Eyal Buks

Introduction to Thermodynamics and Statistical Physics (114016) - Lecture Notes

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Technion
Preface

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1. The Principle of Largest Uncertainty

In this chapter we discuss relations between information theory and statistical mechanics. We show that the canonical and grand canonical distributions can be obtained from Shannon’s principle of maximum uncertainty [1, 2, 3]. Moreover, the time evolution of the entropy of an isolated system and the H theorem are discussed.

1.1 Entropy in Information Theory

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 \( p_m \). The normalization condition reads

\[
\sum_m p_m = 1 . \tag{1.1}
\]

For a given probability distribution \( \{ p_m \} \) the entropy is defined as

\[
\sigma = - \sum_m p_m \log p_m . \tag{1.2}
\]

Below we show that this quantity characterizes the uncertainty in the knowledge of the state of the system.

1.1.1 Example - Two States System

Consider a system which can occupy either state \( e_1 \) with probability \( p \), or state \( e_2 \) with probability \( 1 - p \), where \( 0 \leq p \leq 1 \). The entropy is given by

\[
\sigma = -p \log p - (1-p) \log (1-p) . \tag{1.3}
\]
As expected, the entropy vanishes at $p = 0$ and $p = 1$, since in both cases there is no uncertainty in what is the state which is occupied by the system. The largest uncertainty is obtained at $p = 0.5$, for which $\sigma = \log 2 = 0.69$.

1.1.2 Smallest and Largest Entropy

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

$$\lim_{p \to 0} (-p \log p) = \lim_{p \to 0} \left( -\frac{d \log p}{dp} \frac{1}{p} \right) = 0 . \quad (1.4)$$

From this figure, which shows that $-p \log p \geq 0$ in the range $0 \leq p \leq 1$, it is easy to infer that the smallest possible value of the entropy is zero. Moreover, since $-p \log p = 0$ iff $p = 0$ or $p = 1$, it is evident that $\sigma = 0$ iff the system occupies one of the states with probability one and all the other states with probability zero. In this case there is no uncertainty in what is the state which is occupied by the system.
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

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

(1.5)

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

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

(1.6)

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

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

(1.7)

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

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

(1.8)

In addition the variables $(p_1, p_2, \cdots)$ are subjected to the constrain (1.5). Similarly to Eq. (1.8) we have

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

(1.9)

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

$$ \nabla \sigma = (\nabla \sigma) \parallel + (\nabla \sigma) \perp , $$

(1.10)

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

(1.11)

where $(\nabla \sigma) \parallel$ and $(\delta \bar{p}) \parallel$ are parallel to $\nabla g_0$, and where $(\nabla \sigma) \perp$ and $(\delta \bar{p}) \perp$ are orthogonal to $\nabla g_0$. Using this notation Eq. (1.8) can be expressed as
\[ \delta \sigma = (\nabla \sigma)_{\parallel} \cdot (\delta \vec{p})_{\parallel} + (\nabla \sigma)_{\perp} \cdot (\delta \vec{p})_{\perp}. \]  

(1.12)

Given that the constraint \( g_0 (\vec{p}) = 0 \) 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 \( \nabla g_0 \), 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 \( \nabla g_0 \), namely, \( \delta \vec{p} \cdot \nabla g_0 = 0 \) one has \( 0 = \delta \sigma = \nabla \sigma \cdot \delta \vec{p} \). As can be seen from Eq. (1.12), this condition is fulfilled only when \( (\nabla \sigma)_{\perp} = 0 \), namely only when the vectors \( \nabla \sigma \) and \( \nabla g_0 \) are parallel to each other. In other words, only when

\[ \nabla \sigma = \xi_0 \nabla g_0, \]  

(1.13)

where \( \xi_0 \) is a constant. This constant is called Lagrange multiplier. Using Eqs. (1.2) and (1.5) the condition (1.13) is expressed as

\[ \log p_m + 1 = \xi_0. \]  

(1.14)

Let \( M \) be the number of available states. From Eq. (1.14) we find that all probabilities are equal. Thus using Eq. (1.5), one finds that

\[ p_1 = p_2 = \cdots = \frac{1}{M}. \]  

(1.15)

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 \( \delta \vec{p} \)

\[ \sigma (\vec{p} + \delta \vec{p}) = \exp (\delta \vec{p} \cdot \nabla) \sigma (\vec{p}) 
= \left( 1 + \delta \vec{p} \cdot \nabla + \frac{(\delta \vec{p} \cdot \nabla)^2}{2!} + \cdots \right) \sigma (\vec{p}) 
= \sigma (\vec{p}) + \delta \vec{p} \cdot \nabla \sigma + \frac{(\delta \vec{p} \cdot \nabla)^2}{2!} \sigma + \cdots 
= \sigma (\vec{p}) + \sum_m \frac{\partial \sigma}{\partial p_m} \delta p_m + \frac{1}{2} \sum_{m,m'} \delta p_m \delta p_{m'} \frac{\partial^2 \sigma}{\partial p_m \partial p_{m'}} + \cdots \]  

(1.16)

Using Eq. (1.2) one finds that

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

(1.17)

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
$A(M) = \sigma \left( \frac{1}{M}, \frac{1}{M}, \ldots, \frac{1}{M} \right) = \log M$ , \hspace{1cm} (1.18)

for the probability distribution given by Eq. (1.15). For this probability distribution that maximizes $\sigma$, as expected, the state which is occupied by the system is most uncertain.

1.1.3 The composition property

The composition property is best illustrated using an example.

**Example - A Three States System.** A system can occupy one of the states $e_1$, $e_2$ or $e_3$ with probabilities $p_1$, $p_2$ and $p_3$ respectively. The uncertainty associated with this probability distribution can be estimated in two ways, directly and indirectly. Directly, it is simply given by the definition of entropy in Eq. (1.2)

$$\sigma(p_1, p_2, p_3) = -p_1 \log p_1 - p_2 \log p_2 - p_3 \log p_3 .$$ \hspace{1cm} (1.19)

Alternatively [see Fig. 1.1], the uncertainty can be decomposed as follows: (a) the system can either occupy state $e_1$ with probability $p_1$, or not occupy state $e_1$ with probability $1 - p_1$; (b) given that the system does not occupy state $e_1$, it can either occupy state $e_2$ with probability $p_2/(1 - p_1)$ or occupy state $e_3$ with probability $p_3/(1 - p_1)$. Assuming that uncertainty (entropy) is additive, the total uncertainty (entropy) is given by

$$\sigma_i = \sigma(p_1, 1 - p_1) + (1 - p_1) \sigma\left(\frac{p_2}{1 - p_1}, \frac{p_3}{1 - p_1}\right) .$$ \hspace{1cm} (1.20)

The factor $(1 - p_1)$ in the second term is included since the uncertainty associated with distinction between states $e_2$ and $e_3$ contributes only when state $e_1$ is not occupied, an event which occurs with probability $1 - p_1$. Using the definition (1.2) and the normalization condition

$$p_1 + p_2 + p_3 = 1 ,$$ \hspace{1cm} (1.21)

one finds

$$\begin{align*}
\sigma_i &= -p_1 \log p_1 - (1 - p_1) \log (1 - p_1) \\
&\quad + (1 - p_1) \left[ -\frac{p_2}{1 - p_1} \log \frac{p_2}{1 - p_1} - \frac{p_3}{1 - p_1} \log \frac{p_3}{1 - p_1} \right] \\
&= -p_1 \log p_1 - p_2 \log p_2 - p_3 \log p_3 \\
&\quad - (1 - p_1 - p_2 - p_3) \log (1 - p_1) \\
&= \sigma(p_1, p_2, p_3) ,
\end{align*}$$ \hspace{1cm} (1.22)

that is, for this example the entropy satisfies the decomposition property.
The composition property can be defined as follows. Consider a system which can occupy one of the states \{e_1, e_2, \cdots, e_M\} with probabilities \(q_1, q_2, \cdots, q_M\) respectively. This set of states is grouped as follows. The first group includes the first \(M_1\) states \{e_1, e_2, \cdots, e_{M_1}\}; the second group includes the next \(M_2\) states \{e_{M_1+1}, e_{M_1+2}, \cdots, e_{M_1+M_2}\}, etc., where \(M_1 + M_2 + \cdots = M_0\). The probability that one of the states in the first group is occupied is \(p_1 = q_1 + q_2 + \cdots + q_{M_1}\), the probability that one of the states in the second group is occupied is \(p_2 = q_{M_1+1} + q_{M_1+2} + \cdots + q_{M_1+M_2}\), etc., where

\[
p_1 + p_2 + \cdots = 1. \tag{1.23}
\]

The composition property requires that the following holds [see Fig. 1.2]

\[
\sigma(q_1, q_2, \cdots, q_{M_0}) = \sigma(p_1, p_2, \cdots) \\
+ p_1 \sigma\left(\frac{q_1}{p_1}, \frac{q_2}{p_1}, \cdots, \frac{q_{M_1}}{p_1}\right) \\
+ p_2 \sigma\left(\frac{q_{M_1+1}}{p_2}, \frac{q_{M_1+2}}{p_2}, \cdots, \frac{q_{M_1+M_2}}{p_2}\right) + \cdots
\]

\[
\tag{1.24}
\]

Using the definition (1.2) the following holds

\[
\sigma(p_1, p_2, \cdots) = -p_1 \log p_1 - p_2 \log p_2 - \cdots, \tag{1.25}
\]
1.1. Entropy in Information Theory

Fig. 1.2. The composition property - the general case.

\begin{align}
 p_1 \sigma \left( \frac{q_1}{p_1}, \frac{q_2}{p_1}, \ldots, \frac{q_{M_1}}{p_1} \right) \\
= p_1 \left( \frac{q_1}{p_1} \log \frac{q_1}{p_1} - \frac{q_2}{p_1} \log \frac{q_2}{p_1} - \cdots - \frac{q_{M_1}}{p_1} \log \frac{q_{M_1}}{p_1} \right) \\
= -q_1 \log q_1 - q_2 \log q_2 - \cdots - q_{M_1} \log q_{M_1} \\
+ p_1 \log p_1 ,
\end{align}

(1.26)

dec., thus it is evident that condition (1.24) is indeed satisfied.
1.1.4 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 \( \Lambda (N) = \sigma (1/N, 1/N, \cdots, 1/N) \) 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. (1.24).

**Exercise 1.1.1.** Show that the above definition leads to the entropy given by Eq. (1.2) up to multiplication by a positive constant.

**Solution 1.1.1.** The 1st 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 \( M_0 = M_1 + M_2 + \cdots + M_N \). Using the composition property (1.24) one finds

\[
\Lambda (M_0) = \sigma (p_1, p_2, \cdots, p_N) + p_1 \Lambda (M_1) + p_2 \Lambda (M_2) + \cdots
\]

(1.28)

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

\[
\Lambda (NK) = \Lambda (N) + \Lambda (K).
\]

(1.29)

Taking \( K = N = 1 \) yields

\[
\Lambda (1) = 0.
\]

(1.30)

Taking \( N = 1 + x \) yields

\[
\frac{\Lambda (K + Kx) - \Lambda (K)}{Kx} = \frac{1}{K} \frac{\Lambda (1 + x)}{x}.
\]

(1.31)

Taking the limit \( x \to 0 \) yields

\[
\frac{d\Lambda}{dK} = \frac{C}{K},
\]

(1.32)

where

\[
C = \lim_{x \to 0} \frac{\Lambda (1 + x)}{x}.
\]

(1.33)

Integrating Eq. (1.32) and using the initial condition (1.30) yields

\[
\Lambda (K) = C \log K.
\]

(1.34)
Moreover, the second property requires that $C > 0$. Choosing $C = 1$ and using Eq. (1.28) yields

$$\sigma (p_1, p_2, \cdots, p_N) = \Lambda (M_0) - p_1 \Lambda (M_1) - p_2 \Lambda (M_2) - \cdots$$

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

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

(1.35)

in agreement with the definition (1.2).

### 1.2 Largest Uncertainty Estimator

As before, the possible states of a given system are denoted as $e_m$, where $m = 1, 2, 3, \cdots$, 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

$$\langle X_l \rangle = \sum_m p_m X_l (m),$$

(1.36)

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 (1.36) and the normalization condition (1.1). For each such probability distribution the entropy can be calculated according to the definition (1.2). 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 (1.5) in addition to the constrains (1.36), which can be expressed as

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

(1.37)

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

$$\delta \sigma = \nabla \sigma \cdot \delta \bar{p},$$

(1.38a)

$$\delta g_l = \nabla g_l \cdot \delta \bar{p},$$

(1.38b)
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 $\nabla g_0, \nabla g_1, \nabla g_2, \cdots, \nabla g_L$ one has

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

This condition is fulfilled only when the vector $\nabla \sigma$ belongs to the subspace spanned by the vectors $\{ \nabla g_0, \nabla g_1, \nabla g_2, \cdots, \nabla g_L \}$ [see also the discussion below Eq. (1.12) above]. In other words, only when

$$\nabla \sigma = \xi_0 \nabla g_0 + \xi_1 \nabla g_1 + \xi_2 \nabla g_2 + \cdots + \xi_L \nabla g_L,$$  

where the numbers $\xi_0, \xi_1, \cdots, \xi_L$, which are called Lagrange multipliers, are constants. Using Eqs. (1.2), (1.5) and (1.37) the condition (1.40) can be expressed as

$$-\log p_m - 1 = \xi_0 + \sum_{l=1}^{L} \xi_l X_l (m).$$  

From Eq. (1.41) one obtains

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

The Lagrange multipliers $\xi_0, \xi_1, \cdots, \xi_L$ can be determined from Eqs. (1.5) and (1.37)

$$1 = \sum_m p_m = \exp (-1 - \xi_0) \sum_m \exp \left( - \sum_{l=1}^{L} \xi_l X_l (m) \right),$$  

$$\langle X_l \rangle = \sum_m p_m X_l (m)$$

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

Using Eqs. (1.42) and (1.43) one finds

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

In terms of the partition function $Z$, which is defined as
\[ Z = \sum_{m} \exp \left( -\sum_{l=1}^{L} \xi_l X_l (m) \right), \quad (1.46) \]

one finds

\[ p_m = \frac{1}{Z} \exp \left( -\sum_{l=1}^{L} \xi_l X_l (m) \right). \quad (1.47) \]

Using the same arguments as in section 1.1.2 above [see Eq. (1.16)] it is easy to show that at the stationary point that occurs for the probability distribution given by Eq. (1.47) the entropy obtains its largest value.

1.2.1 Useful Relations

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

\[
\langle X_l \rangle = \sum_{m} p_m X_l (m)
\]
\[
= \frac{1}{Z} \sum_{m} \exp \left( -\sum_{l=1}^{L} \xi_l X_l (m) \right) X_l (m)
\]
\[
= -1 \frac{\partial Z}{Z \partial \xi_l}
\]
\[
= -\frac{\partial \log Z}{\partial \xi_l}.
\]

(1.48)

Similarly, \( \langle X_l^2 \rangle \) can be expressed as

\[
\langle X_l^2 \rangle = \sum_{m} p_m X_l^2 (m)
\]
\[
= \frac{1}{Z} \sum_{m} \exp \left( -\sum_{l=1}^{L} \xi_l X_l (m) \right) X_l^2 (m)
\]
\[
= \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_l^2}.
\]

(1.49)

Using Eqs. (1.48) and (1.49) one finds that the variance of the variable \( X_l \) is given by

\[
\left( \langle \Delta X_l \rangle \right)^2 = \left( \langle X_l - \langle X_l \rangle \rangle \right)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi_l^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_l} \right)^2.
\]

(1.50)

However, using the following identity
\[
\frac{\partial^2 \log Z}{\partial \xi_i^2} = \partial_1 \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \frac{\partial^2 Z}{\partial \xi_i^2} = \left( \frac{1}{Z} \frac{\partial Z}{\partial \xi_i} \right)^2, \quad (1.51)
\]

one finds
\[
\langle (\Delta X_l)^2 \rangle = \frac{\partial^2 \log Z}{\partial \xi_i^2}. \quad (1.52)
\]

Note that the above results Eqs. (1.48) and (1.52) are valid only when \( Z \) is expressed as a function of the the Lagrange multipliers, namely
\[
Z = Z(\xi_1, \xi_2, \cdots, \xi_L). \quad (1.53)
\]

Using the definition of entropy (1.2) and Eq. (1.47) one finds
\[
\sigma = -\sum_m p_m \log p_m = -\sum_m p_m \log \left( \frac{1}{Z} \exp \left( -\sum_{l=1}^L \xi_l X_l(m) \right) \right) = \sum_m p_m \left( \log Z + \sum_{l=1}^L \xi_l X_l(m) \right) = \log Z + \sum_{l=1}^L \xi_l \sum_m p_m X_l(m),
\]
thus
\[
\sigma = \log Z + \sum_{l=1}^L \xi_l \langle X_l \rangle. \quad (1.54)
\]

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
\[
\sigma = \sigma(\langle X_1 \rangle, \langle X_2 \rangle, \cdots, \langle X_L \rangle). \quad (1.55)
\]

Using Eq. (1.55) one has
\[
\frac{\partial \sigma}{\partial \langle X_l \rangle} = \frac{\partial \log Z}{\partial \langle X_l \rangle} + \sum_{l'=1}^L \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \sum_{l'=1}^L \xi_{l'} \frac{\partial \langle X_{l'} \rangle}{\partial \langle X_l \rangle} = \frac{\partial \log Z}{\partial \langle X_l \rangle} + \sum_{l'=1}^L \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \xi_l = \sum_{l'=1}^L \frac{\partial \log Z}{\partial \xi_{l'}} \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \sum_{l'=1}^L \langle X_{l'} \rangle \frac{\partial \xi_{l'}}{\partial \langle X_l \rangle} + \xi_l, \quad (1.57)
\]
thus using Eq. (1.48) one finds
\[
\frac{\partial \sigma}{\partial \langle X_l \rangle} = \xi_l .
\] (1.58)

### 1.2.2 The Free Entropy

The free entropy \( \sigma_F \) is defined as the term \( \log Z \) in Eq. (1.54)
\[
\sigma_F = \log Z
\]
\[
= \sigma - \sum_{l=1}^{L} \xi_l \sum_{m} p_m X_l (m)
\]
\[
= -\sum_{m} p_m \log p_m - \sum_{l=1}^{L} \xi_l \sum_{m} p_m X_l (m) .
\] (1.59)

The free entropy is commonly expressed as a function of the Lagrange multipliers
\[
\sigma_F = \sigma_F (\xi_1, \xi_2, \cdots, \xi_L) .
\] (1.60)

We have seen above that the LUE maximizes \( \sigma \) for given values of expectation values \( \langle X_1 \rangle, \langle X_2 \rangle, \cdots, \langle X_L \rangle \). We show below that a similar result can be obtained for the free energy \( \sigma_F \) with respect to given values of the Lagrange multipliers.

**Claim.** The LUE maximizes \( \sigma_F \) for given values of the Lagrange multipliers \( \xi_1, \xi_2, \cdots, \xi_L \).

**Proof.** As before, the normalization condition is expressed as
\[
0 = g_0 (\bar{p}) = \sum_{m} p_m - 1 .
\] (1.61)

At a stationary point of \( \sigma_F \), as we have seen previously, the following holds
\[
\nabla \sigma_F = \eta \nabla g_0 ,
\] (1.62)

where \( \eta \) is a Lagrange multiplier. Thus
\[
-(\log p_m + 1) - \sum_{l=1}^{L} \xi_l X_l (m) = \eta ,
\] (1.63)

or
\[
p_m = \exp (-\eta - 1) \exp \left( -\sum_{l=1}^{L} \xi_l X_l (m) \right) .
\] (1.64)
Table 1.1. The microcanonical, canonical and grandcanonical distributions.

<table>
<thead>
<tr>
<th></th>
<th>energy</th>
<th>number of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>microcanonical distribution</td>
<td>constrained $U(m) = U$</td>
<td>constrained $N(m) = N$</td>
</tr>
<tr>
<td>canonical distribution</td>
<td>average is given $\langle U \rangle$</td>
<td>constrained $N(m) = N$</td>
</tr>
<tr>
<td>grandcanonical distribution</td>
<td>average is given $\langle U \rangle$</td>
<td>average is given $\langle N \rangle$</td>
</tr>
</tbody>
</table>

This result is the same as the one given by Eq. (1.42). Taking into account the normalization condition (1.61) one obtains the same expression for $p_m$ as the one given by Eq. (1.47). Namely, the stationary point of $\sigma_F$ corresponds to the LUE probability distribution. Since

$$\frac{\partial^2 \sigma_F}{\partial p_m \partial p_{m'}} = -\frac{1}{p_m} \delta_{m,m'} < 0 ,$$  \hspace{1cm} (1.65)

one concludes that this stationary point is a maximum point [see Eq. (1.16)].

1.3 The Principle of Largest Uncertainty in Statistical Mechanics

The energy and number of particles of state $e_m$ are denoted by $U(m)$ and $N(m)$ respectively. The probability that state $e_m$ is occupied is denoted as $p_m$. We consider below three cases (see table 1.1). In the first case (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 the environment, and we assume that its average energy $\langle U \rangle$ 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 the environment, and we assume that both the average energy $\langle U \rangle$ and the average number of particles $\langle N \rangle$ are given. However, in all cases, the probability distribution $\{p_m\}$ is not given.

According to the principle of largest uncertainty in statistical mechanics the LUE is employed to estimate the probability distribution $\{p_m\}$, namely, we will seek a probability distribution 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.

1.3.1 Microcanonical Distribution

In this case no expectation values are given. Thus we seek a probability distribution which is consistent with the normalization condition (1.1), and
which maximizes the entropy. The desired probability distribution is
\[ p_1 = p_2 = \cdots = 1/M , \quad (1.66) \]
where \( M \) is the number of accessible states of the system [see also Eq. (1.18)].
Using Eq. (1.2) the entropy for this case is given by
\[ \sigma = \log M . \quad (1.67) \]

### 1.3.2 Canonical Distribution

Using Eq. (1.47) one finds that the probability distribution is given by
\[ p_m = \frac{1}{Z_c} \exp(-\beta U (m)) , \quad (1.68) \]
where \( \beta \) is the Lagrange multiplier associated with the given expectation value \( \langle U \rangle \), and the partition function is given by
\[ Z_c = \sum_m \exp(-\beta U (m)) . \quad (1.69) \]
The term \( \exp(-\beta U (m)) \) is called Boltzmann factor.
Moreover, Eq. (1.48) yields
\[ \langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} , \quad (1.70) \]
Eq. (1.52) yields
\[ \langle (\Delta U)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2} , \quad (1.71) \]
and Eq. (1.55) yields
\[ \sigma = \log Z_c + \beta \langle U \rangle . \quad (1.72) \]

Using Eq. (1.58) one can expressed the Lagrange multiplier \( \beta \) as
\[ \beta = \frac{\partial \sigma}{\partial U} , \quad (1.73a) \]
The temperature \( \tau = 1/\beta \) is defined as
\[ \frac{1}{\tau} = \beta . \quad (1.74) \]

**Exercise 1.3.1.** Consider a system that can be in one of two states having energies \( \pm \varepsilon/2 \). Calculate the average energy \( \langle U \rangle \) and the variance \( \langle (\Delta U)^2 \rangle \) in thermal equilibrium at temperature \( \tau \).
Solution: The partition function is given by Eq. (1.69)

\[ Z_c = \exp \left( \frac{-\beta \varepsilon}{2} \right) + \exp \left( \frac{\beta \varepsilon}{2} \right) = 2 \cosh \left( \frac{\beta \varepsilon}{2} \right), \]  \hspace{1cm} (1.75)

thus using Eqs. (1.70) and (1.71) one finds

\[ \langle U \rangle = -\frac{\varepsilon}{2} \tanh \left( \frac{\beta \varepsilon}{2} \right), \]  \hspace{1cm} (1.76)

and

\[ \langle (\Delta U)^2 \rangle = \left( \frac{\varepsilon}{2} \right)^2 \frac{1}{\cosh^2 \frac{\beta \varepsilon}{2}}, \]  \hspace{1cm} (1.77)

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

---

1.3.3 Grandcanonical Distribution

Using Eq. (1.47) one finds that the probability distribution is given by

\[ p_m = \frac{1}{Z_{gc}} \exp \left( -\beta U (m) - \eta N (m) \right), \]  \hspace{1cm} (1.78)

where \( \beta \) and \( \eta \) are the Lagrange multipliers associated with the given expectation values \( \langle U \rangle \) and \( \langle N \rangle \) respectively, and the partition function is given by

\[ Z_{gc} = \sum_m \exp \left( -\beta U (m) - \eta N (m) \right). \]  \hspace{1cm} (1.79)

The term \( \exp \left( -\beta U (m) - \eta N (m) \right) \) is called Gibbs factor.

Moreover, Eq. (1.48) yields
1.3. The Principle of Largest Uncertainty in Statistical Mechanics

\[ \langle U \rangle = -\left( \frac{\partial \log Z_{ge}}{\partial \beta} \right)_{\eta} , \quad (1.80) \]

\[ \langle N \rangle = -\left( \frac{\partial \log Z_{ge}}{\partial \eta} \right)_{\beta} \quad (1.81) \]

Eq. (1.52) yields

\[ \langle (\Delta U)^2 \rangle = \left( \frac{\partial^2 \log Z_{ge}}{\partial \beta^2} \right)_{\eta} , \quad (1.82) \]

\[ \langle (\Delta N)^2 \rangle = \left( \frac{\partial^2 \log Z_{ge}}{\partial \eta^2} \right)_{\beta} , \quad (1.83) \]

and Eq. (1.55) yields

\[ \sigma = \log Z_{gc} + \beta \langle U \rangle + \eta \langle N \rangle . \quad (1.84) \]

1.3.4 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. (1.72) can be rewritten as

\[ \sigma = \log Z_{c} + \beta U , \quad (1.85) \]

and the one in Eq. (1.84) as

\[ \sigma = \log Z_{gc} + \beta U + \eta N . \quad (1.86) \]

Using Eq. (1.58) one can expressed the Lagrange multipliers \( \beta \) and \( \eta \) as

\[ \beta = \left( \frac{\partial \sigma}{\partial U} \right)_{N} , \quad (1.87) \]

\[ \eta = \left( \frac{\partial \sigma}{\partial N} \right)_{U} . \quad (1.88) \]

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

\[ \mu = -\tau \eta . \quad (1.89) \]

In the definition (1.2) the entropy \( \sigma \) is dimensionless. Historically, the entropy was defined as

\[ S = k_B \sigma , \quad (1.90) \]

where
Chapter 1. The Principle of Largest Uncertainty

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

(1.91)

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

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

(1.92)

When the grandcanonical partition function is expressed in terms of \( \beta \) and \( \mu \) (instead of in terms of \( \beta \) and \( \eta \)), it is convenient to rewrite Eqs. (1.80) and (1.81) as (see homework exercises 14 of chapter 1).

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

(1.93)

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

(1.94)

where \( \lambda \) is the fugacity, which is defined by

\[ \lambda = \exp(\beta \mu) = e^{-\eta}. \]  

(1.95)

1.4 Time Evolution of Entropy of an Isolated System

Consider a perturbation which results in transitions between the states of an isolated system. Let \( \Gamma_{rs} \) denotes the resulting rate of transition from state \( r \) to state \( s \). The probability that state \( s \) is occupied is denoted as \( p_s \).

The following theorem (H theorem) states that if for every pair of states \( r \) and \( s \)

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

(1.96)

then

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

(1.97)

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

To prove this theorem we express the rate of change in the probability \( p_s \) in terms of these transition rates

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

(1.98)

The first term represents the transitions to state \( r \), whereas the second one represents transitions from state \( r \). Using property (1.96) one finds

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

(1.99)
The last result and the definition (1.2) allows calculating the rate of change of entropy

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

(1.100)

One the other hand, using Eq. (1.96) and exchanging the summation indices allow rewriting the last result as

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

(1.101)

Thus, using both expressions (1.100) and (1.101) yields

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

(1.102)

In general, since \(\log x\) is a monotonic increasing function

\[(p_s - p_r) (\log p_s - \log p_r) \geq 0 , \]

(1.103)

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

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

(1.104)

and equality holds iff \(p_s = p_r\) holds for all pairs is states satisfying \(\Gamma_{sr} \neq 0\). When \(\sigma\) becomes time independent the system is said to be in thermal equilibrium. In thermal equilibrium, when all accessible states have the same probability, one finds using the definition (1.2)

\[
\sigma = \log M ,
\]

(1.105)

where \(M\) is the number of accessible states of the system.

Note that the rates \(\Gamma_{rs}\), which can be calculated using quantum mechanics, indeed satisfy the property (1.96) for the case of an isolated system.

