)^{3/2}, \]
(4.251)

thus

\[ U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \frac{3N\tau}{2}. \]
(4.252)

a) Using Eq. (4.249) one finds that

\[ \langle (\Delta E)^2 \rangle = - \frac{\partial}{\partial \beta} \left[ \frac{3N}{2\beta^2} \right] = \frac{2U^2}{3N}. \]
(4.253)

b) Using Eq. (4.250) one obtains

\[ \langle (\Delta E)^3 \rangle = - \frac{\partial}{\partial \beta} \left[ \frac{3N}{2\beta^2} \right] = \frac{8U^3}{9N^2}. \]
(4.254)

19. The entropy change of the body \( \Delta \sigma_1 \) is given by

\[ \Delta \sigma_1 = C \int_{\tau_a}^{\tau_b} \frac{d\tau}{\tau} = C \log \frac{\tau_b}{\tau_a}, \]
(4.255)

and that of the bath \( \Delta \sigma_2 \) is given by

\[ \Delta \sigma_2 = \frac{\Delta Q}{\tau_b} = \frac{C (\tau_a - \tau_b)}{\tau_b}, \]
(4.256)

thus

\[ \Delta \sigma = C \left( \frac{\tau_a}{\tau_b} - 1 - \log \frac{\tau_a}{\tau_b} \right). \]
(4.257)

The function \( f(x) = x - 1 - \log x \) in the range \( 0 < x < \infty \) satisfy

\( f(x) \geq 0 \), where \( f(x) > 0 \) unless \( x = 1 \).

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20. The efficiency is given by

\[ \eta = 1 + \frac{Q_l}{Q_h} = 1 + \frac{Q_{ca}}{Q_{ab}} = 1 + \frac{c_p (\tau_a - \tau_c)}{c_V (\tau_b - \tau_a)} = 1 - \gamma \frac{p_2 (V_1 - V_2)}{V_2 (p_1 - p_2)}, \]  

(4.258)

where \( \gamma = \frac{c_p}{c_V}. \)

21. Energy conservation requires that \( W = Q_l + Q_h. \) Consider a Carnot heat engine operating between the same thermal baths producing work \( W \) per cycle. The Carnot engine consumes heat \( Q'_h \) from the hot bath per cycle and delivered \(-Q'_l\) heat to the cold one per cycle, where \( W = Q'_l + Q'_h \) and

\[ \eta_c = \frac{W}{Q'_h} = 1 - \frac{\tau_l}{\tau_h}. \]  

(4.259)

According to Clausius principle

\[ Q_l + Q'_l \leq 0, \]  

(4.260)

thus

\[ \gamma = \frac{Q_l}{W} \leq \frac{Q'_l}{W} = \frac{Q'_h - W}{W} = \frac{\tau_h}{\tau_h - \tau_l} - 1 = \frac{\tau_l}{\tau_h - \tau_l}. \]  

(4.261)

22. Using Eq. (4.261) one finds that

\[ \frac{A (\tau_h - \tau_l)}{P} = \frac{\tau_l}{\tau_h - \tau_l}, \]  

(4.262)

thus

\[ \tau_l^2 - 2\tau_l \left( \tau_h + \frac{P}{2A} \right) + \tau_h^2 = 0, \]  

(4.263)

or

\[ \tau_l = \tau_h + \frac{P}{2A} \pm \sqrt{\left( \tau_h + \frac{P}{2A} \right)^2 - \tau_h^2}. \]  

(4.264)

The solution for which \( \tau_l \leq \tau_h \) is given by

\[ \tau_l = \tau_h + \frac{P}{2A} - \sqrt{\left( \tau_h + \frac{P}{2A} \right)^2 - \tau_h^2}. \]  

(4.265)

23. Using Eq. (4.241) one finds that

\[ \left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} - p, \]  

(4.266)
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thus
\[ \frac{B \tau^n}{V} = \frac{3A \tau^3}{V} - p = \frac{2A \tau^3}{V}, \] (4.267)

therefore
\[ B = 2A, \quad n = 3. \] (4.268)

24. Using Eq. (4.237), which is given by
\[
c_p - c_V = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N},
\] (4.270)
on one finds that
\[
c_p - c_V = \frac{A^2 \tau}{\tau} n^2 \tau^{2(n-1)} = n^2 A \tau^{n-1}. \] (4.271)

25. In general the following holds
\[
c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} \right), \] (4.272)
\[
c_p = c_V + N, \] (4.273)

where for the current case
\[ Z_{\text{int}} = 1 + 3 \exp \left( -\frac{A}{\tau} \right), \] (4.274)

thus
a) \( c_V \) is given by
\[
c_V = N \left( \frac{3}{2} + \frac{3 \left( \frac{A}{\tau} \right)^2 e^{-\frac{A}{\tau}}}{1 + 3 e^{-\frac{A}{\tau}}} \right), \] (4.275)

b) and \( c_p \) is given by
\[
c_p = N \left( \frac{5}{2} + \frac{3 \left( \frac{A}{\tau} \right)^2 e^{-\frac{A}{\tau}}}{1 + 3 e^{-\frac{A}{\tau}}} \right). \] (4.276)

26. Consider an infinitesimal change in the temperatures of both bodies \( d\tau_1 \) and \( d\tau_2 \). The total change in entropy associated with the reversible process employed by the heat engine vanishes, thus
\[ 0 = d\sigma = d\sigma_1 + d\sigma_2 = \frac{dQ_1}{\tau_1} + \frac{dQ_2}{\tau_2} = C \left( \frac{d\tau_1}{\tau_1} + \frac{d\tau_2}{\tau_2} \right). \] (4.277)
4.9. Solutions

a) By integration the equation

\[ \frac{d\tau_1}{\tau_1} = - \frac{d\tau_2}{\tau_2}, \tag{4.278} \]

one finds

\[ \int_{\tau_1}^{\tau_f} \frac{d\tau_1}{\tau_1} = - \int_{\tau_2}^{\tau_f} \frac{d\tau_2}{\tau_2}, \tag{4.279} \]

or

\[ \log \frac{\tau_f}{\tau_1} = \log \frac{\tau_2}{\tau_f}, \tag{4.280} \]

thus

\[ \tau_f = \sqrt{\tau_1 \tau_2}. \tag{4.281} \]

b) Energy conservation law yields

\[ W = \Delta U_1 + \Delta U_2 = C (\tau_1 - \tau_f) + C (\tau_2 - \tau_f) = C (\sqrt{\tau_1} - \sqrt{\tau_2})^2. \tag{4.282} \]

27. Energy conservation requires that the temperature of the mixture will remain \( \tau \). The entropy of an ideal gas of density \( n \), which contains \( N \) particles, is given by

\[ \sigma (N, n) = N \left( \log \frac{nQ}{n} + \frac{5}{2} \right), \tag{4.283} \]

where

\[ nQ = \left( \frac{M\tau}{2\pi\hbar^2} \right)^{3/2}, \tag{4.284} \]

\[ n = \frac{N}{V}. \tag{4.285} \]

Using the relation

\[ pV = N\tau, \tag{4.286} \]

one finds that the final pressure of the gas after the partition has been removed and the system has reached thermal equilibrium is given by

\[ p_{\text{final}} = \frac{2p_1p_2}{p_1 + p_2}. \tag{4.287} \]

Thus, the change in entropy is given by
\begin{align*}
\Delta \sigma &= \sigma_{\text{final}} - \sigma_1 - \sigma_2 \\
&= 2N \left( \log \left( \frac{p_1 + p_2}{2p_1p_2} \right) + \frac{5}{2} \right) - N \left( \log \frac{\tau nQ}{p_1} + \frac{5}{2} \right) - N \left( \log \frac{\tau nQ}{p_2} + \frac{5}{2} \right) \\
&= N \log \left( \frac{(p_1 + p_2)^2}{4p_1p_2} \right).
\end{align*}
(4.288)

28. First, consider the case of an ideal gas made of a \textit{unique} type of particles. Recall that the entropy \(\sigma\), \(c_V\) and \(c_p\) are given by [see Eqs. (4.121), (4.122) and (4.123)]

\begin{align*}
\sigma &= N \left( \frac{5}{2} + \log \frac{nQ}{n} + \frac{\partial}{\partial \tau} \left( \tau \log Z_{\text{int}} \right) \right), \\
&= N \left( \frac{5}{2} + h_{\text{int}} \right), \\
c_V &= c_V + N, \quad c_p = c_V + N, \\
&\text{where } n = N/V \text{ is the density,} \\
n_Q &= \left( \frac{M\tau}{2\pi \hbar^2} \right)^{3/2}.
\end{align*}
(4.292)

is the quantum density, \(M\) is the mass of a particle in the gas, and

\[ h_{\text{int}} = \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} = \frac{c_V}{N} - \frac{3}{2}. \]
(4.293)

The requirement that \(h_{\text{int}}\) is temperature independent leads to

\[ \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} = g_{\text{int}} + h_{\text{int}} \log \frac{\tau}{\tau_0}, \]
(4.294)

where both \(g_{\text{int}}\) and \(\tau_0\) are constants. Using this notation, the change in entropy due to a change in \(V\) from \(V_1\) to \(V_2\) and a change in \(\tau\) from \(\tau_1\) to \(\tau_2\) is given by

\begin{align*}
\Delta \sigma &= \sigma_2 - \sigma_1 = N \left( \log \frac{V_2\tau_2^{3/2}}{V_1\tau_1^{3/2}} + \left( \frac{c_V}{N} - \frac{3}{2} \right) \log \frac{\tau_2}{\tau_1} \right) \\
&= N \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{3}{2}} \right).
\end{align*}
(4.295)

Thus the total change in the entropy of the mixture is given by
\[ \Delta \sigma = \Delta \sigma_A + \Delta \sigma_B \]
\[ \Delta \sigma = N_A \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V, A}}{N_A}} \right) + N_B \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V, B}}{N_B}} \right) \]
\[ \Delta \sigma = (N_A + N_B) \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} \right) \]

and the requirement \( \Delta \sigma = 0 \) leads to
\[ \left( \frac{V_2}{V_1} \right) \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} = 1. \]

Alternatively, by employing the equation of state
\[ pV = N \tau, \]
this can be rewritten as
\[ \left( \frac{V_2}{V_1} \right) \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} \left( \frac{p_2}{p_1} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} = 1, \]
or with the help of Eq. (4.291) as
\[ p_2 = p_1 \left( \frac{V_2}{V_1} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} \left( 1 + \frac{c_{V, A} + c_{V, B}}{N_A + N_B} \right) \]
\[ p_1 \left( \frac{V_1}{V_2} \right)^{\frac{c_{V, A} + c_{V, B}}{N_A + N_B}} = 1. \]

29. Using
\[ \sigma = \log Z_c + \beta U = \log Z_{gc} + \beta U + \eta N \]
one finds that
\[ \log Z_c = \log Z_{gc} + \eta N. \]

The following holds for classical ideal gas having no internal degrees of freedom
\[ \log Z_{gc} = N \]
\[ \eta = -\beta \mu = \log \frac{n q V}{N}, \]
where
\[ n_Q = \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2}, \quad (4.304) \]

thus
\[
\log Z_c = N \left( 1 + \log \frac{n_Q V}{N} \right) \\
= N \log (n_Q V) + N - N \log N \\
\simeq N \log (n_Q V) - \log N! \\
= \log \left( \frac{(n_Q V)^N}{N!} \right),
\]

\[ (4.305) \]

or
\[
Z_c = \frac{1}{N!} \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2} V^N.
\]

30. The efficiency is defined as \( \eta = W/Q_h \), where \( W \) is the total work, and \( Q_h \) is the heat extracted from the heat bath at higher temperature. Energy conservation requires that \( W = Q_h + Q_l \), where \( Q_l \) is the heat extracted from the heat bath at lower temperature, thus \( \eta = 1 + Q_l/Q_h \). In the present case \( Q_h \) is associated with process \( a \to b \), while \( Q_l \) is associated with process \( c \to d \). In both isentropic processes \( (b \to c \text{ and } d \to a) \) no heat is exchanged. Hence the efficiency \( \eta \) is given by

\[
\eta = 1 + \frac{Q_l}{Q_h} = 1 + \frac{c_p (\tau_d - \tau_c)}{c_p (\tau_b - \tau_a)}.
\]

\[ (4.307) \]

The relation \( pV = N \tau \) yields

\[
\eta = 1 + \frac{\tau_d - \tau_c}{\tau_b - \tau_a} = 1 + \frac{p_2 (V_d - V_c)}{p_1 (V_b - V_a)}.
\]

\[ (4.308) \]

Along the isentropic process \( pV^\gamma \) is constant, where \( \gamma = c_p/c_V \), thus

\[
\eta = 1 + \frac{p_2}{p_1} \left( \frac{V_a - V_b}{V_b - V_a} \right) = 1 - \left( \frac{p_2}{p_1} \right)^{\gamma-1}.
\]

\[ (4.309) \]

31. No heat is exchanged in the isentropic processes, thus the efficiency \( \eta \) is given by
4.9. Solutions

\[ \eta = 1 + \frac{Q_l}{Q_h} \]
\[ = 1 + \frac{Q_{c-d}}{Q_{a-b}} \]
\[ = 1 + \frac{c_V (\tau_d - \tau_c)}{c_V (\tau_b - \tau_a)}. \]  

(4.310)

Since \( \tau V^{\gamma - 1} \) remains unchanged in an isentropic process, where

\[ \gamma = \frac{c_p}{c_v}, \]  

(4.311)

one finds that

\[ \tau_b V_1^{\gamma - 1} = \tau_c V_2^{\gamma - 1}, \]  

(4.312)

\[ \tau_d V_2^{\gamma - 1} = \tau_a V_1^{\gamma - 1}, \]  

(4.313)

or

\[ \frac{\tau_c}{\tau_b} = \frac{\tau_d}{\tau_a} = \left( \frac{V_2}{V_1} \right)^{1-\gamma}, \]  

(4.314)

thus

\[ \eta = 1 - \left( \frac{V_2}{V_1} \right)^{1-\gamma}. \]  

(4.315)

32. Let \( V_{A1} = N \tau_A / p \) (\( V_{B1} = N \tau_B / p \)) be the initial volume of vessel A (B) and let \( V_{A2} (V_{B2}) \) be the final volume of vessel A (B). In terms of the final temperature of both vessels, which is denoted as \( \tau_f \), one has

\[ V_{A2} = V_{B2} = \frac{N \tau_f}{p}. \]  

(4.316)

The entropy of an ideal gas of density \( n = N/V \), which contains \( N \) particles, is given by

\[ \sigma = N \left( \log \frac{nQ}{n} + \frac{5}{2} \right), \]  

(4.317)

where

\[ nQ = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2}, \]  

(4.318)
or as a function of \( \tau \) and \( p \)

\[ \sigma = N \left( \log \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} \frac{\tau ^{5/2}}{p} + \frac{5}{2} \right), \]  

(4.319)
Chapter 4. Ideal Gas

Thus the change in entropy is given by

\[ \Delta \sigma = \sigma_{\text{final}} - \sigma_{\text{initial}} = \frac{5N}{2} \log \frac{\tau_f^2}{\tau_A \tau_B}. \]  
(4.320)

In general, for an isobaric process the following holds

\[ Q = W + \Delta U = p(V_2 - V_1) + c_V(\tau_2 - \tau_1), \]  
(4.321)

where \( Q \) is the heat that was added to the gas, \( W \) the work done by the gas and \( \Delta U \) the change in internal energy of the gas. Using the equation of state \( pV = N\tau \) this can be written as

\[ Q = (N + c_V)(\tau_2 - \tau_1). \]  
(4.322)

Since no heat is exchanged with the environment during this process the following holds

\[ Q_A + Q_B = 0, \]

where

\[ Q_A = (N + c_V)(\tau_f - \tau_A), \]  
(4.323)
\[ Q_B = (N + c_V)(\tau_f - \tau_B), \]  
(4.324)

thus

\[ \tau_f = \frac{\tau_A + \tau_B}{2}, \]  
(4.325)

and therefore

\[ \Delta \sigma = \frac{5N}{2} \log \frac{(\tau_A + \tau_B)^2}{4\tau_A \tau_B}. \]  
(4.326)
5. Bosonic and Fermionic Systems

In the first part of this chapter two Bosonic systems, namely photons and phonons, are studied. A photon is the quanta of electromagnetic waves whereas a phonon is the quanta of acoustic waves. The second part is devoted to two Fermionic systems, electrons in metals and electrons and holes in semiconductors.

5.1 Electromagnetic Radiation

This section discusses an electromagnetic cavity in thermal equilibrium.

5.1.1 Electromagnetic Cavity

Consider an empty volume surrounded by conductive walls having infinite conductivity. The Maxwell’s equations in SI units for the electric \( E \) and magnetic \( H \) fields are given by

\[
\nabla \times H = \epsilon_0 \frac{\partial E}{\partial t}, \tag{5.1}
\]

\[
\nabla \times E = -\mu_0 \frac{\partial H}{\partial t}, \tag{5.2}
\]

\[
\nabla \cdot E = 0, \tag{5.3}
\]

and

\[
\nabla \cdot H = 0, \tag{5.4}
\]

where \( \epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1} \) and \( \mu_0 = 1.26 \times 10^{-6} \text{ N A}^{-2} \) are the permittivity and permeability respectively of free space, and the following holds

\[
\epsilon_0 \mu_0 = \frac{1}{c^2}, \tag{5.5}
\]

where \( c = 2.99 \times 10^8 \text{ m s}^{-1} \) is the speed of light in vacuum.

In the Coulomb gauge, where the vector potential \( A \) is chosen such that
\[ \nabla \cdot \mathbf{A} = 0, \quad (5.6) \]

the scalar potential \( \phi \) vanishes in the absence of sources (charge and current), and consequently both fields \( \mathbf{E} \) and \( \mathbf{H} \) can be expressed in terms of \( \mathbf{A} \) only as

\[ \mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}, \quad (5.7) \]

and

\[ \mu_0 \mathbf{H} = \nabla \times \mathbf{A}. \quad (5.8) \]

The gauge condition (5.6) and Eqs. (5.7) and (5.8) guarantee that Maxwell’s equations (5.2), (5.3), and (5.4) are satisfied

\[ \nabla \times \mathbf{E} = -\frac{\partial (\nabla \times \mathbf{A})}{\partial t} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}, \quad (5.9) \]

\[ \nabla \cdot \mathbf{E} = -\frac{\partial (\nabla \cdot \mathbf{A})}{\partial t} = 0, \quad (5.10) \]

\[ \nabla \cdot \mathbf{H} = \frac{1}{\mu_0} \nabla \cdot (\nabla \times \mathbf{A}) = 0, \quad (5.11) \]

where in the last equation the general vector identity \( \nabla \cdot (\nabla \times \mathbf{A}) = 0 \) has been employed. Substituting Eqs. (5.7) and (5.8) into the only remaining nontrivial equation, namely into Eq. (5.1), leads to

\[ \nabla \times (\nabla \times \mathbf{A}) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}. \quad (5.12) \]

Using the vector identity

\[ \nabla \times (\nabla \times \mathbf{A}) = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}, \quad (5.13) \]

and the gauge condition (5.6) one finds that

\[ \nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}. \quad (5.14) \]

Consider a solution in the form

\[ \mathbf{A} = q(t) \mathbf{u}(\mathbf{r}), \quad (5.15) \]

where \( q(t) \) is independent on position \( \mathbf{r} \) and \( \mathbf{u}(\mathbf{r}) \) is independent on time \( t \). The gauge condition (5.6) leads to

\[ \nabla \cdot \mathbf{u} = 0. \quad (5.16) \]

From Eq. (5.14) one finds that
\[ q \nabla^2 u = \frac{1}{c^2} \frac{d^2 q}{dt^2}. \] (5.17)

Multiplying by an arbitrary unit vector \( \hat{n} \) leads to
\[ \frac{(\nabla^2 u) \cdot \hat{n}}{\mathbf{u} \cdot \hat{n}} = \frac{1}{c^2} \frac{d^2 q}{dt^2}. \] (5.18)

The left hand side of Eq. (5.18) is a function of \( \mathbf{r} \) only while the right hand side is a function of \( t \) only. Therefore, both should equal a constant, which is denoted as \(-\kappa^2\), thus
\[ \nabla^2 u + \kappa^2 u = 0, \] (5.19)

and
\[ \frac{d^2 q}{dt^2} + \omega^2 \kappa q = 0, \] (5.20)

where
\[ \omega = c \kappa. \] (5.21)

Equation (5.19) should be solved with the boundary conditions of a perfectly conductive surface. Namely, on the surface \( S \) enclosing the cavity we have \( \mathbf{H} \cdot \hat{s} = 0 \) and \( \mathbf{E} \times \hat{s} = 0 \), where \( \hat{s} \) is a unit vector normal to the surface. To satisfy the boundary condition for \( \mathbf{E} \) we require that \( \mathbf{u} \) be normal to the surface, namely, \( \mathbf{u} = \hat{s} (\mathbf{u} \cdot \hat{s}) \) on \( S \). This condition guarantees also that the boundary condition for \( \mathbf{H} \) is satisfied. To see this, we calculate the integral of the normal component of \( \mathbf{H} \) over some arbitrary portion \( S' \) of \( S \). Using Eq. (5.8) and Stoke's theorem one finds that
\[ \int_{S'} (\mathbf{H} \cdot \hat{s}) dS = \frac{q}{\mu_0} \int_{S'} [(\nabla \times \mathbf{u}) \cdot \hat{s}] dS \]
\[ = \frac{q}{\mu_0} \oint_C \mathbf{u} \cdot d\mathbf{l}, \] (5.22)

where the close curve \( C \) encloses the surface \( S' \). Thus, since \( \mathbf{u} \) is normal to the surface one finds that the integral along the close curve \( C \) vanishes, and therefore
\[ \int_{S'} (\mathbf{H} \cdot \hat{s}) dS = 0. \] (5.23)

Since \( S' \) is arbitrary we conclude that \( \mathbf{H} \cdot \hat{s} = 0 \) on \( S \).