### 1.5 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

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

(1.106)

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

$$
\delta \sigma \geq 0 .
$$

(1.107)

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

$$
\tau_1 = \tau_2
$$

(1.108)

and

$$
\mu_1 = \mu_2 .
$$

(1.109)

1.5.1 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

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

(1.110)

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

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

(1.111)
whereas, for particles having mass \( m \) in a constant gravitational field \( g \) one has
\[
\mu_{\text{ex}} = mgz ,
\]
where \( z \) is the height. The thermal equilibrium relation (1.109) is generalized in the presence of externally applied potential energy as
\[
\mu_{\text{tot},1} = \mu_{\text{tot},2} .
\]

1.6 Free Entropy and Free Energies

The free entropy [see Eq. (1.59)] for the canonical distribution is given by [see Eq. (1.85)]
\[
\sigma_{F,c} = \sigma - \beta U ,
\]
whereas for the grandcanonical case it is given by [see Eq. (1.86)]
\[
\sigma_{F,gc} = \sigma - \beta U - \eta N .
\]

We define below two corresponding free energies, the canonical free energy (known also as the Helmholtz free energy)
\[
F = -\tau \sigma_{F,c} = U - \tau \sigma ,
\]
and the grandcanonical free energy
\[
G = -\tau \sigma_{F,gc} = U - \tau \sigma + \tau \eta N = U - \tau \sigma - \mu N .
\]

In section 1.2.2 above we have 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 1.2 below

1.7 Problems Set 1

Note: Problems 1-6 are taken from the book by Reif, chapter 1.
Chapter 1. The Principle of Largest Uncertainty

Table 1.2. Summary of main results.

<table>
<thead>
<tr>
<th></th>
<th>general (M states)</th>
<th>microcanonical</th>
<th>canonical</th>
<th>grandcanonical</th>
</tr>
</thead>
<tbody>
<tr>
<td>given expectation</td>
<td>$\langle X_l \rangle$ where ( l = 1, 2, ..., L )</td>
<td>$\langle U \rangle$</td>
<td>$\langle U \rangle, \langle N \rangle$</td>
<td></td>
</tr>
<tr>
<td>partition function</td>
<td>$Z = \sum_m e^{-\frac{1}{\beta} \xi_l X_l(m)}$</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>$p_m = \frac{1}{\sum\xi_l X_l(m)}$</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>
</tr>
<tr>
<td>$\langle X_l \rangle$</td>
<td>$\langle X_l \rangle = -\frac{\partial \log Z}{\partial \xi_l}$</td>
<td>$\langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta}$</td>
<td>$\langle U \rangle = -\frac{\partial \log Z_{gc}}{\partial \eta}$</td>
<td></td>
</tr>
<tr>
<td>$\langle (\Delta X)^2 \rangle$</td>
<td>$\langle (\Delta X)^2 \rangle = \frac{\partial^2 \log Z}{\partial \xi_l^2}$</td>
<td>$\langle (\Delta U)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2}$</td>
<td>$\langle (\Delta N)^2 \rangle = \frac{\partial^2 \log Z_{gc}}{\partial \eta^2}$</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>
</tbody>
</table>

Lagrange multipliers

| $\xi_l = \left( \frac{\partial \sigma}{\partial \langle X_l \rangle} \right)_{\langle X_n \rangle_{n \neq l}}$ | $\beta = \frac{\partial \sigma}{\partial \beta}$ | $\beta = \left( \frac{\partial \sigma}{\partial \beta} \right)_N$ |
| max principle        | $\sigma_F = \sigma - \sum_l \xi_l \langle X_l \rangle$ | min $F(\tau)$ | $\min G(\tau, \mu)$ |
| $\sigma_F = \sigma_{\min}$ | $F = U - \tau \sigma$ | $G = U - \tau \sigma - \mu N$ |

1. A drunk starts out from a lamppost in the middle of a street, taking steps of equal length either to the right or to the left with equal probability. What is the probability that the man will again be at the lamppost after taking $N$ steps
   a) if $N$ is even?
   b) if $N$ is odd?

2. In the game of Russian roulette, one inserts a single cartridge into the drum of a revolver, leaving the other five chambers of the drum empty. One then spins the drum, aims at one’s head, and pulls the trigger.
   a) What is the probability of being still alive after playing the game $N$ times?
b) What is the probability of surviving \((N - 1)\) turns in this game and then being shot the \(N\)th time one pulls the trigger?

c) What is the mean number of times a player gets the opportunity of pulling the trigger in this macabre game?

3. Consider the random walk problem with \(p = q\) and let \(m = n_1 - n_2\), denote the net displacement to the right. After a total of \(N\) steps, calculate the following mean values: \(\langle m \rangle\), \(\langle m^2 \rangle\), \(\langle m^3 \rangle\), and \(\langle m^4 \rangle\). Hint: Calculate the moment generating function.

4. The probability \(W(n)\), that an event characterized by a probability \(p\) occurs \(n\) times in \(N\) trials was shown to be given by the binomial distribution

\[
W(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} .
\]  

Consider a situation where the probability \(p\) is small \((p \ll 1)\) and where one is interested in the case \(n \ll N\). (Note that if \(N\) is large, \(W(n)\) becomes very small if \(n \rightarrow N\) because of the smallness of the factor \(p^n\) when \(p \ll 1\). Hence \(W(n)\) is indeed only appreciable when \(n \ll N\).) Several approximations can then be made to reduce Eq. (1.117) to simpler form.

a) Using the result \(\ln(1-p) \approx -p\), show that \((1-p)^{N-n} \approx e^{-Np}\).

b) Show that \(N!/(N-n)! \approx N^n\).

c) Hence show that Eq. (1.117) reduces to

\[
W(n) = \frac{\lambda^n}{n!} e^{-\lambda} ,
\]

where \(\lambda \equiv Np\) is the mean number of events. This distribution is called the "Poisson distribution."

5. Consider the Poisson distribution of the preceding problem.

a) Show that it is properly normalized in the sense that \(\sum_{n=0}^{\infty} W(n) = 1\).

(The sum can be extended to infinity to an excellent approximation, since \(W(n)\) is negligibly small when \(n \gtrsim N\).)

b) Use the Poisson distribution to calculate \(\langle n \rangle\).

c) Use the Poisson distribution to calculate \(\langle (\Delta n)^2 \rangle = \langle (n - \langle n \rangle)^2 \rangle\).

6. 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?

7. A multiple choice test contains 20 problems. The correct answer for each problem has to be chosen out of 5 options. Show that the probability to pass the test (namely to have at least 11 correct answers) using guessing only, is \(5.6 \times 10^{-4}\).
8. 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 $N \rightarrow \infty$?

9. 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 $n \in \{0,1,2,\ldots,6\}$. 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?

10. 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.

11. 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.

12. 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

$$ M = m (N_+ - N_-). \tag{1.118} $$

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

$$ N! = (2\pi N)^{1/2} N^N \exp \left( -N + \frac{1}{2N} + \cdots \right) \tag{1.119} $$

to show that

$$ f(M) = \frac{1}{m\sqrt{2\pi N}} \exp \left( -\frac{M^2}{2m^2N} \right). \tag{1.120} $$

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

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13. 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

\[
\langle X \rangle = aN (2p - 1) = aN (p - q) .
\]

b) Show that the variance \( \langle (X - \langle X \rangle)^2 \rangle \) is given by

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

14. 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

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

15. 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).

16. A fair coin is flipped until the first head occurs. Let \( X \) denote the number of flips required.

a) Find the entropy \( \sigma \). In this exercise use log in base 2 in the definition of the entropy, namely \( \sigma = -\sum_i p_i \log_2 p_i \).

b) A random variable \( X \) is drawn according to this distribution. Find an “efficient” sequence of yes-no questions of the form, “Is \( X \) contained in the set \( S \)?” Compare \( \sigma \) to the expected number of questions required to determine \( X \).

17. 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. That is, to correctly calculate this derivative the variable \( z \) has to be expressed as a function of \( x \) and \( y \), namely, \( z = z(x, y) \).

a) Show that:

\[
\left( \frac{\partial z}{\partial x} \right) _y = - \left( \frac{\partial y}{\partial x} \right) _z \left( \frac{\partial z}{\partial y} \right) _x .
\]
b) Show that:

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

(1.125)

18. Let \( Z_{gc} \) be a grand canonical partition function.

a) Show that:

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

(1.126)

where \( \tau \) is the temperature, \( \beta = 1/\tau \), and \( \mu \) is the chemical potential.

b) Show that:

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

(1.127)

where

\[
\lambda = \exp (\beta \mu)
\]

(1.128)

is the fugacity.

19. 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

\[
\tau = \frac{\varepsilon}{2 \tanh^{-1} \left( -\frac{2\langle U \rangle}{N\varepsilon} \right)} ,
\]

(1.129)

where \( \langle U \rangle \) is the average total energy of the array. Note that the temperature can become negative if \( \langle U \rangle > 0 \). Why a negative temperature is possible for this system?

20. 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

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

(1.130)

where \( n = 0, 1, 2, \ldots \) is integer.

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

\[
\langle U \rangle = \frac{N\hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} ,
\]

(1.131)

where \( \beta = 1/\tau \).
b) Show that the variance of the energy of the system is given by
\[
\langle (\Delta U)^2 \rangle = \frac{N \left( \frac{\hbar \omega}{2} \right)^2}{\sinh \frac{\hbar \omega}{2}}. \tag{1.132}
\]

21. 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
\[
\langle U \rangle = -\frac{2N\varepsilon \sinh (\beta \varepsilon)}{1 + 2 \cosh \beta \varepsilon}, \tag{1.133}
\]
where $\beta = 1/\tau$.

b) Show the variance of the energy of the system is given by
\[
\langle (U - \langle U \rangle)^2 \rangle = 2N\varepsilon^2 \frac{\cosh (\beta \varepsilon) + 2}{[1 + 2 \cosh (\beta \varepsilon)]^2}. \tag{1.134}
\]

22. Consider a one dimensional chain containing $N \gg 1$ sections (see figure). 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 in $N\alpha$, 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
\[
\alpha = a \left[ \frac{1 + \tanh \left( \frac{Fa}{2\tau} \right)}{2} \right]. \tag{1.135}
\]

b) Show that in the limit of high temperature the spring constant is given approximately by
\[
k \approx \frac{4\tau}{N \alpha^2}. \tag{1.136}
\]

23. 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
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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

\[
E_{n,l} = \begin{cases} 
\hbar \omega_a \left( n + \frac{1}{2} \right) & \text{for } l = a \\
\hbar \omega_b \left( n + \frac{1}{2} \right) & \text{for } l = b 
\end{cases}, \quad n = 0, 1, 2, \ldots
\]  

(1.137)

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

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

(1.138)

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

24. The elasticity of a rubber band can be described in terms of a one-dimensional model of \( N \) polymer molecules linked together end-to-end. The angle between successive links is equally likely to be 0° or 180°. The length of each polymer is \( d \) and the total length is \( L \). The system is in thermal equilibrium at temperature \( \tau \). Show that the force \( f \) required to maintain a length \( L \) is given by

\[
f = \frac{\tau}{d} \tanh^{-1} \left( \frac{L}{Nd} \right).
\]  

(1.139)

25. 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 \( \varepsilon \). We suppose 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

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

(1.140)

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

26. 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 \( n_1 \gg 1 \) and \( n_2 \gg 1 \)). Consider an energy exchange with a reservoir at temperature \( \tau \) leading to population changes \( n_2 \to n_2 - 1 \) and \( n_1 \to n_1 + 1 \).

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 ratio \( n_2/n_1 \) as a function of \( E_1 \), \( E_2 \) and \( \tau \).
27. 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.

28. 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

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

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

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

where

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

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 $\tau$.

29. The energy of a donor level in a semiconductor is $-\varepsilon$ when occupied by an electron (and the energy is zero otherwise). A donor level can be either occupied by a spin up electron or a spin down electron, however, it cannot be simultaneously occupied by two electrons. Express the average occupation of a donor state $\langle N_d \rangle$ as a function of $\varepsilon$ and the chemical potential $\mu$. 

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1.8 Solutions Set 1

1. Final answers:
   a) \( \frac{N!}{(\frac{N}{2})!(\frac{N}{2})!} \left( \frac{1}{2} \right)^N \)
   b) 0

2. Final answers:
   a) \( \left( \frac{5}{6} \right)^N \)
   b) \( \left( \frac{5}{6} \right)^{N-1} \frac{1}{6} \)
   c) In general
      \[
      \sum_{N=0}^\infty N x^{N-1} = \frac{d}{dx} \sum_{N=0}^\infty x^N = \frac{d}{dx} \frac{1}{1-x} = \frac{1}{(1-x)^2},
      \]
      thus
      \[
      \bar{N} = \frac{1}{6} \sum_{N=0}^\infty N \left( \frac{5}{6} \right)^{N-1} = \frac{1}{\left(1 - \frac{5}{6}\right)^2} = 6.
      \]

3. Let \( W(m) \) be the probability for for taking \( n_1 \) steps to the right and \( n_2 = N - n_1 \) steps to the left, where \( m = n_1 - n_2 \), and \( N = n_1 + n_2 \). Using
   \[
   n_1 = \frac{N + m}{2}, \quad n_2 = \frac{N - m}{2},
   \]
   one finds
   \[
   W(m) = \frac{N!}{(N + m)! (N - m)!} p^\frac{N+m}{2} q^\frac{N-m}{2}.
   \]
   It is convenient to employ the moment generating function, defined as
   \[
   \phi(t) = \langle e^{tm} \rangle.
   \]
   In general, the following holds
   \[
   \phi(t) = \sum_{k=0}^\infty \frac{t^k}{k!} \langle m^k \rangle,
   \]
   thus from the \( k \)th derivative of \( \phi(t) \) one can calculate the \( k \)th moment of \( m \)
   \[
   \langle m^k \rangle = \phi^{(k)}(0).
   \]
1.8. Solutions Set 1

Using $W(m)$ one finds

$$\phi(t) = \sum_{m=-N}^{N} W(m) e^{tm}$$

$$= \sum_{m=-N}^{N} \frac{N!}{(N+m/2)! (N-m/2)!} p^{N+m/2} q^{N-m/2} e^{tm},$$

or using the summation variable

$$n_1 = \frac{N+m}{2},$$

one has

$$\phi(t) = \sum_{n_1=0}^{N} \frac{N!}{n_1! (N-n_1)!} p^{n_1} q^{N-n_1} e^{t(2n_1-N)}$$

$$= e^{-tN} \sum_{n_1=0}^{N} \frac{N!}{n_1! (N-n_1)!} (pe^{2t})^{n_1} q^{N-n_1}$$

$$= e^{-tN} (pe^{2t} + q)^N.$$

Using $p = q = 1/2$

$$\phi(t) = \left(\frac{e^t + e^{-t}}{2}\right)^N = (\cosh t)^N.$$

Thus using the expansion

$$(\cosh t)^N = 1 + \frac{1}{2!} Nt^2 + \frac{1}{4!} [N + 3N (N - 1)] t^4 + O(t^5),$$

one finds

$$\langle m \rangle = 0,$$

$$\langle m^2 \rangle = N,$$

$$\langle m^3 \rangle = 0,$$

$$\langle m^4 \rangle = N (3N - 2).$$

4. Using the binomial distribution

$$W(n) = \frac{N!}{n! (N-n)!} p^n (1-p)^{N-n}$$

$$= \frac{N (N-1) (N-2) \cdots (N-n+1)}{n!} p^n (1-p)^{N-n}$$

$$\approx \frac{(Np)^n}{n!} \exp (-Np).$$
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5.

a) \(\sum_{n=0}^{\infty} W(n) = e^{-\lambda} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} = 1\)

b) As in Ex. 1-6, it is convenient to use the moment generating function

\[\phi(t) = \langle e^{tn} \rangle = \sum_{n=0}^{\infty} e^{tn} W(n) = e^{-\lambda} \sum_{n=0}^{\infty} \frac{\lambda^n e^{tn}}{n!} = e^{-\lambda} \sum_{n=0}^{\infty} \frac{(\lambda e^t)^n}{n!} = \exp[\lambda (e^t - 1)] .\]

Using the expansion

\[\exp[\lambda (e^t - 1)] = 1 + \lambda t + \frac{1}{2!} \lambda (1 + \lambda) t^2 + O(t^3),\]

one finds

\[\langle n \rangle = \lambda .\]

c) Using the same expansion one finds

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

thus

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

6.

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

7.

\[\sum_{n=11}^{20} \frac{20!}{n!(20-n)!} 0.2^n \times 0.8^{20-n} = 5.6 \times 10^{-4} . \quad (1.144)\]

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

\[\begin{align*}
(x_{An}, y_{Am}) &= (S_{Am}, m - S_{Am}) , \\
(x_{Bm}, y_{Bm}) &= (N - S_{Bm}, N - m + S_{Bm}) ,
\end{align*}\]

where

\[\begin{align*}
S_{Am} &= \sum_{n=1}^{m} \sigma_{An} , \quad (1.147) \\
S_{Bm} &= \sum_{n=1}^{m} \sigma_{Bn} . \quad (1.148)
\end{align*}\]
A meeting occurs if for some $m$

$$S_{Am} = N - S_{Bm},$$

$$m - S_{Am} = N - m + S_{Bm},$$  \hspace{1cm} (1.149)

i.e. if

$$\quad S_{Am} + S_{Bm} = N = 2m - N.$$  \hspace{1cm} (1.151)

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

$$p_N = \frac{\binom{2N}{N}}{2^{2N}} = \frac{(2N)!}{(N!2^N)^2}. \hspace{1cm} (1.152)$$

With the help of the Stirling’s formula (1.119) one finds that

$$\lim_{N \to \infty} p_N = \frac{1}{\sqrt{N\pi}}. \hspace{1cm} (1.153)$$

9. The following holds

$$p_0 = 0,$$

$$p_1 = \frac{5}{6}p_0 + \frac{1}{6}p_2,$$

$$p_2 = \frac{4}{6}p_1 + \frac{2}{6}p_3,$$

$$p_3 = \frac{3}{6}p_2 + \frac{3}{6}p_4,$$

$$p_4 = \frac{2}{6}p_3 + \frac{4}{6}p_5,$$

$$p_5 = \frac{1}{6}p_4 + \frac{5}{6}p_6,$$

$$p_6 = 1,$$

and thus

$$p_1 = \frac{1}{32}, \quad p_2 = \frac{3}{16}, \quad p_3 = \frac{1}{2}, \quad p_4 = \frac{13}{16}, \quad p_5 = \frac{31}{32}. \hspace{1cm} (1.154)$$

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

$$p_C = \frac{N \times 2 \times (N - 2)!}{N!} = \frac{2}{N - 1}, \hspace{1cm} (1.154)$$

and for the case of a row

$$p_R = \frac{(2 + (N - 2) \times 2) \times (N - 2)!}{N!} = \frac{2}{N}. \hspace{1cm} (1.155)$$
11. Let the binary representation of $p$ be given by

$$ p = \sum_{m=1}^{\infty} \sigma_m \left( \frac{1}{2} \right)^m, \quad (1.156) $$

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.

12. Using

$$ N_+ + N_- = N, \quad (1.157a) $$
$$ N_+ - N_- = \frac{M}{m}, \quad (1.157b) $$

one has

$$ N_+ = \frac{N}{2} \left( 1 + \frac{M}{mN} \right), \quad (1.158a) $$
$$ N_- = \frac{N}{2} \left( 1 - \frac{M}{mN} \right), \quad (1.158b) $$

or

$$ N_+ = \frac{N}{2} (1 + x), \quad (1.159a) $$
$$ N_- = \frac{N}{2} (1 - x), \quad (1.159b) $$

where

$$ x = \frac{M}{mN}. $$

The number of states having total magnetization $M$ is given by

$$ \Omega(M) = \frac{N!}{N_+!N_-!} = \frac{N!}{\left[ \frac{N}{2} (1 + x) \right]! \left[ \frac{N}{2} (1 - x) \right]!}. \quad (1.160) $$

Since all states have equal probability one has

$$ f(M) = \frac{\Omega(M)}{2^N}. \quad (1.161) $$
Taking the natural logarithm of Stirling’s formula one finds

\[ \log N! = N \log N - N + O \left( \frac{1}{N} \right) , \tag{1.162} \]

thus in the limit \( N \gg 1 \) one has

\[
\begin{align*}
\log f &= - \log 2^N + N \log N - N \\
&= -N \log 2 + N \log N \\
&= -N \log 2 + N \log N \\
&= \left( \frac{N}{2} (1 + x) \right) \log \left( \frac{N}{2} (1 + x) \right) - \left( \frac{N}{2} (1 - x) \right) \log \left( \frac{N}{2} (1 - x) \right) \\
&= \left( -\frac{N}{2} \right) \left\{ -2 \log \frac{N}{2} + (1 + x) \log \left( \frac{N}{2} (1 + x) \right) + (1 - x) \log \left( \frac{N}{2} (1 - x) \right) \right\} \\
&= \left( -\frac{N}{2} \right) \left\{ -2 \log \frac{N}{2} + (1 + x) \left( \log \frac{N}{2} + \log (1 + x) \right) + (1 - x) \left( \log \frac{N}{2} + \log (1 - x) \right) \right\} \\
&= \left( -\frac{N}{2} \right) \left( \log (1 - x^2) + x \log \frac{1 + x}{1 - x} \right) . \tag{1.163}
\end{align*}
\]

The function \( \log f(x) \) has a sharp peak near \( x = 0 \), thus we can approximate it by assuming \( x \ll 1 \). To lowest order

\[ \log (1 - x^2) + x \log \frac{1 + x}{1 - x} = x^2 + O \left( x^3 \right) , \tag{1.164} \]

thus

\[ f(M) = A \exp \left( -\frac{M^2}{2m^2N} \right) , \tag{1.165} \]

where \( A \) is a normalization constant, which is determined by requiring that

\[ 1 = \int_{-\infty}^{\infty} f(M) \, dM . \tag{1.166} \]

Using the identity

\[ \int_{-\infty}^{\infty} \exp (-ay^2) \, dy = \sqrt{\frac{\pi}{a}} , \tag{1.167} \]
one finds
\[ \frac{1}{A} = \int_{-\infty}^{\infty} \exp \left( -\frac{M^2}{2m^2N} \right) \, dM = m\sqrt{2\pi N}, \quad (1.168) \]

thus
\[ f(M) = \frac{1}{m\sqrt{2\pi N}} \exp \left( -\frac{M^2}{2m^2N} \right), \quad (1.169) \]

The expectation value is giving by
\[ \langle M \rangle = \int_{-\infty}^{\infty} M f(M) \, dM = 0, \quad (1.170) \]

and the variance is given by
\[ \langle (M - \langle M \rangle)^2 \rangle = \langle M^2 \rangle = \int_{-\infty}^{\infty} M^2 f(M) \, dM = m^2 N. \quad (1.171) \]

13. The probability to have \( n \) steps to the right is given by
\[ W(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}. \quad (1.172) \]

a)
\[ \langle n \rangle = \sum_{n=0}^{N} \frac{N!n}{n!(N-n)!} p^n q^{N-n} \quad (1.173) \]
\[ = p \frac{\partial}{\partial p} \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n q^{N-n} \]
\[ = p \frac{\partial}{\partial p} (p + q)^N = pN (p + q)^{N-1} = pN. \]

Since
\[ X = an - a(N-n) = a(2n-N) \quad (1.174) \]

we find
\[ \langle X \rangle = aN (2p-1) = aN (p-q). \quad (1.175) \]

b)
\[
\langle n^2 \rangle = \sum_{n=0}^{N} \frac{N! n^2}{n! (N-n)!} p^n q^{N-n} \\
= \sum_{n=0}^{N} \frac{N! n (n-1)}{n! (N-n)!} p^n q^{N-n} + \sum_{n=0}^{N} \frac{N! n}{n! (N-n)!} p^n q^{N-n} \\
= p^2 \frac{\partial^2}{\partial p^2} \sum_{n=0}^{N} \frac{N!}{n! (N-n)!} n p^n q^{N-n} + \langle n \rangle \\
= p^2 \frac{\partial^2}{\partial p^2} (p + q)^N + \langle n \rangle = p^2 N (N - 1) + pN.
\]

Thus
\[
\langle (n - \langle n \rangle)^2 \rangle = p^2 N (N - 1) + pN - p^2 N^2 = Npq ,
\]
and
\[
\langle (X - \langle X \rangle)^2 \rangle = 4a^2 Npq .
\]

14. The total energy is given by
\[
E = k x^2 + \frac{m \dot{x}^2}{2} = \frac{ka^2}{2} ,
\]
where \( a \) is the amplitude of oscillations. The time period \( T \) is given by
\[
T = 2 \int_{-a}^{a} \frac{dx}{\sqrt{\frac{m}{k} x^2}} = 2 \sqrt{\frac{m}{k} \int_{-a}^{a} \frac{dx}{\sqrt{a^2 - x^2}}} = 2 \pi \sqrt{\frac{m}{k}} ,
\]
thus
\[
f(x) = \frac{2}{T |x|} = \frac{1}{\pi \sqrt{a^2 - x^2}} .
\]

15. The six experiments are independent, thus
\[
\sigma = 6 \times \left( -\frac{2}{3} \ln \frac{2}{3} - \frac{1}{3} \ln \frac{1}{3} \right) = 3.8191 .
\]

16. The random variable \( X \) obtains the value \( n \) with probability \( p_n = q^n \), where \( n = 1, 2, 3, \ldots \), and \( q = 1/2 \).

a) The entropy is given by
\[
\sigma = -\sum_{n=1}^{\infty} p_n \log_2 p_n = -\sum_{n=1}^{\infty} q^n \log q^n = \sum_{n=1}^{\infty} nq^n .
\]

This can be rewritten as
\[
\sigma = q \frac{\partial}{\partial q} \sum_{n=1}^{\infty} q^n = q \frac{\partial}{\partial q} \left( \frac{1}{1-q} - 1 \right) = \frac{q}{(1-q)^2} = 2 .
\]
b) A series of questions is of the form: "Was a head obtained in the 1st time?", "Was a head obtained in the 2nd time?", etc. The expected number of questioned required to find \( X \) is

\[
\frac{1}{2} \times 1 + \frac{1}{4} \times 2 + \frac{1}{8} \times 3 + \cdots = 2,
\]

which is exactly the entropy \( \sigma \).

17. a) Consider an infinitesimal change in the variable \( z = z(x, y) \)

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

(1.181)

For a process for which \( z \) is a constant \( \delta z = 0 \), thus

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

(1.182)

Dividing by \( \delta x \) yields

\[
\left( \frac{\partial z}{\partial x} \right)_y = - \left( \frac{\partial z}{\partial y} \right)_x \frac{\delta z}{\delta x}.
\]  

(1.183)

b) Consider a process for which the variable \( w \) is kept constant. An

infinitesimal change in the variable \( z = z(x, y) \) is expressed as

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

(1.184)

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

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

(1.185)

or

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

(1.186)
We have found in class that

\[ \langle U \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta, \quad (1.187) \]

\[ \langle N \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta. \quad (1.188) \]

a) Using relation (1.125) one has

\[ \langle U \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta \]
\[ = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu - \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta \left( \frac{\partial \mu}{\partial \beta} \right)_\eta \]
\[ = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu - \eta \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\beta \]
\[ = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\mu + \tau \mu \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\beta. \quad (1.189) \]

b) Using Eq. (1.188) one has

\[ \langle N \rangle = -\left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta \]
\[ = -\left( \frac{\partial \mu}{\partial \eta} \right)_\beta \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta \]
\[ = \tau \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta, \quad (1.190) \]

or in terms of the fugacity \( \lambda \), which is defined by

\[ \lambda = \exp (\beta \mu) = e^{-\eta}, \quad (1.191) \]

one has

\[ \langle N \rangle = \tau \left( \frac{\partial \log Z_{gc}}{\partial \mu} \right)_\beta \]
\[ = \tau \frac{\partial \lambda}{\partial \mu} \frac{\partial \log Z_{gc}}{\partial \lambda} \]
\[ = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda}. \quad (1.192) \]
19. The canonical partition function is given by

\[ Z_c = Z_1^N, \]  

where

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

Thus

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

and

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

The negative temperature is originated by our assumption that the energy of a single magnet has an upper bound. In reality this is never the case.

20. The canonical partition function is given by

\[ Z_c = Z_1^N, \]  

where

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

a) \[ \langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} = -N \frac{\partial \log Z_1}{\partial \beta} = \frac{N \hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} \]  

b) \[ \left\langle (\Delta U)^2 \right\rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2} = N \frac{\partial^2 \log Z_1}{\partial \beta^2} = \frac{N \left( \frac{\hbar \omega}{2} \right)^2}{\sinh^2 \frac{\beta \hbar \omega}{2}} \]  

21. The canonical partition function is given by

\[ Z_c = [\exp (\beta \varepsilon) + 1 + \exp (-\beta \varepsilon)]^N = [1 + 2 \cosh (\beta \varepsilon)]^N, \]  

where \( \beta = 1/\tau. \)
a) Thus the average energy is
\[
\langle U \rangle = -\frac{\partial \log Z_c}{\partial \beta} = -\frac{2N\varepsilon \sinh (\beta \varepsilon)}{1 + 2 \cosh \beta \varepsilon},
\]
(1.202)
b) and the variance is
\[
\left\langle (U - \langle U \rangle)^2 \right\rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2} = -\frac{\partial \langle U \rangle}{\partial \beta} = \frac{2N\varepsilon^2 \cosh (\beta \varepsilon) + 2}{[1 + 2 \cosh (\beta \varepsilon)]^2}.
\]
(1.203)

22. Each section can be in one of two possible states with corresponding energies 0 and \(-Fa\).

a) By definition, \(\alpha\) is the mean length of each segment, which is given by
\[
\alpha = \frac{a \exp (Fa\beta)}{1 + \exp (Fa\beta)} = a \left[ \frac{1}{2} + \tanh \left( \frac{Fa\beta}{2} \right) \right],
\]
(1.204)
where \(\beta = 1/\tau\).
b) At high temperature \(Fa\beta \ll 1\) the length of the chain \(L = Na\) is given by
\[
L = \frac{Na}{2} \left[ 1 + \tanh \left( \frac{Fa\beta}{2} \right) \right] \approx \frac{Na}{2} \left( 1 + \frac{Fa\beta}{2} \right),
\]
(1.205)
or
\[
F = k \left( L - \frac{Na}{2} \right),
\]
(1.206)
where the spring constant \(k\) is given by
\[
k = \frac{4\tau}{Na^2}.
\]
(1.207)

23. The average length of a single link is given by
\[
\langle l \rangle = \frac{a \exp (\beta Fa) \sum_{n=0}^{\infty} \exp \left[ -\beta\hbar \omega_a \left( n + \frac{1}{2} \right) \right] + b \exp (\beta Fb) \sum_{n=0}^{\infty} \exp \left[ -\beta\hbar \omega_b \left( n + \frac{1}{2} \right) \right]}{\exp (\beta Fa) \sum_{n=0}^{\infty} \exp \left[ -\beta\hbar \omega_a \left( n + \frac{1}{2} \right) \right] + \exp (\beta Fb) \sum_{n=0}^{\infty} \exp \left[ -\beta\hbar \omega_b \left( n + \frac{1}{2} \right) \right]}
\]
(1.208)
\[
= \frac{a \exp (\beta Fa)}{2 \sinh \frac{Fa}{2}} + \frac{b \exp (\beta Fb)}{2 \sinh \frac{Fb}{2}}.
\]
\[= \frac{\exp (\beta Fa)}{2 \sinh \frac{Fa}{2}} + \frac{\exp (\beta Fb)}{2 \sinh \frac{Fb}{2}}.
\]
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To first order in $\beta$

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

(1.209)

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

24. The length $L$ is given by

$$L = N \langle l \rangle,$$

where $\langle l \rangle$ is the average contribution of a single molecule to the total length, which can be either $+d$ or $-d$. The probability of each possibility is determined by the Boltzmann factor. The energy change due to flipping of one link from $0^\circ$ to $180^\circ$ is $2fd$, therefore

$$\langle l \rangle = \frac{e^{\beta fd} - e^{-\beta fd}}{e^{\beta fd} + e^{-\beta fd}} = d \tanh(\beta fd) \ ,$$

where $\beta = 1/\tau$. Thus

$$L = Nd \tanh(\beta fd) \ ,$$

or

$$f = \frac{\tau}{d} \tanh^{-1} \frac{L}{Nd} \ .$$

25. The grand partition function $Z_{gc}$ is given by

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

thus

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \log Z_{gc}}{\partial \mu} = \frac{2}{2 + \exp[\beta(\varepsilon - \mu)]} \ .$$

(1.211)

26.

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

(1.212)

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

(1.213)
c) For a small change near thermal equilibrium one expects $(\Delta \sigma)_{2LS} + (\Delta \sigma)_R = 0$, thus
\[
\frac{n_2}{n_1} = \exp \left( -\frac{E_2 - E_1}{\tau} \right) \tag{1.214}
\]

27. The number of ways to select $N_B$ occupied sites of type B out of $N$ sites is $N!/n!(N-n)!$. Similarly the number of ways to select $N_B$ empty sites of type A out of $N$ sites is $N!/n!(N-n)!$.

a) Thus
\[
\sigma = \log \left( \frac{N!}{N_B!(N-N_B)!} \right)^2 \simeq 2 \left[ N \log N - N_B \log N_B - (N-N_B) \log (N-N_B) \right] \tag{1.215}
\]

b) The energy of the system is given by $U = N_B \varepsilon$. Thus, the Helmholtz free energy is given by
\[
F = U - \tau \sigma = U - 2\tau \left[ N \log N - \frac{U}{\varepsilon} \log \frac{U}{\varepsilon} - \left( N - \frac{U}{\varepsilon} \right) \log \left( N - \frac{U}{\varepsilon} \right) \right] \tag{1.216}
\]

At thermal equilibrium $(\partial F/\partial U)_\tau = 0$, thus
\[
0 = \left( \frac{\partial F}{\partial U} \right)_\tau = 1 + 2\tau \left[ \frac{U}{\varepsilon} - \log \left( \frac{U}{\varepsilon} \right) \right] \tag{1.217}
\]
or
\[
\frac{N - N_B}{N_B} = \exp \left( \frac{\varepsilon}{2\tau} \right) \tag{1.218}
\]

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

Alternatively, one can calculate the chemical potential from the requirement
\[
1 = \frac{N_A}{N} + \frac{N_B}{N} \tag{1.219}
\]
where
\[
\frac{N_A}{N} = \frac{\exp (\beta \mu)}{1 + \exp (\beta \mu)} \tag{1.220a}
\]
\[
\frac{N_B}{N} = \frac{\exp (\beta \mu - \beta \varepsilon)}{1 + \exp (\beta \mu - \beta \varepsilon)} \tag{1.220b}
\]
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which is satisfied when

\[ \mu = \frac{\varepsilon}{2}, \quad (1.221) \]

thus

\[ \langle N_B \rangle = \frac{N}{1 + \exp \left( \frac{\varepsilon}{2T} \right)}. \quad (1.222) \]

28. In general,

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

Moreover

\[ \{ \# \text{ os ways to distribute } m \text{ identical balls in } N \text{ boxes} \} \]
\[ = \{ \# \text{ os ways to arrange } m \text{ identical balls and } N - 1 \text{ identical partitions in a line} \} \]

\[ a) \text{ Therefore} \]
\[ g(N, m) = \frac{(N - 1 + m)!}{(N - 1)!m!}. \quad (1.223) \]

\[ b) \text{ The entropy is given by} \]
\[ \sigma = \log \left( \frac{(N - 1 + m)!}{(N - 1)!m!} \right) \simeq (N + m) \log (N + m) - N \log N - m \log m, \]
\[ (1.224) \]

or in terms of the total energy \( E = \hbar \omega (m + N/2) \)

\[ \sigma = \left[ N + \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \right] \log \left[ N + \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \right] \]
\[ - N \log N - \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right) \log \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right). \]
\[ (1.225) \]
c) The temperature $\tau$ is given by
\[
\frac{1}{\tau} = \frac{\partial \sigma}{\partial E} = 1 - \ln \frac{2h\omega}{2E + Nh\omega} + \ln \frac{2h\omega}{2E - Nh\omega} - 1 \frac{h\omega}{\hbar}\ln \left( \frac{2E + Nh\omega}{2E - Nh\omega} \right).
\] (1.226)

In the thermodynamical limit ($N \gg 1, m \gg 1$) the energy $E$ and its average $U$ are indistinguishable, thus
\[
\exp \left( \frac{h\omega}{\tau} \right) = \frac{2U + Nh\omega}{2U - Nh\omega}, \quad \text{(1.227)}
\]
or
\[
U = \frac{Nh\omega}{2} \coth \frac{h\omega}{2\tau}. \quad \text{(1.228)}
\]

29. The grand canonical partition function is given by
\[
\zeta = 1 + 2\lambda \exp (\beta \varepsilon), \quad \text{(1.229)}
\]
where $\lambda = \exp (\beta \mu)$ is the fugacity, thus
\[
\langle N_{\mu} \rangle = \lambda \frac{\partial \log \zeta}{\partial \lambda} = \frac{2\lambda e^{\beta \varepsilon}}{1 + 2\lambda e^{\beta \varepsilon}} = \frac{1}{1 + \frac{1}{2} e^{-\beta (\varepsilon + \mu)}}. \quad \text{(1.230)}
\]
2. Ideal Gas

In this chapter we study some basic properties of ideal gas of massive identical particles. We start by considering a single particle in a box. We then discuss the statistical properties of an ensemble of identical indistinguishable particles and introduce the concepts of Fermions and Bosons. In the rest of this chapter we mainly focus on the classical limit. For this case we derive expressions for the pressure, heat capacity, energy and entropy and discuss how internal degrees of freedom may modify these results. In the last part of this chapter we discuss an example of an heat engine based on ideal gas (Carnot heat engine). We show 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.

2.1 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

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

(2.1)

The quantum eigenstates and eigenenergies are determined by requiring that the wavefunction \( \psi(x, y, z) \) satisfies the Schrödinger equation

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

(2.2)

In addition, we require that the wavefunction \( \psi \) vanishes on the surfaces of the box. The normalized solutions are given by

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

(2.3)

where

\[
n_x, n_y, n_z = 1, 2, 3, \ldots
\]

(2.4)
The corresponding eigenenergies are given by

$$
\varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{2M} \left( \frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2).
$$

(2.5)

For simplicity we consider the case where the particle doesn’t have any internal degree of freedom (such as spin). Later we will release this assumption and generalize the results for particles having internal degrees of freedom.

The partition function is given by

$$
Z_1 = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left( -\frac{\varepsilon_{n_x, n_y, n_z}}{\tau} \right)
= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left( -\alpha^2 (n_x^2 + n_y^2 + n_z^2) \right).
$$

(2.6)

where

$$
\alpha^2 = \frac{\hbar^2 \pi^2}{2ML^2\tau}.
$$

(2.7)

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

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

(2.8)

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

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

(2.9)

By changing the integration variable \( x = \alpha n_x \) one finds

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

(2.10)

thus

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

(2.11)

where we have introduced the quantum density.
2.1. A Particle in a Box

\[ n_Q = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2}. \]  

(2.12)

The partition function (2.11) together with Eq. (1.70) allows evaluating the average energy (recall that \( \beta = 1/\tau \))

\[
\langle \varepsilon \rangle = -\frac{\partial \log Z_1}{\partial \beta} = -\frac{\partial \log \left( \frac{ML^2}{2\pi \hbar^2 \beta} \right)^{3/2}}{\partial \beta} = -\frac{3 \partial \log \beta}{\partial \beta} = \frac{3\tau}{2}. \]

(2.13)

This result can be written as

\[
\langle \varepsilon \rangle = d\tau^2, \]

(2.14)

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. (1.71)

\[
\langle (\Delta \varepsilon)^2 \rangle = \frac{\partial^2 \log Z_1}{\partial \beta^2} = -\frac{\partial \langle \varepsilon \rangle}{\partial \beta} = -\frac{\partial}{\partial \beta} \left( \frac{3}{2\beta^2} \right) = \frac{3}{2\beta^2}.
\]

(2.15)

Thus, using Eq. (2.13) the standard deviation is given by

\[
\sqrt{\langle (\Delta \varepsilon)^2 \rangle} = \sqrt{\frac{2}{3}} \langle \varepsilon \rangle.
\]

(2.16)

What is the physical meaning of the quantum density? The de Broglie wavelength \( \lambda \) of a particle having mass \( M \) and velocity \( v \) is given by
\[ \lambda = \frac{h}{Mv} , \]  

(2.17)

For a particle having energy equal to the average energy \( \langle \varepsilon \rangle = 3\tau/2 \) one has

\[ \frac{Mv^2}{2} = \frac{3\tau}{2} , \]

(2.18)

thus in this case the de-Broglie wavelength, which is denoted as \( \lambda_T \) (the thermal wavelength)

\[ \lambda_T = \frac{h}{\sqrt{3M\tau}} , \]

(2.19)

and therefore one has (recall that \( \hbar = h/2\pi \))

\[ n_Q = \left( \frac{\pi}{2\sqrt{3M\tau}} \right)^{3/2} = \left( \frac{1}{\lambda_T \sqrt{3}} \right)^{3/2} . \]

(2.20)

Thus the quantum density is inversely proportional to the thermal wavelength cubed.

### 2.2 Gibbs Paradox

In the previous section we have studied the case of a single particle. Let us now consider the case where the box is occupied by \( N \) particles of the same type. For simplicity, we consider the case where the density \( n = N/V \) is sufficiently small to safely allowing to neglect any interaction between the particles. In this case the gas is said to be ideal.

**Definition 2.2.1.** Ideal gas is an ensemble of non-interacting identical particles.

What is the partition function of the ideal gas? Recall that for the single particle case we have found that the partition function is given by [see Eq. (2.6)]

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

(2.21)

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.

Since the total number of particles \( N \) is constrained we need to calculate the canonical partition function. For the case of distinguishable particles one may argue that the canonical partition function is given by
2.2. Gibbs Paradox

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

(2.22)

However, as was demonstrated by Gibbs in his famous paradox, this answer is wrong. To see this, we employ Eqs. (1.72) and (2.11) and assume that the partition function is given by Eq. (2.22) above, thus

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

(2.23)

or in terms of the gas density

\[ n = \frac{N}{V}, \]  

(2.24)

we find

\[ \sigma - \beta U = N \log \left( \frac{n_Q}{n} \right). \]  

(2.25)

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 we will see 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 we divide the box 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

\[ N = N_1 + N_2, \]  

(2.26)

\[ V = V_1 + V_2. \]  

(2.27)

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

\[ n = \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}. \]  

(2.28)

Now we use Eq. (2.25) to evaluate the change in entropy \( \Delta \sigma \) due to the process of dividing the box. Since no energy is required to add (or to remove) the partition one has

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

\[ = N \log \left( \frac{n_Q}{n} \right) - N_1 \log \left( \frac{n_Q}{n} \right) - N_2 \log \left( \frac{n_Q}{n} \right) \]

\[ = N \log N - N_1 \log N_1 - N_2 \log N_2. \]  

(2.29)

Using the Stirling’s formula (1.162)

\[ \log N! \approx N \log N - N, \]  

(2.30)
one finds
\[ \Delta \sigma \simeq \log \frac{N!}{N_1!N_2!} > 0. \] (2.31)

Thus we came to the conclusion that the process of dividing the box leads to 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.

What is wrong with the partition function given by Eq. (2.22)? 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 (2.22) treats the particles as being distinguishable, \( g(N_1, N_2, \cdots) \) may in general be larger than unity. In fact, it is easy to see that
\[ g(N_1, N_2, \cdots) = \frac{N!}{N_1!N_2! \times \cdots}. \] (2.32)

For example, consider the state that is described by Fig. 2.1 below for a gas containing \( N = 3 \) identical particles. The expansion (2.22) contains \( 3!/1!/2! = 3 \) terms having the same occupation numbers \( (N_n = 1 \text{ if } n = 2, N_n = 2 \text{ if } n = 3, \text{ and } N_n = 0 \text{ for all other values of } n) \). 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 \( \{N_1, N_2, \cdots\} \).

### 2.3 Fermions and Bosons

As we saw in the previous section the canonical partition function given by Eq. (2.22) is incorrect. For indistinguishable particles each set of orbital oc-
2.3. Fermions and Bosons

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 particles in nature are divided into two type: Fermion 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 integer.

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

2.3.1 Fermi-Dirac Distribution

In this case the occupation number can take only two possible values: 0 or 1. Thus, by Eq. (1.79) the grandcanonical partition function of an orbital having energy is \( \varepsilon \) is given by

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

where

\[
\lambda = \exp(\beta \mu) \tag{2.34}
\]

is the fugacity [see Eq. (1.95)]. The average occupation of the orbital, which is denoted by \( f_{FD}(\varepsilon) = \langle N(\varepsilon) \rangle \), is found using Eq. (1.94)

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

\[
= \frac{1}{\exp[\beta (\varepsilon - \mu)] + 1} .
\]

(2.35)

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

In this case the occupation number can take any integer value. Thus, by Eq. (1.79) the grandcanonical partition function of an orbital having energy is $\varepsilon$ is given by

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

(2.36)

The average occupation of the orbital, which is denoted by $f_{BE} (\varepsilon) = \langle N (\varepsilon) \rangle$, is found using Eq. (1.94)

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

(2.37)

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

2.3.3 Classical Limit

The classical limit occurs when

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

(2.38)

As can be seen from Eqs. (2.35) and (2.37) the following holds

$$
f_{FD} (\varepsilon) \simeq f_{BE} (\varepsilon) \simeq \exp [\beta (\mu - \varepsilon)] \ll 1 ,
$$

(2.39)

and

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

(2.40)

Thus the classical limit corresponds to the case where the average occupation of an orbital is close to zero, namely the orbital is on average almost empty. The main results of the above discussed cases (Fermi-Dirac distribution, Bose-Einstein distribution and the classical limit) are summarized in table 2.1 below.
## 2.4. 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. (2.40) above. The grandcanonical partition function of the entire system $Z_{gc}$ is found by multiplying $\zeta_n$ of all orbitals

$$Z_{gc} = \prod_n (1 + \lambda \exp(-\beta \varepsilon_n)) .$$  \hspace{1cm} (2.41)

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

$$\lambda \exp(-\beta \varepsilon) \ll 1$$  \hspace{1cm} (2.42)

and employ the first order expansion

$$\log(1 + x) = x + O(x^2)$$  \hspace{1cm} (2.43)

to obtain

### Table 2.1. Fermi-Dirac, Bose-Einstein and classical distributions.

<table>
<thead>
<tr>
<th></th>
<th>orbital partition function</th>
<th>average occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermions</td>
<td>$1 + \lambda \exp(-\beta \varepsilon)$</td>
<td>$\frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}$</td>
</tr>
<tr>
<td>Bosons</td>
<td>$\frac{1}{1 - \lambda \exp(-\beta \varepsilon)}$</td>
<td>$\frac{1}{\exp[\beta(\varepsilon - \mu)] - 1}$</td>
</tr>
<tr>
<td>classical limit</td>
<td>$1 + \lambda \exp(-\beta \varepsilon)$</td>
<td>$\exp[\beta (\mu - \varepsilon)]$</td>
</tr>
</tbody>
</table>
Chapter 2. Ideal Gas

\[ \log Z_{gc} = \sum_n \log (1 + \lambda \exp (-\beta \varepsilon_n)) \]
\[ \simeq \lambda \sum_n \exp (-\beta \varepsilon_n) \]
\[ = \lambda Z_1 , \quad (2.44) \]

where

\[ Z_1 = V \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2} \quad (2.45) \]

[see Eq. (2.11)] 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

\[ \log Z_{gc} = e^{-\eta} V \left( \frac{M}{2 \pi \hbar^2 \beta} \right)^{3/2} . \quad (2.46) \]

The average energy and average number of particle are calculated using Eqs. (1.80) and (1.81) respectively

\[ \langle U \rangle = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \frac{3}{2 \beta} \log Z_{gc} , \quad (2.47) \]
\[ \langle N \rangle = - \left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta = \log Z_{gc} . \quad (2.48) \]

In what follows, to simplify the notation we remove the diagonal brackets and denote \( \langle U \rangle \) and \( \langle N \rangle \) 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. Using this simplified notation and employing Eqs. (2.47) and (2.48) one finds that

\[ U = \frac{3N \tau}{2} . \quad (2.49) \]

Namely, the total energy is \( N \langle \varepsilon \rangle \), where \( \langle \varepsilon \rangle \) is the average single particle energy that is given by Eq. (2.13).

The entropy is evaluate using Eq. (1.86)

\[ \sigma = \log Z_{gc} + \beta U + \eta N \]
\[ = N \left( 1 + \frac{3}{2} - \frac{\mu}{\tau} \right) \]
\[ = N \left( \frac{5}{2} - \mu \beta \right) . \quad (2.50) \]
Furthermore, using Eqs. (2.44), (2.48), (2.11) and (1.95) one finds that
\[ \mu \beta = \log \frac{n}{n^Q}, \] (2.51)
where \( n = N/V \) is the density. This allows expressing the entropy as
\[ \sigma = N \left( \frac{5}{2} + \log \frac{n^Q}{n} \right). \] (2.52)

Using the definition (1.116) and Eqs. (2.49) and (2.52) one finds that the Helmholtz free energy is given by
\[ F = N \tau \left( \log \frac{n}{n^Q} - 1 \right). \] (2.53)

### 2.4.1 Pressure

The pressure \( p \) is defined by
\[ p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,N}. \] (2.54)

Using Eq. (2.53) and keeping in mind that \( n = N/V \) one finds
\[ p = \frac{N \tau}{V}. \] (2.55)

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
\[
\{\text{pressure}\} = \frac{\{\text{force}\}}{\{\text{area}\}} = \frac{\text{rate of momentum change}}{\{\text{area}\}} = 2 \frac{|p_x| \times \frac{|p_x|}{2mL}}{L^2} = \frac{p_x^2}{mV}. \] (2.56)
Chapter 2. Ideal Gas

The average energy of a particle is given by Eq. (2.13)

\[ \frac{3\tau}{2} = \langle \varepsilon \rangle = \frac{\langle p_x^2 + p_y^2 + p_z^2 \rangle}{2m}, \quad (2.57) \]

thus one finds that

\[ \frac{\langle p_x^2 \rangle}{m} = \tau. \quad (2.58) \]

Using this result and Eq. (2.56) one finds that the pressure due to a single particle is \( p = \tau/V \), thus the total pressure is

\[ p = \frac{N\tau}{V}. \quad (2.59) \]

2.4.2 Useful Relations

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

Claim. The following holds

\[ p = -\left( \frac{\partial U}{\partial V} \right)_{\sigma,N} \]

Proof. Using the definition (2.54) and recalling that \( F = U - \tau\sigma \) one finds

\[ -p = \left( \frac{\partial F}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\tau,N} - \left( \frac{\partial (\tau\sigma)}{\partial V} \right)_{\tau,N}. \quad (2.60) \]

Using identity (1.125), which is given by

\[ \left( \frac{\partial z}{\partial x} \right)_{w} = \left( \frac{\partial z}{\partial x} \right)_{y} + \left( \frac{\partial z}{\partial y} \right)_{x} \left( \frac{\partial y}{\partial x} \right)_{w}, \quad (2.61) \]

one finds

\[ \left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \tau \left( \frac{\partial U}{\partial \sigma} \right)_{V,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N}, \quad (2.62) \]

thus

\[ -p = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} - \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} \left( \frac{\partial U}{\partial V} \right)_{\sigma,N}. \quad (2.63) \]
2.4. Ideal Gas in the Classical Limit

In a similar way the following relations can be obtained

\[
p = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{U,N} = - \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} = - \left( \frac{\partial F}{\partial V} \right)_{\tau,N}, \tag{2.64}
\]

\[
\mu = -\tau \left( \frac{\partial \sigma}{\partial N} \right)_{U,V} = \left( \frac{\partial U}{\partial N} \right)_{\sigma,V} = \left( \frac{\partial F}{\partial N} \right)_{\tau,V}. \tag{2.65}
\]

Another useful relation is given below.  

Claim. The following holds

\[
\left( \frac{\partial \sigma}{\partial V} \right)_\tau = \left( \frac{\partial p}{\partial \tau} \right)_V. \tag{2.66}
\]

Proof. See problem 2 of set 2.

2.4.3 Heat Capacity

The heat capacity at constant volume is defined by

\[
c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V, \tag{2.67}
\]

whereas the heat capacity at constant pressure is defined by

\[
c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p. \tag{2.68}
\]

Using Eq. (2.52) and recalling that \( n_Q \propto \tau^{3/2} \) one finds

\[
c_V = \tau \frac{3N}{2\tau} = \frac{3N}{2}. \tag{2.69}
\]

Claim. The following holds

\[
c_p = \frac{5N}{2}. \tag{2.70}
\]

Proof. See problem 1 of set 2.

2.4.4 Internal Degrees of Freedom

In this section we generalize our results for the case where the particles in the gas have internal degrees of freedom. Taking into account internal degrees of freedom the grandcanonical partition function of an orbital having orbital energy \( \varepsilon_n \) for the case of Fermions becomes

\[
\zeta_{FD,n} = \prod_I \left( 1 + \lambda \exp (-\beta \varepsilon_n) \exp (-\beta E_I) \right), \tag{2.71}
\]
where \( \{E_l\} \) are the eigenenergies of a particle due to internal degrees of freedom, and where \( \lambda = \exp(\beta \mu) \) and \( \beta = 1/T \). As is required by the Pauli exclusion principle, no more than one Fermion can occupy a given internal eigenstate. Similarly, for the Bosonic case, where each state can be occupied by any integer number of Bosons, one has

\[
\zeta_{BE,n} = \prod_l \left( \sum_{m=0}^{\infty} \lambda^m \exp(-\beta m \varepsilon_n) \exp(-\beta E_l) \right).
\]

(2.72)

In the classical limit the average occupation of an orbital is close to zero. In this limit, namely when

\[
\lambda \exp(-\beta \varepsilon_n) \ll 1 ,
\]

(2.73)

[see Eq. (2.38)] the following holds

\[
\zeta_{FD,n} \simeq \zeta_{BE,n} \simeq \zeta_n ,
\]

(2.74)

where

\[
\zeta_n = 1 + \lambda \exp(-\beta \varepsilon_n) \ Z_{\text{int}} ,
\]

(2.75)

and where

\[
Z_{\text{int}} = \sum_l \exp(-\beta E_l) ,
\]

(2.76)

is the internal partition function.

Using Eq. (1.94) one finds that the average occupation of the orbital \( f_n \) in the classical limit is given by

\[
f_n = \lambda \frac{\partial \log \zeta_n}{\partial \lambda} = \frac{\lambda Z_{\text{int}} \exp(-\beta \varepsilon_n)}{1 + \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n)} \simeq \lambda Z_{\text{int}} \exp(-\beta \varepsilon_n) .
\]

(2.77)

The total grandcanonical partition function is given by

\[
Z_{gc} = \prod_n \zeta_n ,
\]

(2.78)

thus
2.4. Ideal Gas in the Classical Limit

\[
\log Z_{\text{gc}} = \sum_n \log \zeta_n \\
= \sum_n \log [1 + \lambda Z_{\text{int}} \exp (-\beta \varepsilon_n)] \\
\simeq \lambda Z_{\text{int}} \sum_n \exp (-\beta \varepsilon_n) \\
= \lambda Z_{\text{int}} Z_1 ,
\]

where we have used the fact that in the classical limit \( \lambda Z_{\text{int}} \exp (-\beta \varepsilon_n) \ll 1 \).

Furthermore, using Eq. (2.11) and recalling that \( \eta = -\mu/\tau \) one finds

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

This result together with Eqs. (1.80) and (1.81) yield

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

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

where

\[
\langle E_l \rangle = \frac{\sum_l E_l \exp (-\beta E_l)}{\sum_l \exp (-\beta E_l)} = -\frac{\partial \log Z_{\text{int}}}{\partial \beta} .
\]

Claim. The following hold

\[
\mu = \tau \left( \log \frac{n}{nQ} - \log Z_{\text{int}} \right) ,
\]

\[
U = N \left( \frac{3\tau}{2} - \frac{\partial \log Z_{\text{int}}}{\partial \beta} \right) ,
\]

\[
F = N \tau \left( \log \frac{n}{nQ} - \log Z_{\text{int}} - 1 \right) ,
\]

\[
\sigma = N \left( \frac{5}{2} + \log \frac{nQ}{n} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right) ,
\]

\[
c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} \right) ,
\]

\[
c_p = c_V + N .
\]

Proof. See problem 3 of set 2.
2.5 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

\[
d\sigma = \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} dU + \left( \frac{\partial \sigma}{\partial V} \right)_{U,N} dV + \left( \frac{\partial \sigma}{\partial N} \right)_{U,V} dN . \tag{2.90}
\]

Using Eqs. (1.87), (2.64) and (2.65)

\[
d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV - \frac{\mu}{\tau} dN , \tag{2.91}
\]
or

\[
dU = \tau \sigma - p dV + \mu dN . \tag{2.92}
\]

This relation expresses the change in the energy of the system \( dU \) in terms of

\[
\begin{align*}
dQ &= \tau d\sigma & \text{heat added to the system} \\
dW &= p dV & \text{work done by the system} \\
\mu dN & & \text{energy change due to added particles}
\end{align*}
\]

For processes that keep the number of particles unchanged

\[ dN = 0 , \]

one has

\[
dU = dQ - dW . \tag{2.93}
\]

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

\[
\Delta U = Q - W , \tag{2.94}
\]

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. 2.2):

- 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. (2.67) together with Eq. (1.87) one finds that

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

(2.95)

Furthermore, as can be seen from Eq. (2.85), 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 we conclude that for processes for which \( dN = 0 \) the change in energy \( dU \) can be expressed as

\[
dU = c_V d\tau .
\]  

(2.96)
2.5.1 Isothermal Process

Since \( \tau \) is constant one finds using Eq. (2.96) that \( \Delta U = 0 \). Integrating the relation \( dW = pdV \) and using Eq. (2.55) one finds

\[
Q = W = \int_{V_i}^{V_f} pdV = N\tau \int_{V_i}^{V_f} \frac{dV}{V} = N\tau \log \frac{V_f}{V_i}.
\]

\[(2.97)\]

2.5.2 Isobaric Process

Integrating the relation \( dW = pdV \) for this case where the pressure is constant yields

\[
W = \int_{V_i}^{V_f} pdV = p(V_f - V_i) .
\]

\[(2.98)\]

The change in energy \( \Delta U \) can be found by integrating Eq. (2.96)

\[
\Delta U = \int_{\tau_1}^{\tau_2} c_V d\tau .
\]

\[(2.99)\]

The heat added to the system \( Q \) can be found using Eq. (2.94)

\[
Q = W + \Delta U = p(V_f - V_i) + \int_{\tau_1}^{\tau_2} c_V d\tau .
\]

\[(2.100)\]

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

\[
\Delta U = c_V (\tau_2 - \tau_1) .
\]

\[(2.101)\]
2.5. Processes in Ideal Gas

2.5.3 Isochoric Process

In this case the volume is constant, thus \( W = 0 \). By integrating Eq. (2.96) one finds that

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

(2.102)

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

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

2.5.4 Isentropic Process

In this case the entropy is constant, thus \( dQ = \tau d\sigma = 0 \), and therefore \( dU = -dW \), thus using the relation \( dW = pdV \) and Eq. (2.96) one has

\[
c_V d\tau = -pdV ,
\]

(2.103)

or using Eq. (2.55)

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

(2.104)

This relation can be rewritten using Eq. (2.89) as

\[
\frac{d\tau}{\tau} = (1 - \gamma) \frac{dV}{V} .
\]

(2.105)

where

\[
\gamma = \frac{c_p}{c_V} .
\]

(2.106)

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

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

(2.107)

Thus

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

(2.108)

or using Eq. (2.55)

\[
p_1 V_1^\gamma = p_2 V_2^\gamma .
\]

(2.109)
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 \( dW = pdV \)

\[
-\Delta U = W = \int_{V_i}^{V_f} pdV = p_1V_1^\gamma \int_{V_i}^{V_f} V^{-\gamma}dV = p_1V_1^\gamma \frac{(V_1^{1-\gamma+1} - V_2^{1-\gamma+1})}{\gamma - 1} = \frac{p_2V_2 - p_1V_1}{1 - \gamma} = \frac{N(\tau_2 - \tau_1)}{1 - \gamma} = -c_V(\tau_2 - \tau_1).
\]

(2.110)

### 2.6 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. 2.3 and 2.4)

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. (2.97) 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

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

(2.111)

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

\[
Q_l = N\tau_l \log \frac{V_d}{V_c},
\]

(2.112)

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

\[
W = W_{ab} + W_{cd} + W_{bc} + W_{da} = N\tau_h \log \frac{V_b}{V_a} + N\tau_l \log \frac{V_d}{V_c}
+ \frac{N (\tau_l - \tau_h)}{1 - \gamma} + \frac{N (\tau_h - \tau_l)}{1 - \gamma}
= N \left(\tau_h \log \frac{V_b}{V_a} + \tau_l \log \frac{V_d}{V_c}\right),
\]

(2.113)
where the work in both isothermal processes $W_{ab}$ and $W_{cd}$ is calculated using Eq. (2.97), whereas the work in both isentropic processes $W_{bc}$ and $W_{da}$ is calculated using Eq. (2.110). Note that the following holds

$$W = Q_h + Q_l.$$  \hspace{1cm} (2.114)

This is expected in view of Eq. (2.94) since the gas returns after a full cycle to its initial state and therefore $\Delta U = 0$.