Each solution of Eq. (5.19) that satisfies the boundary conditions is called an eigen mode. As can be seen from Eq. (5.20), the dynamics of a mode amplitude \( q \) is the same as the dynamics of an harmonic oscillator having angular frequency \( \omega = c \kappa \).
5.1.2 Partition Function

What is the partition function of a mode having eigen angular frequency $\omega_\kappa$? We have seen that the mode amplitude has the dynamics of an harmonic oscillator having angular frequency $\omega_\kappa$. Thus, the quantum eigenenergies of the mode are

$$\varepsilon_s = s\hbar \omega_\kappa,$$

(5.24)

where $s = 0, 1, 2, \cdots$ is an integer\(^1\). When the mode is in the eigenstate having energy $\varepsilon_s$ the mode is said to occupy $s$ photons. The canonical partition function of the mode is found using Eq. (3.37)

$$Z_\kappa = \sum_{s=0}^{\infty} \exp(-s\beta\hbar \omega_\kappa)$$

$$= \frac{1}{1 - \exp(-\beta\hbar \omega_\kappa)}.$$

(5.25)

Note the similarity between this result and the orbital partition function $\zeta$ of Bosons given by Eq. (4.31). The average energy is found using

$$\langle \varepsilon_\kappa \rangle = -\frac{\partial \log Z_\kappa}{\partial \beta}$$

$$= \frac{\hbar \omega_\kappa}{e^{\beta \hbar \omega_\kappa} - 1}.$$

(5.26)

The partition function of the entire system is given by

$$Z = \prod_\kappa Z_\kappa,$$

(5.27)

and the average total energy by

$$U = -\frac{\partial \log Z}{\partial \beta} = \sum_\kappa \langle \varepsilon_\kappa \rangle.$$

(5.28)

5.1.3 Cube Cavity

For simplicity, consider the case of a cavity shaped as a cube of volume $V = L^3$. We seek solutions of Eq. (5.19) satisfying the boundary condition

\(^1\) In Eq. (5.24) above the ground state energy was taken to be zero. Note that by taking instead $\varepsilon_s = (s + 1/2)\hbar \omega_\kappa$, one obtains $Z_\kappa = 1/2 \sinh(\beta \hbar \omega_\kappa/2)$ and $\langle \varepsilon_\kappa \rangle = (\hbar \omega_\kappa/2) \coth(\beta \hbar \omega_\kappa/2)$. In some cases the offset energy term $\hbar \omega_\kappa/2$ is very important (e.g., the Casimir force), however, in what follows we disregard it.
that the tangential component of \( \mathbf{u} \) vanishes on the walls. Consider a solution having the form

\[
\begin{align*}
\mathbf{u}_x &= \sqrt{\frac{8}{V}} a_x \cos (k_x x) \sin (k_y y) \sin (k_z z), \\
\mathbf{u}_y &= \sqrt{\frac{8}{V}} a_y \sin (k_x x) \cos (k_y y) \sin (k_z z), \\
\mathbf{u}_z &= \sqrt{\frac{8}{V}} a_z \sin (k_x x) \sin (k_y y) \cos (k_z z).
\end{align*}
\]

(5.29) (5.30) (5.31)

While the boundary condition on the walls \( x = 0, y = 0, \) and \( z = 0 \) is guaranteed to be satisfied, the boundary condition on the walls \( x = L, y = L, \) and \( z = L \) yields

\[
\begin{align*}
k_x &= \frac{n_x}{L} \pi, \\
k_y &= \frac{n_y}{L} \pi, \\
k_z &= \frac{n_z}{L} \pi.
\end{align*}
\]

(5.32) (5.33) (5.34)

where \( n_x, n_y \) and \( n_z \) are integers. This solution clearly satisfies Eq. (5.19) where the eigenvalue \( \kappa \) is given by

\[
\kappa = \sqrt{k_x^2 + k_y^2 + k_z^2}.
\]

(5.35)

Alternatively, using the notation

\[
\mathbf{n} = (n_x, n_y, n_z),
\]

(5.36)

one has

\[
\kappa = \frac{\pi}{L} n,
\]

(5.37)

where

\[
n = \sqrt{n_x^2 + n_y^2 + n_z^2}.
\]

(5.38)

Using Eq. (5.21) one finds that the angular frequency of a mode characterized by the vector of integers \( \mathbf{n} \) is given by

\[
\omega_n = \frac{\pi c}{L} n.
\]

(5.39)

In addition to Eq. (5.19) and the boundary condition, each solution has to satisfy also the transversality condition \( \nabla \cdot \mathbf{u} = 0 \) (5.16), which in the present case reads

\[
\mathbf{n} \cdot \mathbf{a} = 0,
\]

(5.40)
where
\[ a = (a_x, a_y, a_z). \] (5.41)

Thus, for each set of integers \( \{n_x, n_y, n_z\} \) there are two orthogonal modes (polarizations), unless \( n_x = 0 \) or \( n_y = 0 \) or \( n_z = 0 \). In the latter case, only a single solution exists.

### 5.1.4 Average Energy

The average energy \( U \) of the system is found using Eqs. (5.26), (5.28) and (5.39)
\[
U = \sum_n \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1}
= 2\tau \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\alpha n}{e^{\alpha n} - 1},
\] (5.42)

where the dimensionless parameter \( \alpha \) is given by
\[
\alpha = \frac{\beta \hbar \pi c}{L}. \] (5.43)

The following relation can be employed to estimate the dimensionless parameter \( \alpha \)
\[
\alpha = \frac{2.4 \times 10^{-3}}{L \text{ cm} 300\text{K}}. \] (5.44)

In the limit where \( \alpha \ll 1 \) the sum can be approximated by the integral
\[
U \simeq 2\tau \frac{4\pi}{8} \int_0^{\infty} dn \, n^2 \frac{\alpha n}{e^{\alpha n} - 1}. \] (5.45)

By employing the integration variable transformation [see Eq. (5.39)]
\[
n = \frac{L}{\pi c} \omega, \] (5.46)

one finds that the energy per unit volume \( U/V \) can be expressed as
\[
\frac{U}{V} = \int_0^{\infty} d\omega \, u_\omega, \] (5.47)

where (see Fig. 5.1)
5.1. Electromagnetic Radiation

Fig. 5.1. The function $x^3/(e^x - 1)$.

$$u_\omega = \frac{\hbar}{c^3\pi^2} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}. \quad (5.48)$$

This result is known as Planck’s radiation law. The factor $u_\omega$ represents the spectral distribution of the radiation. The peak in $u_\omega$ is obtained at $\beta\hbar\omega_0 = 2.82$. In terms of the wavelength $\lambda_0 = 2\pi c/\omega_0$ one has

$$\frac{\lambda_0}{\mu m} = 5.1 \left( \frac{T}{1000 \text{ K}} \right)^{-1}. \quad (5.49)$$

The total energy is found by integrating Eq. (5.47) and by employing the variable transformation $x = \beta\hbar\omega$

$$\frac{U}{\bar{V}} = \frac{\tau^4}{c^3\pi^2\hbar^3} \int_0^\infty \frac{x^3}{e^x - 1} \, dx = \frac{\pi^2\tau^4}{15\hbar^3c^3}. \quad (5.50)$$

5.1.5 Stefan-Boltzmann Radiation Law

Consider a small hole having area $dA$ drilled into the conductive wall of an electromagnetic (EM) cavity. What is the rate of energy radiation emitted from the hole? We employ below a kinetic approach to answer this question. Consider radiation emitted in a time interval $dt$ in the direction of the unit vector $\hat{u}$. Let $\theta$ be the angle between $\hat{u}$ and the normal to the surface of the hole. Photons emitted during that time interval $dt$ in the direction $\hat{u}$ came from the region in the cavity that is indicated in Fig. 5.2, which has volume
Chapter 5. Bosonic and Fermionic Systems

Fig. 5.2. Radiation emitted through a small hole in the cavity wall.

\[ V_\theta = dA \cos \theta \times c dt. \]  
(5.51)

The average energy in that region can be found using Eq. (5.50). Integrating over all possible directions yields the total rate of energy radiation emitted from the hole per unit area

\[
J = \frac{1}{dAdt} \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\phi \frac{U}{V} V_\theta \\
= \frac{\pi^2 \tau^4}{15\hbar^3c^2} \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \cos \theta \int_0^{2\pi} d\phi \\
= \frac{\pi^2 \tau^4}{60\hbar^3c^2} 
\]  
(5.52)

In terms of the historical definition of temperature \( T = \frac{\tau}{k_B} \) [see Eq. (3.57)] one has

\[ J = \sigma_B T^4, \]  
(5.53)

where \( \sigma_B \), which is given by
5.2 Phonons in Solids

This section is devoted to elastic waves in solids. A one-dimensional example is first discussed, and then some of the results are generalized for the case of a 3D lattice.

5.2.1 One Dimensional Example

Consider the 1D lattice shown in Fig. 5.3 below, which contains $N$ `atoms' having mass $m$ each that are attached to each other by springs having a spring constant $m\omega^2$. The lattice spacing is $a$. The atoms are allowed to move in one dimension along the array axis. The normal mode angular eigen-frequencies $\omega_n$ are given by [see Eq. (5.182) and Fig. 5.4]

$$\omega_n = \omega \sqrt{2 (1 - \cos k_n a)} = 2\omega \left| \sin \frac{k_n a}{2} \right|,$$

where $a$ is the lattice spacing,

$$k_n = \frac{2\pi n}{a N},$$

and $n$ is integer ranging from $-N/2$ to $N/2$.

What is the partition function of an eigen-mode having eigen angular frequency $\omega_n$? The mode amplitude has the dynamics of an harmonic oscillator having angular frequency $\omega_n$. Thus, as we had in the previous section (EM modes), the quantum eigenenergies of the mode are

$$\varepsilon_s = s \hbar \omega_n,$$

where $s = 0, 1, 2, \cdots$ is an integer. When the mode is in an eigenstate having energy $\varepsilon_s$, the mode is said to occupy $s$ phonons. The canonical partition function of the mode is found using Eq. (3.37)
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Fig. 5.4. The function $|\sin(\pi x/2)|$.

$$Z_\kappa = \sum_{s=0}^{\infty} \exp(-s\beta \hbar \omega_\kappa)$$

$$= \frac{1}{1 - \exp(-\beta \hbar \omega_\kappa)}. \quad (5.58)$$

Similarly to the EM case, the average total energy is given by

$$U = \frac{N}{2} \sum_{n=-N/2}^{N/2} \frac{\hbar \omega_n}{\exp(\beta \hbar \omega_n) - 1}, \quad (5.59)$$

where $\beta = 1/\tau$, and the total heat capacity $c_V$ is given by

$$c_V = \frac{\partial U}{\partial \tau} = \sum_{n=-N/2}^{N/2} \frac{(\beta \hbar \omega_n)^2 \exp(\beta \hbar \omega_n)}{[\exp(\beta \hbar \omega_n) - 1]^2}. \quad (5.60)$$

**High Temperature Limit.** In the high temperature limit $\beta \hbar \omega \ll 1$

$$\frac{(\beta \hbar \omega_n)^2 \exp(\beta \hbar \omega_n)}{[\exp(\beta \hbar \omega_n) - 1]^2} \approx 1, \quad (5.61)$$

therefore

$$c_V = N. \quad (5.62)$$

**Low Temperature Limit.** In the low temperature limit $\beta \hbar \omega \gg 1$ the main contribution to the sum in Eq. (5.60) comes from terms for which $|n| \lesssim N/\beta \hbar \omega$. Thus, to a good approximation the dispersion relation can be approximated by
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\[ \omega_n = 2\omega \left| \sin \frac{k_n a}{2} \right| \approx 2\omega \left| \frac{k_n a}{2} \right| = \frac{2\pi}{N} |n| . \quad (5.63) \]

Moreover, in the limit \( N \gg 1 \) the sum in Eq. (5.60) can be approximated by an integral, and to a good approximation the upper limit \( N/2 \) can be substituted by infinity, thus

\[ c_V = \sum_{n=-N/2}^{N/2} \left( \frac{\beta h \omega_n}{N} \right)^2 \exp \left( \frac{\beta h \omega_n}{N} \right) \left[ \exp \left( \frac{\beta h \omega_n}{N} \right) - 1 \right]^2 \]

\[ \approx 2 \sum_{n=0}^{\infty} \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right)^2 \exp \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right) \left[ \exp \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right) - 1 \right]^2 \]

\[ \approx 2 \int_0^{\infty} dn \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right)^2 \exp \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right) \left[ \exp \left( \frac{\beta h \omega \frac{2\pi}{N}}{n} \right) - 1 \right]^2 \]

\[ = \frac{N}{\pi} \frac{\tau}{\hbar \omega} \int_0^{\infty} dx x^2 \exp \left( x \right) \left( \exp(x) - 1 \right)^2 \]

\[ = \frac{N}{3} \frac{\pi}{\hbar \omega \omega} . \quad (5.64) \]

5.2.2 The 3D Case

The case of a 3D lattice is similar to the case of EM cavity that was studied in the previous section. However, there are 3 important distinctions:

1. The number of modes of a lattice containing \( N \) atoms that can move in 3D is finite, \( 3N \) instead of infinity as in the EM case.
2. For any given vector \( k \) there are 3, instead of only 2, orthogonal modes (polarizations).
3. Dispersion: contrary to the EM case, the dispersion relation (namely, the function \( \omega (k) \)) is in general nonlinear [see Eq. (5.182)].

Due to distinctions 1 and 2, the sum over all modes is substituted by an integral according to

\[ \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{4\pi}{3} \int_0^{nD} dn n^2 , \quad (5.65) \]

where the factor of 3 replaces the factor of 2 we had in the EM case. Moreover, the upper limit is \( nD \) instead of infinity, where \( nD \) is determined from the requirement
\[ \frac{3}{8} 4\pi \int_0^{n_D} dn \, n^2 = 3N, \quad (5.66) \]

thus
\[ n_D = \left( \frac{6N}{\pi} \right)^{1/3}. \quad (5.67) \]

Similarly to the EM case, the average total energy is given by
\[ U = \sum_n \frac{\hbar \omega_n}{\exp (\beta \hbar \omega_n) - 1} \quad (5.68) \]
\[ = \frac{3\pi}{2} \int_0^{n_0} dn \, n^2 \frac{\hbar \omega_n}{\exp (\beta \hbar \omega_n) - 1}. \quad (5.69) \]

To proceed with the calculation the dispersion relation \( \omega_n (k_n) \) is needed. Here we assume for simplicity that dispersion can be disregarded to a good approximation, and consequently the dispersion relation can be assumed to be linear
\[ \omega_n = v k_n, \quad (5.70) \]
where \( v \) is the sound velocity. The wave vector \( k_n \) is related to \( n = \sqrt{n_x^2 + n_y^2 + n_z^2} \) by
\[ k_n = \frac{\pi n}{L}, \quad (5.71) \]
where \( L = V^{1/3} \) and \( V \) is the volume. In this approximation one finds using the variable transformation
\[ x = \frac{\beta \hbar v \pi n}{L}, \quad (5.72) \]
that
\[ U = \frac{3\pi}{2} \int_0^{n_0} dn \, n^2 \frac{\hbar v \pi n}{\exp \left( \frac{\beta \hbar v \pi n}{L} \right) - 1} \]
\[ = \frac{3V \pi^4}{2\hbar^3 v^3 \pi^2} \int_0^{x_D} dx \frac{x^3}{\exp x - 1}, \quad (5.73) \]

where
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\[ x_D = \frac{\beta\hbar v \pi n_D}{L} = \frac{\beta\hbar v \pi \left( \frac{6N}{\pi} \right)^{1/3}}{L}. \]

Alternatively, in terms of the Debye temperature, which is defined as

\[ \Theta = \hbar v \left( \frac{6\pi^2 N}{V} \right)^{1/3}, \quad (5.74) \]

one has

\[ x_D = \frac{\Theta}{\tau}, \quad (5.75) \]

and

\[ U = 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{\exp x - 1}. \quad (5.76) \]

As an example \( \Theta/k_B = 88\text{K} \) for Pb, while \( \Theta/k_B = 1860\text{K} \) for diamond. Below we calculate the heat capacity \( c_V = \partial U/\partial \tau \) in two limits.

**High Temperature Limit.** In the high temperature limit \( x_D = \Theta/\tau \ll 1 \), thus

\[
U = 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{\exp x - 1}
\approx 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \ x^2
= 9N\tau \left( \frac{T}{\Theta} \right)^3 \frac{x_D^3}{3}
= 3N\tau , \quad (5.77)
\]

and therefore

\[ c_V = \frac{\partial U}{\partial \tau} = 3N. \quad (5.78) \]

Note that in this limit the averaged energy of each mode is \( \tau \) and consequently \( U = 3N\tau \). This result demonstrates the equal partition theorem of classical statistical mechanics that will be discussed in the next chapter.

**Low Temperature Limit.** In the low temperature limit \( x_D = \Theta/\tau \gg 1 \), thus
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\[ U = 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{\pi/15} dx \frac{x^3}{\exp x - 1} \]

\[ \simeq 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{\infty} dx \frac{x^3}{\exp x - 1} \]

\[ = \frac{3\pi^4}{5} N\tau \left( \frac{T}{\Theta} \right)^3, \]

(5.79)

and therefore

\[ c_v = \frac{\partial U}{\partial \tau} = \frac{12\pi^4}{5} N\tau \left( \frac{T}{\Theta} \right)^3. \]

(5.80)

Note that Eq. (5.79) together with Eq. (5.74) yield

\[ \frac{U}{V} = \frac{3}{2} \frac{\pi^2 \tau^4}{15} \frac{1}{h^3 v^3}. \]

(5.81)

Note the similarity between this result and Eq. (5.50) for the EM case [see Eq. (5.50)].

5.3 Fermi Gas

In this section an ideal gas of Fermions of mass \( m \) is studied. While only the classical limit was considered in chapter 2, here the more general case is considered.

5.3.1 Orbital Partition Function

Consider an orbital having energy \( \varepsilon_n \). When internal degrees of freedom are disregarded, its grandcanonical Fermionic partition function is given by [see Eq. (4.28)]

\[ \zeta_n = 1 + \lambda \exp (-\beta \varepsilon_n), \]

(5.82)

where

\[ \lambda = \exp (\beta \mu) = e^{-\eta}, \]

(5.83)

is the fugacity and \( \beta = 1/\tau \). Taking into account internal degrees of freedom the grandcanonical Fermionic partition function becomes [see Eq. (5.50)]
5.3. Fermi Gas

\[ \zeta_n = \prod_l (1 + \lambda \exp(-\beta \varepsilon_n) \exp(-\beta E_l)) , \]  
(5.84)

where \( \{E_l\} \) are the eigenenergies of a particle due to internal degrees of freedom. As is required by the Pauli exclusion principle, no more than one Fermion can occupy a given internal eigenstate and a given orbital.

5.3.2 Partition Function of the Gas

The grandcanonical partition function of the gas is given by

\[ Z_{gc} = \prod_n \zeta_n . \]  
(5.85)

The orbital eigenenergies of a particle of mass \( m \) in a box are given by Eq. (4.5)

\[ \varepsilon_n = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2 , \]  
(5.86)

where

\[ n = (n_x, n_y, n_z) , \]  
(5.87)

\[ n = \sqrt{n_x^2 + n_y^2 + n_z^2} , \]  
(5.88)

The orbital eigenenergies of a particle due to internal degrees of freedom. As is required by the Pauli exclusion principle, no more than one Fermion can occupy a given internal eigenstate and a given orbital.

\[ \log Z_{gc} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log \zeta_n . \]  
(5.91)

Alternatively, using the notation

\[ \alpha^2 = \frac{\beta \hbar^2 \pi^2}{2mL^2} , \]  
(5.89)

and Eq. (5.84) one finds that

\[ \log Z_{gc} = \sum_l \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log (1 + \lambda \exp(-\alpha^2 n^2) \exp(-\beta E_l)) . \]  
(5.90)

For a macroscopic system \( \alpha \ll 1 \), and consequently the sum over \( n \) can be approximately replaced by an integral

\[ \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{1}{8} \int_0^\infty dn \, n^2 , \]  
(5.91)
thus, one has

$$\log Z_{gc} = \frac{\pi}{2} \sum_{l}^\infty \int_{0}^{\infty} dn \ n^2 \log (1 + \lambda \exp (-\alpha^2 n^2) \exp (-\beta E_l)) .$$  \hspace{1cm} (5.92)$$

This can be further simplified by employing the variable transformation

$$\beta \varepsilon = \alpha^2 n^2 .$$  \hspace{1cm} (5.93)$$

The following holds

$$\frac{\sqrt{\pi}}{2} \left( \frac{\beta}{\alpha^2} \right)^{3/2} d\varepsilon = n^2 dn .$$

Thus, by introducing the density of states

$$D(\varepsilon) = \begin{cases} \frac{V}{2\pi} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} & \varepsilon \geq 0 , \\ 0 & \varepsilon < 0 , \end{cases}$$  \hspace{1cm} (5.94)$$

one has

$$\log Z_{gc} = \frac{1}{2} \sum_{l}^\infty \int_{-\infty}^{\infty} d\varepsilon \ D(\varepsilon) \log (1 + \lambda \exp (-\beta (\varepsilon + E_l))) .$$  \hspace{1cm} (5.95)$$

5.3.3 Energy and Number of Particles

Using Eqs. (3.45) and (3.60) for the energy $U$ and the number of particles $N$, namely using

$$U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta ,$$  \hspace{1cm} (5.96)$$

$$N = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda} ,$$  \hspace{1cm} (5.97)$$

one finds that

$$U = \frac{1}{2} \sum_{l}^\infty \int_{-\infty}^{\infty} d\varepsilon \ D(\varepsilon) \ (\varepsilon + E_l) \ f_{FD}(\varepsilon + E_l) \ ,$$  \hspace{1cm} (5.98)$$

$$N = \frac{1}{2} \sum_{l}^\infty \int_{-\infty}^{\infty} d\varepsilon \ D(\varepsilon) \ f_{FD}(\varepsilon + E_l) \ ,$$  \hspace{1cm} (5.99)$$

where $f_{FD}$ is the Fermi-Dirac distribution function [see Eq. (4.30)]

$$f_{FD}(\epsilon) = \frac{1}{\exp [\beta (\epsilon - \mu)] + 1} .$$  \hspace{1cm} (5.100)$$

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5.3.4 Example: Electrons in Metal

Electrons are Fermions having spin 1/2. The spin degree of freedom gives rise to two orthogonal eigenstates having energies $E_+$ and $E_-$ respectively. In the absence of any external magnetic field these states are degenerate, namely $E_+ = E_-$. For simplicity we take $E_+ = E_- = 0$. Thus, Eqs. (5.98) and (5.99) become

\begin{align*}
U &= \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) \varepsilon f_{FD}(\varepsilon), \\
N &= \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) f_{FD}(\varepsilon),
\end{align*}

Typically for metals at room temperature or below the following holds $\tau \ll \mu$. Thus, it is convenient to employ the following theorem (Sommerfeld expansion) to evaluate these integrals.