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

$$\eta = \frac{W}{Q_h} = 1 + \frac{Q_l}{Q_h}. \hspace{1cm} (2.115)$$

Using Eqs. (2.111) and (2.113) one finds

$$\eta = 1 + \frac{\tau_l \log \gamma_b}{\tau_h \log \gamma_a}. \hspace{1cm} (2.116)$$

Employing Eq. (2.108) for both isentropic processes yields

$$\tau_h \gamma_b^{-1} = \tau_l \gamma_c^{-1}, \hspace{1cm} (2.117)$$

$$\tau_h \gamma_a^{-1} = \tau_l \gamma_d^{-1}, \hspace{1cm} (2.118)$$

thus by dividing these equations one finds

$$\frac{\gamma_b^{-1}}{\gamma_a^{-1}} = \frac{\gamma_c^{-1}}{\gamma_d^{-1}}, \hspace{1cm} (2.119)$$

or

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}. \hspace{1cm} (2.120)$$

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

$$\eta_C = 1 - \frac{\tau_l}{\tau_h}. \hspace{1cm} (2.121)$$

### 2.7 Limits Imposed Upon the Efficiency

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. (2.121)? As we will see 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. We make the following assumptions:

- 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 (2.5) 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 we will see 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. (2.6). 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 we will see below.

To show that the idle heat engine shown in Fig. (2.5) can not be realized we employ the second law and require that the total change in entropy \( \Delta \sigma \) per cycle is non-negative

\[
\Delta \sigma \geq 0.
\]

(2.122)

The only change in entropy per cycle is due to the heat that is subtracted from the heat bath.
\[ \Delta \sigma = -\frac{Q}{\tau}, \]  
(2.123)

thus since \( Q = W \) (energy conservation) we find that

\[ \frac{W}{\tau} \leq 0. \]  
(2.124)

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 convert it all into work.

As we will see 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 2.7.1.** Kelvin’s principle is equivalent to Clausius’s principle.

**Proof.** Assume that Clausius’s principle does not hold. Thus the system shown in Fig. 2.7(a) that transfers heat \( Q_0 > 0 \) from a cold thermal reservoir at temperature \( \tau_1 \) to a hotter one at temperature \( \tau_h > \tau_1 \) is possible. In Fig. 2.7(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. 2.8(a) that extracts heat \( Q_0 \) from a thermal reservoir at temperature \( \tau_h \) and converts it all into work is possible. In Fig. 2.8(b) a refrigerator is added
that employs the work \( W = Q_0 \) to remove heat \( Q \) from a colder thermal reservoir at temperature \( \tau_1 < \tau_h \) 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 we have seen unity efficiency is impossible. What is the largest possible efficiency of an heat engine?

**Theorem 2.7.2.** The efficiency \( \eta \) of a heat engine operating between a hotter and colder heat reservoirs at temperature \( \tau_h \) and \( \tau_1 \) respectively can not exceed the value

\[
\eta_C = 1 - \frac{\tau_1}{\tau_h} .
\]

**(2.125)**

*Proof.* A heat engine (labeled as 'I') is seen in Fig. 2.9. 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

\[
\eta_I = \frac{W}{Q_H} ,
\]

whereas the efficiency of the reversed Carnot heat engine 'C' is given by Eq. (2.121)
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**Fig. 2.8.** The assumption that Kelvin’s principle does not hold.

**Fig. 2.9.** Limit imposed upon engine efficiency.

\[ \eta_C = \frac{W}{Q_h} = 1 - \frac{\tau}{\tau_h}. \]  
(2.127)

For the combined system, the Clausius’s principle requires that

\[ Q'_h - Q_h > 0. \]  
(2.128)

thus

\[ \eta \leq \eta_C = 1 - \frac{\tau}{\tau_h}. \]

The same argument that was employed in the proof above can be used to deduce the following corollary:
Corollary 2.7.1. 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.

Note that a similar bound is imposed upon the efficiency of refrigerators (see problem 16 of set 2).

2.8 Problems Set 2

1. The heat capacity at constant pressure is defined as

\[ C_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p . \]  

(2.129)

Calculate $C_p$ of an classical ideal gas having no internal degrees of freedom.

2. Show that

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau} = \left( \frac{\partial p}{\partial \tau} \right)_V , \]

(2.130)

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

\[ \mu = \tau \left( \log \frac{n}{n_Q} - \log Z_{\text{int}} \right) , \]

(2.131)

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 by the following relation:

\[ U = N \left( \frac{3\tau}{2} - \frac{\partial \log Z_{\text{int}}}{\partial \beta} \right) , \]

(2.132)

where $\beta = bl/\tau$.

c) Show that the Helmholtz free energy is given by

\[ F = N\tau \left( \log \frac{n}{n_Q} - \log Z_{\text{int}} - 1 \right) . \]

(2.133)

d) Show that the entropy is given by

\[ \sigma = N \left( \frac{5}{2} + \log \frac{n_Q}{n} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right) . \]

(2.134)
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e) Show that the heat capacity at constant volume is given by

\[ c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} \right). \quad (2.135) \]

f) Show that the heat capacity at constant pressure is given by

\[ c_p = c_V + N. \quad (2.136) \]

4. The heat capacity \( c \) of a body having entropy \( \sigma \) is given by

\[ c = \tau \frac{\partial \sigma}{\partial \tau}, \quad (2.137) \]

where \( \tau \) is the temperature. Show that

\[ c = \frac{\langle (\Delta U)^2 \rangle}{\tau^2}, \quad (2.138) \]

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

\[ \varepsilon_n = \left( n + \frac{1}{2} \right) \hbar \omega, \quad (2.139) \]

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

\[ p_n = \frac{\lambda^n}{n!} e^{-\lambda}, \quad (2.140) \]

where \( \lambda = Nv/V \).
8. A lattice contains \( N \) sites, each is 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 \( \tau \).
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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

$$M = \frac{N \mu}{2} \left\{ (2J + 1) \coth \left[ (2J + 1) \frac{\mu H}{2\tau} \right] - \coth \left( \frac{\mu H}{2\tau} \right) \right\} .$$

11. 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).

12. 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

$$\lambda = \left( \frac{M}{2\pi \hbar^2} \right)^{-3/2} \tau^{-5/2} p .$$

13. 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

$$c_V = N \left\{ \frac{3}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{[g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)]^2} \right\} ,$$

$$c_p = N \left\{ \frac{5}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{[g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)]^2} \right\} .$$

14. A classical gas is described by the following equation of state

$$p (V - b) = N \tau ,$$

where $p$ is the pressure, $V$ is the volume, $\tau$ is the temperature, $N$ is the number of particles and $b$ is a constant.
2.8. Problems Set 2

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.

15. A classical gas is described by the following equation of state

\[
(p + \frac{a}{V^2})(V - b) = N\tau ,
\]  

(2.152)

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.

16. A classical gas is described by the following equation of state

\[
(p + \frac{a}{V^2})(V - b) = N\tau ,
\]  

(2.153)

where \( p \) is the pressure, \( V \) is the volume, \( \tau \) is the temperature, and \( a \) and \( b \) are constants. 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

\[
W = N\tau_0 \log \frac{V_2 - b}{V_1 - b} - a \frac{V_2 - V_1}{V_2 V_1} ,
\]  

(2.154)

\[
Q = \Delta U + W = N\tau_0 \log \frac{V_2 - b}{V_1 - b} .
\]  

(2.155)

17. 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 \( V \), is in thermal equilibrium at temperature \( \tau \).

a) Calculate \( \langle (\Delta E)^2 \rangle \).

b) Calculate \( \langle (\Delta E)^3 \rangle \).

18. 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 establishes is given by

\[
\Delta \sigma = C \left( \frac{\tau_a}{\tau_b} - 1 - \log \frac{\tau_a}{\tau_b} \right) .
\]  

(2.156)

Use this result to show that \( \Delta \sigma \geq 0 \).

19. The figure below shows a cycle of an engine made of an ideal gas. In the first step \( a \rightarrow b \) the volume is constant \( V_2 \), the second one \( b \rightarrow c \) is
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Fig. 2.10.

an isentropic process, and in the third one the pressure is constant $p_2$. Assume that the heat capacities $C_V$ and $C_p$ are temperature independent. Show that the efficiency of this engine is given by

$$\eta = 1 - \frac{\gamma p_2 (V_1 - V_2)}{V_2 (p_1 - p_2)},$$

(2.157)

where $\gamma = C_p/C_v$.

20. 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

$$\gamma = \frac{Q_l}{W}.$$  

(2.158)

Show that the second law of thermodynamics imposes an upper bound on $\gamma$

$$\gamma \leq \frac{\tau_l}{\tau_h - \tau_l}.$$  

(2.159)

21. 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.

22. The state equation of a given matter is
2.8. Problems Set 2

\[ p = \frac{A\tau^3}{V}, \quad (2.160) \]

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

\[ U = B\tau^n \log \frac{V}{V_0} + f(\tau), \quad (2.161) \]

where \( B \) and \( V_0 \) are constants, \( f(\tau) \) only depends on the temperature. Find \( B \) and \( n \).

23. 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 \( C_p \).

24. 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 \( \tau_f \).
   b) Calculate the total work \( W \), which is delivered by the process.

25. 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.

26. 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 \( \tau \).

27. 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 shown in Fig. 2.11. Assume that the heat capacities \( C_V \) and \( C_p \) are temperature independent. Calculate the efficiency of this engine.

28. 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. 2.12. Assume that the heat capacities $C_V$ and $C_p$ are temperature independent. Calculate the efficiency $\eta$ of this engine.
29. 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 \( \Delta \sigma = \sigma_{\text{final}} - \sigma_{\text{initial}} \).

2.9 Solutions Set 2

1. The entropy is given by

\[
\sigma = N \left\{ \log \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} \frac{V}{N} + \frac{5}{2} \right\},
\]

or using \( pV = N\tau \)

\[
\sigma = N \left\{ \log \left( \frac{M}{2\pi \hbar^2} \right)^{3/2} \left( \frac{\tau V}{5p} \right) + \frac{5}{2} \right\},
\]

thus

\[
C_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p = \frac{5}{2} N.
\]

2. Since

\[
\frac{\partial^2 F}{\partial V \partial \tau} = \frac{\partial^2 F}{\partial \tau \partial V},
\]

where \( F \) is Helmholtz free energy, one has

\[
\left( \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial \tau} \right)_V \right)_\tau = \left( \frac{\partial}{\partial \tau} \left( \frac{\partial F}{\partial V} \right)_\tau \right)_V.
\]

By definition

\[
\left( \frac{\partial F}{\partial V} \right)_\tau = -p.
\]

Moreover, using \( F = U - \tau \sigma \) one finds

\[
\left( \frac{\partial F}{\partial \tau} \right)_V = \left( \frac{\partial U}{\partial \tau} \right)_V - \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V - \sigma
\]
\[
= \left( \frac{\partial U}{\partial \tau} \right)_V - \left( \frac{\partial U}{\partial \sigma} \right)_V \left( \frac{\partial \sigma}{\partial \tau} \right)_V - \sigma
\]
\[
= -\sigma,
\]

(2.167)
thus
\[
\left( \frac{\partial \sigma}{\partial V} \right)_\tau = \left( \frac{\partial p}{\partial \tau} \right)_V .
\] (2.168)

3. We have found in class the following relations
\[
n_Q = \left( \frac{M \tau}{2 \pi \hbar^2} \right)^{3/2},
\] (2.169)
\[
\eta = -\frac{\mu}{\tau},
\] (2.170)
\[
\log Z_{gc} = e^{-\eta} Z_{int} V n_Q ,
\] (2.171)
\[
U = \left( \frac{3 \tau}{2} - \frac{\partial \log Z_{int}}{\partial \beta} \right) \log Z_{gc} ,
\] (2.172)
\[
N = \log Z_{gc} .
\] (2.173)

a) Using Eqs. (2.171) and (2.173) one finds
\[
\log \frac{n}{n_Q Z_{int}} = \frac{\mu}{\tau} ,
\] (2.174)
thus
\[
\mu = \tau \left( \log \frac{n}{n_Q} - \log Z_{int} \right) .
\] (2.175)

b) Using Eqs. (2.172) and (2.173)
\[
U = N \left( \frac{3 \tau}{2} - \frac{\partial \log Z_{int}}{\partial \beta} \right) .
\] (2.176)

c) Using the relations
\[
F = U - \tau \sigma ,
\] (2.177)
\[
\sigma = \log Z_{gc} + \beta U + \eta N ,
\] (2.178)
one finds
\[
F = U - \tau \sigma
\] (2.179)
\[
= N \tau (-\eta - 1)
\] (2.180)
\[
= N \tau \left( \frac{\mu}{\tau} - 1 \right)
\] (2.181)
\[
= N \tau \left( \log \frac{n}{n_Q} - \log Z_{int} - 1 \right) .
\] (2.182)
d) Using the relation

\[ \sigma = - \left( \frac{\partial F}{\partial \tau} \right)_V, \tag{2.184} \]

one finds

\[ \sigma = - \left( \frac{\partial F}{\partial \tau} \right)_V \]

\[ = N \left( - \frac{\partial (\tau \log \frac{n}{n_Q})}{\partial \tau} \right)_V + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \]

\[ = N \left( -\tau \left( \frac{\partial \left( \log \frac{n}{n_Q} \right)}{\partial \tau} \right)_V - \log \frac{n}{n_Q} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \right) \]

\[ = N \left( \frac{3}{2} - \log \frac{n}{n_Q} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} + 1 \right) \]

\[ = N \left( \frac{5}{2} + \log \frac{n}{n_Q} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right). \tag{2.185} \]

e) By definition

\[ c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V \]

\[ = N \left( \frac{3}{2} + \tau \frac{\partial^2 \left( \tau \log Z_{\text{int}} \right)}{\partial \tau^2} \right). \tag{2.186} \]

f) The following holds

\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p \tag{2.187} \]

\[ = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_V + \tau \left( \frac{\partial \sigma}{\partial V} \right)_\tau \left( \frac{\partial V}{\partial \tau} \right)_p \]

\[ = c_V + \tau \left( \frac{\partial \sigma}{\partial V} \right)_\tau \left( \frac{\partial V}{\partial \tau} \right)_p. \]

Using \( V_p = N\tau \) and Eq. (2.185) one finds

\[ c_p = c_V + \tau \frac{N N}{V_p} = c_V + N. \tag{2.188} \]
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4. With the help of Eqs. (1.87), (1.70) and (1.71) together with the following relation
\[ \frac{\partial}{\partial \tau} = -\frac{1}{\tau^2} \frac{\partial}{\partial \beta}, \] (2.189)
one finds that
\[ c = \tau \frac{\partial \sigma}{\partial \tau} = \frac{\partial U}{\partial \tau} = -\frac{1}{\tau^2} \frac{\partial U}{\partial \beta} = \left\langle \frac{(\Delta U)^2}{\tau^2} \right\rangle. \] (2.190)

5. The internal partition function is given by
\[ Z_{\text{int}} = \frac{1}{2 \sinh \frac{\hbar \omega}{2 \tau}} \simeq \frac{\tau}{\hbar \omega}, \] (2.191)
thus using Eqs. (2.186) and (2.188)
\[ c_V = N \left( \frac{3}{2} + \tau \frac{\partial^2}{\partial \tau^2} \frac{(\tau \log \frac{\tau}{\hbar \omega})}{\hbar \omega} \right) = \frac{5N}{2}, \] (2.192)
\[ c_p = \frac{7N}{2}. \] (2.193)

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
\[ \Delta \sigma = \sigma_{\text{mix}} - \sigma_A - \sigma_B \]
\[ = \sigma \left( \frac{N_A}{V_A + V_B} \right) + \sigma \left( \frac{N_B}{V_A + V_B} \right) - \sigma \left( \frac{N_A}{V_A} \right) - \sigma \left( \frac{N_B}{V_B} \right) \]
\[ = N_A \log \frac{V_A + V_B}{V_A} + N_B \log \frac{V_A + V_B}{V_B}. \]

7. The probability to find a molecule in the volume \( v \) is given by \( p = v/V \).
Thus, \( p_n \) is given by
\[ p_n = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}. \] (2.194)
Using the solution of problem 4 of set 1
\[ p_n = \frac{\lambda^n}{n!} e^{-\lambda}, \]
where \( \lambda = Nv/V \).
8. The partition function of a single atom is given by

\[ Z_1 = \exp(\mu_0 H \beta) + \exp(-\mu_0 H \beta) = 2 \cosh(\mu_0 H \beta), \]

where \( \beta = 1/\tau \), thus the partition function of the entire system is

\[ Z = (2 \cosh(\mu_0 H \beta))^N, \]

a) The free energy is given by

\[ F = -\tau \log Z = -N\tau \log(2 \cosh(\mu_0 H \beta)). \quad (2.195) \]

The magnetization is given by

\[ M = -\left( \frac{\partial F}{\partial H} \right)_\tau = N\mu_0 \tanh(\mu_0 H \beta). \quad (2.196) \]

b) The energy \( U \) is given by

\[ U = -\frac{\partial \log Z}{\partial \beta} = -N\mu_0 H \tanh(\mu_0 H \beta), \quad (2.197) \]

thus

\[ C = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_H \]
\[ = \left( \frac{\partial U}{\partial \tau} \right)_H \]
\[ = -N\mu_0 H \left( \frac{\partial \tanh(\mu_0 H \tau)}{\partial \tau} \right)_H \]
\[ = N \left( \frac{\mu_0 H}{\tau} \frac{1}{\cosh(\mu_0 H \tau)} \right)^2. \quad (2.198) \]

c) The entropy \( \sigma \), which is given by

\[ \sigma = \beta (U - F) \]
\[ = N \left[ \log \left( 2 \cosh(\mu_0 H \tau) \right) - \frac{\mu_0 H}{\tau} \tanh(\mu_0 H \tau) \right], \quad (2.199) \]

and which remains constant, is a function of the ratio \( H/\tau \), therefore

\[ \tau_2 = \tau_1 \frac{H_2}{H_1}. \quad (2.200) \]

9. The partition function of a single atom is given by
\[ Z = \sum_{m=-1}^{1} \exp(-\beta \varepsilon_m) \]
\[ = 1 + 2 \exp(\beta \Delta) \cosh(\beta \mu_0 H) , \]  
\[ (2.201) \]

where \( \beta = 1/\tau \). The free energy is given by
\[ F = -N \tau \log Z , \]  
\[ (2.202) \]

thus the magnetization is given by
\[ M = -\left( \frac{\partial F}{\partial H} \right) \tau \]
\[ = \frac{2N \mu_0 \exp(\beta \Delta) \sinh(\beta \mu_0 H)}{1 + 2 \exp(\beta \Delta) \cosh(\beta \mu_0 H)} . \]  
\[ (2.203) \]

and the magnetic susceptibility is given by
\[ \chi = \frac{N \mu_0^2}{\tau (1 + \frac{1}{2} \exp(-\beta \Delta))} , \]  
\[ (2.204) \]

10. The partition function of a single atom is given by
\[ Z = \sum_{m=-J}^{J} \exp(m \mu H \beta) , \]

where \( \beta = 1/\tau \). By multiplying by a factor \( \sinh(\mu H \beta / 2) \) one finds
\[ \sinh \left( \frac{\mu H \beta}{2} \right) Z = \frac{1}{2} \left[ \exp \left( \frac{\mu H \beta}{2} \right) - \exp \left( -\frac{\mu H \beta}{2} \right) \right] \sum_{m=-J}^{J} \exp(m \mu H \beta) \]
\[ = \frac{1}{2} \left[ \exp \left[ \left( J + \frac{1}{2} \right) \mu H \beta \right] - \exp \left[ -\left( J + \frac{1}{2} \right) \mu H \beta \right] \right] , \]  
\[ (2.205) \]

thus
\[ Z = \frac{\sinh \left[ \left( J + \frac{1}{2} \right) \mu H \beta \right]}{\sinh \left( \frac{\mu H \beta}{2} \right)} . \]  
\[ (2.206) \]

a) The free energy is given by
\[ F = -N \tau \log Z = -N \tau \log \left[ \frac{\sinh \left[ \left( J + \frac{1}{2} \right) \mu H \beta \right]}{\sinh \left( \frac{\mu H \beta}{2} \right)} \right] . \]  
\[ (2.207) \]
b) The magnetization is given by
\[
M = - \left( \frac{\partial F}{\partial H} \right)_\tau = \frac{N\mu}{2} \left\{ (2J+1) \coth \left[ (2J+1) \frac{\mu H}{2\tau} \right] - \coth \left( \frac{\mu H}{2\tau} \right) \right\}.
\] (2.208)

11. The internal chemical potential \( \mu_g \) is given by Eq. (2.131). In thermal equilibrium the total chemical potential
\[
\mu_{\text{tot}} = \mu_g + mgz,
\] (2.209)
(m is the mass of the each diatomic molecule \( N_2 \), \( g \) is the gravity acceleration constant, and \( z \) is the height) is \( z \) independent. Thus, the density \( n \) as a function of height above see level \( z \) can be expressed as
\[
n(z) = n(0) \exp \left( -\frac{mgz}{k_BT} \right).
\] (2.210)
The condition \( n(z) = 0.5 \times n(0) \) yields
\[
z = \frac{k_BT \ln 2}{mg} = \frac{1.3806568 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K} \times \ln 2}{14 \times 1.6605402 \times 10^{-27} \text{ kg} \times 9.8 \text{ m s}^{-2}} = 12.6 \text{ km}.
\] (2.211)

12. The Helmholtz free energy of an ideal gas of \( N \) particles is given by
\[
F = -\tau N \log \left[ \left( \frac{M\tau}{2\pi\hbar^2} \right)^{3/2} V \right] + \tau N \log N - \tau N,
\] (2.212)
thus the chemical potential is
\[
\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau,V} = -\tau \log \left( \left( \frac{M\tau}{2\pi\hbar^2} \right)^{3/2} V \right) + \tau \log N,
\] (2.213)
and the pressure is
\[
p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,V} = \frac{N\tau}{V}.
\] (2.214)
Using these results the fugacity \( \lambda = \exp(\beta\mu) \) can be expressed in terms of \( p \)
\[
\lambda = e^{\beta\mu} = \left( \frac{M\tau}{2\pi\hbar^2} \right)^{-3/2} \frac{N}{V} = \left( \frac{M}{2\pi\hbar^2} \right)^{-3/2} \tau^{-5/2} p.
\] (2.215)
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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\[ Z = 1 + e^{\beta \mu} + e^{\beta(2\mu - \varepsilon)} , \]  
(2.216)

or in terms of the fugacity \( \lambda = \exp(\beta \mu) \)

\[ Z = 1 + \lambda + \lambda^2 e^{-\beta \varepsilon} . \]  
(2.217)

Thus

\[ \langle N_a \rangle = N_0 \lambda \frac{\partial \log Z}{\partial \lambda} = N_0 \frac{\lambda + 2\lambda^2 e^{-\beta \varepsilon}}{1 + \lambda + \lambda^2 e^{-\beta \varepsilon}} , \]  
(2.218)

where \( \lambda \) is given by Eq. (2.215).