**Theorem 5.3.1.** Let $g(\varepsilon)$ be a function that vanishes in the limit $\varepsilon \to -\infty$, and that diverges no more rapidly than some power of $\varepsilon$ as $\varepsilon \to \infty$. Then, the following holds

\begin{equation}
\int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) f_{FD}(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon \, g(\varepsilon) + \frac{\pi^2 g'(\mu)}{6\beta^2} + O\left(\frac{1}{\beta\mu}\right)^4.
\end{equation}

**Proof.** Let

\begin{equation}
G(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' \, g(\varepsilon').
\end{equation}

Integration by parts yields

\begin{align*}
I &= \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) f_{FD}(\varepsilon) \\
&= \left[G(\varepsilon) f_{FD}(\varepsilon)\right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} d\varepsilon \, G(\varepsilon) \left( -\frac{\partial f_{FD}}{\partial \varepsilon} \right),
\end{align*}

(5.105)
where the following holds

\[- \frac{\partial f_{FD}}{\partial \varepsilon} = \frac{\beta e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon - \mu)} + 1)^2} = \frac{\beta}{4 \cosh^2 \frac{\beta(\varepsilon - \mu)}{2}}. \tag{5.106}\]

Using the Taylor expansion of \( G(\varepsilon) \) about \( \varepsilon - \mu \), which has the form

\[ G(\varepsilon) = \sum_{n=0}^{\infty} \frac{G^{(n)}(\mu)}{n!} (\varepsilon - \mu)^n, \tag{5.107}\]

yields

\[ I = \sum_{n=0}^{\infty} \frac{G^{(n)}(\mu)}{n!} \int_{-\infty}^{\infty} \frac{\beta (\varepsilon - \mu)^n d\varepsilon}{4 \cosh^2 \frac{\beta(\varepsilon - \mu)}{2}}. \tag{5.108}\]

Employing the variable transformation

\[ x = \beta (\varepsilon - \mu), \tag{5.109}\]

and exploiting the fact that \((-\partial f_{FD}/\partial \varepsilon)\) is an even function of \( \varepsilon - \mu \) leads to

\[ I = \sum_{n=0}^{\infty} \frac{G^{(2n)}(\mu)}{(2n)! \beta^{2n}} \int_{-\infty}^{\infty} \frac{x^{2n} dx}{4 \cosh^2 \frac{\beta x}{2}}. \tag{5.110}\]

With the help of the identities

\[ \int_{-\infty}^{\infty} \frac{dx}{4 \cosh^2 \frac{\beta x}{2}} = 1, \tag{5.111}\]

\[ \int_{-\infty}^{\infty} \frac{x^2 dx}{4 \cosh^2 \frac{\beta x}{2}} = \frac{\pi^2}{3}, \tag{5.112}\]

one finds that

\[ I = G(\mu) + \frac{\pi^2 G^{(2)}(\mu)}{6 \beta^2} + O \left( \frac{1}{\beta \mu} \right)^4 \]

\[ = \int_{-\infty}^{\mu} d\varepsilon \ g(\varepsilon) + \frac{\pi^2 g'(\mu)}{6 \beta^2} + O \left( \frac{1}{\beta \mu} \right)^4. \tag{5.113}\]

With the help of this theorem (5.103) one finds that the number of particles \( N \) to second order in \( \tau \) is given by
5.3. Fermi Gas

\[ N = \int_{-\infty}^{\mu} d\varepsilon \, D(\varepsilon) + \frac{\pi^2 \tau^2 D'(\mu)}{6}. \quad (5.114) \]

Moreover, at low temperatures, the chemical potential is expected to be close the the Fermi energy \( \varepsilon_F \), which is defined by

\[ \varepsilon_F = \lim_{\tau \to 0} \mu. \quad (5.115) \]

Thus, to lowest order in \( \mu - \varepsilon_F \) one has

\[ \int_{-\infty}^{\mu} d\varepsilon \, D(\varepsilon) = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) + (\mu - \varepsilon_F) D(\varepsilon_F) + O((\mu - \varepsilon_F)^2), \quad (5.116) \]

and therefore

\[ N = N_0 + (\mu - \varepsilon_F) D(\varepsilon_F) + \frac{\pi^2 \tau^2 D'(\varepsilon_F)}{6}, \quad (5.117) \]

where

\[ N_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon), \quad (5.118) \]

is the number of electrons at zero temperature. The number of electrons \( N \) in metals is expected to be temperature independent, namely \( N = N_0 \) and consequently

\[ \mu = \varepsilon_F - \frac{\pi^2 D'(\varepsilon_F)}{6 \beta^2 D(\varepsilon_F)}. \quad (5.119) \]

Similarly, the energy \( U \) at low temperatures is given approximately by

\[
U = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \varepsilon f_{FD}(\varepsilon) \\
= \left. \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \varepsilon + (\mu - \varepsilon_F) D(\varepsilon_F) \varepsilon_F + \frac{\pi^2 \tau^2}{6} (D'(\varepsilon_F) \varepsilon_F + D(\varepsilon_F)) \right|_{U_0} \\
= U_0 - \frac{\pi^2 \tau^2 D'(\varepsilon_F)}{6 D(\varepsilon_F)} D(\varepsilon_F) \varepsilon_F + \frac{\pi^2 \tau^2}{6} (D'(\varepsilon_F) \varepsilon_F + D(\varepsilon_F)) \\
= U_0 + \frac{\pi^2 \tau^2}{6} D(\varepsilon_F),
\]

\[ (5.120) \]
where

\[ U_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon \ D(\varepsilon) \varepsilon . \]  

(5.121)

From this result one finds that the electronic heat capacity is given by

\[ c_V = \frac{\partial U}{\partial T} = \frac{\pi}{3} \frac{\varepsilon_F^2 \tau}{D(\varepsilon_F)} . \]  

(5.122)

Comparing this result with Eq. (5.80) for the phonons heat capacity, which is proportional to \( \tau^3 \) at low temperatures, suggests that typically, while the electronic contribution is the dominant one at very low temperatures, at higher temperatures the phonons’ contribution becomes dominant.

### 5.4 Semiconductor Statistics

Consider a semiconductor having energy gap

\[ E_g = \varepsilon_c - \varepsilon_v , \]  

(5.123)

between its conduction and valence bands, where \( \varepsilon_c \) (\( \varepsilon_v \)) is the lowest (highest) energy of the conduction (valence) band (see Fig. 5.5). The energy density of states \( D_c(\varepsilon) \) and \( D_v(\varepsilon) \) of the conduction and valence bands, respectively, are given by

\[ D_c(\varepsilon) = \frac{2^{1/2} m_c^{3/2}}{\pi^2 h^3} \sqrt{\varepsilon - \varepsilon_c} , \]  

(5.124)

\[ D_v(\varepsilon) = \frac{2^{1/2} m_v^{3/2}}{\pi^2 h^3} \sqrt{\varepsilon_v - \varepsilon} , \]  

(5.125)

where \( m_c \) (\( m_v \)) is the effective mass of the conduction (valence) band.

Let \( N_d \) (\( N_a \)) be the density, i.e. number per unit volume, of donor (acceptor) impurities. It is assumed that each donor (acceptor) impurity can supply a single electron (hole) to the conduction (valence) band. The density of electrons (holes) in the conduction (valence) band is denoted by \( n_c \) (\( n_v \)), and the density of electrons (holes) localized in a donor (acceptor) state is denoted by \( n_d \) (\( n_a \)). Charge conservation implies that

\[ N_d - N_a = n_c + n_d - n_v - n_a . \]  

(5.126)

The densities \( n_c \) and \( n_v \) are given by

\[ n_c = \int_{\varepsilon_c}^{\infty} d\varepsilon \ D_c(\varepsilon) f_{FD}(\varepsilon) , \]  

(5.127)
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Fig. 5.5. The energy gap is $E_g = \varepsilon_c - \varepsilon_v$, where $\varepsilon_c$ ($\varepsilon_v$) is the lowest (highest) energy of the conduction (valence) band. The energy of a localized donor (acceptor) state is denoted by $\varepsilon_d$ ($\varepsilon_a$).

and

$$n_v = \int_{-\infty}^{\varepsilon_v} d\varepsilon \ D_v(\varepsilon) \ (1 - f_{FD}(\varepsilon)) ,$$ (5.128)

where $f_{FD}(\varepsilon) = 1/(exp[\beta(\varepsilon - \mu)] + 1)$ is the Fermi-Dirac function [see Eq. (4.30)], $\beta^{-1}$ is the temperature, and $\mu$ is the chemical potential.

Below it will be assumed that the occupation probability of electron (hole) states in the conduction (valence) band is small, i.e. $\beta(\varepsilon_c - \mu) \gg 1$ ($\beta(\mu - \varepsilon_v) \gg 1$). In this classical limit the approximation [see Eq. (4.34)]

$$\frac{1}{\exp(\beta(\varepsilon - \mu)) + 1} \simeq \exp(-\beta(\varepsilon - \mu)) ,$$ (5.129)

can be employed for calculating the density $n_c$ of electrons in the conduction band [see Eq. (5.127)]
\[ n_c \simeq \frac{2^{1/2} m_c^{3/2}}{\pi^{1/2} h^3} \int_{\varepsilon_c}^{\infty} d\varepsilon \sqrt{\varepsilon - \varepsilon_c} \exp(-\beta (\varepsilon - \mu)) \]
\[ = \frac{2^{1/2} m_c^{3/2}}{\pi^2 h^3 \beta} \int_{\beta(\varepsilon_c - \mu)}^{\infty} dx \sqrt{\frac{x}{\beta} + \mu} - \varepsilon_c \exp(-x) \]
\[ = \left( \frac{m_c}{2^{1/3} \pi h^2 \beta} \right)^{3/2} e^{-\beta(\varepsilon_c - \mu)}, \]
\[(5.130)\]

and the approximation
\[ 1 - \frac{1}{\exp(\beta (\varepsilon - \mu)) + 1} \approx \frac{1}{\exp(\beta (\mu - \varepsilon)) + 1} \simeq \exp(-\beta (\mu - \varepsilon)), \quad (5.131) \]
can be employed for calculating the density \( n_v \) of holes in the valence band [see Eq. (5.128)]
\[ n_v = \int_{-\infty}^{\varepsilon_v} d\varepsilon \frac{2^{1/2} m_v^{3/2}}{\pi^2 h^3} \sqrt{\varepsilon_v - \varepsilon} \exp(-\beta (\mu - \varepsilon)) \]
\[ = \frac{2^{1/2} m_v^{3/2}}{\pi^2 h^3 \beta} \int_{-\infty}^{\beta(\varepsilon_v - \mu)} dx \sqrt{\varepsilon_v - \left( \frac{x}{\beta} + \mu \right)} \exp(x) \]
\[ = \left( \frac{m_v}{2^{1/3} \pi h^2 \beta} \right)^{3/2} e^{-\beta(\mu - \varepsilon_v)}. \]
\[(5.132)\]

Note that the product \( n_c n_v \) is independent on the chemical potential [see Eqs. (5.123), (5.130) and (5.132)]
\[ n_c n_v = \left( \frac{m_c m_v}{2^{2/3} \pi^2 h^4 \beta^2} \right)^{3/2} e^{-\beta E_g}. \]
\[(5.133)\]

The energy of a localized donor (acceptor) state is denoted by \( \varepsilon_d \) (\( \varepsilon_a \)) (see Fig. 5.5). A donor (acceptor) level can be either occupied by a spin up electron (hole) or a spin down electron (hole). However, for both cases the probability of occupations by two particles (two electrons or two holes) is assumed to be negligibly small (due to strong Coulomb repulsion). For the case of a donor impurity, the grand canonical partition function \( \zeta \) is given by [see Eq. (3.44)]
\[ \zeta = 1 + 2 \lambda \exp(-\beta \varepsilon_d), \]
\[(5.134)\]
where \( \lambda = \exp(\beta \mu) \) is the fugacity, thus
\[ n_d = N_d \frac{\partial \log \zeta}{\partial \lambda} = \frac{N_d}{2 e^{2(\varepsilon_d - \mu)} + 1}; \]
\[(5.135)\]
Similarly, for an acceptor impurity

\[ n_a = \frac{N_a}{2e^{\beta(\mu-\varepsilon_a)} + 1}. \]  

(5.136)

The chemical potential \( \mu \) can be found from the charge conservation relation (5.126).

5.5 Problems

1. Calculate the average number of photons \( N \) in equilibrium at temperature \( \tau \) in a cavity of volume \( V \). Use this result to estimate the number of photons in the universe assuming it to be a spherical cavity of radius \( 10^{26} \) m and at temperature \( \tau = k_B \times 3 \) K.

2. Write a relation between the temperature of the surface of a planet and its distance from the Sun, on the assumption that as a black body in thermal equilibrium, it reradiates as much thermal radiation, as it receives from the Sun. Assume also, that the surface of the planet is at constant temperature over the day-night cycle. Use \( T_{\text{Sun}} = 5800 \) K; \( R_{\text{Sun}} = 6.96 \times 10^8 \) m; and the Mars-Sun distance of \( D_{\text{M-S}} = 2.28 \times 10^{11} \) m and calculate the temperature of Mars surface.

3. Consider two parallel planar surfaces having absorption coefficients \( \alpha_1 \) and \( \alpha_2 \), and temperatures \( T_1 \) and \( T_2 \), respectively. Calculate the net energy flow per unit area \( J_{21} \) between the first surface and the second one.

4. Calculate the Helmholtz free energy \( F \) of photon gas having total energy \( U \) and volume \( V \) and use your result to show that the pressure is given by

\[ p = \frac{U}{3V}. \]  

(5.137)

5. Consider a photon gas initially at temperature \( \tau_1 \) and volume \( V_1 \). The gas is adiabatically compressed from volume \( V_1 \) to volume \( V_2 \) in an isentropic process. Calculate the final temperature \( \tau_2 \) and final pressure \( p_2 \).

6. Consider a one-dimensional lattice of \( N \) identical point particles of mass \( m \), interacting via nearest-neighbor spring-like forces with spring constant \( m\omega^2 \) (see Fig. 5.3). Denote the lattice spacing by \( a \). Show that the normal mode eigen-frequencies are given by

\[ \omega_n = \omega \sqrt{2 \left( 1 - \cos k_n a \right)}, \]  

(5.138)

where \( k_n = 2\pi n/aN \), and \( n \) is integer ranging from \(-N/2\) to \(N/2\) (assume \( N \gg 1 \)).

7. Two identical non-interacting particles, each having mass \( M \), are confined in a one dimensional parabolic potential given by
where the angular frequency $\omega$ is a constant.

a) Calculate the canonical partition function of the system $Z_{c,B}$ for the case where the particles are Bosons.

b) Calculate the canonical partition function of the system $Z_{c,F}$ for the case where the particles are Fermions.

8. Consider an orbital with energy $\epsilon$ in an ideal gas. The system is in thermal equilibrium at temperature $T$ and chemical potential $\mu$.

a) Show that the probability that the orbital is occupied by $n$ particles is given by

$$p_F(n) = \frac{\exp[n(\mu - \epsilon)\beta]}{1 + \exp[(\mu - \epsilon)\beta]} ,$$

for the case of Fermions, where $n \in \{0, 1\}$, and by

$$p_B(n) = \{1 - \exp[(\mu - \epsilon)\beta]\} \exp[n(\mu - \epsilon)\beta] ,$$

where $n \in \{0, 1, 2, \cdots\}$, for the case of Bosons.

b) Show that the variance $(\Delta n)_F^2 = \left\langle (n - \langle n \rangle)_F^2 \right\rangle$ is given by

$$(\Delta n)_F^2 = \langle n \rangle_F (1 - \langle n \rangle_F) ,$$

for the case of Fermions, and by

$$(\Delta n)_B^2 = \langle n \rangle_B (1 + \langle n \rangle_B) ,$$

for the case of Bosons.

9. Consider a metal at zero temperature having Fermi energy $\epsilon_F$, number of electrons $N$ and volume $V$.

a) Calculate the mean energy of electrons.

b) Calculate the ratio $\alpha$ of the mean-square-speed of electrons to the square of the mean speed

$$\alpha = \frac{\langle v^2 \rangle}{\langle v \rangle^2} .$$

9. Consider an ideal classical gas containing $N$ identical particles having each mass $M$, in the extreme relativistic limit. The gas is contained in a vessel having a cube shape with volume of $V = L^3$. In the extreme relativistic limit the dispersion relation $\epsilon(k)$ is modified: the energy $\epsilon(k)$ of a single particle quantum state having a wavefunction $\psi$ given by
\[ \psi(x, y, z) = \left( \frac{2}{L} \right)^{3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z) , \]

is given by
\[ \varepsilon(k) = \hbar c , \]

where \( c \) is the speed of light and where \( k = \sqrt{k_x^2 + k_y^2 + k_z^2} \) (contrary to the non-relativistic case where it is given by \( \varepsilon(k) = \hbar^2 k^2 / 2M \)). The system is in thermal equilibrium at temperature \( \tau \). Calculate:

a) the total energy \( U \) of the system.

b) the pressure \( p \).

11. Consider an ideal gas made of \( N \) electrons in the \textit{extreme relativistic limit}. The gas is contained in a box having a cube shape with a volume \( V = L^3 \). In the extreme relativistic limit the dispersion relation \( \varepsilon(k) \) is given by Eq. (5.146). The system is in thermal equilibrium at zero temperature \( \tau = 0 \). Calculate the ratio \( p/U \) between the pressure \( p \) and the total energy of the system \( U \).

12. A gas of two dimensional electrons is free to move in a plane. The mass of each electron is \( m_e \), the density (number of electrons per unit area) is \( n \), and the temperature is \( \tau \). Show that the chemical potential \( \mu \) is given by
\[ \mu = \tau \log \left[ \exp \left( \frac{n \pi \hbar^2}{m_e \tau} \right) - 1 \right] . \]

13. Consider a one dimensional gas containing \( N \) non-interacting electrons moving along the \( x \) direction. The electrons are confined to a section of length \( L \). At zero temperature \( \tau = 0 \) calculate the ratio \( U/\varepsilon_F \) between the total energy of the system \( U \) and the Fermi energy \( \varepsilon_F \).

14. Consider a one dimensional gas containing \( N \) non-interacting electrons moving along the \( x \) direction. The electrons are confined by a potential given by
\[ V(x) = \frac{1}{2} m \omega^2 x^2 , \]

where \( m \) is the electron mass and where \( \omega \) is the angular frequency of oscillations. Calculate the chemical potential \( \mu \)

a) in the limit of zero temperature \( \tau = 0 \).

b) in the limit of high temperatures \( \tau \gg \hbar \omega \).

5.6 Solutions

1. The density of states of the photon gas is given by
\[ dg = \frac{V \varepsilon^2}{\pi^2 \hbar^3 c^3} d\varepsilon, \quad (5.149) \]

thus
\[ N = \frac{V}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\varepsilon^2}{e^{\varepsilon/\tau} - 1} d\varepsilon = \left( \frac{\tau}{\hbar c} \right)^3 \alpha, \quad (5.150) \]

where
\[ \alpha = \frac{1}{\pi^2} \int_0^\infty \frac{x^2}{e^x - 1} dx. \quad (5.151) \]

The number \( \alpha \) is calculated numerically
\[ \alpha = 0.24359. \quad (5.152) \]

For the universe
\[ N = \frac{4\pi}{3} \left( 10^{20} \text{ m} \right)^3 \left( \frac{1.3806568 \times 10^{-23} \text{ J K}^{-1} \text{ K}}{1.05457266 \times 10^{-34} \text{ Js} 2.99792458 \times 10^8 \text{ m s}^{-1}} \right)^3 \times 0.24359 \]
\[ \simeq 2.29 \times 10^{87}. \quad (5.153) \]

2. The energy emitted by the Sun is
\[ E_{\text{Sun}} = 4\pi R_{\text{Sun}}^2 \sigma_B T_{\text{Sun}}^4, \quad (5.154) \]

and the energy emitted by a planet is
\[ E_{\text{planet}} = 4\pi R_{\text{planet}}^2 \sigma_B T_{\text{planet}}^4. \quad (5.155) \]

The fraction of Sun energy that planet receives is
\[ \frac{\pi R_{\text{planet}}^2}{4\pi D_{\text{M-S}}^2} E_{\text{Sun}}, \quad (5.156) \]

and this equals to the energy it reradiates. Therefore
\[ \frac{\pi R_{\text{planet}}^2}{4\pi D^2} E_{\text{Sun}} = E_{\text{planet}}, \quad (5.157) \]

thus
5.6. Solutions

\[ T_{\text{planet}} = \sqrt{\frac{R_{\text{Sun}}}{2D}} T_{\text{Sun}}, \]  
(5.158)

and for Mars

\[ T_{\text{Mars}} = \sqrt{\frac{6.96 \times 10^8 \text{ m}}{2 \times 2.28 \times 10^{11} \text{ m}}} \times 5800 \text{ K} = 226 \text{ K}. \]  
(5.159)

3. Note that energy conservation implies that the energy radiated per unit area (ERPUA) \( J_r \) from a surface having absorption coefficient \( \alpha \) and temperature \( T \) is given by \( J_r = J_B \alpha \) [see Eq. (5.53)]. The ERPUA from the first (second) surface can be expressed as \( J_{r1} = J_{a11} + J_{a21} \) \( (J_{r2} = J_{a12} + J_{a22}) \), where \( J_{amm} \) denotes the energy absorbed per unit area (EAPUA) by surface \( m \) due to ERPUA originating from surface \( n \), and the following holds

\[ J_{a11} = J_{r1} (1 - \alpha_2) \alpha_1 s, \]  
(5.160)

\[ J_{a21} = J_{r1} \alpha_2 s, \]  
(5.161)

\[ J_{a12} = J_{r2} \alpha_1 s, \]  
(5.162)

\[ J_{a22} = J_{r2} (1 - \alpha_1) \alpha_2 s, \]  
(5.163)

where

\[ s = \sum_{n=0}^{\infty} (1 - \alpha_1)^n (1 - \alpha_2)^n \]
\[ = \frac{1}{1 - (1 - \alpha_1)(1 - \alpha_2)}, \]  
(5.164)

thus

\[ J_{21} = J_{r1} - J_{a11} - J_{a12} \]
\[ = (J_B - J_{B2}) \alpha_1 \alpha_2 s \]
\[ = \frac{\sigma_B (T_1^4 - T_2^4)}{\frac{1}{\alpha_1} + \frac{1}{\alpha_2} - 1}. \]  
(5.165)

4. The partition function is given by

\[ Z = \prod_n \sum_{s=0}^{\infty} \exp (s \beta \omega_n) = \prod_n \frac{1}{1 - \exp (-\beta \omega_n)}, \]  
(5.166)

thus the free energy is given by

\[ F = -\tau \log Z = \tau \sum_n \log [1 - \exp (-\beta \omega_n)]. \]  
(5.167)
Transforming the sum over modes into integral yields

\[ F = \tau \pi \int_0^\infty dn \ n^2 \log [1 - \exp (-\beta \hbar \omega_n)] \]

\[ = \tau \pi \int_0^\infty dn \ n^2 \log \left[ 1 - \exp \left(-\frac{\beta \hbar \pi cn}{L}\right) \right], \quad (5.168) \]

or, by integrating by parts

\[ F = -\frac{1}{3} \frac{\hbar \pi^2 c}{L} \int_0^\infty dn \ n^3 \exp \left(-\frac{\beta \hbar \pi cn}{L}\right) - 1 = -\frac{1}{3} U, \quad (5.169) \]

where

\[ U = \frac{\pi^2 \tau^4 V}{15 \hbar^3 c^3}, \quad (5.170) \]

thus

\[ p = -\left( \frac{\partial F}{\partial V} \right)_\tau = \frac{U}{3V}. \quad (5.171) \]

5. The Helmholtz free energy is given by [see Eq. (5.169)]

\[ F = -\frac{U}{3} = -\frac{\pi^2 \tau^4 V}{45 \hbar^3 c^3}, \quad (5.172) \]

hence the entropy \( \sigma \) is given by

\[ \sigma = -\left( \frac{\partial F}{\partial \tau} \right)_V = \frac{4 \pi^2 \tau^3 V}{45 \hbar^3 c^3}. \quad (5.173) \]