13. The internal partition function is given by

\[ Z_{\text{int}} = g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right) . \]  
(2.219)

Using Eq. (2.135)

\[ c_V = \frac{3}{2} N + N \tau \left[ \frac{\partial^2}{\partial \tau^2} (\tau \log Z_{\text{int}}) \right]_V \]

\[ = N \left\{ \frac{3}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{[g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)]^2} \right\} . \]  
(2.220)

Using Eq. (2.136)

\[ c_p = N \left\{ \frac{5}{2} + \left( \frac{\varepsilon}{\tau} \right)^2 \frac{g_1 g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)}{[g_1 + g_2 \exp \left( -\frac{\varepsilon}{\tau} \right)]^2} \right\} . \]  
(2.221)

14. Using Maxwell's relation

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N} , \]  
(2.222)

and the equation of state one finds that

\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \frac{N}{V - b} . \]  
(2.223)

a) Using the definitions

\[ c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{V,N} , \]  
(2.224)

\[ c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{p,N} , \]  
(2.225)
and the general identity
\[
\left( \frac{\partial z}{\partial x} \right)_\alpha = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_\alpha ,
\]
(2.226)
one finds
\[
c_p - c_V = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} \left( \frac{\partial V}{\partial \sigma} \right)_{p,N} ,
\]
(2.227)
or with the help of Eq. (2.223) and the equation of state
\[
c_p - c_V = N \frac{N\tau}{p(V-b)} = N .
\]
(2.228)
b) Using the identity
\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial V} \right)_{\sigma,N} + \left( \frac{\partial U}{\partial \sigma} \right)_{V,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} ,
\]
(2.229)
 together with Eq. (2.223) yields
\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = -p + \frac{N\tau}{V-b} = 0 .
\]
(2.230)
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
\[
dU = c_V d\tau .
\]
(2.231)
For an isentropic process no heat is exchanged, and therefore \( dW = -dU \), thus since \( c_V \) is independent on temperature one has
\[
W = -\Delta U = -c_V (\tau_2 - \tau_1) .
\]
(2.232)
15. Using the definitions
\[
c_V = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{V,N} ,
\]
(2.233)
\[
c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_{p,N} ,
\]
(2.234)
and the general identity
\[
\left( \frac{\partial z}{\partial x} \right)_\alpha = \left( \frac{\partial z}{\partial x} \right)_y + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial x} \right)_\alpha ,
\]
(2.235)
one finds
\[ c_p - c_V = \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N} . \] (2.236)

Using Maxwell’s relation
\[ \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N} , \] (2.237)
and the equation of state
\[ \left( p + \frac{a}{V^2} \right) (V - b) = N\tau , \] (2.238)
one finds
\[ c_p - c_V = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} \left( \frac{\partial V}{\partial \tau} \right)_{p,N} \]
\[ = \frac{\tau N}{(V-b)} 
- \frac{-aV + 2ab + pV}{N V^2} 
+ \frac{N}{1 + \frac{-2aV + 2ab}{V^2(p + \frac{a}{V^2})}} \] (2.239)
or
\[ c_p - c_V = \frac{N}{1 - \frac{2a(1-b)}{V\tau}} . \] (2.240)

16. The work \( W \) is given by
\[ W = \int_{V_1}^{V_2} p dV . \] (2.241)

Using
\[ \left( p + \frac{a}{V^2} \right) (V - b) = N\tau , \] (2.242)
one finds
\[ W = \int_{V_1}^{V_2} \left( \frac{N\tau_0}{V-b} - \frac{a}{V^2} \right) dV = N\tau_0 \log \frac{V_2 - b}{V_1 - b} - a \frac{V_2 - V_1}{V_2 V_1} . \] (2.243)

Using the identity
\[ \left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \left( \frac{\partial U}{\partial \tau} \right)_{\sigma,N} + \left( \frac{\partial U}{\partial \sigma} \right)_{V,N} \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = -p + \tau \left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} , \]
and Maxwell's relation

\[
\left( \frac{\partial \sigma}{\partial V} \right)_{\tau,N} = \left( \frac{\partial p}{\partial \tau} \right)_{V,N},
\]

(2.245)

one finds

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

(2.246)

In the present case

\[
\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \frac{N \tau}{V - b} - p = \frac{a}{V^2},
\]

(2.247)

thus

\[
\Delta U = \int_{V_1}^{V_2} \left( \frac{\partial U}{\partial V} \right)_{\tau,N} \, dV = a \int_{V_1}^{V_2} \frac{dV}{V^2} = a \frac{V_2 - V_1}{V_2 V_1},
\]

(2.248)

and

\[
Q = \Delta U + W = N \tau_0 \log \frac{V_2 - b}{V_1 - b}.
\]

(2.249)

17. In general the following holds

\[
\langle E^n \rangle = \frac{1}{Z_{gc}} \left( - \frac{\partial^n Z_{gc}}{\partial \beta^n} \right)_{\eta},
\]

(2.250)

and

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

(2.251)

Thus the variance is given by

\[
\left\langle (\Delta E)^2 \right\rangle = \langle E^2 \rangle - \langle E \rangle^2
\]

\[
= \frac{1}{Z_{gc}} \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_{\eta} - \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_{\eta}^2
\]

\[
= \left( \frac{\partial^2 \log Z_{gc}}{\partial \beta^2} \right)_{\eta}.
\]

(2.252)

Furthermore, the following holds:
\[ \left\langle (\Delta E)^3 \right\rangle = \left\langle E^3 - 3E^2U + 3EU^2 - U^3 \right\rangle = \left\langle E^3 \right\rangle - 3U \left\langle E^2 \right\rangle + 2U^3 \]

\[ = - \left[ 1 \left( \frac{\partial^3 Z_{gc}}{\partial \beta^3 \eta} \right)_\eta - \frac{3}{Z_{gc}} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_\eta + \frac{2}{Z_{gc}^3} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta^3 \right] \]

\[ = - \frac{\partial}{\partial \beta} \left[ 1 \left( \frac{\partial^2 Z_{gc}}{\partial \beta^2} \right)_\eta - \frac{1}{Z_{gc}} \left( \frac{\partial Z_{gc}}{\partial \beta} \right)_\eta \right] \]

\[ = - \left( \frac{\partial^3 \log Z_{gc}}{\partial \beta^3 \eta} \right)_\eta . \]  

(2.253)

For classical gas having no internal degrees of freedom one has

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

(2.254)

thus

\[ U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \frac{3N\tau}{2}. \]  

(2.255)

a) Using Eq. (2.252)

\[ \left\langle (\Delta E)^2 \right\rangle = - \frac{\partial}{\partial \beta} \left( \frac{3N}{2\beta^2} \right) = \frac{3N}{2} \frac{2U^2}{3N}. \]  

(2.256)

b) Using Eq. (2.253)

\[ \left\langle (\Delta E)^3 \right\rangle = - \frac{\partial}{\partial \beta} \left( \frac{3N}{\beta^3} \right) = \frac{3N}{\beta^3} = \frac{8U^3}{9N^2}. \]  

(2.257)

18. The entropy change of the body is

\[ \Delta \sigma_1 = C \int_{\tau_a}^{\tau_b} \frac{d\tau}{\tau} = C \log \frac{\tau_b}{\tau_a}, \]

(2.258)

and that of the bath is

\[ \Delta \sigma_2 = \frac{\Delta Q}{\tau_b} = \frac{C(\tau_a - \tau_b)}{\tau_b}, \]

(2.259)

thus

\[ \Delta \sigma = C \left( \frac{\tau_a}{\tau_b} - 1 - \log \frac{\tau_a}{\tau_b} \right). \]  

(2.260)

The function \( f(x) = x - 1 - \log x \) in the range \( 0 < x < \infty \) satisfy \( f(x) \geq 0 \), where \( f(x) > 0 \) unless \( x = 1 \).
19. The efficiency is given by

$$\eta = 1 + \frac{Q_l}{Q_h} = 1 + \frac{Q_{ca}}{Q_{ab}} = 1 + \frac{C_p (\tau_a - \tau_c)}{C_v (\tau_b - \tau_a)} = 1 - \frac{\gamma p_2 (V_1 - V_2)}{V_2 (p_1 - p_2)}, \quad (2.261)$$

where $\gamma = C_p/C_v$.

20. 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

$$\eta_c = \frac{W}{Q'_h} = 1 - \frac{\tau_l}{\tau_h}. \quad (2.262)$$

According to Clausius principle

$$Q_l + Q'_l \leq 0, \quad (2.263)$$

thus

$$\gamma = \frac{Q_l}{W} \leq -\frac{Q'_l}{W} = \frac{Q'_h - W}{W} = \frac{\tau_h}{\tau_h - \tau_l} - 1 = \frac{\tau_l}{\tau_h - \tau_l}. \quad (2.264)$$

21. Using Eq. (2.264)

$$\frac{A (\tau_h - \tau_l)}{P} = \frac{\tau_l}{\tau_h - \tau_l}, \quad (2.265)$$

thus

$$\tau_l^2 - 2\tau_l \left( \tau_h + \frac{P}{2A} \right) + \tau_h^2 = 0, \quad (2.266)$$

or

$$\tau_l = \tau_h + \frac{P}{2A} \pm \sqrt{\left( \tau_h + \frac{P}{2A} \right)^2 - \tau_h^2}. \quad (2.267)$$

The solution for which $\tau_l \leq \tau_h$ is

$$\tau_l = \tau_h + \frac{P}{2A} - \sqrt{\left( \tau_h + \frac{P}{2A} \right)^2 - \tau_h^2}. \quad (2.268)$$

22. Using Eq. (2.244)

$$\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \tau \left( \frac{\partial p}{\partial \tau} \right)_{V,N} - p, \quad (2.269)$$
Chapter 2. Ideal Gas

thus
\[ \frac{B\tau^n}{V} = 3A\tau^3 - p = \frac{2A\tau^3}{V}, \quad (2.270) \]

therefore
\[ B = 2A, \quad (2.271) \]
\[ n = 3. \quad (2.272) \]

23. In general the following holds
\[ C_V = N \left( \frac{3}{2} + \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} \right), \quad (2.273) \]
\[ C_p = c_v + N, \quad (2.274) \]

where in our case
\[ Z_{\text{int}} = 1 + 3 \exp \left( -\frac{\Delta}{\tau} \right), \quad (2.275) \]

thus
a) \[ C_V \] is given by
\[ C_V = N \left( \frac{3}{2} + 3 \frac{\left( \frac{\Delta}{\tau} \right)^2 e^{-\frac{\Delta}{\tau}}}{\left( 1 + 3e^{-\frac{\Delta}{\tau}} \right)^2} \right), \quad (2.276) \]
b) and \[ C_p \] is given by
\[ C_p = N \left( \frac{5}{2} + 3 \frac{\left( \frac{\Delta}{\tau} \right)^2 e^{-\frac{\Delta}{\tau}}}{\left( 1 + 3e^{-\frac{\Delta}{\tau}} \right)^2} \right), \quad (2.277) \]

24. 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
\[ 0 = d\sigma = d\sigma_1 + d\sigma_2 = \frac{dQ_1}{\tau_1} + \frac{dQ_2}{\tau_2} = C \left( \frac{d\tau_1}{\tau_1} + \frac{d\tau_2}{\tau_2} \right). \quad (2.278) \]

a) Thus, by integration the equation
\[ \frac{d\tau_1}{\tau_1} = -\frac{d\tau_2}{\tau_2}, \quad (2.279) \]
on one finds
\[ \int_{\tau_1}^{\tau_f} \frac{d\tau_1}{\tau_1} = - \int_{\tau_2}^{\tau_f} \frac{d\tau_2}{\tau_2}, \]  
\[ \text{or} \quad \log \frac{\tau_f}{\tau_1} = \log \frac{\tau_2}{\tau_f}, \]

thus

\[ \tau_f = \sqrt{\tau_1 \tau_2}. \]

b) Employing energy conservation law yields

\[ W = \Delta U_1 + \Delta U_2 = C (\tau_1 - \tau_f) + C (\tau_2 - \tau_f) = C (\sqrt{\tau_1} - \sqrt{\tau_2})^2. \]

25. 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

\[ \sigma(N, n) = N \left( \log \frac{nQ}{n} + \frac{5}{2} \right), \]

where

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

\[ n = \frac{N}{V}. \]

Using the relation

\[ pV = N\tau, \]

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

\[ p_{\text{final}} = \frac{2p_1 p_2}{p_1 + p_2}. \]

Thus, the change in entropy is given by

\[ \Delta \sigma = \sigma_{\text{final}} - \sigma_1 - \sigma_2 \]
\[ = 2N \left( \log \frac{(p_1 + p_2) \tau n_Q}{2p_1 p_2} + \frac{5}{2} \right) - N \left( \log \frac{\tau n_Q}{p_1} + \frac{5}{2} \right) - N \left( \log \frac{\tau n_Q}{p_2} + \frac{5}{2} \right) \]
\[ = N \log \frac{(p_1 + p_2)^2}{4p_1 p_2}. \]
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26. Using

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

one finds

\[ \log Z_c = \log Z_{gc} + \eta N . \] (2.289)

The following holds for classical ideal gas having no internal degrees of freedom

\[ \log Z_{gc} = N \]
\[ \eta = -\beta \mu = \log \frac{n_Q V}{N} , \] (2.290)

where

\[ n_Q = \left( \frac{M \tau}{2\pi\hbar^2} \right)^{3/2} , \] (2.291)

thus

\[ \log Z_c = N \left( 1 + \log \frac{n_Q V}{N} \right) \]
\[ = N \log (n_Q V) + N - N \log N \]
\[ \simeq N \log (n_Q V) - \log N! \]
\[ = \log \left( \frac{n_Q V}{N} \right)^N , \] (2.292)

or

\[ Z_c = \frac{1}{N!} \left( \frac{M \tau}{2\pi\hbar^2} \right)^{3/2} V^N . \] (2.293)

27. 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 \( b \to c \) and \( d \to a \) no heat is exchanged. Thus

\[ \eta = 1 + \frac{Q_l}{Q_h} = 1 + \frac{C_p (\tau_d - \tau_c)}{C_p (\tau_b - \tau_a)} . \] (2.294)
Using $pV = N\tau$ yields

$$\eta = 1 + \frac{\tau_d - \tau_c}{\tau_b - \tau_a} = 1 + \frac{p_2 (V_d - V_c)}{p_1 (V_b - V_a)}.$$ \hspace{1cm} (2.295)

Along the isentropic process $pV^\gamma$ is constant, where $\gamma = C_p/C_v$, thus

$$\eta = 1 + \frac{p_2 \left( \frac{p_1}{p_2} \right)^\gamma (V_a - V_b)}{V_b - V_a} = 1 - \left( \frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}}.$$ \hspace{1cm} (2.296)

28. No heat is exchanged in the isentropic processes, thus the efficiency is given by

$$\eta = 1 + \frac{Q_h}{Q_{h'}} = 1 + \frac{Q_{c-d}}{Q_{a-b}} = 1 + \frac{c_v (\tau_d - \tau_c)}{c_v (\tau_b - \tau_a)}.$$ \hspace{1cm} (2.297)

Since $\tau V^{\gamma-1}$ remains unchanged in an isentropic process, where

$$\gamma = \frac{c_p}{c_v},$$ \hspace{1cm} (2.298)

one finds that

$$\tau_b V_1^{\gamma-1} = \tau_c V_2^{\gamma-1},$$ \hspace{1cm} (2.299)

$$\tau_d V_2^{\gamma-1} = \tau_a V_1^{\gamma-1},$$ \hspace{1cm} (2.300)

or

$$\frac{\tau_c}{\tau_b} = \frac{\tau_d}{\tau_a} = \left( \frac{V_2}{V_1} \right)^{1-\gamma},$$ \hspace{1cm} (2.301)

thus

$$\eta = 1 - \left( \frac{V_2}{V_1} \right)^{1-\gamma}.$$ \hspace{1cm} (2.302)

29. 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

$$V_{A2} = V_{B2} = \frac{N\tau_f}{p}.$$ \hspace{1cm} (2.303)
The entropy of an ideal gas of density \( n = N/V \), which contains \( N \) particles, is given by

\[
\sigma = N \left( \log \frac{n_Q}{n} + \frac{5}{2} \right),
\]

where

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

or as a function of \( \tau \) and \( p \)

\[
\sigma = N \left( \log \left( \frac{M}{2\pi\hbar^2} \right)^{3/2} \frac{\tau^{5/2}}{p} + \frac{5}{2} \right).
\]

Thus the change in entropy is given by

\[
\Delta \sigma = \sigma_{\text{final}} - \sigma_{\text{initial}} = \frac{5N}{2} \log \frac{\tau_f^2}{\tau_A \tau_B}.
\]

In general, for an isobaric process the following holds

\[
Q = W + \Delta U = p(V_2 - V_1) + c_V(\tau_2 - \tau_1),
\]

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

\[
Q = (N + c_V)(\tau_2 - \tau_1).
\]

Since no heat is exchanged with the environment during this process the following holds

\[
Q_A + Q_B = 0,
\]

where

\[
Q_A = (N + c_V)(\tau_f - \tau_A),
Q_B = (N + c_V)(\tau_f - \tau_B),
\]

thus

\[
\tau_f = \frac{\tau_A + \tau_B}{2},
\]

and therefore

\[
\Delta \sigma = \frac{5N}{2} \log \frac{(\tau_A + \tau_B)^2}{4\tau_A \tau_B}.
\]
3. Bosonic and Fermionic Systems

In the first part of this chapter we study two Bosonic systems, namely photons and phonons. A photon is the quanta of electromagnetic waves whereas a phonon is the quanta of acoustic waves. In the second part we study two Fermionic systems, namely electrons in metals and electrons and holes in semiconductors.

3.1 Electromagnetic Radiation

In this section we study an electromagnetic cavity in thermal equilibrium.

3.1.1 Electromagnetic Cavity

Consider an empty volume surrounded by conductive walls having infinite conductivity. The Maxwell’s equations in SI units are given by

\[ \nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}, \]  
\[ (3.1) \]

\[ \nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t}, \]  
\[ (3.2) \]

\[ \nabla \cdot \mathbf{E} = 0, \]  
\[ (3.3) \]

and

\[ \nabla \cdot \mathbf{H} = 0, \]  
\[ (3.4) \]

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

\[ \epsilon_0 \mu_0 = \frac{1}{c^2}, \]  
\[ (3.5) \]

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 \( \mathbf{A} \) is chosen such that

\[ \nabla \cdot \mathbf{A} = 0, \]  
\[ (3.6) \]
Chapter 3. Bosonic and Fermionic Systems

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

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t},$$

(3.7)

and

$$\mu_0 \mathbf{H} = \nabla \times \mathbf{A}.$$  

(3.8)

The gauge condition (3.6) and Eqs. (3.7) and (3.8) guarantee that Maxwell’s equations (3.2), (3.3), and (3.4) are satisfied

$$\nabla \times \mathbf{E} = -\frac{\partial (\nabla \times \mathbf{A})}{\partial t} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t},$$

(3.9)

$$\nabla \cdot \mathbf{E} = -\frac{\partial (\nabla \cdot \mathbf{A})}{\partial t} = 0,$$

(3.10)

$$\nabla \cdot \mathbf{H} = \frac{1}{\mu_0} \nabla \cdot (\nabla \times \mathbf{A}) = 0,$$

(3.11)

where in the last equation the general vector identity $\nabla \cdot (\nabla \times \mathbf{A}) = 0$ has been employed. Substituting Eqs. (3.7) and (3.8) into the only remaining nontrivial equation, namely into Eq. (3.1), leads to

$$\nabla \times (\nabla \times \mathbf{A}) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}.$$  

(3.12)

Using the vector identity

$$\nabla \times (\nabla \times \mathbf{A}) = \nabla (\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A},$$  

(3.13)

and the gauge condition (3.6) one finds that

$$\nabla^2 \mathbf{A} = \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2}.$$  

(3.14)

Consider a solution in the form

$$\mathbf{A} = q(t) \mathbf{u}(r),$$

(3.15)

where $q(t)$ is independent on position $\mathbf{r}$ and $\mathbf{u}(\mathbf{r})$ is independent on time $t$. The gauge condition (3.6) leads to

$$\nabla \cdot \mathbf{u} = 0.$$  

(3.16)

From Eq. (3.14) one finds that

$$q \nabla^2 \mathbf{u} = \frac{1}{c^2} \mathbf{u} \frac{d^2 q}{dt^2}.$$  

(3.17)
Multiplying by an arbitrary unit vector $\hat{n}$ leads to

$$
\left(\nabla^2 u + \kappa^2 u\right) = \frac{1}{c^2 q} \frac{d^2 q}{dt^2}.
$$

(3.18)

The left hand side of Eq. (3.18) is a function of $r$ 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

$$
\nabla^2 u + \kappa^2 u = 0,
$$

(3.19)

and

$$
\frac{d^2 q}{dt^2} + \omega^2 \kappa q = 0,
$$

(3.20)

where

$$
\omega \kappa = c \kappa.
$$

(3.21)

Equation (3.19) should be solved with the boundary conditions of a perfectly conductive surface. Namely, on the surface $S$ enclosing the cavity we have $H \cdot \hat{s} = 0$ and $E \times \hat{s} = 0$, where $\hat{s}$ is a unit vector normal to the surface. To satisfy the boundary condition for $E$ we require that $u$ be normal to the surface, namely, $u = \hat{s} (u \cdot \hat{s})$ on $S$. This condition guarantees also that the boundary condition for $H$ is satisfied. To see this we calculate the integral of the normal component of $H$ over some arbitrary portion $S'$ of $S$. Using Eq. (3.8) and Stoke’s theorem one finds that

$$
\int_{S'} (H \cdot \hat{s}) \, ds = \frac{q}{\mu_0} \int_{S'} \left[(\nabla \times u) \cdot \hat{s}\right] \, ds
$$

$$
= \frac{q}{\mu_0} \int_{C} u \cdot dl,
$$

(3.22)

where the close curve $C$ encloses the surface $S'$. Thus, since $u$ is normal to the surface one finds that the integral along the close curve $C$ vanishes, and therefore

$$
\int_{S'} (H \cdot \hat{s}) \, ds = 0.
$$

(3.23)

Since $S'$ is arbitrary we conclude that $H \cdot \hat{s} = 0$ on $S$.

Each solution of Eq. (3.19) that satisfies the boundary conditions is called an eigen mode. As can be seen from Eq. (3.20), the dynamics of a mode amplitude $q$ is the same as the dynamics of an harmonic oscillator having angular frequency $\omega_\kappa = c \kappa$. 

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3.1.2 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

$$\varepsilon_s = s \hbar \omega_\kappa,$$

(3.24)

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. (1.69)

$$Z_\kappa = \sum_{s=0}^{\infty} \exp (-s \beta \hbar \omega_\kappa) = \frac{1}{1 - \exp (-\beta \hbar \omega_\kappa)}.$$

(3.25)

Note the similarity between this result and the orbital partition function $\zeta$ of Bosons given by Eq. (2.36). The average energy is found using

$$\langle \varepsilon_\kappa \rangle = -\frac{\partial \log Z_\kappa}{\partial \beta} = \frac{\hbar \omega_\kappa}{e^{\beta \hbar \omega_\kappa} - 1}.$$

(3.26)

The partition function of the entire system is given by

$$Z = \prod_\kappa Z_\kappa,$$

(3.27)

and the average total energy by

$$U = -\frac{\partial \log Z}{\partial \beta} = \sum_\kappa \langle \varepsilon_\kappa \rangle.$$

(3.28)

3.1.3 Cube Cavity

For simplicity, consider the case of a cavity shaped as a cube of volume $V = L^3$. We seek solutions of Eq. (3.19) satisfying the boundary condition

\(^1\)In Eq. (3.24) 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 \( u \) vanishes on the walls. Consider a solution having the form

\[
\begin{align*}
u_x &= \sqrt{\frac{8}{V}} a_x \cos (k_x x) \sin (k_y y) \sin (k_z z), \\
u_y &= \sqrt{\frac{8}{V}} a_y \sin (k_x x) \cos (k_y y) \sin (k_z z), \\
u_z &= \sqrt{\frac{8}{V}} a_z \sin (k_x x) \sin (k_y y) \cos (k_z z).
\end{align*}
\tag{3.29}
\]

(3.29)

\[
\begin{align*}
u_x &= \sqrt{\frac{8}{V}} a_x \cos (k_x x) \sin (k_y y) \sin (k_z z), \\
u_y &= \sqrt{\frac{8}{V}} a_y \sin (k_x x) \cos (k_y y) \sin (k_z z), \\
u_z &= \sqrt{\frac{8}{V}} a_z \sin (k_x x) \sin (k_y y) \cos (k_z z).
\end{align*}
\tag{3.30}
\]

(3.30)

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

\[
\begin{align*}
k_x &= \frac{n_x \pi}{L}, \\
k_y &= \frac{n_y \pi}{L}, \\
k_z &= \frac{n_z \pi}{L},
\end{align*}
\tag{3.32}
\]

(3.32)

\[
\begin{align*}
k_x &= \frac{n_x \pi}{L}, \\
k_y &= \frac{n_y \pi}{L}, \\
k_z &= \frac{n_z \pi}{L},
\end{align*}
\tag{3.33}
\]

(3.33)

\[
\begin{align*}
k_x &= \frac{n_x \pi}{L}, \\
k_y &= \frac{n_y \pi}{L}, \\
k_z &= \frac{n_z \pi}{L},
\end{align*}
\tag{3.34}
\]

(3.34)

where \( n_x, n_y \) and \( n_z \) are integers. This solution clearly satisfies Eq. (3.19) where the eigen value \( \kappa \) is given by

\[
\kappa = \sqrt{k_x^2 + k_y^2 + k_z^2}.
\tag{3.35}
\]

(3.35)

Alternatively, using the notation

\[
\mathbf{n} = (n_x, n_y, n_z),
\tag{3.36}
\]

(3.36)

one has

\[
\kappa = \frac{\pi}{L} \mathbf{n},
\tag{3.37}
\]

(3.37)

where

\[
n = \sqrt{n_x^2 + n_y^2 + n_z^2}.
\tag{3.38}
\]

(3.38)

Using Eq. (3.21) one finds that the angular frequency of a mode characterized by the vector of integers \( \mathbf{n} \) is given by

\[
\omega_{\mathbf{n}} = \frac{\pi c}{L} n.
\tag{3.39}
\]

(3.39)

In addition to Eq. (3.19) and the boundary condition, each solution has to satisfy also the transversality condition \( \nabla \cdot \mathbf{u} = 0 \) (3.16), which in the present case reads

\[
\mathbf{n} \cdot \mathbf{a} = 0.
\tag{3.40}
\]

(3.40)
where
\[ a = (a_x, a_y, a_z) \] .

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.

### 3.1.4 Average Energy

The average energy \( U \) of the system is found using Eqs. (3.26), (3.28) and (3.39)

\[
U = \sum_n \frac{\hbar \omega_n}{e^{\beta \hbar \omega_n} - 1} = 2\tau \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{\alpha n}{e^{\alpha n} - 1},
\]

(3.42)

where the dimensionless parameter \( \alpha \) is given by
\[ \alpha = \frac{\beta \hbar \pi c}{L} \].

(3.43)

The following relation can be employed to estimate the dimensionless parameter \( \alpha \)
\[ \alpha = \frac{2.4 \times 10^{-3}}{L \text{ cm} \ 300 \text{ K}} \].

(3.44)

In the limit where
\[ \alpha \ll 1 \]

(3.45)

the sum can be approximated by the integral
\[ U \simeq 2\tau \frac{4\pi}{8} \int_0^{\infty} dn \ n^2 \frac{\alpha n}{e^{\alpha n} - 1} \].

(3.46)

Employing the integration variable transformation [see Eq. (3.39)]
\[ n = \frac{L}{\pi c} \omega \],

(3.47)

allows expressing the energy per unit volume \( U/V \) as
\[ \frac{U}{V} = \int_0^{\infty} d\omega \ u_\omega \],

(3.48)
3.1. Electromagnetic Radiation

where

\[ u_\omega = \frac{{\hbar \omega^3}}{c^3\pi^2 e^{\beta \hbar \omega} - 1}. \]  \hspace{1cm} (3.49)

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

\[ \frac{\lambda_0}{\mu m} = 5.1 \left( \frac{T}{1000 \text{ K}} \right)^{-1}. \]  \hspace{1cm} (3.50)

The function \( x^3/(e^x - 1) \).

The total energy is found by integrating Eq. (3.48) and by employing the variable transformation \( x = \beta \hbar \omega \)

\[ \frac{U}{V} = \frac{\tau^4}{c^3\pi^2 \hbar^3} \int_0^\infty \frac{x^3dx}{e^x - 1} \]

\[ = \frac{\pi^2 \tau^4}{15 \hbar^3 c^3}. \]  \hspace{1cm} (3.51)

3.1.5 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. 3.1, which has volume
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Fig. 3.1. Radiation emitted through a small hole in the cavity wall.

\[ V_\theta = dA \cos \theta \times c dt . \] (3.52)

The average energy in that region can be found using Eq. (3.51). Integrating over all possible directions yields the total rate of energy radiation emitted from the hole per unit area

\[
J = \frac{1}{dA dt} \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\varphi \frac{U}{V} V_\theta
\]

\[
= \frac{\pi^2 \tau^4}{15 \hbar^3 c^2} \frac{1}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \cos \theta \int_0^{2\pi} d\varphi
\]

\[
= \frac{\pi^2 \tau^4}{60 \hbar^3 c^2}
\] (3.53)

In terms of the historical definition of temperature \( T = \tau/k_B \) [see Eq. (1.92)] one has

\[ J = \sigma_B T^4 , \] (3.54)

where \( \sigma_B \), which is given by

\[ \sigma_B = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \frac{W}{m^2 K^4} , \] (3.55)

is the Stefan-Boltzmann constant.
3.2 Phonons in Solids

In this section we study elastic waves in solids. We start with a one-dimensional example, and then generalize some of the results for the case of a 3D lattice.

3.2.1 One Dimensional Example

Consider the 1D lattice shown in Fig. 3.2 below, which contains \( N \) 'atoms' having mass \( m \) each that are attached to each other by springs having spring constant \( m\omega^2 \). The lattice spacing is \( a \). The atoms are allowed to move in one dimension along the array axis. In problem 5 of set 3 one finds that the normal mode angular eigen-frequencies are given by

\[
\omega_n = \omega \sqrt{2 \left( 1 - \cos k_n a \right)} = 2\omega \left| \sin \frac{k_n a}{2} \right|,
\]

where \( a \) is the lattice spacing,

\[
k_n = \frac{2\pi n}{aN},
\]

and \( n \) is integer ranging from \(-N/2\) to \(N/2\).
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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, where we have discussed EM modes, the quantum eigenenergies of the mode are

$$\varepsilon_s = s \hbar \omega_n$$

(3.58)

where $s = 0, 1, 2, \ldots$ 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. (1.69)

$$Z_\kappa = \sum_{s=0}^{\infty} \exp (-s \beta \hbar \omega_\kappa) = \frac{1}{1 - \exp (-\beta \hbar \omega_\kappa)}$$

(3.59)

Similarly to the EM case, the average total energy is given by

$$U = \sum_{n=-N/2}^{N/2} \frac{\hbar \omega_n}{\exp (\beta \hbar \omega_n) - 1}$$

(3.60)

where $\beta = 1/\tau$, and the total heat capacity is given by

$$C_V = \frac{\partial U}{\partial \tau} = \sum_{n=-N/2}^{N/2} \frac{(\beta \hbar \omega_n)^2 \exp (\beta \hbar \omega_n)}{[\exp (\beta \hbar \omega_n) - 1]^2}$$

(3.61)

**High Temperature Limit.** In the high temperature limit $\beta \hbar \omega \ll 1$

$$\frac{(\beta \hbar \omega_n)^2 \exp (\beta \hbar \omega_n)}{[\exp (\beta \hbar \omega_n) - 1]^2} \simeq 1$$

(3.62)

therefore

$$C_V = N$$

(3.63)

**Low Temperature Limit.** In the low temperature limit $\beta \hbar \omega \gg 1$ the main contribution to the sum in Eq. (3.61) comes from terms for which $|n| \lesssim N/\beta \hbar \omega$. Thus, to a good approximation the dispersion relation can be approximated by

$$\omega_n = 2 \omega \left| \sin \frac{k_n a}{2} \right| \simeq 2 \omega \left| \frac{k_n a}{2} \right| = \omega \frac{2 \pi}{N} |n|$$

(3.64)

Moreover, in the limit $N \gg 1$ the sum in Eq. (3.61) can be approximated by an integral, and to a good approximation the upper limit $N/2$ can be substituted by infinity, thus
3.2. Phonons in Solids

\[ C_V = \sum_{n=-N/2}^{N/2} \frac{(\beta \hbar \omega_n)^2 \exp(\beta \hbar \omega_n)}{[\exp(\beta \hbar \omega_n) - 1]^2} \]

\[ \simeq 2 \sum_{n=0}^{\infty} \frac{(\beta \hbar \omega_2 \pi n)^2 \exp(\beta \hbar \omega_2 \pi n)}{[\exp(\beta \hbar \omega_2 \pi n) - 1]^2} \]

\[ \simeq 2 \int_0^{\infty} dn \frac{(\beta \hbar \omega_2 \pi n)^2 \exp(\beta \hbar \omega_2 \pi n)}{[\exp(\beta \hbar \omega_2 \pi n) - 1]^2} \]

\[ = \frac{N \tau}{\pi \hbar \omega} \int_0^{\infty} dx \frac{x^2 \exp(x)}{(\exp(x) - 1)^2} \]

\[ = \frac{N \pi \tau}{3 \hbar \omega} . \]  \hspace{1cm} (3.65)

3.2.2 The 3D Case

The case of a 3D lattice is similar to the case of EM cavity that we have 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 \( \mathbf{k} \) there are 3, instead of only 2, orthogonal modes (polarizations).
3. Dispersion: contrary to the EM case, the dispersion relation (namely, the function \( \omega(\mathbf{k}) \)) is in general nonlinear.