For an isentropic process, for which \( \sigma \) is a constant, one has

\[ \tau_2 = \tau_1 \left( \frac{V_1}{V_2} \right)^{1/3}. \quad (5.174) \]

The pressure \( p \) is given by \( p = U / (3V) \) [see Eq. (5.137)], thus

\[ p = \frac{\pi^2 \tau^4}{45 \hbar^3 c^3}, \quad (5.175) \]

hence

\[ p_2 = \left( \frac{\pi^2 \tau_2^4}{45 \hbar^3 c^3} \right) \left( \frac{V_1}{V_2} \right)^{4/3}. \quad (5.176) \]
6. Let \( u(na) \) be the displacement of point particle number \( n \). The equations of motion are given by

\[
m\ddot{u}(na) = -m\omega^2 \{2u(na) - u[(n - 1) a] - u[(n + 1) a]\}. \tag{5.177}
\]

Consider a solution having the form

\[
u(na, t) = e^{i(kna - \omega_n t)}. \tag{5.178}
\]

Periodic boundary condition requires that

\[
e^{ikNa} = 1, \tag{5.179}
\]

thus

\[
k_n = \frac{2\pi n}{aN}. \tag{5.180}
\]

Substituting into Eq. 5.177 yields

\[
-m\omega_n^2 u(na) = -m\omega^2 \left[2u(na) - u(na) e^{-ika} - u(na) e^{ika}\right], \tag{5.181}
\]

or

\[
\omega_n = \omega \sqrt{2(1 - \cos k_n a)} = 2\omega \left|\sin \frac{k_n a}{2}\right|. \tag{5.182}
\]

7. The single particle eigen energies are given by

\[
\epsilon_n = \hbar \omega \left(n + \frac{1}{2}\right), \tag{5.183}
\]

where \( n = 0, 1, 2, \ldots \).

a) For Bosons

\[
Z_{c,B} = \frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \exp \left[-\beta (\epsilon_n + \epsilon_m)\right] + \frac{1}{2} \sum_{n=0}^{\infty} \exp (-2\beta \epsilon_n)
\]

\[
= \frac{1}{2} \left(\sum_{n=0}^{\infty} \exp (-\beta \epsilon_n)\right)^2 + \frac{1}{2} \sum_{n=0}^{\infty} \exp (-2\beta \epsilon_n)
\]

\[
= \frac{\exp (-\beta \hbar \omega)}{2(1 - \exp (-\beta \hbar \omega))} + \frac{\exp (-\beta \hbar \omega)}{2(1 - \exp (-2\beta \hbar \omega))}. \tag{5.184}
\]

Note that the average energy \( U_B \) is given by

\[
U_B = -\frac{\partial \log Z_{c,B}}{\partial \beta} = \hbar \omega \frac{1 + 2e^{-2\beta \hbar \omega} + e^{-\beta \hbar \omega}}{1 - e^{-2\beta \hbar \omega}}. \tag{5.185}
\]
b) For Fermions

\[ Z_{c,F} = \frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \exp \left[ \beta (\epsilon_n + \epsilon_m) \right] - \frac{1}{2} \sum_{n=0}^{\infty} \exp \left( -2\beta \epsilon_n \right) \]

\[ = \exp \left( -\beta \hbar \omega \right) \frac{2 (1 - \exp (-\beta \hbar \omega))}{2 (1 - \exp (-2\beta \hbar \omega))} \cdot \]

Note that for this case the average energy \( U_F \) is given by

\[ U_F = -\frac{\partial \log Z_{c,F}}{\partial \beta} = \hbar \omega \frac{2 + e^{-2\beta \hbar \omega} + e^{-\beta \hbar \omega}}{1 - e^{-2\beta \hbar \omega}}. \]  

(5.186)

8. In general, by using the Gibbs factor

\[ p(n) = \frac{\exp \left[ n (\mu - \epsilon) \beta \right]}{\sum_{n'} \exp \left[ n' (\mu - \epsilon) \beta \right]}, \]  

\[ p_{F}(n) = \frac{\exp \left[ n (\mu - \epsilon) \beta \right]}{1 + \exp \left[ (\mu - \epsilon) \beta \right]}, \]  

\[ p_{B}(n) = \frac{\exp \left[ n (\mu - \epsilon) \beta \right]}{\sum_{n'=0}^{\infty} \exp \left[ n' (\mu - \epsilon) \beta \right]} \{1 - \exp \left[ (\mu - \epsilon) \beta \right]\} \exp \left[ n (\mu - \epsilon) \beta \right], \]  

\[ \{1 - \exp \left[ (\mu - \epsilon) \beta \right]\} \exp \left[ n (\mu - \epsilon) \beta \right], \]  

\[ \{1 - \exp \left[ (\mu - \epsilon) \beta \right]\} \exp \left[ n (\mu - \epsilon) \beta \right], \]  

where \( n \in \{0, 1\} \), and for Bosons

\[ = \{1 - \exp \left[ (\mu - \epsilon) \beta \right]\} \exp \left[ n (\mu - \epsilon) \beta \right], \]  

(5.190)

where \( n \in \{0, 1, 2, \cdots \} \). The expectation value of \( \langle n \rangle \) in general is given by

\[ \langle n \rangle = \sum_{n'} n' p(n') = \sum_{n'} n' \exp \left[ n (\mu - \epsilon) \beta \right] \]  

\[ = \sum_{n'} \frac{n' \exp \left[ n (\mu - \epsilon) \beta \right]}{\sum_{n'} \exp \left[ n' (\mu - \epsilon) \beta \right]}, \]  

(5.191)

thus for Fermions

\[ \langle n \rangle_F = \frac{1}{\exp \left[ (\epsilon - \mu) \beta \right] + 1}, \]  

(5.192)

and for Bosons
\[ \langle n \rangle_B = \left\{ 1 - \exp \left[ (\mu - \varepsilon) \beta \right] \right\} \sum_{n'=0}^{\infty} n' \exp \left[ n' (\mu - \varepsilon) \beta \right] \]
\[ = \left\{ 1 - \exp \left[ (\mu - \varepsilon) \beta \right] \right\} \frac{\exp \left[ (\mu - \varepsilon) \beta \right]}{(1 - \exp \left[ (\mu - \varepsilon) \beta \right])^2} \]
\[ = \frac{1}{\exp \left[ (\varepsilon - \mu) \beta \right] - 1}. \] (5.193)

In general, the following holds

\[ \tau \left( \frac{\partial \langle n \rangle}{\partial \mu} \right)_\varepsilon = \frac{\sum n'' \langle (n'')^2 \rangle \exp \left[ n (\mu - \varepsilon) \beta \right]}{\sum n' \exp \left[ n' (\mu - \varepsilon) \beta \right]} - \left( \frac{\sum n' \exp \left[ n' (\mu - \varepsilon) \beta \right]}{\sum n' \exp \left[ n' (\mu - \varepsilon) \beta \right]} \right)^2 \]
\[ = \langle n^2 \rangle - \langle n \rangle^2 = \left\langle (n - \langle n \rangle)^2 \right\rangle. \] (5.194)

Thus

\[ (\Delta n)_F^2 = \frac{\exp \left[ (\varepsilon - \mu) \beta \right]}{\left( \exp \left[ (\varepsilon - \mu) \beta \right] + 1 \right)^2} = \langle n \rangle_F (1 - \langle n \rangle_F), \] (5.195)

\[ (\Delta n)_B^2 = \frac{\exp \left[ (\varepsilon - \mu) \beta \right]}{\left( \exp \left[ (\varepsilon - \mu) \beta \right] - 1 \right)^2} = \langle n \rangle_B (1 + \langle n \rangle_B). \] (5.196)

9. In general, at zero temperature the average of the energy \( \varepsilon \) to the power \( n \) is given by

\[ \langle \varepsilon^n \rangle = \frac{\int_0^\varepsilon D(\varepsilon) \varepsilon^n \, d\varepsilon}{\int_0^\varepsilon D(\varepsilon) \, d\varepsilon}, \] (5.197)

where \( D(\varepsilon) \) is the density of states

\[ D(\varepsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}, \] (5.198)

thus

\[ \langle \varepsilon^n \rangle = \frac{\frac{\varepsilon^n}{n} + 1}{\frac{\varepsilon^2}{4} + 1}. \] (5.199)

a) Using Eq. (5.199) one finds that

\[ \langle \varepsilon \rangle = \frac{3\varepsilon_F}{5}. \] (5.200)
b) The speed \( v \) is related to the energy by

\[
v = \sqrt{\frac{2\varepsilon}{m}},
\]

thus

\[
\alpha = \frac{\langle \varepsilon \rangle}{\langle \varepsilon^{1/2} \rangle^2} = \frac{\frac{\varepsilon_F}{3 + 1}}{\frac{\varepsilon_F^{1/2}}{3 + 1}} = \frac{16}{15}.
\]

(5.201)

(5.202)

c) The number of electrons \( N \) is given by

\[
N = \int_0^\varepsilon \! d\varepsilon \, D(\varepsilon) = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \int_0^\varepsilon \! d\varepsilon \, \varepsilon^{1/2} = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \frac{2}{3} \varepsilon_F^{3/2},
\]

thus

\[
\varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3},
\]

(5.203)

(5.204)

and therefore

\[
U = \frac{3N}{5} \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.
\]

(5.205)

Moreover, at zero temperature the Helmholtz free energy \( F = U - \tau \sigma = \tau \sigma = U \), thus the pressure is given by

\[
p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,N}
= -\left( \frac{\partial U}{\partial V} \right)_{\tau,N}
= \frac{3N}{5} \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \frac{2}{3V}
= \frac{2N\varepsilon_F}{5V}.
\]

(5.206)

(5.207)

10. The \( \mathbf{k} \) vector is restricted due to boundary conditions to the values

\[
\mathbf{k} = \frac{\pi \mathbf{n}}{L},
\]

(5.208)

where

\[
\mathbf{n} = (n_x, n_y, n_z)
\]
and \( n_x, n_y, n_z = 1, 2, 3, \ldots \). The single particle partition function is given by

\[
Z_1 = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left( -\frac{\varepsilon(k)}{\tau} \right).
\]  
(5.209)

Approximating the discrete sum by a continuous integral according to

\[
\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{4\pi}{8} \int_0^{\infty} dn n^2, 
\]  
(5.210)

one has

\[
Z_1 = \frac{4\pi}{8} \int_0^{\infty} dn n^2 \exp \left( -\frac{n\hbar\pi c}{L\tau} \right)
= \frac{4V\tau^3}{8\pi^2\hbar^3c^3} \int_0^{\infty} dx x^2 \exp (-x) 
= \frac{V\tau^3}{\pi^2\hbar^3c^3}. 
\]  
(5.211)

In the classical limit the grandcanonical partition function \( Z_{gc} \) is given by [see Eq. (4.39)]

\[
\log Z_{gc} = \lambda Z_1 ,
\]  
(5.212)

where \( \lambda = \exp (\beta \mu) \) is the fugacity. In terms of the Lagrange multipliers \( \eta = -\mu/\tau \) and \( \beta = 1/\tau \) the last result can be rewritten as

\[
\log Z_{gc} = e^{-\eta} \frac{V}{\pi^2\hbar^3c^3\beta^3}.
\]  
(5.213)

\( a \) The average energy \( U \) and average number of particle \( N \) are calculated using Eqs. (3.45) and (3.46) respectively

\[
U = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \frac{3}{\beta} \log Z_{gc},
\]  
(5.214)

\[
N = -\left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta = \log Z_{gc},
\]  
(5.215)

thus

\[
U = 3N\tau ,
\]  
(5.216)

and

\[
\eta = \log \left( \frac{V\tau^3}{\pi^2\hbar^3c^3} \right).
\]  
(5.217)
b) The entropy $\sigma$ is evaluated using Eq. (3.51)

$$\sigma = \log Z_{gc} + \beta U + \eta N$$

$$= N (1 + 3 + \eta)$$

$$= N \left[ 4 + \log \left( \frac{V\tau^3}{\pi^2 N \hbar^3 c^3} \right) \right],$$

and the Helmholtz free energy by the definition (3.89)

$$F = U - \tau \sigma = -N \tau \left[ 1 + \log \left( \frac{V\tau^3}{\pi^2 N \hbar^3 c^3} \right) \right],$$

thus the pressure $p$ is given by

$$p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,N} = \frac{N \tau}{V}.$$ (5.220)

11. The grandcanonical partition function of the gas is given by

$$Z_{gc} = \prod_n \zeta_n,$$ (5.221)

where

$$\zeta_n = \prod_l \left( 1 + \lambda \exp \left( -\beta \varepsilon_n \right) \exp \left( -\beta E_l \right) \right)$$ (5.222)

is a grandcanonical Fermionic partition function of an orbital having energy $\varepsilon_n$ given by

$$\varepsilon_n = \frac{\pi \hbar c n}{L},$$ (5.223)

where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, $n_x, n_y, n_z = 1, 2, 3, \cdots$,

$$\lambda = \exp (\beta \mu) = e^{-\eta}$$ (5.224)

is the fugacity, $\beta = 1/\tau$ and $\{E_l\}$ are the eigenenergies of a particle due to internal degrees of freedom. For electrons, in the absence of magnetic field both spin states have the same energy, which is taken to be zero. Thus, log $Z_{gc}$ can be written as

$$\log Z_{gc} = \sum_{l} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log \left( 1 + \lambda \exp \left( -\beta \varepsilon_n \right) \exp \left( -\beta E_l \right) \right).$$ (5.225)

For a macroscopic system the sum over $n$ can be approximately replaced by an integral.
\[ \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{4\pi}{8} \int_{0}^{\infty} dn \ n^2, \quad (5.226) \]

thus, one has

\[
\log Z_{gc} = 2 \frac{4\pi}{8} \int_{0}^{\infty} dn \ n^2 \log \left(1 + \lambda \exp \left( -\frac{\beta \hbar c}{L} \right) \right). \quad (5.227)
\]

By employing the variable transformation

\[
\varepsilon = \frac{\pi \hbar c n}{L}. \quad (5.228)
\]

one has

\[
\log Z_{gc} = \int_{0}^{\infty} d\varepsilon \ \frac{V \varepsilon^2}{\pi^2 \hbar^2 c^3} \log \left(1 + \lambda \exp \left( -\beta \varepsilon \right) \right). \quad (5.229)
\]

The energy \( U \) and the number of particles \( N \) are given by

\[
U = -\left( \frac{\partial}{\partial \beta} \log Z_{gc} \right)_\eta = \int_{0}^{\infty} d\varepsilon \ \frac{V \varepsilon^3}{\pi^2 \hbar^2 c^3} f_{FD} (\varepsilon), \quad (5.230)
\]

\[
N = \lambda \left( \frac{\partial}{\partial \lambda} \log Z_{gc} \right) = \int_{0}^{\infty} d\varepsilon \ \frac{V \varepsilon^2}{\pi^2 \hbar^2 c^3} f_{FD} (\varepsilon), \quad (5.231)
\]

where \( f_{FD} \) is the Fermi-Dirac distribution function [see Eq. (4.30)]

\[
f_{FD} (\varepsilon) = \frac{1}{\exp[\beta (\varepsilon - \mu)] + 1}. \quad (5.232)
\]

At zero temperature

\[
U = \int_{0}^{\varepsilon_F} d\varepsilon \ \frac{V \varepsilon^3}{\pi^2 \hbar^2 c^3} = \frac{V}{\pi^2 \hbar^2 c^3} \frac{\varepsilon_F^4}{4}, \quad (5.233)
\]

\[
N = \int_{0}^{\varepsilon_F} d\varepsilon \ \frac{V \varepsilon^2}{\pi^2 \hbar^2 c^3} = \frac{V}{\pi^2 \hbar^2 c^3} \frac{\varepsilon_F^3}{3}, \quad (5.234)
\]

and therefore

\[
U = \frac{3N}{4} \varepsilon_F. \quad (5.235)
\]

The energy \( U \) can be expressed as a function of \( V \) and \( N \) as
\[ U = \left( \frac{3N}{4} \right)^{4/3} \left( \frac{\pi^2 h^3 c}{3} \right)^{1/3} V^{-1/3} \frac{\pi}{4} \cdot \frac{1}{\sqrt[3]{V}} - \frac{1}{\sqrt[3]{V}} \frac{4}{3}. \]

At zero temperature the Helmholtz free energy \( F \) equals the energy \( U \), thus the pressure \( p \) is given by

\[ p = - \left( \frac{\partial F}{\partial V} \right)_{\tau,N} = - \left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \frac{1}{3} \left( \frac{3N}{4} \right)^{4/3} \left( \frac{\pi^2 h^3 c}{3} \right)^{1/3} \frac{\pi}{4}, \quad (5.236) \]

thus

\[ \frac{p}{U} = \frac{1}{3V}. \quad (5.237) \]

12. The energy of an electron having a wave function proportional to \( \exp(ik_x x) \exp(ik_y y) \) is \( (\hbar^2 / (2m_e)) (k_x^2 + k_y^2) \). For periodic boundary conditions one has

\[ k_x = \frac{2\pi n_x}{L_x}, \quad (5.238) \]
\[ k_y = \frac{2\pi n_y}{L_y}, \quad (5.239) \]

where the sample is of area \( L_x L_y \), and \( n_x \) and \( n_y \) are both integers. The number of states having energy smaller than \( E' \) is given by (including both spin directions)

\[ 2\pi \frac{2m_e E'}{\hbar^2} \frac{L_x L_y}{4\pi^2}, \quad (5.240) \]

thus, the density of state per unit area is given by

\[ D(E) = \begin{cases} \frac{m_e}{\pi \hbar^2} & E > 0 \\ 0 & E < 0 \end{cases}, \quad (5.241) \]

Using Fermi-Dirac function

\[ f(E) = \frac{1}{1 + \exp[\beta (E - \mu)]}, \quad (5.242) \]

where \( \beta = 1/\tau \), one finds that the density \( n \) is given by

\[ n = \int_{-\infty}^{\infty} D(E) f(E) dE \]
\[ = \frac{m_e}{\pi \hbar^2} \int_{0}^{\infty} \frac{dE}{1 + \exp[\beta (E - \mu)]} \]
\[ = \frac{m_e \tau}{\pi \hbar^2} \log \left( 1 + e^{\beta \mu} \right), \quad (5.243) \]

thus

\[ \mu = \tau \log \left[ \exp \left( \frac{n\pi \hbar^2}{m_e \tau} \right) - 1 \right]. \quad (5.244) \]
13. The orbital eigenenergies are given by

$$\varepsilon_n = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2,$$

where \( n = 1, 2, 3, \ldots \). The grandcanonical partition function \( Z_{gc} \) of the gas is given by

$$Z_{gc} = \prod_n \zeta_n,$$

where

$$\zeta_n = \prod_l (1 + \lambda \exp(-\beta \varepsilon_n) \exp(-\beta E_l)),$$

is the orbital grandcanonical Fermionic partition function, where,

$$\lambda = \exp(\beta \mu) = e^{-\eta},$$

is the fugacity, \( \beta = 1/\tau \) and \( \{E_l\} \) are the eigenenergies of a particle due to internal degrees of freedom. For electrons, in the absence of magnetic field both spin states have the same energy, which is taken to be zero. Thus, \( \log Z_{gc} \) can be written as

$$\log Z_{gc} = \sum_{n=1}^{\infty} \log \zeta_n$$

$$= 2 \sum_{n=1}^{\infty} \log(1 + \lambda \exp(-\beta \varepsilon_n))$$

$$\simeq 2 \int_0^{\infty} d\varepsilon \log \left(1 + \lambda \exp \left(-\beta \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2 \right) \right).$$

(5.249)

By employing the variable transformation

$$\varepsilon = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2,$$

one obtains

$$\log Z_{gc} = \frac{1}{2} \int_0^{\infty} d\varepsilon \ D(\varepsilon) \log (1 + \lambda \exp(-\beta \varepsilon)),$$

(5.251)

where

$$D(\varepsilon) = \begin{cases} \frac{2L}{\pi} \sqrt{\frac{2m}{\hbar^2} \varepsilon^{-1/2}} & \varepsilon \geq 0 \\ 0 & \varepsilon < 0 \end{cases}$$

(5.252)
is the 1D density of states. Using Eqs. (3.45) and (3.60) for the energy $U$ and the number of particles $N$, namely using

$$U = -\left(\frac{\partial \log Z_{gc}}{\partial \beta}\right)_{\eta},$$

$$N = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda},$$

one finds that

$$U = \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) \varepsilon f_{FD}(\varepsilon),$$

$$N = \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) f_{FD}(\varepsilon),$$

where $f_{FD}$ is the Fermi-Dirac distribution function [see Eq. (4.30)]

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta (\varepsilon - \mu)] + 1}.$$ (5.257)

At zero temperature, where $\mu = \varepsilon_F$ one has

$$U = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} = \frac{2D(\varepsilon_F)}{3} \varepsilon_F^2,$$

$$N = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{-1/2} = 2D(\varepsilon_F) \varepsilon_F,$$

thus

$$\frac{U}{\varepsilon_F} = \frac{N}{3}.$$ (5.260)

14. The orbital eigenenergies in this case are given by

$$\varepsilon_n = \hbar \omega \left(n + \frac{1}{2}\right),$$

where $n = 0, 1, 2, \cdots$. The grandcanonical partition function of the gas is given by

$$Z_{gc} = \prod_n \zeta_n,$$

where

$$\zeta_n = \prod_l \left(1 + \lambda \exp(-\beta \varepsilon_n) \exp(-\beta E_l)\right).$$ (5.263)
is the orbital grandcanonical Fermionic partition function where,
\[ \lambda = \exp(\beta \mu) = e^{-\eta} \]  
(5.264)
is the fugacity, \( \beta = 1/\tau \) and \( \{ E_i \} \) are the eigenenergies of a particle due to internal degrees of freedom. For electrons, in the absence of magnetic field both spin states have the same energy, which is taken to be zero. Thus, \( \log Z_{gc} \) can be written as
\[
\log Z_{gc} = \sum_{n=0}^{\infty} \log \zeta_n \\
= \sum_{n=0}^{\infty} \log (1 + \lambda \exp(-\beta \varepsilon_n)). 
\]  
(5.265)
The number of particles \( N \) is given by
\[
N = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda} = 2 \sum_{n=0}^{\infty} f_{FD}(\varepsilon_n), 
\]  
(5.266)
where \( f_{FD} \) is the Fermi-Dirac distribution function
\[
f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}. 
\]  
(5.267)
a) At zero temperature the chemical potential \( \mu \) is the Fermi energy \( \varepsilon_F \), and the Fermi-Dirac distribution function becomes a step function, thus with the help of Eq. (5.266) one finds that
\[
N = \frac{2\varepsilon_F}{\hbar \omega}, 
\]  
(5.268)
thus
\[
\mu = \varepsilon_F = \frac{N \hbar \omega}{2}. 
\]  
(5.269)
b) Using the approximation
\[
f_{FD}(\varepsilon) \simeq \exp[-\beta (\varepsilon - \mu)], 
\]  
(5.270)
for the the limit of high temperatures and approximating the sum by an integral one has
\[
N = 2 \sum_{n=0}^{\infty} \exp \left[ -\beta \left( \hbar \omega \left( n + \frac{1}{2} \right) - \mu \right) \right] \\
= 2 \exp \left( \beta \left( \mu - \frac{\hbar \omega}{2} \right) \right) \int_0^{\infty} dn \exp(-\beta \hbar \omega n) \\
= \frac{2 \exp \left( \beta \left( \mu - \frac{\hbar \omega}{2} \right) \right)}{\beta \hbar \omega}, 
\]  
(5.271)
thus

\[ \mu = \tau \left( \log \left( \frac{N \beta \hbar \omega}{2} \right) + \frac{\beta \hbar \omega}{2} \right) \]

\[ \simeq \tau \log \left( \frac{N \beta \hbar \omega}{2} \right). \]

(5.272)
6. Classical Limit of Statistical Mechanics

In this chapter the classical limit of statistical mechanics is discussed. The Hamilton’s formalism is introduced, and the Hamilton-Jacobi equations of motion are presented. The density function in thermal equilibrium is used to prove the equipartition theorem.

6.1 Classical Hamiltonian

In this section the Hamilton’s formalism, which is analogous to Newton’s laws of classical mechanics, is briefly reviewed. Consider a classical system having \( d \) degrees of freedom. The system is described using the vector of coordinates

\[
\vec{q} = (q_1, q_2, \cdots, q_d).
\]  

(6.1)

Let \( E \) be the total energy of the system. For simplicity we restrict the discussion to a special case where \( E \) is a sum of two terms

\[
E = T + V,
\]

where \( T \) depends only on velocities, namely \( T = T(\dot{\vec{q}}) \), and where \( V \) depends only on coordinates, namely \( V = V(\vec{q}) \). The notation overdot is used to express time derivative, namely

\[
\dot{\vec{q}} = \left( \frac{dq_1}{dt}, \frac{dq_2}{dt}, \cdots, \frac{dq_d}{dt} \right).
\]  

(6.2)

The first term \( T \) is referred to as kinetic energy and to the second one \( V \) as potential energy.

The canonical conjugate momentum \( p_i \) of the coordinate \( q_i \) is defined as

\[
p_i = \frac{\partial T}{\partial \dot{q}_i}.
\]  

(6.3)

The classical Hamiltonian \( \mathcal{H} \) of the system is expressed as a function of the vector of coordinates \( \vec{q} \) and as a function of the vector of canonical conjugate momentum variables...
\[ \vec{p} = (p_1, p_2, \cdots, p_d), \]  

namely

\[ \mathcal{H} = \mathcal{H}(\vec{q}, \vec{p}), \]  

and it is defined by

\[ \mathcal{H} = \sum_{i=1}^{d} p_i \dot{q}_i - T + V. \]  

### 6.1.1 Hamilton-Jacobi Equations

The equations of motion of the system are given by

\[ \dot{q}_i = \frac{\partial \mathcal{H}}{\partial \dot{p}_i}, \]  
\[ \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \]

where \( i = 1, 2, \cdots d. \)

### 6.1.2 Example

Consider a particle having mass \( m \) in a one dimensional potential \( V(q) \) (see Fig. 6.1). The kinetic energy is given by \( T = m\dot{q}^2/2 \), thus the canonical conjugate momentum is given by [see Eq. (6.3)] \( p = m\dot{q} \). Thus for this example the canonical conjugate momentum equals the mechanical momentum. Note, however, that this is not necessarily always the case. Using the definition (6.6) one finds that the Hamiltonian is given by

\[ \mathcal{H} = m\dot{q}^2 - \frac{m\dot{q}^2}{2} + V(q) \]

\[ = \frac{p^2}{2m} + V(q). \]  

Hamilton-Jacobi equations (6.7) and (6.8) read

\[ \ddot{q} = \frac{p}{m}, \]  
\[ \dot{p} = -\frac{\partial V}{\partial q}. \]

The second equation, which can be rewritten as

\[ m\ddot{q} = -\frac{\partial V}{\partial q}, \]

expresses Newton’s second law.
6.2 Density Function

Consider a classical system in thermal equilibrium. The density function $\rho(\bar{q}, \bar{p})$ is the probability distribution to find the system in the point $(\bar{q}, \bar{p})$. 

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Fig. 6.2. A capacitor having capacitance $C$ connected in parallel to an inductor having inductance $L$.

The following theorem is given without a proof. Let $\mathcal{H}(\bar{q}, \bar{p})$ be an Hamiltonian of a system, and assume that $\mathcal{H}$ has the following form

$$\mathcal{H} = \sum_{i=1}^{d} A_i p_i^2 + V(\bar{q}),$$

(6.17)

where $A_i$ are constants. Then in the classical limit, namely in the limit where Plank’s constant approaches zero $h \to 0$, the density function is given by

$$\rho(\bar{q}, \bar{p}) = N \exp\left(-\beta \mathcal{H}(\bar{q}, \bar{p})\right),$$

(6.18)

where

$$N = \frac{1}{\int d\bar{q} \int d\bar{p} \exp\left(-\beta \mathcal{H}(\bar{q}, \bar{p})\right)}$$

(6.19)

is a normalization constant, $\beta = 1/\tau$, and $\tau$ is the temperature. The notation $\int d\bar{q}$ indicates integration over all coordinates, namely $\int d\bar{q} = \int dq_1 \int dq_1 \cdot \cdot \cdot \int dq_d$, and similarly $\int d\bar{p}$.

Let $A(\bar{q}, \bar{p})$ be a variable which depends on the coordinates $\bar{q}$ and their canonical conjugate momentum variables $\bar{p}$. Using the above theorem the average value of $A$ can be calculates as:

$$\langle A(\bar{q}, \bar{p}) \rangle = \int d\bar{q} \int d\bar{p} \ A(\bar{q}, \bar{p}) \rho(\bar{q}, \bar{p})$$

$$= \frac{\int d\bar{q} \int d\bar{p} \ A(\bar{q}, \bar{p}) \exp(-\beta \mathcal{H}(\bar{q}, \bar{p}))}{\int d\bar{q} \int d\bar{p} \ \exp(-\beta \mathcal{H}(\bar{q}, \bar{p}))}.$$

(6.20)
6.2.1 Equipartition Theorem

Theorem 6.2.1. Assume that the Hamiltonian has the following form

\[ H = B_i q_i^2 + \tilde{H}, \]  

(6.21)

where \( B_i \) is a constant and where \( \tilde{H} \) is independent of \( q_i \). Then the following holds

\[ \langle B_i q_i^2 \rangle = \frac{\tau}{2}. \]  

(6.22)

Similarly, assume that the Hamiltonian has the following form

\[ H = A_i p_i^2 + \tilde{H}, \]  

(6.23)

where \( A_i \) is a constant and where \( \tilde{H} \) is independent of \( p_i \). Then the following holds

\[ \langle A_i p_i^2 \rangle = \frac{\tau}{2}. \]  

(6.24)

Proof. With the help of Eq. (6.20) one finds the first case that

\[ \langle B_i q_i^2 \rangle = \frac{\partial}{\partial \beta} \log \left( \int dq_i B_i q_i^2 \exp \left( -\beta H(q, \tilde{p}) \right) \right) \]

\[ = \frac{\partial}{\partial \beta} \log \left( \int dq_i \exp \left( -\beta B_i q_i^2 \right) \right) \]

\[ = \frac{1}{2\beta}. \]  

(6.25)

The proof for the second case is similar.

Exercise 6.2.1. Consider a particle having mass \( m \) in a one dimensional parabolic potential given by \( V(q) = (1/2) kq^2 \), where \( k \) is the spring constant (harmonic oscillator). The kinetic energy is given by \( p^2/2m \), where \( p \) is the canonical momentum variable conjugate to \( q \). The Hamiltonian is given by

\[ H = \frac{p^2}{2m} + \frac{kq^2}{2}. \]  

(6.26)

Calculate the average energy \( U \) in the classical limit. Compare the result to the more general result that is derived using a quantum treatment.
Chapter 6. Classical Limit of Statistical Mechanics

**Solution 6.2.1.** In the classical limit the average energy of the system can be easily calculated using the equipartition theorem

\[ U = \langle \mathcal{H} \rangle = \tau . \]  

(6.27)

In the quantum treatment, the system has discrete energy levels \( E_s \) given by

\[ E_s = s \hbar \omega , \]

where \( s = 0, 1, 2, \cdots \), and where \( \omega = \sqrt{k/m} \) is the angular resonance frequency. The partition function is given by

\[ Z = \sum_{s=0}^{\infty} \exp \left( -s \beta \hbar \omega \right) = \frac{1}{1 - \exp \left( -\beta \hbar \omega \right)} , \]

(6.28)

thus the average energy \( U \) is given by

\[ U = -\frac{\partial \log Z}{\partial \beta} = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} . \]

(6.29)

Using the expansion

\[ U = \beta^{-1} + O(\beta) , \]

(6.30)

one finds that in the limit of high temperatures, namely when \( \beta \hbar \omega \ll 1 \), the quantum result [Eq. (6.30)] coincides with the classical limit [Eq. (6.27)].

### 6.3 Problems

1. A gas at temperature \( \tau \) emits a spectral line at wavelength \( \lambda_0 \). The width of the observed spectral line is broadened due to motion of the molecules (this is called Doppler broadening). Show that the relation between spectral line intensity \( I \) and wavelength is given by

\[ I(\lambda) \propto \exp \left[ -\frac{mc^2(\lambda - \lambda_0)^2}{2\lambda_0^5 \tau} \right] , \]

(6.31)

where \( c \) is velocity of light, and \( m \) is mass of a molecule.

2. Consider two particles, both having the same mass \( m \), moving in a one-dimensional potential with coordinates \( x_1 \) and \( x_2 \) respectively. The potential energy is given by

\[ V(x_1, x_2) = \frac{m\omega^2 x_1^2}{2} + \frac{m\omega^2 x_2^2}{2} + m\Omega^2 (x_1 - x_2)^2 , \]

(6.32)

where the angular frequencies \( \omega \) and \( \Omega \) are real constants Assume that the temperature \( \tau \) of the system is sufficiently high to allow treating it classically. Calculate the following average values \( \langle x_1^2 \rangle \) and \( \langle (x_1 - x_2)^2 \rangle \).
6.3. Problems

3. A classical system is described using a set of coordinates \( \{ q_1, q_2, \ldots, q_N \} \) and the corresponding canonically conjugate variables \( \{ p_1, p_2, \ldots, p_N \} \). The Hamiltonian of the system is given by

\[
H = \sum_{n=1}^{N} A_n p_n^s B_n q_n^t,
\]

where \( A_n \) and \( B_n \) are positive constants, and \( s \) and \( t \) are even positive integers. Show that the average energy of the system in equilibrium at temperature \( \tau \) is given by

\[
\langle U \rangle = N \tau \left( \frac{1}{s} + \frac{1}{t} \right).
\]

4. A small hole of area \( A \) is made in the wall of a vessel of volume \( V \) containing a classical ideal gas of \( N \) particles of mass \( M \) in equilibrium at temperature \( \tau \). Calculate the number of particles \( dN \), which escape through the opening during the infinitesimal time interval \( dt \).

5. Consider an ideal gas of Fermions having mass \( M \) and having no internal degrees of freedom at temperature \( \tau \). The velocity of a particle is denoted as \( v = \sqrt{v_x^2 + v_y^2 + v_z^2} \). Calculate the quantity

\[
\langle v \rangle \left\langle \frac{1}{v} \right\rangle
\]

(the symbol \( \langle \rangle \) denoted averaging) in the:

a) classical limit (high temperatures).

b) zero temperature.

6. Consider an ideal classical gas of particles having mass \( M \) and having no internal degrees of freedom at temperature \( \tau \). Let \( v = \sqrt{v_x^2 + v_y^2 + v_z^2} \) be the velocity of a particle. Calculate

a) \( \langle v \rangle \)

b) \( \sqrt{\langle v^2 \rangle} \)

7. Consider an ideal gas of \( N \) molecules, each of mass \( M \), contained in a centrifuge of radius \( R \) and length \( L \) rotating with angular velocity \( \omega \) about its axis. Neglect the effect of gravity. The system is in equilibrium at temperature \( \tau = 1/\beta \). Calculate the particle density \( n(r) \) as a function of the radial distance from the axis \( r \) (where \( 0 \leq r \leq R \)).

8. A mixture of two classical ideal gases, consisting of \( N_1 \) and \( N_2 \) particles of mass \( M_1 \) and \( M_2 \), respectively, is enclosed in a cylindrical vessel of height \( h \) and area of bottom and top side \( S \). The vessel is placed in a gravitational field having acceleration \( g \). The system is in thermal equilibrium at temperature \( \tau \). Find the pressure exerted on the upper wall of the cylinder.
6.4 Solutions

1. Let $\lambda$ be the wavelength measured by an observer, and let $\lambda_0$ be the wavelength of the emitted light in the reference frame where the molecule is at rest. Let $v_x$ be the velocity of the molecule in the direction of the light ray from the molecule to the observer. Due to Doppler effect (to first order in $v_x/c$, i.e. in the non-relativistic limit)

$$\lambda = \lambda_0 \left(1 + \frac{v_x}{c}\right). \quad (6.35)$$

The probability distribution $f(v_x)$ is proportional to

$$f(v_x) \propto \exp \left(-\frac{mv_x^2}{2\tau}\right), \quad (6.36)$$

thus using

$$v_x = c \left(\frac{\lambda - \lambda_0}{\lambda_0}\right), \quad (6.37)$$

one finds that the probability distribution $I(\lambda)$ is proportional to

$$I(\lambda) \propto \exp \left[-\frac{mc^2(\lambda - \lambda_0)^2}{2\lambda_0^2 \tau}\right]. \quad (6.38)$$

2. It is convenient to employ the coordinate transformation

$$x_+ = \frac{x_1 + x_2}{\sqrt{2}}, \quad (6.39)$$
$$x_- = \frac{x_1 - x_2}{\sqrt{2}}. \quad (6.40)$$

The inverse transformation is given by

$$x_1 = \frac{x_+ + x_-}{\sqrt{2}}, \quad (6.41)$$
$$x_2 = \frac{x_+ - x_-}{\sqrt{2}}. \quad (6.42)$$

The following holds

$$x_1^2 + x_2^2 = x_+^2 + x_-^2, \quad (6.43)$$

and

$$\dot{x}_1^2 + \dot{x}_2^2 = \dot{x}_+^2 + \dot{x}_-^2, \quad (6.44)$$

thus, the kinetic energy $T$ of the system is given by

$$T = \frac{m (\dot{x}_1^2 + \dot{x}_2^2)}{2} = \frac{m (\dot{x}_+^2 + \dot{x}_-^2)}{2}, \quad (6.45)$$
and the potential energy $V$ is given by

$$V(x_1, x_2) = \frac{m\omega^2}{2} x_1^2 + \frac{m\omega^2}{2} x_2^2 + m\Omega^2 (x_1 - x_2)^2$$

$$= \frac{m\omega^2}{2} x_1^2 + \frac{m(\omega^2 + 4\Omega^2)}{2} x_2^2.$$  

(6.46)

The equipartition theorem yields

$$\frac{m\omega^2}{2} \langle x_1^2 \rangle = \frac{m(\omega^2 + 4\Omega^2)}{2} \langle x_2^2 \rangle = \frac{\tau}{2},$$

(6.47)

thus

$$\langle (x_1 + x_2)^2 \rangle = \frac{2\tau}{m\omega^2},$$

(6.48)

and

$$\langle (x_1 - x_2)^2 \rangle = \frac{2\tau}{m(\omega^2 + 4\Omega^2)}.$$  

(6.49)

Furthermore, since by symmetry $\langle x_+ x_- \rangle = 0$, one has

$$\langle x_1^2 \rangle = \frac{1}{2} \langle (x_+ + x_-)^2 \rangle$$

$$= \frac{1}{2} \left( \langle x_+^2 \rangle + \langle x_-^2 \rangle \right)$$

$$= \frac{\tau}{m\omega^2} \left( 1 - \frac{4\Omega^2}{\omega^2} \right).$$

(6.50)

3. The following holds

$$\langle B_n q_n^t \rangle = \frac{\int_{-\infty}^{\infty} dq_n B_n q_n^t \exp(-\beta B_n q_n^t)}{\int_{-\infty}^{\infty} dq_n \exp(-\beta B_n q_n^t)}$$

$$= \frac{\int_0^{\infty} dq_n B_n q_n^t \exp(-\beta B_n q_n^t)}{\int_0^{\infty} dq_n \exp(-\beta B_n q_n^t)}$$

$$= -\frac{d}{d\beta} \log \int_0^{\infty} dq_n \exp(-\beta B_n q_n^t),$$

(6.51)

where $\beta = 1/\tau$. The integration variable transformation

$$x = \beta B_n q_n^t,$$

(6.52)

$$dx = t\beta B_n q_n^{t-1} dq_n,$$

(6.53)
leads to
\[
\langle B_n q_n^t \rangle = -\frac{d}{d\beta} \log \left( (\beta B_n)^{\frac{1}{t}} t^{-1} \int_0^\infty x^{\frac{1}{t}-1} e^{-x} dx \right) = \frac{\tau}{t}, \tag{6.54}
\]
thus
\[
\langle U \rangle = \sum_{n=1}^N \langle A_n p_n^s \rangle + \langle B_n q_n^t \rangle = N \tau \left( \frac{1}{s} + \frac{1}{t} \right). \tag{6.55}
\]

4. Let \( f(v) \) be the probability distribution of velocity \( v \) of particles in the gas. The vector \( \mathbf{u} \) is expressed in spherical coordinates, where the \( z \) axis is chosen in the direction of the normal outward direction
\[
v = v (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta). \tag{6.56}
\]
By symmetry, \( f(v) \) is independent of \( \theta \) and \( \varphi \). The number \( dN \) is calculated by integrating over all possible values of the velocity of the leaving particles (note that \( \theta \) can be only in the range \( 0 \leq \theta \leq \pi/2 \))
\[
dN = \int_0^\infty dv \int_0^1 d(\cos \theta) \int_0^{2\pi} d\varphi \, v^2 v \langle dv \rangle A \cos \theta N \frac{f(v)}{V}. \tag{6.57}
\]
Note that \( v \langle dv \rangle A \cos \theta \) represents the volume of a cylinder, from which particles of velocity \( v \) can escape during the time interval \( dt \). Since \( f(v) \) is normalized
\[
1 = \int_0^\infty dv \int_0^1 d(\cos \theta) \int_0^{2\pi} d\varphi \, v^2 f(v) = 4\pi \int_0^\infty dv v^2 f(v), \tag{6.58}
\]
thus
\[
\frac{dN}{dt} = \pi N A \frac{\langle v \rangle}{V} = \int_0^\infty dv v^2 v f(v) = \frac{N A \langle v \rangle}{4V}. \tag{6.59}
\]
In the classical limit
\[
f(v) \propto \exp \left( -\frac{Mv^2}{2\tau} \right), \tag{6.60}
\]
thus, by changing the integration variable \( x = Mv^2/(2\tau) \) one finds that
\[
\langle v \rangle = \frac{\int_0^\infty dv v^3 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dv v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)}
\]
\[
= \frac{2\tau}{M} \left( \frac{8\tau}{\pi M} \right)^{1/2} \int_0^\infty dx x^{1/2} \exp(-x)
\]
\[
= \frac{8\tau}{\pi M}^{1/2}, \tag{6.61}
\]
6.4. Solutions

\[ \frac{dN}{dt} = \frac{NA}{4V} \left( \frac{8\pi}{\pi M} \right)^{1/2}. \]  

(6.62)

5. The probability that an orbital having energy \( \varepsilon \) is occupied is given by

\[ f_F(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \mu}{\beta}\right)}, \]

(6.63)

where \( \beta = \frac{1}{\tau} \) and \( \mu \) is the chemical potential. The velocity \( v \) of such an orbital is related to the energy \( \varepsilon \) by

\[ \varepsilon = \frac{Mv^2}{2}. \]

(6.64)

The 3D density of state per unit volume is given by

\[ g(\varepsilon) = \frac{1}{2\pi^2} \left( \frac{2M}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}, \]

(6.65)

thus

\[ \langle v \rangle = \left( \int_0^\infty d\varepsilon \varepsilon f_F(\varepsilon) f_F(\varepsilon) \frac{1}{\varepsilon} \right) \left( \int_0^\infty d\varepsilon f_F(\varepsilon) \right)^2. \]

(6.66)

a) In the classical limit

\[ f_F(\varepsilon) \propto \exp\left(\frac{-\beta \varepsilon}{\varepsilon}\right), \]

(6.67)

thus using the identities

\[ \int_0^\infty d\varepsilon \varepsilon^n \exp\left(\frac{-\beta \varepsilon}{\varepsilon}\right) = \Gamma(n) \frac{n^n}{\beta^n}, \]

(6.68)

\[ \int_0^\infty d\varepsilon \exp\left(\frac{-\beta \varepsilon}{\varepsilon}\right) = \frac{1}{\beta}, \]

(6.69)

\[ \Gamma(1) = 1, \]

(6.70)

\[ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}, \]

(6.71)
one finds that
\[
\langle v \rangle \langle \frac{1}{v} \rangle = \frac{\left( \int_0^\infty d\varepsilon \varepsilon \exp(-\beta\varepsilon) \right) \left( \int_0^\infty d\varepsilon \exp(-\beta\varepsilon) \right) \left( \int_0^\infty d\varepsilon \varepsilon^{1/2} \exp(-\beta\varepsilon) \right)^2}{\left( \int_0^\infty d\varepsilon \varepsilon^{1/2} \exp(-\beta\varepsilon) \right)^2}
\]
\[
= \frac{\Gamma(1) \beta^{-1} \frac{1}{\pi} \pi^2}{\left( \Gamma\left(\frac{3}{2}\right) \beta^{-1/2} \frac{1}{2\pi} \right)^2}
\]
\[
= \frac{4}{\pi}.
\]

(6.72)

b) Using the identity
\[
\int_0^{\varepsilon_F} d\varepsilon \varepsilon^n = \frac{\varepsilon_F^{n+1}}{n+1},
\]
(6.73)

one finds that
\[
\langle v \rangle \langle \frac{1}{v} \rangle = \frac{\left( \int_0^{\varepsilon_F} d\varepsilon \varepsilon \right) \left( \int_0^{\varepsilon_F} d\varepsilon \right) \left( \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} \right)^2}{\left( \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} \right)^2}
\]
\[
= \frac{\varepsilon_F^2}{\pi} \frac{\varepsilon_F^2}{\pi} \frac{\varepsilon_F^3}{2}
\]
\[
= \frac{9}{8}.
\]

(6.74)