Due to distinctions 1 and 2, the sum over all modes is substituted by an integral according to

\[ \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \rightarrow \frac{3}{8} \int_0^{n_D} dn \ n^2 , \]  \hspace{1cm} (3.66)

where the factor of 3 replaces the factor of 2 we had in the EM case. Moreover, the upper limit is \( n_D \) instead of infinity, where \( n_D \) is determined from the requirement

\[ \frac{3}{8} \int_0^{n_D} dn \ n^2 = 3N , \]  \hspace{1cm} (3.67)

thus

\[ n_D = \left( \frac{6N}{\pi} \right)^{1/3} . \]  \hspace{1cm} (3.68)
Similarly to the EM case, the average total energy is given by

\[ U = \sum_n \frac{\hbar \omega_n}{\exp (\beta \hbar \omega_n) - 1} \]

\[ = \frac{3\pi}{2} \int_0^{n_D} dn \ n^2 \frac{\hbar \omega_n}{\exp (\beta \hbar \omega_n) - 1}. \]

(3.69)  

(3.70)

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

\[ \omega_n = v k_n, \]

(3.71)

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

\[ k_n = \frac{\pi n}{L}, \]

(3.72)

where \( L = V^{1/3} \) and \( V \) is the volume. In this approximation one finds using the variable transformation

\[ x = \frac{\beta \hbar \nu \pi n}{L}, \]

(3.73)

that

\[ U = \frac{3\pi}{2} \int_0^{n_D} dn \ n^2 \frac{\hbar \nu \pi n}{L} \frac{\frac{\hbar \nu n}{L}}{\exp \left( \frac{\beta \hbar \nu n}{L} \right) - 1} \]

\[ = \frac{3V \tau^4}{2\hbar^3 v^3 \pi^3} \int_0^{x_D} dx \ x^3 \frac{\exp x - 1}{\exp x - 1}. \]

(3.74)

where

\[ x_D = \frac{\beta \hbar \nu \pi n_D}{L} = \frac{\beta \hbar \nu \pi \left( \frac{2N}{V} \right)^{1/3}}{L}. \]

Alternatively, in terms of the Debye temperature, which is defined as

\[ \Theta = \hbar v \left( \frac{6\pi^2 N}{V} \right)^{1/3}, \]

(3.75)

one has
3.2. Phonons in Solids

\[ x_D = \frac{\Theta}{\tau}, \quad (3.76) \]

and

\[ U = 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{\exp x - 1}. \quad (3.77) \]

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

\[
\begin{align*}
U &\approx 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^\infty dx \, x^2 \\
&= 9N\tau \left( \frac{T}{\Theta} \right)^3 \frac{x_D^3}{3} \\
&= 3N\tau, \quad (3.78)
\end{align*}
\]

and therefore

\[ C_V = \frac{\partial U}{\partial \tau} = 3N. \quad (3.79) \]

Note that in this limit the average 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

\[
\begin{align*}
U &\approx 9N\tau \left( \frac{T}{\Theta} \right)^3 \int_0^\infty dx \frac{x^3}{\exp x - 1} \\
&\approx \frac{3\pi^4}{5} N\tau \left( \frac{T}{\Theta} \right)^3,
\end{align*}
\]

(3.80)
and therefore
\[ C_V = \frac{\partial U}{\partial \tau} = \frac{12\pi^4}{5} N \left( \frac{\tau}{\Theta} \right)^3. \] (3.81)

Note that Eq. (3.80) together with Eq. (3.75) yield
\[ \frac{U}{V} = 3 \frac{\pi^2 \tau^4}{2 \frac{15}{2} \hbar^3 \nu^3}. \] (3.82)

Note the similarity between this result and Eq. (3.51) for the EM case.

### 3.3 Fermi Gas

In this section we study an ideal gas of Fermions of mass \( m \). While only the classical limit was considered in chapter 2, here we consider the more general case.

#### 3.3.1 Orbital Partition Function

Consider an orbital having energy \( \varepsilon_n \). Disregarding internal degrees of freedom, its grandcanonical Fermionic partition function is given by [see Eq. (2.33)]
\[ \zeta_n = 1 + \lambda \exp(-\beta \varepsilon_n), \] (3.83)
where
\[ \lambda = \exp(\beta \mu) = e^{-\eta}, \] (3.84)
is the fugacity and \( \beta = 1/\tau \). Taking into account internal degrees of freedom the grandcanonical Fermionic partition function becomes
\[ \zeta_n = \prod_l (1 + \lambda \exp(-\beta \varepsilon_n) \exp(-\beta E_l)), \] (3.85)
where \( \{E_l\} \) are the eigenenergies of a particle due to internal degrees of freedom [see Eq. (2.71)]. As is required by the Pauli exclusion principle, no more than one Fermion can occupy a given internal eigenstate and a given orbital.

#### 3.3.2 Partition Function of the Gas

The grandcanonical partition function of the gas is given by
\[ Z_{gc} = \prod_n \zeta_n. \] (3.86)
As we have seen in chapter 2, the orbital eigenenergies of a particle of mass $m$ in a box are given by Eq. (2.5)

$$\varepsilon_n = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2,$$

where

$$n = (n_x, n_y, n_z),$$

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2},$$

$$n_x, n_y, n_z = 1, 2, 3, \ldots,$$

and $L^3 = V$ is the volume of the box. Thus, $\log Z_{gc}$ can be written as

$$\log Z_{gc} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log \zeta_n.$$  \hspace{1cm} (3.91)

Alternatively, using the notation

$$\alpha^2 = \frac{\beta \hbar^2 \pi^2}{2mL^2},$$

and Eq. (3.85) one has

$$\log Z_{gc} = \sum_{l} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log \left(1 + \lambda \exp \left(-\alpha^2 n^2\right) \exp \left(-\beta E_l\right)\right).$$  \hspace{1cm} (3.93)

For a macroscopic system $\alpha \ll 1$, and consequently the sum over $n$ can be approximately replaced by an integral

$$\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{1}{8} \frac{1}{4} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} dn n^2,$$

thus, one has

$$\log Z_{gc} = \frac{\pi}{2} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \frac{1}{1^2} \frac{1}{4} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} dn n^2 \log \left(1 + \lambda \exp \left(-\alpha^2 n^2\right) \exp \left(-\beta E_l\right)\right).$$  \hspace{1cm} (3.95)

This can be further simplified by employing the variable transformation

$$\beta \varepsilon = \alpha^2 n^2.$$  \hspace{1cm} (3.96)

The following holds
\[
\frac{\sqrt{\frac{2}{\beta}}}{\sqrt{\alpha^2}}^{3/2} d\varepsilon = n^2 dn.
\]
Thus, by introducing the density of states
\[
D(\varepsilon) = \begin{cases} 
\frac{V}{\pi} (\frac{2m}{\hbar^2})^{3/2} \varepsilon^{1/2} & \varepsilon \geq 0, \\
0 & \varepsilon < 0,
\end{cases}
\]  
(3.97)
one has
\[
\log Z_{gc} = \frac{1}{2} \sum_l \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) \log (1 + \lambda \exp (-\beta (\varepsilon + E_l))).
\]  
(3.98)

### 3.3.3 Energy and Number of Particles

Using Eqs. (1.80) and (1.94) for the energy \( U \) and the number of particles \( N \), namely using
\[
U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right) \eta,
\]  
(3.99)
\[
N = \lambda \left( \frac{\partial \log Z_{gc}}{\partial \lambda} \right),
\]  
(3.100)
one finds that
\[
U = \frac{1}{2} \sum_l \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) (\varepsilon + E_l) f_{FD}(\varepsilon + E_l),
\]  
(3.101)
\[
N = \frac{1}{2} \sum_l \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) f_{FD}(\varepsilon + E_l),
\]  
(3.102)
where \( f_{FD} \) is the Fermi-Dirac distribution function [see Eq. (2.35)]
\[
f_{FD}(\varepsilon) = \frac{1}{\exp(\beta (\varepsilon - \mu)) + 1}.
\]  
(3.103)

### 3.3.4 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. (3.101) and (3.102) become
3.3. Fermi Gas

\[ U = \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) \varepsilon f_{FD}(\varepsilon), \]  

(3.104)

\[ N = \int_{-\infty}^{\infty} d\varepsilon \, D(\varepsilon) f_{FD}(\varepsilon), \]  

(3.105)

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 3.3.1.** 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

\[
\int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) f_{FD}(\varepsilon) \\
= \int_{-\infty}^{\mu} d\varepsilon \, g(\varepsilon) + \frac{\pi^2 g'(\mu)}{6\beta^2} + O \left( \frac{1}{\beta \mu} \right)^4.
\]

**Proof.** See problem 7 of set 3.

With the help of this theorem the number of particles \( N \) to second order in \( \tau \) is given by

\[ N = \int_{-\infty}^{\mu} d\varepsilon \, D(\varepsilon) + \frac{\pi^2 \tau^2 D'(\mu)}{6}. \]  

(3.106)

Moreover, at low temperatures, the chemical potential is expected to be close the the Fermi energy \( \varepsilon_F \), which is defined by

\[ \varepsilon_F = \lim_{\tau \to 0} \mu. \]  

(3.107)

Thus, to lowest order in \( \mu - \varepsilon_F \) one has

\[
\int_{-\infty}^{\mu} d\varepsilon \, D(\varepsilon) = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) + (\mu - \varepsilon_F) D(\varepsilon_F) + O(\mu - \varepsilon_F)^2,
\]

(3.108)

and therefore

\[ N = N_0 + (\mu - \varepsilon_F) D(\varepsilon_F) + \frac{\pi^2 \tau^2 D'(\varepsilon_F)}{6}, \]  

(3.109)

where
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\[ N_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) , \quad (3.110) \]

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

\[ \mu = \varepsilon_F - \frac{\pi^2 D'(\varepsilon_F)}{6 \beta^2 D(\varepsilon_F)} . \quad (3.111) \]

Similarly, the energy \( U \) at low temperatures is given approximately by

\[
U = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \left[ \varepsilon f_{FD}(\varepsilon) \right.
\]

\[
= \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \left[ \varepsilon + (\mu - \varepsilon_F) D(\varepsilon) \right] + \varepsilon_F D(\varepsilon) D(\varepsilon) + \varepsilon_F D(\varepsilon) \right]
\]

\[
= U_0 - \frac{\pi^2 \tau^2 D'(\varepsilon_F)}{6 D(\varepsilon_F)} D(\varepsilon) \varepsilon_F + \frac{\pi^2 \tau^2}{6 D(\varepsilon_F)} D'(\varepsilon) \varepsilon_F + D(\varepsilon_F))
\]

\[
= U_0 + \frac{\pi^2 \tau^2}{6} D(\varepsilon_F) , \quad (3.112)
\]

where

\[ U_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \varepsilon . \quad (3.113) \]

From this result one finds that the electronic heat capacity is given by

\[ C_V = \frac{\partial U}{\partial \tau} = \frac{\pi^2 \tau^2}{3} D(\varepsilon_F) . \quad (3.114) \]

Comparing this result with Eq. (3.81) 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.

### 3.4 Semiconductor Statistics

To be written...
3.5 Problems Set 3

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 $\tau = k_B \times 3\, \text{K}$.

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 $T_{\text{Sun}} = 5800\, \text{K}$; $R_{\text{Sun}} = 6.96 \times 10^8$ 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

$$p = \frac{U}{3V}. \quad (3.115)$$

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. 3.2). Denote the lattice spacing by $a$. Show that the normal mode eigen-frequencies are given by

$$\omega_n = \omega \sqrt{2(1 - \cos k_n a)} \quad (3.116)$$

where $k_n = 2\pi n/aN$, and $n$ is integer ranging from $-N/2$ to $N/2$ (assume $N \gg 1$).

7. Consider an orbital with energy $\varepsilon$ in an ideal gas. The system is in thermal equilibrium at temperature $\tau$ and chemical potential $\mu$.

a) Show that the probability that the orbital is occupied by $n$ particles is given by

$$p_F(n) = \frac{\exp [n(\mu - \varepsilon)\beta]}{1 + \exp [(\mu - \varepsilon)\beta]}, \quad (3.117)$$

for the case of Fermions, where $n \in \{0, 1\}$, and by

$$p_B(n) = (1 - \exp [(\mu - \varepsilon)\beta]) \exp [n(\mu - \varepsilon)\beta], \quad (3.118)$$

where $n \in \{0, 1, 2, \cdots\}$, for the case of Bosons.

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b) Show that the variance \( (\Delta n)^2 = \langle (n - \langle n \rangle)^2 \rangle \) is given by

\[
(\Delta n)^2_F = \langle n \rangle_F (1 - \langle n \rangle_F) ,
\]

for the case of Fermions, and by

\[
(\Delta n)^2_B = \langle n \rangle_B (1 + \langle n \rangle_B) ,
\]

for the case of Bosons.

8. 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 \( \varepsilon \to \infty \). Show that the following holds (Sommerfeld expansion)

\[
I = \int_{-\infty}^{\infty} d\varepsilon \ g(\varepsilon) \ f_{FD}(\varepsilon)
= \int_{-\infty}^{\mu} d\varepsilon \ g(\varepsilon) + \frac{\pi^2 g'(\mu)}{6\beta^2} + O \left( \frac{1}{\beta \mu} \right)^4 .
\]

9. Consider a metal at zero temperature having Fermi energy \( \varepsilon_F \), 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

\[
\alpha = \frac{\langle v^2 \rangle}{\langle v \rangle^2} .
\]

(3.121)

c) Calculate the pressure exerted by an electron gas at zero temperature.

10. For electrons with energy \( \varepsilon \gg mc^2 \) (relativistic fermi gas), the energy is given by \( \varepsilon = pc \). Find the fermi energy of this gas and show that the ground state energy is

\[
E(T = 0) = \frac{3}{4} N \varepsilon_F
\]

(3.122)

11. 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

\[
\mu = \tau \log \left[ \exp \left( \frac{n \pi \hbar^2}{m_e \tau} \right) - 1 \right] .
\]

(3.123)
3.6 Solutions Set 3

1. The density of states of the photon gas is given by

\[ dg = \frac{V \varepsilon^2}{\pi^2 \hbar^3 c^3} d\varepsilon. \]  

(3.124)

Thus

\[ N = \frac{V}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\varepsilon^2}{e^{\varepsilon/\tau} - 1} d\varepsilon \]

\[ = V \left( \frac{\tau}{\hbar c} \right)^3 \alpha, \]

(3.125)

where

\[ \alpha = \frac{1}{\pi^2} \int_0^\infty \frac{x^2}{e^x - 1} dx. \]

(3.126)

The number \( \alpha \) is calculated numerically

\[ \alpha = 0.24359. \]

(3.127)

For the universe

\[ N = \frac{4\pi}{3} \left( 10^{26} \text{ m} \right)^3 \left( \frac{1.380568 \times 10^{-23} \text{ J K}^{-1} \text{ K}}{1.05457266 \times 10^{-34} \text{ Js}2.99792458 \times 10^8 \text{ m s}^{-1}} \right)^3 \times 0.24359 \]

\[ \simeq 2.29 \times 10^{87}. \]

(3.128)

2. The energy emitted by the Sun is

\[ E_{\text{Sun}} = 4\pi R_{\text{Sun}}^2 \sigma_B T_{\text{Sun}}^4, \]

(3.129)

and the energy emitted by a planet is

\[ E_{\text{planet}} = 4\pi R_{\text{planet}}^2 \sigma_B T_{\text{planet}}^4. \]

(3.130)

The fraction of Sun energy that planet receives is

\[ \frac{\pi R_{\text{planet}}^2}{4\pi D_{\text{M-S}}^2} E_{\text{Sun}}, \]

(3.131)

and this equals to the energy it reradiates. Therefore

\[ \frac{\pi R_{\text{planet}}^2}{4\pi D^2} E_{\text{Sun}} = E_{\text{planet}}, \]
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thus

\[ T_{\text{planet}} = \sqrt{\frac{R_{\text{Sun}}}{2D} T_{\text{Sun}}} , \]

and for Mars

\[ T_{\text{Mars}} = \sqrt{\frac{6.96 \times 10^8 \, \text{m}}{2 \times 2.28 \times 10^{11} \, \text{m}}} 5800 \, \text{K} = 226 \, \text{K} . \]

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 \( J_r = J_B \alpha \), where \( J_B = \sigma_B T^4 \) [see Eq. (3.54)]. The ERPUA from the first (second) surface can be expressed as \( J_{r1} = J_{a11} + J_{a21} \) (\( J_{r2} = J_{a12} + J_{a22} \)), where \( J_{amn} \) denotes the energy absorbed per unit area (EAPUA) by surface \( m \) due to ERPUA originating from surface \( n \), and the following holds

\[
J_{a11} = J_{r1} (1 - \alpha_2) \alpha_1 s , \hspace{1cm} (3.132)
\]

\[
J_{a21} = J_{r1} \alpha_2 s , \hspace{1cm} (3.133)
\]

\[
J_{a12} = J_{r2} \alpha_1 s , \hspace{1cm} (3.134)
\]

\[
J_{a22} = J_{r2} (1 - \alpha_1) \alpha_2 s , \hspace{1cm} (3.135)
\]

where

\[
s = \sum_{n=0}^{\infty} (1 - \alpha_1)^n (1 - \alpha_2)^n = \frac{1}{1 - (1 - \alpha_1)(1 - \alpha_2)} , \hspace{1cm} (3.136)
\]

thus

\[
J_{21} = J_{r1} - J_{a11} - J_{a12}
\]

\[
= (J_{B1} - J_{B2}) \alpha_1 \alpha_2 s
\]

\[
= \sigma_B (T_1^4 - T_2^4) \frac{1}{\alpha_1 + \alpha_2 - 1} . \hspace{1cm} (3.137)
\]

4. The partition function is given by

\[
Z = \prod_{n}^{\infty} \sum_{s=0}^{\infty} \exp (s \beta \hbar \omega_n) = \prod_{n}^{\infty} \frac{1}{1 - \exp (-\beta \hbar \omega_n)} ,
\]

thus the free energy is given by

\[
F = -\tau \log Z = \tau \sum_{n} \log [1 - \exp (-\beta \hbar \omega_n)] .
\]
Transforming the sum over modes into integral yields

\[ F = \tau \pi \int_0^\infty dnn^2 \log \left[ 1 - \exp \left( -\beta \hbar \omega_n \right) \right] \]

or, by integrating by parts

\[ F = -\frac{1}{3} \frac{\hbar \pi^2 c}{L} \int_0^\infty dnn^3 \frac{n^3}{\exp \left( \frac{\beta \hbar \pi c n}{L} \right) - 1} = \frac{1}{3} U , \]

where

\[ U = \frac{\pi^2 \tau^4 V}{45 \hbar^3 c^3} . \]  

Thus

\[ p = -\left( \frac{\partial F}{\partial V} \right)_T = \frac{U}{3V} . \]  

5. Using the expression for Helmholtz free energy, which was derived in the previous problem,

\[ F = -\frac{U}{3} = -\frac{\pi^2 \tau^4 V}{45 \hbar^3 c^3} , \]

one finds that the entropy is given by

\[ \sigma = -\left( \frac{\partial F}{\partial \tau} \right)_V = \frac{4\pi^2 \tau^3 V}{45 \hbar^3 c^3} . \]

Thus, for an isentropic process, for which \( \sigma \) is a constant, one has

\[ \tau_2 = \tau_1 \left( \frac{V_1}{V_2} \right)^{1/3} . \]

Using again the previous problem, the pressure \( p \) is given by

\[ p = \frac{U}{3V} , \]

thus

\[ p = \frac{\pi^2 \tau^4}{45 \hbar^3 c^3} , \]

and

\[ p_2 = \frac{\pi^2 \tau^4}{45 \hbar^3 c^3} \left( \frac{V_1}{V_2} \right)^{4/3} . \]
6. Let $u(na)$ be the displacement of point particle number $n$. The equations of motion are given by

$$m\ddot{u}(na) = -m\omega^2 \{2u(na) - u[(n-1)a] - u[(n+1)a]\}. \quad (3.141)$$

Consider a solution of the form

$$u(na, t) = e^{i(kn a - \omega_n t)}. \quad (3.142)$$

Periodic boundary condition requires that

$$e^{ik Na} = 1, \quad (3.143)$$

thus

$$k_n = \frac{2\pi n}{da}. \quad (3.144)$$

Substituting in Eq. 3.141 yields

$$-m\omega^2 u(na) = -m\omega^2 \left[2u(na) - u(na)e^{-ika} - u(na)e^{ika}\right], \quad (3.145)$$

or

$$\omega_n = \omega \sqrt{2(1 - \cos k_n a)} = 2\omega \left|\sin \frac{k_n a}{2}\right|. \quad (3.146)$$

7. In general using Gibbs factor

$$p(n) = \frac{\exp \left[n(\mu - \varepsilon)\beta\right]}{\sum_{n'} \exp \left[n'(\mu - \varepsilon)\beta\right]}, \quad (3.147)$$

where $\beta = 1/\tau$, one finds for Fermions

$$p_F(n) = \frac{\exp \left[n(\mu - \varepsilon)\beta\right]}{1 + \exp \left[(\mu - \varepsilon)\beta\right]}, \quad (3.148)$$

where $n \in \{0, 1\}$, and for Bosons

$$p_B(n) = \frac{\exp \left[n(\mu - \varepsilon)\beta\right]}{\sum_{n'=0}^{\infty} \exp \left[n'(\mu - \varepsilon)\beta\right]} = \{1 - \exp \left[(\mu - \varepsilon)\beta\right]\} \exp \left[n(\mu - \varepsilon)\beta\right], \quad (3.149)$$

where $n \in \{0, 1, 2, \cdots \}$. The expectation value of $\langle n \rangle$ in general is given by
\[ \langle n \rangle = \sum_{n'} n' p(n') = \frac{\sum_{n'} n' \exp \left[ n (\mu - \varepsilon) \beta \right]}{\sum_{n'} \exp \left[ n' (\mu - \varepsilon) \beta \right]} , \quad (3.150) \]

thus for Fermions
\[ \langle n \rangle_F = \frac{1}{\exp \left[ (\varepsilon - \mu) \beta \right] + 1} , \quad (3.151) \]

and for Bosons
\[ \langle n \rangle_B = \{ 1 - \exp \left[ (\mu - \varepsilon) \beta \right] \} \sum_{n'=0}^{\infty} n' \exp \left[ n' (\mu - \varepsilon) \beta \right] \]
\[ = \{ 1 - \exp \left[ (\mu - \varepsilon) \beta \right] \} \frac{\exp \left[ (\mu - \varepsilon) \beta \right]}{\left( 1 - \exp \left[ (\mu - \varepsilon) \beta \right] \right)^2} \]
\[ = \frac{1}{\exp \left[ (\varepsilon - \mu) \beta \right] - 1} . \quad (3.152) \]

In general, the following holds
\[ \tau \left( \frac{\partial \langle n \rangle}{\partial \mu} \right)_\tau = \frac{\sum_{n''} (n'')^2 \exp \left[ n (\mu - \varepsilon) \beta \right]}{\sum_{n'} \exp \left[ n' (\mu - \varepsilon) \beta \right]} - \left( \frac{\sum_{n'} n' \exp \left[ n' (\mu - \varepsilon) \beta \right]}{\sum_{n'} \exp \left[ n' (\mu - \varepsilon) \beta \right]} \right)^2 \]
\[ = \langle n^2 \rangle - \langle n \rangle^2 = \langle (n - \langle n \rangle)^2 \rangle . \quad (3.153) \]

Thus
\[ (\Delta n)_F^2 = \frac{\exp \left[ (\varepsilon - \mu) \beta \right]}{\left( \exp \left[ (\varepsilon - \mu) \beta \right] + 1 \right)^2} = \langle n \rangle_F (1 - \langle n \rangle_F) , \quad (3.154) \]
\[ (\Delta n)_B^2 = \frac{\exp \left[ (\varepsilon - \mu) \beta \right]}{\left( \exp \left[ (\varepsilon - \mu) \beta \right] - 1 \right)^2} = \langle n \rangle_B (1 + \langle n \rangle_B) . \quad (3.155) \]

8. Let
\[ G(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' g(\varepsilon') . \quad (3.156) \]

Integration by parts yields
Chapter 3. Bosonic and Fermionic Systems

\[
I = \int_{-\infty}^{\infty} d\varepsilon \ g(\varepsilon) \ f_{FD}(\varepsilon)
\]

\[
= \left[ G(\varepsilon) f_{FD}(\varepsilon) \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} d\varepsilon \ \frac{\partial f_{FD}}{\partial \varepsilon}(\varepsilon), \tag{3.157}
\]

where the following holds

\[
\left( -\frac{\partial f_{FD}}{\partial \varepsilon} \right) = \frac{\beta e^{\beta(\varepsilon-\mu)}}{(e^{\beta(\varepsilon-\mu)} + 1)^2} = \frac{\beta}{4 \cosh^2 \left( \frac{\beta}{2} (\varepsilon - \mu) \right)}. \tag{3.158}
\]

Using the Taylor expansion of \( G(\varepsilon) \) about \( \varepsilon - \mu \), which has the form

\[
G(\varepsilon) = \sum_{n=0}^{\infty} \frac{G^{(n)}(\mu)}{n!} (\varepsilon - \mu)^n, \tag{3.159}
\]

yields

\[
I = \sum_{n=0}^{\infty} \frac{G^{(n)}(\mu)}{n!} \int_{-\infty}^{\infty} \frac{\beta (\varepsilon - \mu)^n d\varepsilon}{4 \cosh^2 \left( \frac{\beta}{2} (\varepsilon - \mu) \right)}. \tag{3.160}
\]

Employing the variable transformation

\[
x = \beta (\varepsilon - \mu), \tag{3.161}
\]

and exploiting the fact that \( -\partial f_{FD}/\partial \varepsilon \) is an even function of \( \varepsilon - \mu \) leads to

\[
I = \sum_{n=0}^{\infty} \frac{G^{(2n)}(\mu)}{(2n)! \beta^{2n}} \int_{-\infty}^{\infty} \frac{x^{2n} dx}{4 \cosh^2 \frac{x}{\beta}}. \tag{3.162}
\]

With the help of the identities

\[
\int_{-\infty}^{\infty} \frac{dx}{4 \cosh^2 \frac{x}{\beta}} = 1, \tag{3.163}
\]

\[
\int_{-\infty}^{\infty} \frac{x^2 dx}{4 \cosh^2 \frac{x}{\beta}} = \frac{\pi^2}{3}, \tag{3.164}
\]

one finds
3.6. Solutions Set 3

\[ I = G(\mu) + \frac{\pi^2 G^{(2)}(\mu)}{6\beta^2} + O \left( \frac{1}{\beta\mu} \right)^4 \]

\[ = \int_{-\infty}^{\mu} d\varepsilon \, g(\varepsilon) + \frac{\pi^2 g'(\mu)}{6\beta^2} + O \left( \frac{1}{\beta\mu} \right)^4. \]

(3.165)

9. In general, at zero temperature the average of the energy \( \varepsilon \) to the power \( n \) is given by

\[ \langle \varepsilon^n \rangle = \frac{\int_0^{\varepsilon_F} d\varepsilon \, D(\varepsilon) \varepsilon^n}{\int_0^{\varepsilon_F} d\varepsilon \, D(\varepsilon)}, \]

(3.166)

where \( D(\varepsilon) \) is the density of states

\[ D(\varepsilon) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}, \]

(3.167)

thus

\[ \langle \varepsilon^n \rangle = \frac{\varepsilon_F^n}{\frac{2n}{3} + 1}. \]

(3.168)

a) Using Eq. (3.168) one finds that

\[ \langle \varepsilon \rangle = \frac{3\varepsilon_F}{5}. \]

(3.169)

b) The speed \( v \) is related to the energy by

\[ v = \sqrt{\frac{2\varepsilon}{m}}, \]

(3.170)

thus

\[ \alpha = \left( \frac{\langle \varepsilon \rangle}{\langle \varepsilon^{1/2} \rangle^2} \right)^2 = \left( \frac{\varepsilon_F}{\frac{3}{2} + 1} \right)^2 = \frac{16}{15}. \]

(3.171)

c) The number of electrons \( N \) is given by

\[ N = \int_0^{\varepsilon_F} d\varepsilon \, D(\varepsilon) = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \int_0^{\varepsilon_F} d\varepsilon \, \varepsilon^{1/2} = \frac{D(\varepsilon_F)}{\varepsilon_F^{1/2}} \frac{2}{3} \varepsilon_F^{3/2}, \]

thus

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\[ \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}, \]  
(3.172)

and therefore

\[ U = \frac{3N}{5} \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}. \]  
(3.173)

Moreover, at zero temperature the Helmholtz free energy \( F = U - T \sigma = U \), thus the pressure is given by

\[
\begin{align*}
p &= -\left( \frac{\partial F}{\partial V} \right)_{\tau,N} \\
&= -\left( \frac{\partial U}{\partial V} \right)_{\tau,N} \\
&= \frac{3N}{5} \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \frac{2}{3V} \\
&= \frac{2N\varepsilon_F}{5V}. \\
\end{align*}
\]

(3.174)

10. The energy of the particles are

\[ \varepsilon_{n,z} = pc \]  
(3.175)

where \( p = \hbar k \), and \( k = \frac{\pi n}{L} \), \( n = \sqrt{n_x^2 + n_y^2 + n_z^2} \) and \( n_i = 1, 2, \cdots \).