6. In the classical limit the probability distribution of the velocity vector \( \mathbf{v} \) satisfies
\[
f(\mathbf{v}) \propto \exp\left(-\frac{Mv^2}{2\tau}\right),
\]
(6.75)

where \( v = |\mathbf{v}| \).

a) By changing the integration variable
\[
x = \frac{Mv^2}{2\tau}
\]
(6.76)

one finds
6.4. Solutions

\[ \langle v \rangle = \frac{\int_0^\infty dv \, v^3 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dv \, v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \frac{2\tau}{M} \frac{\int_0^\infty dx \, x \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dx \, x^{1/2} \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \left( \frac{8\tau}{\pi M} \right)^{1/2} . \]  

(6.77)

\[ \langle v^2 \rangle = \frac{\int_0^\infty dv \, v^4 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dv \, v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \frac{2\tau}{M} \frac{\int_0^\infty dx \, x^{3/2} \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dx \, x^{1/2} \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \frac{2\tau}{M} \frac{3}{2} , \]  

(6.78)

b) Similarly

\[ \langle v^2 \rangle = \frac{\int_0^\infty dv \, v^4 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dv \, v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \frac{2\tau}{M} \frac{\int_0^\infty dx \, x^{3/2} \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_0^\infty dx \, x^{1/2} \exp \left( -\frac{Mv^2}{2\tau} \right)} \]

\[ = \frac{2\tau}{M} \frac{3}{2} , \]  

(6.79)

thus

\[ \sqrt{\langle v^2 \rangle} = \left( \frac{3\tau}{M} \right)^{1/2} = \left( \frac{3\pi}{8} \right)^{1/2} \langle v \rangle . \]  

(6.80)

7. The effect of rotation is the same as an additional external field with potential energy given by

\[ U (r) = -\frac{1}{2} M\omega^2 r^2 , \]  

(6.81)

thus

\[ n (r) = A \exp \left[ -\beta U (r) \right] = A \exp \left( \frac{\beta M\omega^2}{2} r^2 \right) , \]  

(6.82)

where the normalization constant \( A \) is found from the condition

\[ N = 2\pi L \int_0^R n (r) r dr \]

\[ = 2\pi LA \int_0^R \exp \left( \frac{\beta M\omega^2}{2} r^2 \right) r dr \]

\[ = \frac{2\pi LA}{\beta M\omega^2} \left[ \exp \left( \frac{\beta M\omega^2}{2} R^2 \right) - 1 \right] , \]  

(6.83)
thus
\[
n(r) = \frac{N\beta M \omega^2}{2\pi L} \left[ \exp\left(\frac{\beta M \omega^2}{2} R^2\right) - 1 \right] \exp\left(\frac{\beta M \omega^2}{2} r^2\right).
\] (6.84)

8. For each gas the density is given by
\[
n_l(z) = n_l(0) \exp(-\beta M_l g z),
\]
where \( l \in \{1, 2\} \), \( 0 \leq z \leq h \) and the normalization constant is found from the requirement
\[
S \int_0^h dz \ n(z) = N_l,
\] (6.85)
therefore
\[
n_l(0) = \frac{N_l}{S \int_0^h dz \ \exp(-\beta M_l g z)} = \frac{\beta M_l g N_l}{S \left(1 - e^{-\beta M_l g h}\right)}.
\] (6.86)

Using the equation of state \( p = n \tau \), where \( n = N/V \) is the density, one finds that the pressure on the upper wall of the cylinder is given by
\[
p = \left( n_1(h) + n_2(h) \right) \tau
= \left( \frac{M_1 N_1}{\exp(\beta M_1 g h) - 1} + \frac{M_2 N_2}{\exp(\beta M_2 g h) - 1} \right) \frac{g}{S}.
\] (6.87)
7. Noise

This chapter reviews the Langevin and Fokker-Planck equations, and analyzes noise originating from electrical resistance (Nyquist noise) and phase noise of oscillators.

7.1 Stationary Random Signals

Consider a complex signal \( z(t) \) randomly varying in time. As will be discussed below, the random signal \( z(t) \) can be characterized by a variety of statistical properties. In this section it will be assumed that \( z(t) \) is stationary. This assumption implies that all statistical properties of \( z(t) \) remain unchanged when \( z(t) \) is replaced by \( z(t - t_0) \), where \( t_0 \) is a constant (i.e. when the signal is shifted in time).

7.1.1 Power Spectrum

Let \( z_T(t) \) be a sampling of the signal \( z(t) \) in the time interval \((-T/2, T/2)\), namely

\[
z_T(t) = \begin{cases} 
z(t) & -T/2 < t < T/2 \\
0 & \text{else}
\end{cases}
\]  

(7.1)

The signal \( z_T(t) \) can be expressed in terms of its Fourier transform (FT) \( z_T(\omega) \) as

\[
z_T(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ z_T(\omega) e^{-i\omega t}.
\]  

(7.2)

Definition 7.1.1. The power spectrum \( S_z(\omega) \) of \( z_T(t) \) is defined by

\[
S_z(\omega) \equiv \lim_{T \to \infty} \frac{1}{T} |z_T(\omega)|^2.
\]  

(7.3)

Let \( O(z(t)) \) be a functional of the random signal \( z(t) \). The expectation value of \( O(z(t)) \) is defined by

\[
\langle O(z(t)) \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ O(z_T(t)).
\]  

(7.4)
Chapter 7. Noise

Claim. The following holds

\[ \langle |z|^2 \rangle = \int_{-\infty}^{\infty} d\omega \, S_z(\omega) \, . \quad (7.5) \]

Proof. According to the definition (7.4) one has

\[ \langle |z|^2 \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \, z_T^*(t) \, z_T(t) \, , \quad (7.6) \]

thus with the help of Eq. (7.2) one finds that

\[
\begin{align*}
\langle |z|^2 \rangle &= \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{\infty} d\omega' \, z_{T}^{*}(\omega') \, e^{i\omega't} \\
&\quad \times \int_{-\infty}^{\infty} d\omega \, z_{T}(\omega) \, e^{-i\omega t} \\
&= \lim_{T \to \infty} \frac{1}{2\pi T} \int_{-\infty}^{\infty} d\omega' \, z_{T}^{*}(\omega') \int_{-\infty}^{\infty} d\omega \, z_{T}(\omega) \\
&\quad \times \int_{-\infty}^{+\infty} dt \, e^{-i(\omega-\omega')t} \\
&= \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \, |z_T(\omega)|^2 \, . \\
\end{align*}
\]

(7.7)

thus [see Eq. (7.3)]

\[ \langle |z|^2 \rangle = \int_{-\infty}^{\infty} d\omega \, S_z(\omega) \, . \quad (7.8) \]

7.1.2 Autocorrelation Function

Definition 7.1.2. The autocorrelation function \( C_z(t) \) is defined by

\[ C_z(t') = \langle z^*(t + t') z(t) \rangle \, . \quad (7.9) \]

Note that the assumption that \( z(t) \) is stationary implies that the quantity \( \langle z^*(t + t') z(t) \rangle \) is independent on \( t \).

Claim (Wiener-Khinchine Theorem). The following holds

\[ C_z(t') = \int_{-\infty}^{\infty} d\omega \, e^{i\omega t'} S_z(\omega) \, . \quad (7.10) \]
Proof. According to the definition (7.4) one has

\[ C_z(t') = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ z^*_T(t + t') z_T(t) , \tag{7.11} \]

thus with the help of Eq. (7.2) one finds that

\[
C_z(t') = \lim_{T \to \infty} \frac{1}{2\pi T} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\omega' \ z^*_T(\omega') e^{i\omega'(t+t')}
\times \int_{-\infty}^{+\infty} d\omega \ z_T(\omega) e^{-i\omega t}
\]
\[
= \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} d\omega' \ z^*_T(\omega') e^{i\omega t'} \int_{-\infty}^{+\infty} d\omega \ z_T(\omega)
\times \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \ e^{-i(\omega-\omega')t}
\]
\[
= \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} \lim_{T \to \infty} \frac{1}{T} |z_T(\omega)|^2 ,
\tag{7.12}
\]

thus [see Eq. (7.3)]

\[ C_z(t') = \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} S_z(\omega) . \tag{7.13} \]

Claim. The following holds

\[ \langle z^*(\omega') z(\omega) \rangle = 2\pi S_z(\omega) \delta(\omega - \omega') . \tag{7.14} \]

Proof. Inverting the FT in Eq. (7.2) yields

\[ z_T(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt \ z_T(t) e^{i\omega t} , \tag{7.15} \]

thus [see Eq. (7.9)]

\[
\langle z^*(\omega') z(\omega) \rangle
= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt \ e^{i(\omega t - \omega' t')} \langle z^*(t') z(t) \rangle
= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt \ e^{i(\omega t - \omega' t')} C_z(t' - t) . \tag{7.16}
\]

The variable transformation \( t'' = t' - t \) leads to
\[
\left\langle z^* (\omega') z (\omega) \right\rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' e^{-i\omega' t'} e^{i\omega (t'-t'')} C_z (t'') \\
= \int_{-\infty}^{\infty} dt'' e^{-i\omega t''} C_z (t'') \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' e^{i(\omega-\omega')t'} \right\} \delta(\omega-\omega')
\]  
(7.17)

thus, with the help of Eq. (7.10) one finds that
\[
\left\langle z^* (\omega') z (\omega) \right\rangle = \int_{-\infty}^{\infty} dt'' e^{-i\omega t''} C_z (t'') \delta(\omega-\omega') \\
= \int_{-\infty}^{\infty} d\omega'' S_z (\omega'') \delta(\omega-\omega') \int_{-\infty}^{\infty} dt'' e^{i(\omega''-\omega)t''} \\
= 2\pi S_z (\omega) \delta(\omega-\omega') .
\]  
(7.18)

### 7.1.3 Estimator

Let \( X (t) \) be a real stationary random signal, which is assumed to be given by
\[
X (t) = X_0 + X_N (t) ,
\]  
(7.19)
where \( X_0 \) is a real constant and where \( X_N (t) \) is a real stationary random signal, which is assumed to have a vanishing expectation value, i.e. \( \left\langle X_N (t) \right\rangle = 0 \). Let \( X_T (t) \) be a sampling of the signal \( X (t) \) in the time interval \((-T/2,T/2)\), namely
\[
X_T (t) = \begin{cases} 
X (t) & -T/2 < t < T/2 \\
0 & \text{else}
\end{cases} .
\]  
(7.20)

Let \( \hat{X}_0 \) be an estimator of the parameter \( X_0 \) (i.e. estimator of the average value of \( X (t) \)), which is taken to be given by
\[
\hat{X}_0 = \frac{1}{T} \int_{-\infty}^{\infty} dt \ X_T (t) .
\]  
(7.21)

Clearly, \( \left\langle \hat{X}_0 \right\rangle = X_0 \) (since \( \left\langle X_N (t) \right\rangle = 0 \)), and therefore the estimator \( \hat{X}_0 \) is unbiased, i.e. on average it yields the desired result. However, due to the fluctuating noise the variance \( \left( \hat{X}_0 - \left\langle \hat{X}_0 \right\rangle \right)^2 \) of the estimator \( X_0 \) may have a finite value when the sampling time \( T \) is finite.
Claim. The following holds

$$\lim_{T \to \infty} T \left( \hat{X}_0 - \langle \hat{X}_0 \rangle \right)^2 = 2\pi S_{X_N} (0),$$

(7.22)

where $S_{X_N} (0)$ is the zero frequency power spectrum of $X_N (t)$.

Proof. Using Eq. (7.19) and the relation $$\langle \hat{X}_0 \rangle = X_0$$ one finds that

$$\hat{X}_0 - \langle \hat{X}_0 \rangle = \frac{1}{T} \int_{-\infty}^{\infty} dt X_{NT} (t),$$

(7.23)

where $X_{NT} (t)$ is a sampling of $X_N (t)$ in the time interval $(-T/2, T/2)$, i.e.

$$X_{NT} (t) = \begin{cases} X_N (t) & -T/2 < t < T/2 \\ 0 & \text{else} \end{cases},$$

(7.24)

thus, in terms of the autocorrelation function $C_{X_N} (t)$ of $X_N (t)$ one has

$$\lim_{T \to \infty} T \left( \hat{X}_0 - \langle \hat{X}_0 \rangle \right)^2 = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt X_{NT} (t) X_{NT} (t')$$

$$= \int_{-\infty}^{\infty} dt'' \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt' X_{NT} (t' + t'') X_{NT} (t')$$

$$= \int_{-\infty}^{\infty} dt'' C_{X_N} (t'').$$

(7.25)

Finally, the Wiener-Khinchine theorem (7.10) leads to

$$\lim_{T \to \infty} T \left( \hat{X}_0 - \langle \hat{X}_0 \rangle \right)^2 = \int_{-\infty}^{\infty} dt'' \int_{-\infty}^{\infty} d\omega e^{i\omega t''} S_{X_N} (\omega)$$

$$= \int_{-\infty}^{\infty} d\omega \left[ S_{X_N} (\omega) \int_{-\infty}^{\infty} dt'' e^{i\omega t''} \right] = 2\pi \delta (\omega),$$

(7.26)

thus

$$\lim_{T \to \infty} T \left( \hat{X}_0 - \langle \hat{X}_0 \rangle \right)^2 = 2\pi S_{X_N} (0).$$

(7.27)
7.2 Nyquist noise

What is the voltage noise across a resistor? Consider the circuit shown in Fig. 7.1, which consists of a capacitor having capacitance $C$, an inductor having inductance $L$, and a resistor having resistance $R$, all serially connected. The system is assumed to be in thermal equilibrium at temperature $\tau$. To model the effect of thermal fluctuations we add a fictitious voltage source, which produces a random fluctuating voltage denoted by $V(t)$. Let $q(t)$ be the charge stored in the capacitor at time $t$. The classical equation of motion, which is given by

$$\frac{q}{C} + L\ddot{q} + R\dot{q} = V(t),$$

(7.28)

represents Kirchhoff’s voltage law.

Consider a sampling of the fluctuating function $q(t)$ in the time interval $(-T/2, T/2)$, namely [see Eq. (7.1)]

$$q_T(t) = \begin{cases} q(t) & -T/2 < t < T/2 \\ 0 & \text{else} \end{cases}.$$  

(7.29)

The energy stored in the capacitor is given by $q^2/2C$. Using the equipartition theorem (6.22) one finds

$$\frac{\langle q^2 \rangle}{2C} = \frac{\tau}{2},$$

(7.30)

where $\langle q^2 \rangle$ is obtained by averaging $q^2(t)$, namely
7.2. Nyquist noise

\[ \langle q^2 \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ q_T^2 (t) \ . \]  

(7.31)

The Fourier transformed function \( q_T (\omega) \) is related to \( q_T (t) \) by

\[ q_T (t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ q_T (\omega) e^{-i\omega t} , \]  

(7.32)

and the following holds [see Eq. (7.5)]

\[ \langle q^2 \rangle = \int_{-\infty}^{\infty} d\omega \ S_q (\omega) . \]  

(7.33)

where the power spectrum \( S_q (\omega) \) of \( q (t) \) is given by

\[ S_q (\omega) = \lim_{T \to \infty} \frac{1}{T} |q_T (\omega)|^2 . \]  

(7.34)

The Wiener-Khinchine theorem (7.10) yields

\[ \langle q (t) q (t + t') \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ q_T (t) q_T (t + t') = \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} S_q (\omega) . \]  

(7.35)

Taking the Fourier transform of Eq. (7.28) yields

\[ \left( \frac{1}{C} - i\omega R - \omega_0^2 \right) q (\omega) = V (\omega) , \]  

(7.36)

where \( V (\omega) \) is the Fourier transform of \( V (t) \), namely

\[ V (t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ V (\omega) e^{-i\omega t} . \]  

(7.37)

In terms of the resonance frequency

\[ \omega_0 = \sqrt{\frac{1}{LC}} , \]  

(7.38)

one has

\[ [ L (\omega_0^2 - \omega^2) - i\omega R] q (\omega) = V (\omega) . \]  

(7.39)

Taking the absolute value squared yields

\[ S_q (\omega) = \frac{S_V (\omega)}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2} , \]  

(7.40)

where \( S_V (\omega) \) is the power spectrum of \( V (t) \). Integrating the last result yields
\[
\int_{-\infty}^{\infty} d\omega \, S_q(\omega) = \int_{-\infty}^{\infty} d\omega \, \frac{S_V(\omega)}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2}
= \frac{1}{L^2} \int_{-\infty}^{\infty} d\omega \, \frac{S_V(\omega)}{(\omega_0 + \omega)^2 (\omega_0 - \omega)^2 + \omega^2 R^2}.
\]

(7.41)

The integrand has a peak near \( \omega_0 \), having a width \( \simeq R/2L \). The Quality factor \( Q \) is defined as
\[
\frac{\omega_0}{Q} = \frac{R}{2L}.
\]

(7.42)

Assuming \( S_V(\omega) \) is a smooth function near \( \omega_0 \) on the scale \( \omega_0/Q \), and assuming \( Q \gg 1 \) yield
\[
\int_{-\infty}^{\infty} d\omega \, S_q(\omega) \simeq \frac{S_V(\omega_0)}{L^2} \int_{-\infty}^{\infty} d\omega \, \frac{1}{(\omega_0 + \omega)^2 (\omega_0 - \omega)^2 + \left(\frac{2\omega_0}{Q}\right)^2}
\simeq \frac{S_V(\omega_0)}{4\omega_0^3 L^2} \int_{-\infty}^{\infty} d\omega \, \left(\frac{\omega_0 - \omega}{\omega_0}\right)^2 + \left(\frac{1}{Q}\right)^2
= \frac{S_V(\omega_0)}{4\omega_0^3 L^2} \int_{-\infty}^{\infty} dx \, \left(\frac{1}{x^2 + \left(\frac{1}{Q}\right)^2}\right)
\simeq \frac{S_V(\omega_0)}{4\omega_0^3 L^2} \pi Q.
\]

(7.43)

On the other hand, using Eqs. (7.30) and (7.33) one finds
\[
\int_{-\infty}^{\infty} d\omega \, S_q(\omega) = \langle q^2 \rangle = Ct,
\]

(7.44)

therefore
\[
S_V(\omega_0) = \frac{4C\omega_0^2 L^2}{\pi Q} t,
\]

(7.45)

or [see Eqs. (7.38) and (7.42)]
\[
S_V(\omega_0) = \frac{2Rt}{\pi},
\]

(7.46)

thus, Eq. (7.40) can be rewritten as
\[
S_q(\omega) = \frac{2Rt}{\pi} \frac{1}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2}.
\]

(7.47)
7.3. Thermal equilibrium from stochastic processes

Note that the spectral density of $V$ given by Eq. (7.46) is frequency independent. Consider a measurement of the fluctuating voltage $V(t)$ in a frequency band having width $\Delta f$. Using the relation

$$\langle V^2 \rangle = \int_{-\infty}^{\infty} d\omega S_V(\omega) , \quad (7.48)$$

one finds that the variance in such a measurement $\langle V^2 \rangle_{\Delta f}$ is given by

$$\langle V^2 \rangle_{\Delta f} = 4R\tau\Delta f . \quad (7.49)$$

The last result is the Nyquist’s noise formula. The fact that $\lim_{\Delta f \to \infty} \langle V^2 \rangle_{\Delta f} = \infty$ is historically called the ultraviolet catastrophe. This divergence is resolved in the quantum treatment.

7.3 Thermal equilibrium from stochastic processes

This section demonstrates that under appropriate conditions a stochastic process can lead to thermal equilibrium in steady state.

7.3.1 Langevin Equation

Consider the Langevin equation

$$\dot{x} = A(x, t) + q(t) , \quad (7.50)$$

where $x$ is a vector of coordinates that depends on the time $t$, overdot denotes time derivative, the vector $A(x, t)$ is a deterministic function of $x$ and $t$, and the vector $q(t)$ represents random noise that satisfies

$$\langle q(t) \rangle = 0 , \quad (7.51)$$

and

$$\langle q_i(t) q_j(t') \rangle = g_{ij}\delta(t-t') . \quad (7.52)$$

Let

$$\delta x = x(t+\delta t) - x(t) . \quad (7.53)$$

To first order in $\delta t$ one finds by integrating Eq. (7.50) that

$$\langle \delta x \rangle_i = A_i(x, t) \delta t + \int_{t}^{t+\delta t} dt' g_i(t') + O\left((\delta t)^2\right) . \quad (7.54)$$

With the help of Eqs. (7.51) and (7.52) one finds that
\[(\delta x)_i = A_i(x, t) \delta t + O((\delta t)^2) , \quad (7.55)\]

and
\[
\langle (\delta x)_i (\delta x)_j \rangle = A_i(x, t) A_j(x, t) (\delta t)^2 \\
+ \int_t^{t+\delta t} dt' \int_t^{t+\delta t} dt'' (g_i(t') g_j(t'')) + \cdots \\
= A_i(x, t) A_j(x, t) (\delta t)^2 + g_{ij} \delta t + \cdots , \quad (7.56)
\]

thus to first order in \(\delta t\)
\[
\langle (\delta x)_i (\delta x)_j \rangle = g_{ij} \delta t + O((\delta t)^2) . \quad (7.57)
\]

In a similar way one can show that all higher order moments (e.g. third order moments \(\langle (\delta x)_i (\delta x)_j (\delta x)_k \rangle\)) vanish to first order in \(\delta t\).

### 7.3.2 The Smoluchowski-Chapman-Kolmogorov relation

Let \(p_1(x, t)\) be the probability density to find the system at point \(x\) at time \(t\), let \(p_2(x'', t''; x', t')\) be the probability density to find the system at point \(x'\) at time \(t'\) and at point \(x''\) at time \(t''\), and similarly let \(p_3(x''', t'''; x'', t''; x', t')\) be the probability density to find the system at point \(x''\) at time \(t''\), at point \(x'''\) at time \(t'''\) and at point \(x''\) at time \(t''\). The following holds
\[
p_2(x_3, t_3; x_1, t_1) = \int dx_2 p_3(x_3, t_3; x_2, t_2; x_1, t_1) . \quad (7.58)
\]

Let \(P(x, t|x', t')\) be the conditional probability density to find the system at point \(x\) at time \(t\), given that it was (or will be) at point \(x'\) at time \(t'\). The following holds
\[
p_2(x_3, t_3; x_1, t_1) = P(x_3, t_3|x_1, t_1) p_1(x_1, t_1) . \quad (7.59)
\]

Moreover, by assuming that \(t_1 \leq t_2 \leq t_3\) and by assuming the case of a Markov process, i.e. the case where the future \((t_3)\) depends on the present \((t_2)\), but not on the past \((t_1)\), one finds that
\[
p_3(x_3, t_3; x_2, t_2; x_1, t_1) \\
= P(x_3, t_3|x_2, t_2) P(x_2, t_2|x_1, t_1) p_1(x_1, t_1) . \quad (7.60)
\]

With the help of these relations Eq. (7.58) becomes
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\[ p(x_3, t_3 | x_1, t_1) p_1 (x_1, t_1) = \int dx_2 \, \mathcal{P}(x_3, t_3 | x_2, t_2) \mathcal{P}(x_2, t_2 | x_1, t_1) p_1 (x_1, t_1) , \]  
(7.61)

thus by dividing by \( p_1 (x_1, t_1) \) one finds that

\[ \mathcal{P}(x_3, t_3 | x_1, t_1) = \int dx_2 \, \mathcal{P}(x_3, t_3 | x_2, t_2) \mathcal{P}(x_2, t_2 | x_1, t_1) . \]  
(7.62)

7.3.3 The Fokker-Planck Equation

Equation (7.62) can be written as

\[ \mathcal{P}(x, t + \delta t | x_0, t_0) = \int dx' \, \mathcal{P}(x, t + \delta t | x', t') \mathcal{P}(x', t' | x_0, t_0) . \]  
(7.63)

On the other hand

\[ \mathcal{P}(x, t + \delta t | x', t') = \langle \delta (x - \delta x - x') \rangle , \]  
(7.64)

where

\[ \delta x = x(t + \delta t) - x(t) . \]  
(7.65)

For a general scalar function \( F \) of \( x' \) the following holds

\[ F(x' + \delta x) = \exp(\delta x \cdot \nabla') F = F(x') + (\delta x)_i \left( \frac{dF}{dx'_i} \right) + \frac{(\delta x)_i (\delta x)_j}{2!} \left( \frac{d^2F}{dx'_i dx'_j} \right) + \cdots , \]  
(7.66)

thus

\[ \delta (x - \delta x - x') = \delta (x - x') \]
\[ + (\delta x)_i \left( \frac{d\delta (x - x')}{dx'_i} \right) \]
\[ + \frac{(\delta x)_i (\delta x)_j}{2!} \left( \frac{d^2\delta (x - x')}{dx'_i dx'_j} \right) + \cdots . \]  
(7.67)

Inserting this result into Eq. (7.63) yields
\[ \mathcal{P}(\mathbf{x}, t + \delta t|\mathbf{x}_0, t_0) = \int d\mathbf{x}' \left\langle \delta (\mathbf{x} - \delta \mathbf{x} - \mathbf{x}') \right\rangle \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0) \]
\[ = \int d\mathbf{x}' \delta (\mathbf{x} - \mathbf{x}') \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0) \]
\[ + \int d\mathbf{x}' \left\langle (\delta \mathbf{x})_i \right\rangle \frac{d\delta (\mathbf{x} - \mathbf{x}')}{dx'_i} \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0) \]
\[ + \frac{1}{2} \int d\mathbf{x}' \left\langle (\delta \mathbf{x})_i (\delta \mathbf{x})_j \right\rangle \frac{d^2\delta (\mathbf{x} - \mathbf{x}')}{dx'_i dx'_j} \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0), \]
\[ + \cdots . \]  
\[ (7.68) \]

Dividing by \( \delta t \), and taking the limit \( \delta t \to 0 \) leads to [see Eqs. (7.55) and (7.57), and recall that higher order moments vanish to first order in \( \delta t \)].

\[ \frac{\partial \mathcal{P}}{\partial t} = \int d\mathbf{x}' A_i (\mathbf{x}', t) \frac{d\delta (\mathbf{x} - \mathbf{x}')}{dx'_i} \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0) \]
\[ + \frac{1}{2} \int d\mathbf{x}' g_{ij} \frac{d^2\delta (\mathbf{x} - \mathbf{x}')}{dx'_i dx'_j} \mathcal{P} (\mathbf{x}', t'|\mathbf{x}_0, t_0). \]
\[ (7.69) \]

Finally, integrating by parts and assuming that \( \mathcal{P} \to 0 \) in the limit \( \mathbf{x} \to \pm \infty \) yield

\[ \frac{\partial \mathcal{P}}{\partial t} = -\frac{d}{dx'_i} (A_i \mathcal{P}) + \frac{1}{2} \frac{d^2}{dx'_i dx'_j} (g_{ij} \mathcal{P}) . \]
\[ (7.70) \]

This result, which is known as the Fokker-Planck equation, can also be written as

\[ \frac{\partial \mathcal{P}}{\partial t} + \nabla \cdot \mathbf{J} = 0 , \]
\[ (7.71) \]

where the probability current density \( \mathbf{J} \) is given by

\[ J_i = A_i \mathcal{P} - \frac{1}{2} \frac{d}{dx'_j} (g_{ij} \mathcal{P}) . \]
\[ (7.72) \]

In steady state the Fokker-Planck equation (7.71) becomes

\[ \nabla \cdot \mathbf{J} = 0 . \]
\[ (7.73) \]

### 7.3.4 The Potential Condition

Consider the case where \( \mathbf{A} \) can be expressed in terms of a scalar 'Hamiltonian' \( \mathcal{H} \) as (the potential condition)
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\[ \mathbf{A}(\mathbf{x}, t) = -\nabla \mathcal{H} . \]  
(7.74)

Moreover, for simplicity assume that

\[ g_{ij} = 2\tau \delta_{ij} , \]  
(7.75)

where the 'temperature' \( \tau \) is a constant. For this case one has

\[ J_i = -\mathcal{P} \frac{\partial \mathcal{H}}{\partial x'_i} - \tau \frac{\partial \mathcal{P}}{\partial x'_i} , \]  
(7.76)

thus

\[ \mathbf{J} = -\mathcal{P} \nabla \mathcal{H} - \tau \nabla \mathcal{P} \]  
\[ = -\mathcal{P} \nabla (\mathcal{H} + \tau \log \mathcal{P}) . \]  
(7.77)

Substituting a solution having the form

\[ \mathcal{P} = N e^{-\frac{\mathcal{H}}{\tau}} \]  
(7.78)

yields

\[ \mathbf{J} = -\tau N e^{-\frac{\mathcal{H}}{\tau}} \nabla (\log N) = -\tau e^{-\frac{\mathcal{H}}{\tau}} \nabla N , \]  
(7.79)

and thus

\[ \nabla \cdot \mathbf{J} = [\nabla \mathcal{H} \cdot \nabla N - \tau \nabla \cdot (\nabla N)] e^{-\frac{\mathcal{H}}{\tau}} . \]  
(7.80)

In terms of \( N \), the Fokker-Planck equation (7.71) becomes

\[ \frac{\partial N}{\partial t} + [\nabla \mathcal{H} \cdot \nabla N - \tau \nabla \cdot (\nabla N)] = 0 . \]  
(7.81)

In steady state Eq. (7.81) yields

\[ \nabla \mathcal{H} \cdot \nabla N = \tau \nabla \cdot (\nabla N) . \]  
(7.82)

This equation can be solved by choosing \( N \) to be a constant, which can be determined by the normalization condition. In terms of the partition function \( Z \), where \( Z = 1/N \), the steady state solution is expressed as

\[ \mathcal{P} = \frac{1}{Z} e^{-\frac{\mathcal{H}}{\tau}} , \]  
(7.83)

where

\[ Z = \int d\mathbf{x}' \mathcal{P} . \]  
(7.84)
7.3.5 Free Energy

The free energy functional is defined by

\[ F(P) = U - \tau \sigma, \]  

(7.85)

where \( U \) is the energy

\[ U = \int dx' \, H P, \]  

(7.86)

and \( \sigma \) is the entropy

\[ \sigma = -\int dx' \, P \log P. \]  

(7.87)

The distribution \( P \) is constrained to satisfy the normalization constrain

\[ G(P) = \int dx' \, P - 1 = 0. \]  

(7.88)

Minimizing \( F(P) \) under the constrain (7.88) is done by introducing the Lagrange multiplier \( \eta \)

\[ \delta (F(P) + \eta G(P)) = \int dx' \left[ \mathcal{H} + \tau (1 + \log P) + \eta \right] \delta P. \]  

(7.89)

At a stationary point the following holds

\[ \mathcal{H} + \tau (1 + \log P) + \eta = 0, \]  

(7.90)

thus

\[ P = e^{-\frac{\eta}{\tau} - 1} e^{-\frac{\mathcal{H}}{\tau}}, \]  

(7.91)

where the constant \( e^{-\frac{\eta}{\tau} - 1} \) is determined by the normalization condition, i.e. the obtained distribution is identical to the steady state solution of the Fokker-Planck equation (7.83).

7.3.6 Fokker-Planck Equation in One Dimension

In one dimension the Fokker-Planck equation (7.71) becomes [see Eq. (7.76)]

\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( P \frac{\partial \mathcal{H}}{\partial x} + \tau \frac{\partial P}{\partial x} \right), \]  

(7.92)

or
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\[
\frac{\partial P}{\partial t} = \mathcal{L} P, \quad (7.93)
\]

where the operator \( \mathcal{L} \) is given by

\[
\mathcal{L} = \frac{\partial}{\partial x} \frac{\partial H}{\partial x} + \tau \frac{\partial^2}{\partial x^2}. \quad (7.94)
\]

It is convenient to define the operator \( \hat{\mathcal{L}} \), which is given by

\[
\hat{\mathcal{L}} = e^{\frac{2H}{\tau}} L e^{-\frac{2H}{\tau}}. \quad (7.95)
\]

The following holds

\[
\hat{\mathcal{L}} = e^{\frac{2H}{\tau}} \left( \frac{\partial}{\partial x} \frac{\partial H}{\partial x} e^{-\frac{2H}{\tau}} \right) + \frac{\partial^2}{\partial x^2} e^{-\frac{2H}{\tau}}
\]

\[
+ \tau e^{\frac{2H}{\tau}} \left( \frac{\partial^2}{\partial x^2} e^{-\frac{2H}{\tau}} \right) + 2 \tau e^{\frac{2H}{\tau}} \left( \frac{\partial}{\partial x} e^{-\frac{2H}{\tau}} \right) \frac{\partial}{\partial x} + \tau \frac{\partial^2}{\partial x^2}
\]

\[
= \frac{\partial^2 H}{\partial x^2} - \frac{1}{2\tau} \left( \frac{\partial H}{\partial x} \right)^2 + \frac{\partial H}{\partial x} \frac{\partial}{\partial x} + \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 - \frac{\partial H}{\partial x} \frac{\partial}{\partial x} + \tau \frac{\partial^2}{\partial x^2}
\]

\[
= \frac{1}{2} \frac{\partial^2 H}{\partial x^2} - \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 + \tau \frac{\partial^2}{\partial x^2}, \quad (7.96)
\]

thus

\[
\hat{\mathcal{L}} = \tau \frac{\partial^2}{\partial x^2} - \hat{V}, \quad (7.97)
\]

where the potential \( \hat{V} \) is given by

\[
\hat{V} = \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 - \frac{1}{2} \frac{\partial^2 H}{\partial x^2}. \quad (7.98)
\]

Note that while the operator \( \mathcal{L} \) is not Hermitian, the operator \( \hat{\mathcal{L}} \) is since

\[
\hat{\mathcal{L}} = e^{-\frac{2H}{\tau}} \mathcal{L} e^{\frac{2H}{\tau}}
\]

\[
= e^{-\frac{2H}{\tau}} \mathcal{L} e^{\frac{2H}{\tau}} e^{-\frac{2H}{\tau}}
\]

\[
= e^{\frac{2H}{\tau}} \mathcal{L} e^{-\frac{2H}{\tau}}
\]

\[
= e^{\frac{2H}{\tau}} \mathcal{L} e^{-\frac{2H}{\tau}} = \hat{\mathcal{L}}. \quad (7.99)
\]
In terms of $\hat{L}$ Eq. (7.93) becomes (it is assume that $\mathcal{H}$ is time independent)

$$\frac{\partial \hat{\mathcal{P}}}{\partial t} = \hat{L} \hat{\mathcal{P}},$$

(7.100)

where

$$\hat{\mathcal{P}} = e^{\frac{\mathcal{H}}{2\tau}} \mathcal{P} e^{-\frac{\mathcal{H}}{2\tau}}.$$ (7.101)

Let $\psi_n(x)$ be a set of eigenvectors of $\hat{L}$

$$\hat{L} \psi_n = \lambda_n \psi_n.$$ (7.102)

The following holds [see Eq. (7.95)]

$$\mathcal{L} \varphi_n = \lambda_n \varphi_n,$$ (7.103)

where

$$\varphi_n = e^{-\frac{\mathcal{H}}{2\tau}} \psi_n.$$ (7.104)

The conditional probability distribution $\mathcal{P}(x,t|x',t')$ is given by [see Eq. (7.93)]

$$\mathcal{P}(x,t|x',t') = e^{\mathcal{L}(t-t')} \delta(x-x').$$ (7.105)

With the help of the closure relation (recall that $\hat{L}$ is Hermitian)

$$\delta(x-x') = \sum_n \psi_n(x') \psi_n(x)$$
$$= e^{\frac{\mathcal{H}(x) + \mathcal{H}(x')}{2\tau}} \sum_n \varphi_n(x') \varphi_n(x)$$
$$= e^{\frac{\mathcal{H}(x')}{2\tau}} \sum_n \varphi_n(x') \varphi_n(x),$$

(7.106)

one finds that

$$\mathcal{P}(x,t|x',t') = e^{\mathcal{L}(x)(t-t')} e^{\frac{\mathcal{H}(x')}{2\tau}} \sum_n \varphi_n(x') \varphi_n(x)$$
$$= e^{\frac{\mathcal{H}(x')}{2\tau}} \sum_n \varphi_n(x') e^{\mathcal{L}(x)(t-t')} \varphi_n(x)$$
$$= e^{\frac{\mathcal{H}(x')}{2\tau}} \sum_n \varphi_n(x') e^{\lambda_n(t-t')} \varphi_n(x)$$
$$= e^{\frac{\mathcal{H}(x')}{2\tau}} \sum_n e^{-\frac{\mathcal{H}(x')}{2\tau}} \psi_n(x') e^{\lambda_n(t-t')} e^{-\frac{\mathcal{H}(x)}{2\tau}} \psi_n(x),$$

(7.107)
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thus

\[ P(x, t|x', t') = e^{\frac{-H(x') - H(x)}{2\tau}} \sum_n \psi_n^*(x') \psi_n(x) e^{\lambda_n(t-t')} . \] (7.108)

### 7.3.7 Ornstein–Uhlenbeck Process in One Dimension

Consider the following Langevin equation

\[ \dot{x} + \Gamma x = q(t) , \] (7.109)

where \( x \) can take any real value, \( \Gamma \) is a positive constant and where the real noise term \( q(t) \) satisfies \( \langle q(t) \rangle = 0 \) and

\[ \langle q(t) q(t') \rangle = 2\tau \delta(t-t') , \] (7.110)

where \( \tau \) is positive.

For this case [see Eq. (7.74)]

\[ H(x) = \frac{\Gamma x^2}{2} , \] (7.111)

the Fokker-Planck equation for the conditional probability distribution \( P \) is given by [see Eq. (7.71)]

\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( P \Gamma x + \tau \frac{\partial P}{\partial x} \right) , \] (7.112)

and the operator \( \hat{L} \) is given by [see Eq. (7.97)]

\[ \hat{L} = -\frac{\Gamma}{2} \left[ -\left( \frac{\partial}{\partial \left( \frac{x}{x_0} \right)} \right)^2 + \left( \frac{x}{x_0} \right)^2 - 1 \right] , \]

where

\[ x_0 = \sqrt{\frac{2\tau}{\Gamma}} . \] (7.113)

The eigenvectors of \( \hat{L} \) are given by [see Eq. (7.178)]

\[ \psi_n(x) = \frac{e^{-\frac{1}{2}\left( \frac{x}{x_0} \right)^2} H_n \left( \frac{x}{x_0} \right)}{\pi^{1/4} x_0^{1/2} \sqrt{2^n n!}} \] , (7.114)

and the corresponding eigenvalues by

\[ \lambda_n = -\Gamma \left( n + \frac{1}{2} - \frac{1}{2} \right) , \] (7.115)
where \( n = 0, 1, 2, \cdots \).

Using these results one finds that \( P \) is given by [see Eq. (7.108)]
\[
P(x, t| x', t') = e^{-\left(\frac{x^2}{x_0^2}\right)} \sum_n \frac{H_n \left(\frac{x}{x_0}\right) H_n \left(\frac{x'}{x_0}\right) e^{-\Gamma n(t-t')}}{\sqrt{\pi x_0^2 n!}}.
\] (7.116)

With the help of the general identity (7.185) one finds that the following holds
\[
\frac{\alpha e^{-X^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(\frac{\alpha}{2})^n H_n(Y) H_n(X)}{n!} = \exp\left(\frac{-(Y-X\alpha^{-1})^2}{\alpha \sqrt{\pi}}\right),
\] (7.117)

thus Eq. (7.116) becomes
\[
P(x, t| x', t') = \exp\left(\frac{-\left(\frac{x-x'e^{-\frac{1}{\delta}}(t-t')}{\sqrt{\pi \delta}}\right)^2}{\sqrt{\pi \delta}}\right),
\] (7.118)

where
\[
\delta = \sqrt{x_0^2 \left(1 - e^{-2\Gamma(t-t')}\right)} = \sqrt{\frac{2\tau \left(1 - e^{-2\Gamma(t-t')}\right)}{\Gamma}}.
\] (7.119)

### 7.4 Oscillator

An ideal oscillator is a device that outputs an alternating signal at a fixed frequency. Consider an oscillator having a single coordinate \( x(t) \), which can be expressed in terms of a complex amplitude \( A \) as \( x(t) = 2 \text{Re}(A) \). For sufficiently small \( |A| \) it is assumed that \( A \) evolves in time \( t \) according to
\[
\dot{A} + (\Gamma_{\text{eff}} + i\Omega_{\text{eff}}) A = \xi(t),
\] (7.120)

where both the effective resonance frequency \( \Omega_{\text{eff}} \) and the effective damping rate \( \Gamma_{\text{eff}} \) are real even functions of \( |A| \). To second order in \( |A| \) they are given by
\[
\Gamma_{\text{eff}} = \Gamma_0 + \Gamma_2 |A|^2, \quad \Omega_{\text{eff}} = \Omega_0 + \Omega_2 |A|^2,
\] (7.121)

where \( \Gamma_0, \Gamma_2, \Omega_0 \) and \( \Omega_2 \) are real. The fluctuating term \( \xi(t) = \xi_x(t) + i\xi_y(t) \), where both \( \xi_x \) and \( \xi_y \) are real, represents white noise and the following is assumed to hold
\[
\langle \xi_x(t) \xi_x(t') \rangle = 2\Theta \delta(t - t'),
\] (7.122)
\[
\langle \xi_y(t) \xi_y(t') \rangle = 2\Theta \delta(t - t'),
\] (7.123)
\[
\langle \xi_x(t) \xi_y(t') \rangle = 0
\] (7.124)

where \( \Theta \) is positive.
**7.4. Oscillator**

**Exercise 7.4.1.** Consider the case that the potential energy of the oscillator is given by $(1/2)m\Omega_0^2 x^2 + O(|A|^4)$, where $m$ is an effective mass. Express the parameter $\Theta$ in terms of the temperature $\tau_A$.

**Solution 7.4.1.** By introducing the Fourier transform of the sampling of the signals $A(t)$ and $\xi(t)$ [see Eq. (7.2)]

\[
A_T(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ A_T(\omega) e^{-i\omega t},
\]

\[
(7.125)
\]

\[
\xi_T(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ \xi_T(\omega) e^{-i\omega t},
\]

\[
(7.126)
\]

and employing Eq. (7.120) for the case where $\Gamma_2 = 0$ and $\Omega_2 = 0$ (linear response) one finds that

\[
A_T(\omega) = \frac{\xi_T(\omega)}{I_0 + i(\Omega_0 - \omega)}.
\]

\[
(7.127)
\]

Thus the power spectrum (7.34) $S_A(\omega)$ of $A(t)$ is related to the power spectrum $S_\xi(\omega)$ of $\xi(t)$ by [see Eq. (7.3)]

\[
S_A(\omega) = \frac{S_\xi(\omega)}{I_0^2 + (\Omega_0 - \omega)^2}.
\]

\[
(7.128)
\]

The assumption that $S_\xi(\omega)$ is frequency independent (i.e. the assumption that the input noise is white) together with Eq. (7.5) yield

\[
\left\langle |A|^2 \right\rangle = \int_{-\infty}^{\infty} d\omega \ S_A(\omega)
\approx S_\xi \int_{-\infty}^{\infty} \frac{d\omega}{I_0^2 + (\Omega_0 - \omega)^2}
= \frac{\pi S_\xi}{I_0}.
\]

\[
(7.129)
\]

On the other hand the relation $x(t) = 2 \text{Re} \ A$ implies that

\[
\left\langle (x(t))^2 \right\rangle = \left\langle (A + A^*)^2 \right\rangle = 2 \left\langle |A|^2 \right\rangle.
\]

\[
(7.130)
\]

The effective noise temperature $\tau_A$ is defined in a way consistent with the equipartition theorem

\[
\left\langle (x(t))^2 \right\rangle = \frac{\tau_A}{m\Omega_0^2},
\]

\[
(7.131)
\]

where $m$ is an effective mass, and thus
\[ S_\xi = \frac{\Gamma_0 \tau_A}{2\pi m\Omega_0^2}. \quad (7.132) \]

With the help of Wiener-Khinchine theorem [see Eq. (7.10)] one finds that
\[
\langle \xi^* (t + t') \xi (t) \rangle = \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} S_\xi (\omega)
= \frac{\Gamma_0 \tau_A}{m\Omega_0^2} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'}
= \frac{\Gamma_0 \tau_A}{m\Omega_0^2} \delta (t'). \quad (7.133)
\]

On the other hand Eqs. (7.122), (7.123) and (7.124) imply that
\[
\langle \xi^* (t + t') \xi (t) \rangle = 4\Theta \delta (t'), \quad (7.134)
\]
thus
\[
\Theta = \frac{\Gamma_0 \tau_A}{4m\Omega_0^2}. \quad (7.135)
\]

7.4.1 Radial Coordinates

The real and imaginary parts of Eq. (7.120) are given by
\[
\dot{A}_x - \Omega_{\text{eff}} A_y + \Gamma_{\text{eff}} A_x = \xi_x (t), \quad (7.136)
\]
\[
\dot{A}_y + \Omega_{\text{eff}} A_x + \Gamma_{\text{eff}} A_y = \xi_y (t), \quad (7.137)
\]
where \( A = A_x + iA_y \) and where both \( A_x \) and \( A_y \) are real. In cylindrical coordinates \( A \) is expressed as \( A = A_re^{iA_\theta} \), where \( A_r = \sqrt{A_x^2 + A_y^2} \) is positive and \( A_\theta \) is real. The following holds
\[
\dot{A}_r = \frac{\partial A_r}{\partial A_x} \dot{A}_x + \frac{\partial A_r}{\partial A_y} \dot{A}_y
= -\frac{A_x^2 + A_y^2}{A_r} \Gamma_{\text{eff}} + \frac{A_x \xi_x (t) + A_y \xi_y (t)}{A_r}, \quad (7.138)
\]
thus
\[
\dot{A}_r + A_r \Gamma_{\text{eff}} = \xi_r (t), \quad (7.139)
\]
where
\[
\xi_r (t) = \frac{A_x \xi_x (t) + A_y \xi_y (t)}{A_r}. \quad (7.140)
\]
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With the help of Eqs. (7.122), (7.123) and (7.124) one finds that

\[ \langle \xi_r(t) \xi_r(t') \rangle = 2\Theta \delta(t - t') . \]  

(7.141)

Similarly, for \( A_\theta = \tan^{-1}(A_y/A_x) \) one finds that

\[
\dot{A}_\theta = \frac{\partial A_\theta}{\partial A_x} \dot{A}_x + \frac{\partial A_\theta}{\partial A_y} \dot{A}_y \\
= -\frac{A_y}{A_x^2 + A_y^2} (\Omega_{\text{eff}} A_y - \Gamma_{\text{eff}} A_x + \xi_x(t)) \\
+ \frac{A_x}{A_x^2 + A_y^2} (-\Omega_{\text{eff}} A_x - \Gamma_{\text{eff}} A_y + \xi_y(t)),
\]

(7.142)

thus

\[
\dot{A}_\theta + \Omega_{\text{eff}} (A_r) = \frac{1}{A_r} \xi_\theta (t),
\]

(7.143)

where

\[
\xi_\theta (t) = \frac{A_x \xi_y (t) - A_y \xi_x (t)}{A_r},
\]

(7.144)

and where

\[
\langle \xi_\theta (t) \xi_\theta (t') \rangle = 2\Theta \delta(t - t') ,
\]

(7.145)

\[
\langle \xi_r (t) \xi_\theta (t') \rangle = 0 .
\]

(7.146)

7.4.2 Phase Space Distribution

Consider the case where \( \Gamma_2 > 0 \). For this a so-called supercritical Hopf bifurcation occurs when the linear damping coefficient \( \Gamma_0 \) vanishes. Above threshold, i.e. when \( \Gamma_0 \) becomes negative, Eq. (7.139) has a steady state solution (when noise is disregarded) at the point \( r_0 = \sqrt{-\Gamma_0/\Gamma_2} \) [see Eq. (7.121)].