Therefore

\[
\begin{align*}
N &= 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_F^3 = \frac{\pi}{3} n_F^3 \\
n_F &= \left( \frac{3N}{\pi} \right)^{1/3} \\
\varepsilon_F &= \frac{\hbar c \pi}{L} \left( \frac{3N}{\pi} \right)^{1/3} = \hbar c \pi \left( \frac{3N}{\pi V} \right)^{1/3}
\end{align*}
\]

(3.176)

The energy is given by

\[
\begin{align*}
E (T = 0) &= \int_0^{\varepsilon_F} \varepsilon g (\varepsilon) d\varepsilon \\
&= \frac{L^3}{\pi^2 \hbar^3 c^3} \int_0^{\varepsilon_F} \varepsilon^3 d\varepsilon \\
&= \frac{L^3}{\pi^2 \hbar^3 c^3} \times \frac{\varepsilon_F^4}{4} = \frac{1}{4} \frac{L^3}{\pi^2 \hbar^3 c^3} \varepsilon_F^3 \times \varepsilon_F = \\
&= \frac{1}{4} \frac{L^3}{\pi^2 \hbar^3 c^3} \frac{3\pi^2 \hbar^3 c^3 N}{L^3} \varepsilon_F = \frac{3}{4} N \varepsilon_F
\end{align*}
\]

(3.177)
11. The energy of an electron having a wave function proportional to \( \exp(ik_x x) \exp(ik_y y) \) is

\[
\frac{\hbar^2}{2m_e} \left( k_x^2 + k_y^2 \right) .
\]  

(3.178)

For periodic boundary conditions one has

\[
k_x = \frac{2\pi n_x}{L_x} ,
\]  

(3.179)

\[
k_y = \frac{2\pi n_y}{L_y} ,
\]  

(3.180)

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)

\[
\frac{2\pi}{\hbar^2} \frac{2m_e E'}{L_x L_y} \frac{E'}{4\pi^2} ,
\]  

(3.181)

thus, the density of state per unit area is given by

\[
D(E) = \begin{cases} 
\frac{m_e}{\pi \hbar^2} & E > 0 \\
0 & E < 0 
\end{cases} .
\]  

(3.182)

Using Fermi-Dirac function

\[
f(E) = \frac{1}{1 + \exp \left[ \beta(E - \mu) \right]} ,
\]  

(3.183)

where \( \beta = 1/\tau \), the density \( n \) is given by

\[
n = \int_{-\infty}^{\infty} D(E) f(E) \, dE
\]

\[
= \frac{m_e}{\pi \hbar^2} \int_0^{\infty} \frac{dE}{1 + \exp \left[ \beta(E - \mu) \right]}
\]

\[
= \frac{m_e \tau}{\pi \hbar^2} \log \left( 1 + e^{\beta \mu} \right) ,
\]  

(3.184)

thus

\[
\mu = \tau \log \left( \exp \left( \frac{n \pi \hbar^2}{m_e \tau} \right) - 1 \right) .
\]  

(3.185)
4. Classical Limit of Statistical Mechanics

In this chapter we discuss the classical limit of statistical mechanics. We discuss Hamilton’s formalism, define the Hamiltonian and present the Hamilton-Jacobi equations of motion. The density function in thermal equilibrium is used to prove the equipartition theorem. This theorem is then employed to analyze an electrical circuit in thermal equilibrium, and to calculate voltage noise across a resistor (Nyquist noise formula).

4.1 Classical Hamiltonian

In this section we briefly review Hamilton’s formalism, which is analogous to Newton’s laws of classical mechanics. Consider a classical system having $d$ degrees of freedom. The system is described using the vector of coordinates

$$\vec{q} = (q_1, q_2, \cdots, q_d).\tag{4.1}$$

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

$$\dot{\vec{q}} = \left(\frac{dq_1}{dt}, \frac{dq_2}{dt}, \cdots, \frac{dq_d}{dt}\right).\tag{4.2}$$

We refer to the first term $T$ 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

$$p_i = \frac{\partial T}{\partial \dot{q}_i}.\tag{4.3}$$

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
\( \vec{p} = (p_1, p_2, \cdots, p_d) \), \hspace{1cm} (4.4)

namely

\( \mathcal{H} = \mathcal{H}(\vec{q}, \vec{p}) \), \hspace{1cm} (4.5)

and it is defined by

\[ \mathcal{H} = \sum_{i=1}^{d} p_i \dot{q}_i - T + V. \] \hspace{1cm} (4.6)

### 4.1.1 Hamilton-Jacobi Equations

The equations of motion of the system are given by

\[ \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \] \hspace{1cm} (4.7)

\[ \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \] \hspace{1cm} (4.8)

where \( i = 1, 2, \cdots d \).

### 4.1.2 Example

Consider a particle having mass \( m \) in a one dimensional potential \( V(q) \). The kinetic energy is given by \( T = m \dot{q}^2 / 2 \), thus the canonical conjugate momentum is given by [see Eq. (4.3)] \( p = m \dot{q} \). 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 (4.6) one finds that the Hamiltonian is given by
4.1. Classical Hamiltonian

\[ H = m\dot{q}^2 - \frac{m\dot{q}^2}{2} + V(q) \]
\[ = \frac{p^2}{2m} + V(q) . \]  

(4.9)

Hamilton-Jacobi equations (4.7) and (4.8) read

\[ \dot{q} = \frac{p}{m} \]  

(4.10)

\[ \dot{p} = -\frac{\partial V}{\partial q} . \]  

(4.11)

The second equation, which can be rewritten as

\[ m\ddot{q} = -\frac{\partial V}{\partial q} , \]  

(4.12)

expresses Newton’s second law.

4.1.3 Example

\[ L \quad C \]

Consider a capacitor having capacitance \( C \) connected in parallel to an inductor having inductance \( L \). Let \( q \) be the charge stored in the capacitor. The kinetic energy in this case \( T = \frac{Lq^2}{2} \) is the energy stored in the inductor, and the potential energy \( V = \frac{q^2}{2C} \) is the energy stored in the capacitor. The canonical conjugate momentum is given by [see Eq. (4.3)] \( p = L\dot{q} \), and the Hamiltonian (4.6) is given by

\[ H = \frac{p^2}{2L} + \frac{q^2}{2C} . \]  

(4.13)

Hamilton-Jacobi equations (4.7) and (4.8) read

\[ \dot{q} = \frac{p}{L} \]  

(4.14)

\[ \dot{p} = -\frac{q}{C} . \]  

(4.15)

The second equation, which can be rewritten as

\[ L\ddot{q} + \frac{q}{C} = 0 , \]  

(4.16)

expresses the requirement that the voltage across the capacitor is the same as the one across the inductor.
4.2 Density Function

Consider a classical system in thermal equilibrium. The density function \( \rho(\vec{q}, \vec{p}) \) is the probability distribution to find the system in the point \((\vec{q}, \vec{p})\).

The following theorem is given without a proof. Let \( H(\vec{q}, \vec{p}) \) be an Hamiltonian of a system, and assume that \( H \) has the following form

\[
H = \sum_{i=1}^{d} A_i p_i^2 + V(\vec{q}),
\]

(4.17)

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

\[
\rho(\vec{q}, \vec{p}) = N \exp(-\beta H(\vec{q}, \vec{p})),
\]

(4.18)

where

\[
N = \frac{1}{\int d\vec{q} \int d\vec{p} \exp(-\beta H(\vec{q}, \vec{p}))}
\]

(4.19)

is a normalization constant, \( \beta = 1/\tau \), and \( \tau \) is the temperature. The notation \( \int d\vec{q} \) indicates integration over all coordinates, namely \( \int d\vec{q} = \int dq_1 \int dq_1 \cdots \int dq_d \). Similarly, \( \int d\vec{p} = \int dp_1 \int dp_1 \cdots \int dp_d \).

Let \( A(\vec{q}, \vec{p}) \) be a variable which depends on the coordinates \( \vec{q} \) and their canonical conjugate momentum variables \( \vec{p} \). Using the above theorem the average value of \( A \) can be calculates as:

\[
\langle A(\vec{q}, \vec{p}) \rangle = \int d\vec{q} \int d\vec{p} A(\vec{q}, \vec{p}) \rho(\vec{q}, \vec{p})
\]

\[
= \frac{\int d\vec{q} \int d\vec{p} A(\vec{q}, \vec{p}) \exp(-\beta H(\vec{q}, \vec{p}))}{\int d\vec{q} \int d\vec{p} \exp(-\beta H(\vec{q}, \vec{p}))}.
\]

(4.20)

4.2.1 Equipartition Theorem

Assume that the Hamiltonian has the following form

\[
\mathcal{H} = B_i q_i^2 + \tilde{H},
\]

(4.21)

where \( B_i \) is a constant and where \( \tilde{H} \) is independent of \( q_i \). Then the following holds

\[
\langle B_i q_i^2 \rangle = \frac{\tau}{2}.
\]

(4.22)

Similarly, assume that the Hamiltonian has the following form
\[ H = A_i p_i^2 + \tilde{H}, \quad (4.23) \]

where \( A_i \) is a constant and where \( \tilde{H} \) is independent of \( p_i \). Then the following holds

\[ \langle A_i p_i^2 \rangle = \tau. \quad (4.24) \]

To prove the theorem for the first case we use Eq. (4.20)

\[
\langle B_i q_i^2 \rangle = \frac{\int dq \int d\bar{p} B_i q_i^2 \exp (-\beta H(q, \bar{p}))}{\int dq \int d\bar{p} \exp (-\beta H(q, \bar{p}))} \\
= \frac{\int dq_i B_i q_i^2 \exp (-\beta B_i q_i^2)}{\int dq_i \exp (-\beta B_i q_i^2)} \\
= -\frac{\partial}{\partial \beta} \log \left( \int dq_i \exp (-\beta B_i q_i^2) \right) \\
= -\frac{\partial}{\partial \beta} \log \left( \sqrt{\frac{\pi}{\beta B_i}} \right) \\
= \frac{1}{2\beta}. \quad (4.25)
\]

The proof for the second case is similar.

### 4.2.2 Example

Here we calculate the average energy of a harmonic oscillator using both, classical and quantum approaches. 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. The kinetic energy is given by \( p^2/2m \), where \( p \) is the canonical momentum variable conjugate to \( q \). The Hamiltonian is given by

\[ H = \frac{p^2}{2m} + \frac{kq^2}{2}. \quad (4.26) \]

In the classical limit the average energy of the system can be easily calculated using the equipartition theorem

\[ U = \langle H \rangle = \tau. \quad (4.27) \]

In the quantum treatment the system has energy levels given by

\[ E_s = sh\omega, \]

where \( s = 0, 1, 2, \cdots \), and where \( \omega = \sqrt{k/m} \) is the angular resonance frequency. The partition function is given by
Chapter 4. Classical Limit of Statistical Mechanics

\[ Z = \sum_{s=0}^{\infty} \exp \left( -s\beta \hbar \omega \right) = \frac{1}{1 - \exp (-\beta \hbar \omega)} , \]  

(4.28)

thus the average energy \( U \) is given by

\[ U = -\frac{\partial \log Z}{\partial \beta} = \frac{\hbar \omega e^{\beta \hbar \omega} - 1}{e^{\beta \hbar \omega} - 1} . \]  

(4.29)

Using the expansion

\[ U = \beta^{-1} + O (\beta) , \]  

(4.30)

one finds that in the limit of high temperatures, namely when \( \beta \hbar \omega \ll 1 \), the quantum result [Eq. (4.30)] coincides with the classical limit [Eq. (4.27)].

4.3 Nyquist Noise

Here we employ the equipartition theorem in order to evaluate voltage noise across a resistor. Consider the circuit shown in the figure below, 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 \( V(t) \). Let \( q(t) \) be the charge stored in the capacitor at time \( t \). The classical equation of motion, which is given by

\[ \frac{q}{C} + Lq + R\dot{q} = V(t) , \]  

(4.31)

represents Kirchhoff's voltage law.

Fig. 4.1.
Consider a sampling of the fluctuating function $q(t)$ in the time interval $(-T/2, T/2)$, namely

$$q_T(t) = \begin{cases} 
q(t) & -T/2 < t < T/2 \\
0 & \text{else}
\end{cases}$$  \hspace{1cm} (4.32)

The energy stored in the capacitor is given by $q^2/2C$. Using the equipartition theorem one finds

$$\langle q^2 \rangle C = \frac{\tau}{2},$$ \hspace{1cm} (4.33)

where $\langle q^2 \rangle$ is obtained by averaging $q^2(t)$, namely

$$\langle q^2 \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ q_T^2(t).$$ \hspace{1cm} (4.34)

Introducing the Fourier transform:

$$q_T(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) e^{-i\omega t},$$ \hspace{1cm} (4.35)

one finds

$$\langle q^2 \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) e^{-i\omega t} \ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega' \ q_T(\omega') e^{-i\omega' t}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) \int_{-\infty}^{\infty} d\omega' q_T(\omega') \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dte^{-i(\omega+\omega')t}$$

$$= \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \ q_T(\omega)q_T(-\omega).$$ \hspace{1cm} (4.36)

Moreover, using the fact that $q(t)$ is real one finds

$$\langle q^2 \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \ |q_T(\omega)|^2.$$ \hspace{1cm} (4.37)

In terms of the power spectrum $S_q(\omega)$ of $q(t)$, which is defined as

$$S_q(\omega) = \lim_{T \to \infty} \frac{1}{T} |q_T(\omega)|^2,$$ \hspace{1cm} (4.38)

one finds

$$\langle q^2 \rangle = \int_{-\infty}^{\infty} d\omega \ S_q(\omega).$$ \hspace{1cm} (4.39)
Taking the Fourier transform of Eq. (4.31) yields
\[ \left( \frac{1}{C} - i\omega R - L\omega^2 \right) q(\omega) = V(\omega) , \] (4.40)
where \( V(\omega) \) is the Fourier transform of \( V(t) \), namely
\[ V(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ V(\omega)e^{-i\omega t} . \] (4.41)
In terms of the resonance frequency
\[ \omega_0 = \sqrt{\frac{1}{LC}} , \] (4.42)
one has
\[ \left[ L (\omega_0^2 - \omega^2) - i\omega R \right] q(\omega) = V(\omega) . \] (4.43)
Taking the absolute value squared yields
\[ S_q(\omega) = \frac{S_V(\omega)}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2} , \] (4.44)
where \( S_V(\omega) \) is the power spectrum of \( V(t) \). Integrating the last result yields
\[ \int_{-\infty}^{\infty} d\omega \ S_q(\omega) = \int_{-\infty}^{\infty} d\omega \ \frac{S_V(\omega)}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2} \]
\[ = \frac{1}{L^2} \int_{-\infty}^{\infty} d\omega \ \frac{S_V(\omega)}{(\omega_0 + \omega)^2 (\omega_0 - \omega)^2 + \omega^2 R^2} . \] (4.45)
The integrand has a peak near \( \omega_0 \), having a width \( \approx R/2L \). The Quality factor \( Q \) is defined as
\[ \frac{\omega_0}{Q} = \frac{R}{2L} . \] (4.46)
Assuming \( S_V(\omega) \) is a smooth function near \( \omega_0 \) on the scale \( \omega_0/Q \), and assuming \( Q \gg 1 \) yield
\[
\int_{-\infty}^{\infty} d\omega \ S_q(\omega) \simeq \frac{S_V(\omega_0)}{L^2} \int_{-\infty}^{\infty} \frac{d\omega}{(\omega_0 + \omega)^2 (\omega_0 - \omega)^2 + \left(\frac{2 \omega_0 \omega}{Q}\right)^2}
\]
\[
\simeq \frac{S_V(\omega_0)}{4 \omega_0^4 L^2} \int_{-\infty}^{\infty} \frac{d\omega}{(\frac{\omega - \omega_0}{\omega_0})^2 + \left(\frac{1}{Q}\right)^2}
\]
\[
= \frac{S_V(\omega_0)}{4 \omega_0^2 L^2} \int_{-\infty}^{\infty} \frac{dx}{x^2 + \left(\frac{1}{Q}\right)^2} \pi Q
\]
\[
= \frac{S_V(\omega_0)\pi Q}{4 \omega_0^2 L^2}.
\] (4.47)

On the other hand, using Eqs. (4.33) and (4.39) one finds
\[
\int_{-\infty}^{\infty} d\omega \ S_q(\omega) = \langle q^2 \rangle = C \tau,
\] (4.48)
therefore
\[
S_V(\omega_0) = \frac{4C \omega_0^3 L^2}{\pi Q} \tau,
\] (4.49)
or using Eqs. (4.42) and (4.46)
\[
S_V(\omega_0) = \frac{2R \tau}{\pi}.
\] (4.50)
Thus, Eq. (4.44) can be rewritten as
\[
S_q(\omega) = \frac{2R \tau}{\pi} \frac{1}{L^2 (\omega_0^2 - \omega^2)^2 + \omega^2 R^2}.
\] (4.51)

Note that the spectral density of \( V \) given by Eq. (4.50) is frequency independent. Consider a measurement of the fluctuating voltage \( V(t) \) in a frequency band having width \( \Delta f \). Using the relation
\[
\langle V^2 \rangle = \int_{-\infty}^{\infty} d\omega \ S_V(\omega),
\] (4.52)
one finds that the variance in such a measurement \( \langle V^2 \rangle_{\Delta f} \) is given by
\[
\langle V^2 \rangle_{\Delta f} = 4R \tau \Delta f.
\] (4.53)
The last result is the Nyquist's noise formula.
4.4 Thermal Equilibrium From Stochastic Processes

This section demonstrates that under appropriate conditions a stochastic process can lead to thermal equilibrium in steady state.

4.4.1 Langevin Equation

Consider the Langevin equation

\[ \dot{x} = A(x, t) + q(t) \tag{4.54} \]

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

\[ \langle q(t) \rangle = 0 \tag{4.55} \]

and

\[ \langle q_i(t) q_j(t') \rangle = g_{ij} \delta(t - t') \tag{4.56} \]

Let

\[ \delta x = x(t + \delta t) - x(t) \tag{4.57} \]

To first order in \( \delta t \) one finds by integrating Eq. (4.54) that

\[ \langle \delta x \rangle_i = A_i(x, t) \delta t + \int_t^{t+\delta t} dt' q_i(t') + O((\delta t)^2) \tag{4.58} \]

With the help of Eqs. (4.55) and (4.56) one finds that

\[ \langle (\delta x)_i \rangle = A_i(x, t) \delta t + O((\delta t)^2) \tag{4.59} \]

and

\[ \langle (\delta x)_i (\delta x)_j \rangle = A_i(x, t) A_j(x, t) \delta t + \int_t^{t+\delta t} dt' \int_t^{t+\delta t} dt'' q_i(t') q_j(t'') + \cdots \tag{4.60} \]

thus to first order in \( \delta t \)

\[ \langle (\delta x)_i (\delta x)_j \rangle = g_{ij} \delta t + O((\delta t)^2) \tag{4.61} \]

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 \( \delta t \).
4.4.2 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

\[
p_2 (x_3, t_3; x_1, t_1) = \int dx_2 \ p_3 (x_3, t_3; x_2, t_2; x_1, t_1) . \tag{4.62}
\]

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

\[
p_2 (x_3, t_3; x_1, t_1) = P (x_3, t_3|x_1, t_1) p_1 (x_1, t_1) . \tag{4.63}
\]

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

\[
p_3 (x_3, t_3; x_2, t_2; x_1, t_1) \\
= P (x_3, t_3|x_2, t_2) P (x_2, t_2|x_1, t_1) p_1 (x_1, t_1) .
\]

With the help of these relations Eq. (4.62) becomes

\[
P (x_3, t_3|x_1, t_1) p_1 (x_1, t_1) \\
= \int dx_2 \ P (x_3, t_3|x_2, t_2) P (x_2, t_2|x_1, t_1) p_1 (x_1, t_1) , \tag{4.64}
\]

thus by dividing by \( p_1 (x_1, t_1) \) one finds that

\[
P (x_3, t_3|x_1, t_1) = \int dx_2 \ P (x_3, t_3|x_2, t_2) P (x_2, t_2|x_1, t_1) . \tag{4.65}
\]

4.4.3 The Fokker-Planck Equation

Equation (4.65) can be written as

\[
P (x, t+\delta t|x_0, t_0) = \int dx' \ P (x, t+\delta t|x', t') P (x', t'|x_0, t_0) . \tag{4.66}
\]

On the other hand

\[
P (x, t+\delta t|x', t') = \delta (x - \delta x - x') , \tag{4.67}
\]
where
\[ \delta x = x(t + \delta t) - x(t). \] (4.68)

For a general scalar function \( F \) of \( x' \) the following holds
\[
F(x' + \delta x) = \exp(\delta x \cdot \nabla') F = F(x') + (\delta x)_i \frac{dF}{dx'_i} + \frac{(\delta x)_i (\delta x)_j}{2!} \frac{d^2 F}{dx'_i dx'_j} + \cdots,
\] (4.69)

thus
\[
\delta (x - \delta x - x') = \delta (x - x') + (\delta x)_i \frac{d\delta (x - x')}{dx'_i} + \frac{(\delta x)_i (\delta x)_j}{2!} \frac{d^2 \delta (x - x')}{dx'_i dx'_j} + \cdots.
\] (4.70)

Inserting this result into Eq. (4.66)
\[
\mathcal{P}(x, t + \delta t | x_0, t_0) = \int dx' \langle \delta (x - \delta x - x') \rangle \mathcal{P}(x', t'|x_0, t_0)
= \int dx' \delta (x - x') \mathcal{P}(x', t|x_0, t_0)
+ \int dx' \langle (\delta x)_i \rangle \frac{d\delta (x - x')}{dx'_i} \mathcal{P}(x', t'|x_0, t_0)
+ \frac{1}{2} \int dx' \langle (\delta x)_i (\delta x)_j \rangle \frac{d^2 \delta (x - x')}{dx'_i dx'_j} \mathcal{P}(x', t'|x_0, t_0)
+ \cdots,
\] (4.71)

employing Eqs. (4.59) and (4.61) (recall that higher order moments vanish to first order in \( \delta t \)), dividing by \( \delta t \), taking the limit \( \delta t \to 0 \)
\[
\frac{\partial \mathcal{P}}{\partial t} = \int dx' A_i(x', t) \frac{d\delta (x - x')}{dx'_i} \mathcal{P}(x', t'|x_0, t_0)
+ \frac{1}{2} \int dx' g_{ij} \frac{d^2 \delta (x - x')}{dx'_i dx'_j} \mathcal{P}(x', t'|x_0, t_0),
\] (4.72)
and finally integrating by parts and assuming that \( P \to 0 \) in the limit \( x \to \pm \infty \) yield

\[
\frac{\partial P}{\partial t} = -\frac{d}{dx_i'} (A_i P) + \frac{1}{2} \frac{d^2}{dx_i'dx_j'} (g_{ij} P) .
\] (4.73)

This result, which is known as the Fokker-Planck equation, can also be written as

\[
\frac{\partial P}{\partial t} + \nabla \cdot J = 0 ,
\] (4.74)

where the probability current density \( J \) is given by

\[
J_i = A_i P - \frac{1}{2} \frac{d}{dx_j'} (g_{ij} P) .
\] (4.75)

In steady state the Fokker-Planck equation (4.74) becomes

\[
\nabla \cdot J = 0 .
\] (4.76)

### 4.4.4 The Potential Condition

Consider the case where \( A \) can be expressed in terms of a scalar ’Hamiltonian’ \( \mathcal{H} \) as (the potential condition)

\[
A (x, t) = -\nabla \mathcal{H} .
\] (4.77)

Moreover, for simplicity assume that

\[
g_{ij} = 2\tau \delta_{ij} ,
\] (4.78)

where the ’temperature’ \( \tau \) is a constant. For this case one has

\[
J_i = -\mathcal{P} \frac{d\mathcal{H}}{dx_i'} - \tau \frac{d\mathcal{P}}{dx_i'} ,
\] (4.79)

thus

\[
J = -\mathcal{P} \nabla \mathcal{H} - \tau \nabla \mathcal{P} \\
= -\mathcal{P} \nabla (\mathcal{H} + \tau \log \mathcal{P}) .
\] (4.80)

Substituting a solution having the form

\[
\mathcal{P} = Ne^{-\frac{\mathcal{H}}{\tau}}
\] (4.81)

yields
\mathbf{J} = -\tau Ne^{-\frac{\mathcal{H}}{\tau}} \nabla (\log N) = -\tau e^{-\frac{\mathcal{H}}{\tau}} \nabla N , \quad (4.82)

and thus
\nabla \cdot \mathbf{J} = [\nabla \mathcal{H} \cdot \nabla N - \tau \nabla \cdot (\nabla N)] e^{-\frac{\mathcal{H}}{\tau}} . \quad (4.83)

In terms of \( N \) the Fokker-Planck equation (4.74) becomes
\[ \frac{\partial N}{\partial t} + [\nabla \mathcal{H} \cdot \nabla N - \tau \nabla \cdot (\nabla N)] = 0 . \quad (4.84) \]

In steady state Eq. (4.84) becomes
\nabla \mathcal{H} \cdot \nabla N = \tau \nabla \cdot (\nabla N) . \quad (4.85)

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
\[ \mathcal{P} = \frac{1}{Z} e^{-\frac{\mathcal{H}}{\tau}} , \quad (4.86) \]
where
\[ Z = \int d\mathbf{x}' \mathcal{P} . \quad (4.87) \]

4.4.5 Free Energy

The free energy functional is defined by
\[ F(\mathcal{P}) = U - \tau \sigma , \quad (4.88) \]
where \( U \) is the energy
\[ U = \int d\mathbf{x}' \mathcal{H}\mathcal{P} , \quad (4.89) \]
and \( \sigma \) is the entropy
\[ \sigma = -\int d\mathbf{x}' \mathcal{P} \log \mathcal{P} . \quad (4.90) \]

The distribution \( \mathcal{P} \) is constrained to satisfy the normalization constrain
\[ G(\mathcal{P}) = \int d\mathbf{x}' \mathcal{P} - 1 = 0 . \quad (4.91) \]
Minimizing \( F(\mathcal{P}) \) under the constrain (4.91) is done by introducing the Lagrange multiplier \( \eta \).
4.4. Thermal Equilibrium From Stochastic Processes

\[ \delta (F(P) + \eta G(P)) \]
\[ = \int d\mathbf{x}' \left[ \mathcal{H} + \tau (1 + \log P) + \eta \right] \delta P . \]  
(4.92)

At a stationary point the following holds

\[ \mathcal{H} + \tau (1 + \log P) + \eta = 0 , \]  
(4.93)

thus

\[ P = e^{-\frac{\eta}{\tau} - 1} e^{-\frac{\mathcal{H}}{\tau}} , \]  
(4.94)

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 (4.86).