The Langevin Eq. (7.139) can be written as [see Eq. (7.121)]

\[
\dot{A}_r + \frac{\partial H}{\partial A_r} = \xi_r (t),
\]

(7.147)

where

\[
H(A_r) = \frac{\Gamma_0 A_r^2}{2} + \frac{\Gamma_2 A_r^4}{4} \\
= \Theta \left[ \left( \frac{A_r}{\delta_0} \right)^2 + \frac{1}{4\nu^2} \left( \frac{A_r}{\delta_0} \right)^4 \right],
\]

(7.148)
is the Hamiltonian, $\delta_0$ is given by

$$\delta_0^2 = \frac{2\Theta}{\Gamma_0},$$  \hspace{1cm} (7.149)

and $\nu$ is given by

$$\nu = \frac{\Gamma_0}{\sqrt{4\Theta}}.$$  \hspace{1cm} (7.150)

In steady state the normalized phase space probability distribution function is given by [see Eqs. (7.147), (7.74) and (7.83)]

$$P = e^{-\left(\frac{r_0}{\delta_0}\right)^2 - \frac{1}{4\nu^2} \left(\frac{r_0}{\nu}\right)^4} \frac{\pi^{\frac{3}{2}} \delta_0^2 \nu e^{\nu^2} (1 - \text{erf} \nu)}{\pi \delta_0^{\frac{3}{2}} \nu e^{\nu^2} (1 - \text{erf} \nu)},$$  \hspace{1cm} (7.151)

where $A_r = \sqrt{A_x^2 + A_y^2}$, or

$$P = e^{-\left(\frac{r_0}{\delta_0}\right)^2 \left(1 - \frac{1}{4\nu^2} \left(\frac{r_0}{\nu}\right)^2\right)} \frac{\pi^{\frac{3}{2}} \delta_0^2 \nu e^{\nu^2} (1 - \text{erf} \nu)}{\pi \delta_0^{\frac{3}{2}} \nu e^{\nu^2} (1 - \text{erf} \nu)}.$$  \hspace{1cm} (7.152)

**Exercise 7.4.2.** Find approximations for $P$ for the regions well below and well above threshold.

**Solution 7.4.2.** Well below the threshold, where $\nu \gg 1$, Eq. (7.151) becomes (the relation $\lim_{\nu \to \infty} \pi^{\frac{3}{2}} \nu e^{\nu^2} (1 - \text{erf} \nu) = \pi$ is being used)

$$P = e^{-\left(\frac{r_0}{\delta_0}\right)^2} \frac{\pi^{\frac{3}{2}} \delta_0^2 e^{\nu^2}}{\pi \delta_0^{\frac{3}{2}} \nu e^{\nu^2} (1 - \text{erf} \nu)}.$$  \hspace{1cm} (7.153)

On the other hand, well above threshold, near the peak at $A_r = r_0$ one has

$$-A_r^2 \left(1 - \frac{A_r^2}{2r_0^2}\right) = -\frac{1}{2} \frac{r_0^2}{\delta_0^2} + \frac{2\rho^2}{\delta_0^2} + O(\rho^3),$$  \hspace{1cm} (7.154)

where

$$A_r = r_0 + \rho,$$  \hspace{1cm} (7.155)

thus to lowest nonvanishing order in $\rho$ one finds that [see Eq. (7.151)]

$$P \propto e^{2\left(\frac{A_r - r_0}{\delta_0}\right)^2}.$$  \hspace{1cm} (7.156)
### 7.4.3 Allan variance

Above threshold Eqs. (7.139) and (7.143) can be linearized. Using the notation (7.155) one finds to lowest nonvanishing order in \( \rho \) that

\[
A_r \Gamma_{\text{eff}} = -2\Gamma_0 \rho + O(\rho^2) .
\]  

(7.157)

Moreover

\[
\Omega_{\text{eff}} = \Omega_H + \zeta_0 \rho + O(\rho^2) ,
\]

(7.158)

where \( \Omega_H = \Omega_{\text{eff}}(r_0) \) and where \( \zeta_0 = d\Omega_{\text{eff}}/dA_r \) at the point \( r_0 \). Using the notation

\[
A_\theta = -\Omega_Ht + \phi ,
\]

(7.159)

the equations (7.139) and (7.143) become to lowest nonvanishing order in \( \rho \)

\[
\dot{\rho} - 2\Gamma_0 \rho = \xi_r(t) ,
\]

(7.160)

and

\[
\dot{\phi} + \zeta_0 \rho = \frac{\xi_\theta(t)}{r_0} .
\]

(7.161)

**Exercise 7.4.3.** Calculate the correlation functions \( \langle \rho(t) \rho(t') \rangle \) and \( \langle \dot{\phi}(t) \dot{\phi}(t') \rangle \).

**Solution 7.4.3.** Multiplying Eq. (7.160) by the integration factor \( e^{-2\Gamma_0 t} \) yields

\[
\frac{d}{dt} (\rho e^{-2\Gamma_0 t}) = e^{-2\Gamma_0 t} \xi_r(t) ,
\]

(7.162)

thus by integration one finds that

\[
\rho(t) = \rho(0) e^{2\Gamma_0 t} + \int_0^t dt'' e^{2\Gamma_0 (t-t'')} \xi_r(t'') .
\]

(7.163)

In steady state (i.e. in the limit \( t \to \infty \)) the first term can be disregarded (recall that \( \Gamma_0 < 0 \)). With the help of Eq. (7.141) the correlation function of \( \rho(t) \) is found to be given by

\[
\langle \rho(t) \rho(t') \rangle = \int_0^t dt'' \int_0^{t'} dt''' e^{2\Gamma_0 (t-t''+t'-t''')} \langle \xi_r(t'') \xi_r(t''') \rangle
\]

\[
= 2\Theta \int_0^t dt'' \int_0^{t'} dt''' e^{2\Gamma_0 (t-t''+t'-t''')} \delta(t'' - t''') .
\]

(7.164)
For the case where \( t \geq t' \) one has
\[
\langle \rho(t) \rho(t') \rangle = 2\Theta \int_0^t dt'' \int_0^{t'} dt''' e^{2\Gamma_0 (t-t''+t'-t''')} \delta(t''-t''')
\]
\[
= 2\Theta e^{2\Gamma_0 (t+t')} \int_0^{t'} dt'' e^{-4\Gamma_0 t''}
\]
\[
= 2\Theta e^{2\Gamma_0 (t+t')} \frac{1-e^{-4\Gamma_0 t'}}{4\Gamma_0}
\]
\[
= \Theta \frac{e^{2\Gamma_0 (t+t')}-e^{2\Gamma_0 (t-t')}}{2\Gamma_0}.
\]
(7.165)

In steady state the first term vanishes. The result for the general case \((t \geq t'\) or \(t < t'\)) is expressed as
\[
\langle \rho(t) \rho(t') \rangle = -\frac{\Theta}{2\Gamma_0} e^{2\Gamma_0 |t-t'|}.
\]
(7.166)

The last result together with Eqs. (7.145), (7.146) and (7.161) allow evaluating the correlation function of \( \dot{\phi} \)
\[
\langle \dot{\phi}(t) \dot{\phi}(t') \rangle = -\Theta \left[ \frac{\zeta_0^2}{2\Gamma_0} e^{2\Gamma_0 |t-t'|} + 2\frac{\Gamma_2}{\Gamma_0} \delta(t-t') \right].
\]
or
\[
\langle \dot{\phi}(t) \dot{\phi}(t') \rangle = \frac{\Theta \zeta_0^2}{2 |\Gamma_0|^2} \left[ |\Gamma_0| e^{2\Gamma_0 |t-t'|} + \frac{4\Gamma_2 |\Gamma_0|}{\zeta_0^2} \delta(t-t') \right].
\]
(7.167)

Note that the integral from \(-\infty\) to \(\infty\) of both factors \( |\Gamma_0| e^{2\Gamma_0 |t-t'|} \) and \( \delta(t-t') \) is unity.

**Exercise 7.4.4.** Calculate the power spectrum of \( \dot{\phi} \).

**Solution 7.4.4.** In general, by multiplying Eq. (7.10) by \( e^{-i\omega' t'} \) and integration over \( t' \) one finds that
\[
\int_{-\infty}^{\infty} dt' e^{-i\omega' t'} C_z(t')
\]
\[
= \int_{-\infty}^{\infty} d\omega \ S_z(\omega) \int_{-\infty}^{\infty} dt' e^{i(\omega-\omega')t'}
\]
\[
= \frac{1}{2\pi \delta(\omega-\omega')}
\]
(7.168)

thus
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\[ S_z(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' e^{-i\omega t'} C_z(t') \]  

(7.169)

The last result together with Eq. (7.167) allow evaluating the power spectrum of \( \dot{\phi} \)

\[ S_\dot{\phi}(\omega) = \frac{\Theta \zeta_0^2}{4\pi |\Gamma_0|} \int_{-\infty}^{\infty} dt' e^{-i\omega t'} e^{2\Gamma_0|t'|} \]

\[ + \frac{\Theta \Gamma_2}{\pi |\Gamma_0|} \int_{-\infty}^{\infty} dt' e^{-i\omega t'} \delta(t') \]

\[ = \frac{\Theta \zeta_0^2}{4\pi |\Gamma_0|} \int_{-\infty}^{0} dt' e^{-i\omega t'} e^{-2\Gamma_0 t'} \]

\[ + \frac{\Theta \zeta_0^2}{4\pi |\Gamma_0|} \int_{0}^{\infty} dt' e^{-i\omega t'} e^{2\Gamma_0 t'} \]

\[ + \frac{\Theta \Gamma_2}{\pi |\Gamma_0|} , \]  

(7.170)

thus

\[ S_\dot{\phi}(\omega) = \frac{1}{\pi} \frac{\Theta \zeta_0^2}{4\Gamma_0^2 + \omega^2} + \frac{\Theta \Gamma_2}{\pi |\Gamma_0|} . \]

(7.171)

The signal \( y(t) \), which is defined by

\[ y(t) = \frac{\dot{\phi}}{\Omega_H} , \]

(7.172)

represents the normalized deviation of the momentary angular frequency \( \Omega + \dot{\phi} \) from its average value. The average value of \( y(t) \) is estimated by monitoring the signal \( y(t) \) in a time interval \( T \)

\[ \hat{y}(T) = \frac{1}{T} \int_{-T/2}^{T/2} dt \ y(t) . \]

(7.173)

In the limit of steady state, i.e. when \( T \gg 1/|\Gamma_0| \), the variance \( \sigma_y^2(T) \) of the estimator \( \hat{y}(T) \), which is called the Allan variance, is given by [see Eq. (7.27)]

\[ \sigma_y^2(T) = \frac{2\pi S_y(0)}{T} = \frac{2\pi S_\dot{\phi}(0)}{\Omega_H^2 T} , \]

(7.174)

thus

\[ \sigma_y^2(T) = \frac{2}{\Omega_H^2 T} \left( \frac{\Theta \zeta_0^2}{4\Gamma_0^2} + \frac{\Theta \Gamma_2}{|\Gamma_0|} \right) \]

\[ = \frac{2\Theta}{\Omega_H^2 \zeta_0^2 T} \left( 1 + \frac{\zeta_0^2}{4|\Gamma_0| \Gamma_2} \right) . \]

(7.175)
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Fig. 7.2.

7.5 Problems

1. Let \( z(t) \) be a real stationary random signal. Show that the quantity \( P_z(\omega) \), which is defined by

\[
P_z(\omega) = \frac{1}{2\pi} \lim_{T \to \infty} \frac{1}{T} \left[ \left( \int_{-T/2}^{T/2} dt \, z(t) \cos(\omega t) \right)^2 + \left( \int_{-T/2}^{T/2} dt \, z(t) \sin(\omega t) \right)^2 \right].
\]

(7.176)

is the power spectrum of \( z(t) \).

2. The circuit seen in Fig. 7.2, which contains a resistor \( R \), capacitor \( C \), and an inductor \( L \), is at thermal equilibrium at temperature \( \tau \). Calculate the average value \( \langle I^2 \rangle \), where \( I \) is the current in the inductor.

3. Consider a resonator made of a capacitor \( C \), an inductor \( L \), and a resistor \( R \) connected in series (see Fig. 7.1). Let \( I(t) \) be the current in the circuit. Calculate the spectral density \( S_I(\omega) \) of \( I \) at thermal equilibrium. Show that in the limit of high quality factor, namely when

\[
Q = \frac{2}{\pi} \frac{\sqrt{L/C}}{R} \gg 1,
\]

(7.177)

the result is consistent with the equipartition theorem applied for the energy stored by the inductor.

4. The Hermite polynomial \( H_n(X) \) of order \( n \) is defined by

\[
H_n(X) = \exp \left( \frac{X^2}{2} \right) \left( X - \frac{d}{dX} \right)^n \exp \left( -\frac{X^2}{2} \right).
\]

(7.178)
For some low values of $n$ the Hermite polynomials are given by

$$H_0(X) = 1,$$  \hspace{1cm} (7.179)

$$H_1(X) = 2X,$$  \hspace{1cm} (7.180)

$$H_2(X) = 4X^2 - 2,$$  \hspace{1cm} (7.181)

$$H_3(X) = 8X^3 - 12X,$$  \hspace{1cm} (7.182)

$$H_4(X) = 16X^4 - 48X^2 + 12.$$  \hspace{1cm} (7.183)

Show that

$$\exp \left( 2Xt - t^2 \right) = \sum_{n=0}^{\infty} H_n(X) \frac{t^n}{n!}. \hspace{1cm} (7.184)$$

5. Show that

$$\sum_{n=0}^{\infty} \left( \frac{t}{X} \right)^n H_n(X) H_n(Y) = \frac{\exp \left( \frac{\alpha(2XY - \alpha X^2 - \alpha Y^2)}{1 - \alpha^2} \right)}{\sqrt{1 - \alpha^2}}. \hspace{1cm} (7.185)$$

### 7.6 Solutions

1. The following holds

$$\left( \int_{-T/2}^{T/2} dt \ z(t) \cos(\omega t) \right)^2 + \left( \int_{-T/2}^{T/2} dt \ z(t) \sin(\omega t) \right)^2$$

$$= \int_{-T/2}^{T/2} dt \int_{-T/2}^{T/2} dt' \ z(t) \ z(t') \cos(\omega (t - t')) , \hspace{1cm} (7.186)$$

thus in terms of the sampling function $z_T(t)$, which is defined by [see Eq. (7.1)]

$$z_T(t) = \begin{cases} z(t) & \text{if } -T/2 < t < T/2 \\ 0 & \text{else} \end{cases}, \hspace{1cm} (7.187)$$

one finds that

$$P_z(\omega) = \frac{1}{2\pi} \lim_{T \to \infty} \frac{1}{T} \times \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \ z_T(t) \ z_T(t') \cos(\omega (t - t')) . \hspace{1cm} (7.188)$$
The variable transformation $t' = t - t'$ leads to

$$ P_z (\omega) = \frac{1}{2\pi} \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' \ z_T (t' + t'') z_T (t') \cos (\omega t'') $$

$$ P_z (\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt'' \ \cos (\omega t'') $$

$$ \times \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} dt' \ z_T (t' + t'') z_T (t') , $$

(7.189)

thus in terms of the autocorrelation function $C_z (t)$ [see Eq. (7.9)] one finds that

$$ P_z (\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt'' \ \cos (\omega t'') C_z (t'') . $$

(7.190)

According to the Wiener-Khinchine Theorem [see Eq. (7.10)] the following holds

$$ C_z (t'') = \int_{-\infty}^{\infty} d\omega' \ e^{i\omega' t''} S_z (\omega') , $$

(7.191)

where $S_z (\omega)$ is the power spectrum of $z (t)$, thus

$$ P_z (\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt'' \ \cos (\omega t'') \int_{-\infty}^{\infty} d\omega' \ e^{i\omega' t''} S_z (\omega') $$

$$ = \int_{-\infty}^{\infty} d\omega' \ S_z (\omega') $n

$$ \times \frac{1}{2\pi} \int_{-\infty}^{\infty} dt'' \ e^{i(\omega + \omega') t''} + e^{-i(\omega - \omega') t''} $$

$$ = \int_{-\infty}^{\infty} d\omega' \ e^{i(\omega + \omega') t''} + e^{-i(\omega - \omega') t''} $$

$$ = \frac{S_z (-\omega) + S_z (\omega)}{2} . $$

(7.192)

Using the fact that $z (t)$ is real one finds that $z_T (\omega) = z_T^* (\omega)$ [see Eq. (7.2)] and consequently [see Eq. (7.3)] $S_z (-\omega) = S_z (\omega)$, thus $P_z (\omega) = S_z (\omega)$.
2. The energy stored in the inductor $U_L$ is given by $U_L = LI^2/2$, thus by using the equipartition theorem, which states that $\langle U_L \rangle = \tau/2$, one finds that

$$\langle I^2 \rangle = \frac{\tau}{L}.$$  \hspace{1cm} (7.193)

3. Using $I(\omega) = -i\omega q(\omega)$ and $\langle q^2 \rangle = C\tau$, one finds for the case $Q \gg 1$ that

$$\langle I^2 \rangle = \int_{-\infty}^{\infty} d\omega S_I(\omega) \simeq \omega_0^2 \int_{-\infty}^{\infty} d\omega S_q(\omega) = \omega_0^2 \langle q^2 \rangle = \frac{\tau}{L},$$  \hspace{1cm} (7.194)

in agreement with the equipartition theorem for the energy stored in the inductor $LI^2/2$.

4. The relation (7.184), which is a Taylor expansion of the function $f(t) = \exp(2Xt - t^2)$ around the point $t = 0$, implies that

$$H_n(X) = \frac{d^n}{dt^n} \exp(2Xt - t^2) \bigg|_{t=0}.$$  \hspace{1cm} (7.195)

The identity $2Xt - t^2 = X^2 - (X - t)^2$ yields

$$H_n(X) = \exp(X^2) \frac{d^n}{dt^n} \exp(- (X - t)^2) \bigg|_{t=0}.$$  \hspace{1cm} (7.196)

Moreover, using the relation

$$\frac{d}{dt} \exp(- (X - t)^2) = \frac{d}{dX} \exp(- (X - t)^2),$$  \hspace{1cm} (7.197)

one finds that

$$H_n(X) = \exp(X^2) (-1)^n \frac{d^n}{dX^n} \exp(- (X - t)^2) \bigg|_{t=0}
= \exp(X^2) (-1)^n \frac{d^n}{dX^n} \exp(- X^2).$$  \hspace{1cm} (7.198)

Note that for an arbitrary function $g(X)$ the following holds

$$- \exp(X^2) \frac{d}{dX} \exp(- X^2) g = \left(2X - \frac{d}{dX}\right) g,$$  \hspace{1cm} (7.199)

and

$$\exp\left(\frac{X^2}{2}\right) \left(X - \frac{d}{dX}\right) \exp\left(- \frac{X^2}{2}\right) g = \left(2X - \frac{d}{dX}\right) g,$$  \hspace{1cm} (7.200)

thus

$$H_n(X) = \exp\left(\frac{X^2}{2}\right) \left(X - \frac{d}{dX}\right)^n \exp\left(- \frac{X^2}{2}\right).$$  \hspace{1cm} (7.201)
5. With the help of Eq. (7.198) and the general identity
\[
\int_{-\infty}^{\infty} dx \exp(-ax^2 + bx + c) = \sqrt{\frac{\pi}{a}} e^{\frac{b^2 - 4ac}{4a}},
\] (7.202)
according to which the following holds (for the case \( a = 1, b = 2iX \) and \( c = 0 \))
\[
\exp(-X^2) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-x^2 + 2iXx),
\] (7.203)
one finds that
\[
H_n(X) = \frac{\exp(X^2)}{\sqrt{\pi}} \left( \frac{-d}{dX} \right)^n \int_{-\infty}^{\infty} dx \exp(-x^2 + 2iXx)
\]
\[
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx (-2ix)^n \exp(X^2 - x^2 + 2iXx)
\]
\[
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx (-2ix)^n e^{(X+ix)^2},
\] (7.204)
thus the following holds [see Eq. (7.202)]
\[
\sum_{n=0}^{\infty} \left( \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \ e^{(X+iX)^2} e^{(Y+iY)^2} \sum_{n=0}^{\infty} \frac{(-2\alpha xy)^n}{n!} e^{-2\alpha xy} \right)
\]
\[
= \frac{1}{\pi} \int_{-\infty}^{\infty} dx \ e^{(X+iX)^2} \int_{-\infty}^{\infty} dy \ e^{(Y+iY)^2} e^{-2\alpha xy}
\]
\[
\sqrt{\pi e^{\alpha x(\alpha x - 2Y)}}
\]
\[
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \ e^{(-\alpha^2) x^2 + 2(\alpha x + Y) x + Y^2}
\]
\[
\exp\left( \frac{\alpha (2XY - \alpha X^2 - \alpha Y^2)}{1-\alpha^2} \right)
\]
\[
= \frac{1}{\sqrt{1-\alpha^2}}.
\] (7.205)
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