4.4.6 Fokker-Planck Equation in One Dimension

In one dimension the Fokker-Planck equation (4.74) becomes [see Eq. (4.79)]

\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( P \frac{\partial \mathcal{H}}{\partial x} + \tau \frac{\partial P}{\partial x} \right) , \]  
(4.95)

or

\[ \frac{\partial P}{\partial t} = \mathcal{L} P , \]  
(4.96)

where the operator \( \mathcal{L} \) is given by

\[ \mathcal{L} = \frac{\partial}{\partial x} \frac{\partial \mathcal{H}}{\partial x} + \tau \frac{\partial^2}{\partial x^2} . \]  
(4.97)

It is convenient to define the operator \( \hat{\mathcal{L}} \), which is given by

\[ \hat{\mathcal{L}} = e^{\frac{\mathcal{H}}{\tau}} \mathcal{L} e^{-\frac{\mathcal{H}}{\tau}} . \]  
(4.98)

The following holds
\[ \hat{L} = e^{\frac{\pi}{\tau}} \frac{\partial}{\partial x} \left( \frac{\partial H}{\partial x} e^{-\frac{\pi}{\tau}} \right) + \frac{\partial^2}{\partial x^2} e^{-\frac{\pi}{\tau}} \]

\[ = e^{\frac{\pi}{\tau}} \frac{\partial}{\partial x} \left( \frac{\partial H}{\partial x} e^{-\frac{\pi}{\tau}} \right) + \frac{\partial^2}{\partial x^2} e^{-\frac{\pi}{\tau}} \]

\[ + \tau e^{\frac{\pi}{\tau}} \left( \frac{\partial^2}{\partial x^2} e^{-\frac{\pi}{\tau}} \right) + 2 \tau e^{\frac{\pi}{\tau}} \frac{\partial e^{-\frac{\pi}{\tau}}}{\partial x} \frac{\partial}{\partial x} + \tau e^{\frac{\pi}{\tau}} \frac{\partial^2}{\partial x^2} \]

\[ = \frac{\partial^2}{\partial x^2} \frac{1}{2} \frac{\partial H}{\partial x} - \frac{1}{2\tau} \left( \frac{\partial H}{\partial x} \right)^2 + \frac{\partial^2}{\partial x^2} \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 - \frac{\partial H}{\partial x} \frac{\partial}{\partial x} + \tau \frac{\partial^2}{\partial x^2} \]

\[ = \frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 + \tau \frac{\partial^2}{\partial x^2} , \]

(4.99)

Thus

\[ \hat{L} = \tau \frac{\partial^2}{\partial x^2} - \hat{V} , \]

(4.100)

where the potential \( \hat{V} \) is given by

\[ \hat{V} = \frac{1}{4\tau} \left( \frac{\partial H}{\partial x} \right)^2 - \frac{1}{2} \frac{\partial^2 H}{\partial x^2} . \]

(4.101)

Note that while the operator \( \mathcal{L} \) is not Hermitian, the operator \( \hat{\mathcal{L}} \) is since

\[ \hat{\mathcal{L}}^\dagger = e^{-\frac{\pi}{\tau}} \mathcal{L}^\dagger e^{\frac{\pi}{\tau}} \]

\[ = e^{-\frac{\pi}{\tau}} \mathcal{L}^\dagger e^{\frac{\pi}{\tau}} \]

\[ = e^{-\frac{\pi}{\tau}} \mathcal{L} e^{-\frac{\pi}{\tau}} \]

\[ = e^{\frac{\pi}{\tau}} \mathcal{L} e^{-\frac{\pi}{\tau}} = \hat{\mathcal{L}} . \]

(4.102)

In terms of \( \hat{\mathcal{L}} \), Eq. (4.96) becomes (it is assume that \( H \) is time independent)

\[ \frac{\partial \hat{\mathcal{P}}}{\partial t} = \hat{\mathcal{L}} \hat{\mathcal{P}} , \]

(4.103)

where

\[ \hat{\mathcal{P}} = e^{\frac{\pi}{\tau}} \mathcal{P} e^{-\frac{\pi}{\tau}} . \]

(4.104)

Let \( \psi_n(x) \) be a set of eigenvectors of \( \hat{\mathcal{L}} \)

\[ \hat{\mathcal{L}} \psi_n = \lambda_n \psi_n . \]

(4.105)
The following holds [see Eq. (4.98)]

\[ \mathcal{L}\!\phi_n = \lambda_n \phi_n , \]  

(4.106)

where

\[ \phi_n = e^{-\frac{2t}{\tau} \psi_n} . \]  

(4.107)

The conditional probability distribution \( \mathcal{P}(x, t| x', t') \) is given by [see Eq. (4.96)]

\[ \mathcal{P}(x, t| x', t') = e^{\mathcal{L}(t-t')} \delta(x-x') . \]  

(4.108)

With the help of the closure relation (recall that \( \hat{\mathcal{L}} \) is Hermitian)

\[ \delta(x-x') = \sum_n \psi_n^*(x') \psi_n(x) \]
\[ = e^{\frac{\gamma(x) + \gamma(x')}{2\tau}} \sum_n \varphi_n^*(x') \varphi_n(x) \]
\[ = e^{\frac{\gamma(x')}{\tau}} \sum_n \varphi_n^*(x') \varphi_n(x) , \]  

(4.109)

one finds that

\[ \mathcal{P}(x, t| x', t') = e^{\mathcal{L}(x)(t-t')} e^{\frac{\gamma(x')}{\tau}} \sum_n \varphi_n^*(x') \varphi_n(x) \]
\[ = e^{\frac{\gamma(x')}{\tau}} \sum_n \varphi_n^*(x') e^{\mathcal{L}(x)(t-t')} \varphi_n(x) \]
\[ = e^{\frac{\gamma(x')}{\tau}} \sum_n \varphi_n^*(x') e^{\lambda_n(t-t')} \varphi_n(x) \]
\[ = e^{\frac{\gamma(x')}{\tau}} \sum_n e^{-\frac{\gamma(x')}{2\tau} \psi_n^*(x')} e^{\lambda_n(t-t')} e^{-\frac{\gamma(x)}{2\tau} \psi_n(x)} , \]  

(4.110)

thus

\[ \mathcal{P}(x, t| x', t') = e^{\frac{\gamma(x')}{\tau} \frac{\gamma(x)}{2\tau}} \sum_n \psi_n^*(x') \psi_n(x) e^{\lambda_n(t-t')} . \]  

(4.111)

### 4.4.7 Ornstein–Uhlenbeck Process in One Dimension

Consider the following Langevin equation
\[ \dot{x} + \Gamma x = q(t), \quad (4.112) \]

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

\[ \langle q(t) q(t') \rangle = 2\tau \delta(t-t'), \quad (4.113) \]

where \( \tau \) is positive.

For this case [see Eq. (4.77)]

\[ \mathcal{H}(x) = \frac{\Gamma x^2}{2}, \quad (4.114) \]

the Fokker-Planck equation for the conditional probability distribution \( P \) is given by [see Eq. (4.74)]

\[ \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} \left( P \Gamma x + \tau \frac{\partial P}{\partial x} \right), \quad (4.115) \]

and the operator \( \hat{L} \) is given by [see Eq. (4.100)]

\[ \hat{L} = -\frac{\Gamma}{2} \left[ -\left( \frac{\partial}{\partial \left( \frac{x}{x_0} \right)} \right)^2 + \left( \frac{x}{x_0} \right)^2 - 1 \right], \]

where

\[ x_0 = \sqrt{\frac{2\tau}{\Gamma}}. \quad (4.116) \]

The eigenvectors of \( \hat{L} \) are given by [see Eq. (4.131)]

\[ \psi_n(x) = \frac{e^{-\frac{1}{2} \left( \frac{x}{x_0} \right)^2} H_n \left( \frac{x}{x_0} \right)}{\pi^{1/4} x_0^{1/2} \sqrt{2^n n!}}, \quad (4.117) \]

and the corresponding eigenvalues by

\[ \lambda_n = -\Gamma \left( n + \frac{1}{2} - \frac{1}{2} \right), \quad (4.118) \]

where \( n = 0, 1, 2, \ldots \).

Using these results one finds that \( P \) is given by [see Eq. (4.111)]

\[ P(x,t|x',t') = e^{-\left( \frac{x}{x_0} \right)^2} \sum_n \frac{H_n \left( \frac{x}{x_0} \right) H_n \left( \frac{x'}{x_0} \right) e^{-\Gamma n(t-t')}}{\sqrt{n!} x_0^{2n} n!}. \quad (4.119) \]
With the help of the general identity (4.138) one finds that the following holds

\[
\frac{\alpha e^{-x^2}}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{\left(\frac{x}{\sqrt{2}}\right)^n H_n(Y) H_n(X)}{n!} = \frac{\exp\left(-\left(\frac{Y-Xa^{-1}}{\sqrt{\alpha^2-1}}\right)^2\right)}{\sqrt{\pi (\alpha^2 - 1)}},
\]

thus Eq. (4.119) becomes

\[
P(x, t|x', t') = \frac{\exp\left(-\left(\frac{x-x' e^{-\Gamma(t-t')}}{\delta}\right)^2\right)}{\sqrt{\pi \delta}},
\]

where

\[
\delta = \sqrt{x_0^2 (1 - e^{-2\Gamma(t-t')}}) = \sqrt{\frac{2\tau (1 - e^{-2\Gamma(t-t')}}}{\tau}}.
\]

4.5 Problems Set 4

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

\[
I(\lambda) \propto \exp\left[-\frac{mc^2 (\lambda - \lambda_0)^2}{2\lambda_0^2 \tau}\right],
\]

where \(c\) is velocity of light, and \(m\) is mass of a molecule.

2. The circuit seen in the figure below, 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 random real signal \( q(t) \) varying in time. Let \( q_T(t) \) be a sampling of the signal \( q(t) \) in the time interval \( (-T/2, T/2) \), namely

\[
q_T(t) = \begin{cases} 
q(t) & -T/2 < t < T/2 \\
0 & \text{else} 
\end{cases} 
\]  
(4.124)

The Fourier transform is given by

\[
q_T(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \, q_T(\omega) e^{-i\omega t} ,
\]  
(4.125)

and the power spectrum is given by

\[
S_q(\omega) = \lim_{T \to \infty} \frac{1}{T} |q_T(\omega)|^2 .
\]

a) Show that

\[
\langle q^2 \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \, q_T^2(t) = \int_{-\infty}^{\infty} d\omega \, S_q(\omega) .
\]  
(4.126)

b) **Wiener-Khinchine Theorem** - show that the correlation function of the random signal \( q(t) \) is given by

\[
\langle q(t) q(t+t') \rangle \equiv \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \, q_T(t) q_T(t+t') = \int_{-\infty}^{\infty} d\omega \, e^{i\omega t'} S_q(\omega) .
\]  
(4.127)

4. Consider a resonator made of a capacitor \( C \), an inductor \( L \), and a resistor \( R \) connected in series, as was done in class. Let \( I(t) \) be the current in the circuit. Using the results obtained in class calculate the spectral density \( S_I(\omega) \) of \( I \) at thermal equilibrium. Show that in the limit of high quality factor, namely when

\[
Q = \frac{2}{\tau \sqrt{LC}} \gg 1 ,
\]  
(4.128)

your result is consistent with the equipartition theorem applied for the energy stored in the inductor.

5. A classical system is described using a set of coordinates \( \{q_1, q_2, \cdots, q_N\} \) and the corresponding canonically conjugate variables \( \{p_1, p_2, \cdots, p_N\} \). The Hamiltonian of the system is given by

\[
H = \sum_{n=1}^{N} A_n p_n^s + B_n q_n^t ,
\]  
(4.129)

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
\[ \langle U \rangle = N\tau \left( \frac{1}{s} + \frac{1}{t} \right), \]

6. A small hole of area \( A \) is made in the walls of a vessel of volume \( V \) containing a classical ideal gas of \( N \) particles of mass \( M \) each in equilibrium at temperature \( \tau \). Calculate the number of particles \( dN \), which escape through the opening during the infinitesimal time interval \( dt \).

7. 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

\[ \langle v \rangle \left( \frac{1}{v} \right) \]

(the symbol \( \langle \rangle \) denoted averaging) in the:

a) classical limit (high temperatures).

b) zero temperature.

8. 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 \( 0 \leq r \leq R \)).

9. 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) \( \sqrt{\langle v^2 \rangle} \)

10. 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.

11. The Hermite polynomial \( H_n(X) \) of order \( n \) is defined by

\[ H_n(X) = \exp \left( \frac{X^2}{2} \right) \left( X - \frac{d}{dX} \right)^n \exp \left( -\frac{X^2}{2} \right). \]

For some low values of \( n \) the Hermite polynomials are given by

\[ H_0(X) = 1, \]

\[ H_1(X) = 2X, \]

\[ H_2(X) = 4X^2 - 2, \]

\[ H_3(X) = 8X^3 - 12X, \]

\[ H_4(X) = 16X^4 - 48X^2 + 12. \]
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Show that
\[
\exp \left( 2Xt - t^2 \right) = \sum_{n=0}^{\infty} H_n (X) \frac{t^n}{n!}.
\] (4.137)

12. Show that
\[
\sum_{n=0}^{\infty} \frac{(\alpha)^n}{n!} H_n (X) H_n (Y) \exp \left( \frac{\alpha(2XY - \alpha X^2 - \alpha Y^2)}{1 - \alpha^2} \right) \sqrt{1 - \alpha^2}.
\] (4.138)

4.6 Solutions Set 4

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
\[
\lambda = \lambda_0 \left( 1 + \frac{v_x}{c} \right).
\] (4.139)

The probability distribution \( f(v_x) \) is proportional to
\[
f(v_x) \propto \exp \left( -\frac{mv_x^2}{2\tau} \right),
\] (4.140)

thus using
\[
v_x = \frac{c (\lambda - \lambda_0)}{\lambda_0},
\] (4.141)

the probability distribution \( I(\lambda) \) is proportional to
\[
I(\lambda) \propto \exp \left( -\frac{mc^2 (\lambda - \lambda_0)^2}{2\lambda_0^2 \tau} \right).
\] (4.142)

2. The energy stored in the inductor is \( U_L = LI^2 / 2 \). Using the equipartition theorem \( \langle U_L \rangle = \tau / 2 \), thus
\[
\langle I^2 \rangle = \frac{\tau}{L}.
\] (4.143)

3. a)
\[ \langle q^2 \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) e^{-i\omega t} \left( \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega' \ q_T(\omega') e^{-i\omega' t} \right) \]

\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) \int_{-\infty}^{\infty} d\omega' \ q_T(\omega') \ \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ e^{-i(\omega+\omega') t} \]

\[ = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \ q_T(\omega) q_T(-\omega) \ . \quad (4.144) \]

Since \( q(t) \) is real one has \( q_T(-\omega) = q_T^{*}(\omega) \), thus

\[ \langle q^2 \rangle = \int_{-\infty}^{\infty} d\omega \ S_q(\omega) \ . \quad (4.145) \]

b)

\[ \langle q(t) q(t+t') \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ q_T(t) q_T(t+t') \]

\[ = \frac{1}{2\pi} \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ \int_{-\infty}^{\infty} d\omega \ q_T(\omega) e^{-i\omega t} \left( \int_{-\infty}^{\infty} d\omega' \ q_T(\omega') e^{-i\omega' (t+t')} \right) \]

\[ = \frac{1}{2\pi} \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \ e^{-i\omega t'} q_T(\omega) \int_{-\infty}^{\infty} d\omega' \ q_T(\omega') \left( \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{+\infty} dt \ e^{-i(\omega+\omega') t} \right) \]

\[ = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} q_T(\omega) q_T(-\omega) \]

\[ = \int_{-\infty}^{\infty} d\omega \ e^{i\omega t'} S_f(\omega) \ . \quad (4.146) \]

4. Using \( I(\omega) = -i\omega q(\omega) \) and \( \langle q^2 \rangle = C \tau \) one finds for the case \( Q \gg 1 \)

\[ \langle I^2 \rangle = \int_{-\infty}^{\infty} d\omega \ S_I(\omega) \simeq \omega_0^2 \int_{-\infty}^{\infty} d\omega \ S_q(\omega) = \omega_0^2 \langle q^2 \rangle = \frac{\tau}{T} \ . \quad (4.147) \]

in agreement with the equipartition theorem for the energy stored in the inductor \( LI^2/2 \).

5. Calculate for example
\[ \langle B_n^q t_n^q \rangle = \frac{\int_{-\infty}^{\infty} B_n^q t_n^q \exp(-\beta B_n^q t_n^q) \, dq_n}{\int_{-\infty}^{\infty} \exp(-\beta B_n^q t_n^q) \, dq_n} = \frac{\int_{0}^{\infty} B_n^q t_n^q \exp(-\beta B_n^q t_n^q) \, dq_n}{\int_{0}^{\infty} \exp(-\beta B_n^q t_n^q) \, dq_n} = -\frac{d}{d\beta} \log \int_{0}^{\infty} \exp(-\beta B_n^q t_n^q) \, dq_n. \] (4.148)

where \( \beta = 1/\tau \). Changing integration variable

\[ x = \beta B_n^q t_n^q, \] (4.149)
\[ dx = t\beta B_n^q t_n^q - 1 \, dq_n, \] (4.150)

leads to

\[ \langle B_n^q t_n^q \rangle = -\frac{d}{d\beta} \log \left[ (\beta B_n)^{-\frac{1}{t}} \int_{0}^{\infty} x^{\frac{1}{s}-1} e^{-x} \, dx \right] = \frac{\tau}{t}. \] (4.151)

Thus

\[ \langle U \rangle = \sum_{n=1}^{N} \langle A_n p_n^{q} \rangle + \langle B_n q_n^{t} \rangle = N\tau \left( \frac{1}{s} + \frac{1}{t} \right). \] (4.152)

6. Let \( f(v) \) be the probability distribution of velocity \( v \) of particles in the gas. The vector \( u \) is expressed in spherical coordinates, where the \( z \) axis is chosen in the direction of the normal outward direction

\[ v = v (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta). \] (4.153)

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 \( 0 \leq \theta \leq \pi/2 \))

\[ dN = \int_{0}^{\infty} dv \int_{0}^{1} d\cos \theta \int_{0}^{2\pi} d\varphi v^2 f(v) A \cos \theta = \frac{N}{V} f(v). \] (4.154)

Note that \( v (dt) A \cos \theta \) represents the volume of a cylinder from which particles of velocity \( v \) can escape during the time interval \( dt \). Since \( f(v) \) is normalized

\[ 1 = \int_{0}^{\infty} dv \int_{0}^{1} d\cos \theta \int_{0}^{2\pi} d\varphi v^2 f(v) = 4\pi \int_{0}^{\infty} dv v^2 f(v), \] (4.155)

thus

\[ \frac{dN}{dt} = \frac{\pi NA}{V} \int_{0}^{\infty} dv v^2 f(v) = \frac{NA \langle v \rangle}{4V}. \] (4.156)
In the classical limit

\[ f(v) \propto \exp \left( -\frac{Mv^2}{2\tau} \right) \],

(4.157)

thus, by changing the integration variable

\[ x = \frac{Mv^2}{2\tau} \]

(4.158)

one finds

\[
\langle v \rangle = \int_0^\infty dv v^3 \exp \left( -\frac{Mv^2}{2\tau} \right) = \left( \frac{2\tau}{M} \right)^{1/2} \int_0^\infty dx x \exp \left( -\frac{Mv^2}{2\tau} \right) = \left( \frac{8\tau}{\pi M} \right)^{1/2},
\]

(4.159)

and

\[
\frac{dN}{dt} = \frac{NA}{4V} \left( \frac{8\tau}{\pi M} \right)^{1/2}.
\]

(4.160)

7. The probability that an orbital having energy \( \varepsilon \) is occupied is given by

\[ f_F(\varepsilon) = \frac{1}{1 + \exp \left[ (\varepsilon - \mu) \beta \right]} \],

(4.161)

where \( \beta = 1/\tau \) and \( \mu \) is the chemical potential. The velocity \( v \) of such an orbital is related to the energy \( \varepsilon \) by

\[ \varepsilon = \frac{Mv^2}{2} \].

(4.162)

The 3D density of state per unit volume is given by

\[ g(\varepsilon) = \frac{1}{2\pi^2} \left( \frac{2M}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \].

(4.163)

Thus
\begin{align*}
\langle v \rangle \langle \frac{1}{v} \rangle &= \frac{\int_0^\infty d\varepsilon g(\varepsilon) f_F(\varepsilon) v \int_0^\infty d\varepsilon g(\varepsilon) f_F(\varepsilon) \frac{1}{v}}{\int_0^\infty d\varepsilon g(\varepsilon) f_F(\varepsilon) \int_0^\infty d\varepsilon g(\varepsilon) f_F(\varepsilon)} \\
&= \frac{\left( \int_0^\infty d\varepsilon f_F(\varepsilon) \right) \left( \int_0^\infty d\varepsilon f_F(\varepsilon) \right)}{\left( \int_0^\infty d\varepsilon \varepsilon^{1/2} f_F(\varepsilon) \right)^2}.
\end{align*}

(4.164)

\textbf{a)} In the classical limit
\begin{equation}
\mathcal{F}(\varepsilon) \propto \exp(-\beta \varepsilon),
\end{equation}
thus using the identities
\begin{align*}
\int_0^\infty d\varepsilon \varepsilon^n \exp(-\beta \varepsilon) &= \Gamma(n) \beta^{-n} \frac{n}{\beta} \\
\int_0^\infty d\varepsilon \exp(-\beta \varepsilon) &= \frac{1}{\beta} \\
\Gamma(1) &= 1 \\
\Gamma\left(\frac{1}{2}\right) &= \sqrt{\pi}
\end{align*}
on one finds
\begin{align*}
\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} \\
&= \frac{\Gamma(1) \beta^{-1} \frac{1}{\beta} \frac{1}{\beta}}{\left( \Gamma\left(\frac{1}{2}\right) \beta^{-1/2} \frac{1}{2\beta} \right)^2} \\
&= \frac{4}{\pi}.
\end{align*}

(4.165)

\textbf{b)} Using the identity
\begin{equation}
\int_0^\varepsilon d\varepsilon \varepsilon^n = \frac{\varepsilon^{n+1}}{n+1}
\end{equation}
one finds
\[
\langle v \rangle = \left( \frac{\int_0^\varepsilon \varepsilon \, d\varepsilon}{\int_0^\varepsilon \varepsilon^{1/2} \, d\varepsilon} \right)^2 = \frac{2^2 \varepsilon F}{(2^3 \varepsilon F)^2} = \frac{9}{8}.
\]
(4.167)

8. The effect of rotation is the same as an additional external field with potential energy given by
\[
U (r) = -\frac{1}{2} M \omega^2 r^2 ,
\]
(4.168)
thus
\[
n (r) = A \exp \left[ -\beta U (r) \right] = A \exp \left( \frac{\beta M \omega^2}{2} r^2 \right) ,
\]
(4.169)
where the normalization constant \( A \) is found from the condition
\[
N = 2\pi L \int_0^R n (r) r \, dr
= 2\pi LA \int_0^R \exp \left( \frac{\beta M \omega^2}{2} r^2 \right) r \, dr
= \frac{2\pi LA}{\beta M \omega^2} \left[ \exp \left( \frac{\beta M \omega^2}{2} R^2 \right) - 1 \right] ,
\]
(4.170)
thus
\[
n (r) = \frac{N \beta M \omega^2}{2\pi L} \left[ \exp \left( \frac{\beta M \omega^2}{2} R^2 \right) - 1 \right] \exp \left( \frac{\beta M \omega^2}{2} r^2 \right) .
\]
(4.171)

9. In the classical limit the probability distribution of the velocity vector \( \mathbf{v} \) satisfies
\[
f (\mathbf{v}) \propto \exp \left( -\frac{Mv^2}{2\tau} \right) ,
\]
(4.172)
where \( \tau = |\mathbf{v}| \).

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a) By changing the integration variable
\[ x = \frac{Mv^2}{2\tau} \]  
(4.173)

one finds
\[ \langle v \rangle = \frac{\int_{0}^{\infty} dv v^3 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_{0}^{\infty} dv v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)} \]
\[ = \left( \frac{2\tau}{M} \right)^{1/2} \frac{\int_{0}^{\infty} dx x^3 \exp(-x)}{\int_{0}^{\infty} dx x^2 \exp(-x)} \]
\[ = \left( \frac{8\tau}{\pi M} \right)^{1/2} . \]
(4.174)

b) Similarly
\[ \langle v^2 \rangle = \frac{\int_{0}^{\infty} dv v^4 \exp \left( -\frac{Mv^2}{2\tau} \right)}{\int_{0}^{\infty} dv v^2 \exp \left( -\frac{Mv^2}{2\tau} \right)} \]
\[ = \frac{2\tau}{M} \frac{\int_{0}^{\infty} dx x^3 \exp(-x)}{\int_{0}^{\infty} dx x^2 \exp(-x)} \]
\[ = \frac{2\tau}{M} \left( \frac{3}{2} \right) \]
(4.175)

thus
\[ \sqrt{\langle v^2 \rangle} = \left( \frac{3\tau}{M} \right)^{1/2} = \left( \frac{3\pi}{8} \right)^{1/2} \langle v \rangle . \]
(4.176)

10. 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
\[ S \int_{0}^{h} n (z) dz = N_l , \]
(4.178)

therefore
\[ n_l (0) = \frac{N_l}{S \int_{0}^{h} \exp (-\beta M_l g z) dz} = \frac{\beta M_l g N_l}{S (1 - e^{-\beta M_l g h})} . \]
(4.179)
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

\[
p = \left( \frac{M_1 N_1}{\exp(\beta M_1 gh) - 1} + \frac{M_2 N_2}{\exp(\beta M_2 gh) - 1} \right) \frac{g S}{\tau}.
\]

(4.180)

11. The relation (4.137), which is a Taylor expansion of the function \( f(t) = \exp(2Xt - t^2) \) around the point \( t = 0 \), implies that

\[
H_n(X) = \left. \frac{d^n}{dt^n} \exp(2Xt - t^2) \right|_{t=0}.
\]

(4.181)

The identity \( 2Xt - t^2 = X^2 - (X - t)^2 \) yields

\[
H_n(X) = \left. \exp(X^2) \frac{d^n}{dt^n} \exp(- (X - t)^2) \right|_{t=0}.
\]

(4.182)

Moreover, using the relation

\[
\frac{d}{dt} \exp(-(X - t)^2) = -\frac{d}{dX} \exp(-(X - t)^2) ,
\]

(4.183)

one finds that

\[
H_n(X) = \exp(X^2) (-1)^n \left. \frac{d^n}{dX^n} \exp(-(X - t)^2) \right|_{t=0}
= \exp(X^2) (-1)^n \left. \frac{d^n}{dX^n} \exp(-X^2) \right|_{t=0}.
\]

(4.184)

Note that for an arbitrary function \( g(X) \) the following holds

\[
-\exp(X^2) \frac{d}{dX} \exp(-X^2) g = \left( 2X - \frac{d}{dX} \right) g ,
\]

(4.185)

and

\[
\exp\left( \frac{X^2}{2} \right) \left( X - \frac{d}{dX} \right) \exp\left( -\frac{X^2}{2} \right) g = \left( 2X - \frac{d}{dX} \right) g ,
\]

(4.186)

thus

\[
H_n(X) = \exp\left( \frac{X^2}{2} \right) \left( X - \frac{d}{dX} \right)^n \exp\left( -\frac{X^2}{2} \right) .
\]

(4.187)
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12. With the help of Eq. (4.184) and the general identity

\[
\int_{-\infty}^{\infty} \exp(-ax^2 + bx + c) \, dx = \sqrt{\frac{\pi}{a}} e^{\frac{4bc+2b^2}{a}},
\]

(4.188)

according to which the following holds (for the case \(a = 1, b = 2iX\) and \(c = 0\))

\[
\exp(-X^2) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-x^2 + 2iXx) \, dx,
\]

(4.189)

one finds that

\[
H_n(X) = \frac{\exp(X^2)}{\sqrt{\pi}} \left(-\frac{d}{dx}\right)^n \int_{-\infty}^{\infty} \exp(-x^2 + 2iXx) \, dx
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} (-2ix)^n \exp(X^2 - x^2 + 2iXx) \, dx
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} (-2ix)^n e^{(X+ix)^2} \, dx,
\]

(4.190)

thus the following holds [see Eq. (4.188)]

\[
\sum_{n=0}^{\infty} \left(\frac{\alpha}{2}\right)^n H_n(X) H_n(Y)
= \frac{1}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dy \, e^{(X+iy)^2} e^{(Y+iy)^2} \sum_{n=0}^{\infty} \left(-\frac{2\alpha xy}{n!}\right)^n e^{-2\alpha xy}
= \frac{1}{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sqrt{\pi} e^{\alpha xy(2x+2iY)} e^{-2\alpha xy}
= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \, e^{-(1-\alpha^2)x^2+2(2XY-\alpha X)x+X^2}
= \exp\left(\frac{\alpha(2XY-\alpha X-\alpha Y^2)}{1-\alpha^2}\right)
= \sqrt{\frac{\pi}{1-\alpha^2}}.
\]

(4.191)
5. Exercises

5.1 Problems

1. Two identical non-interacting particles each having mass \( M \) are confined in a one dimensional parabolic potential given by

\[
V(x) = \frac{1}{2}M\omega^2 x^2 ,
\]  

(5.1)

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.

2. Consider a one dimension 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 \( \varepsilon_F \).

3. Consider an ideal classical gas at temperature \( \tau \). The set of internal eigenstates of each particle in the gas, 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. Calculate the magnetization of the system, which is defined by

\[
M = -\left( \frac{\partial F}{\partial H} \right)_\tau ,
\]  

(5.2)

where \( F \) is the Helmholtz free energy.

4. (Note: replace this with Ex. 3.9 in the lecture notes) Consider an ideal gas made of \( N \) electrons in the 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 modified: the energy \( \varepsilon \) of a single particle quantum state having a wavefunction \( \psi \) given by

\[
\psi(x,y,z) = \left( \frac{2}{L} \right)^{3/2} \sin \left( \frac{k_x x}{L} \right) \sin \left( \frac{k_y y}{L} \right) \sin \left( \frac{k_z z}{L} \right) ,
\]  

(5.3)
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is given by

$$\varepsilon(k) = \hbar kc,$$

(5.4)

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 $\varepsilon(k) = \frac{\hbar^2 k^2}{2M}$). 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 $U$.

5. 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 $p_2$.

6. 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

$$V(x_1, x_2) = \frac{m\omega^2 x_1^2}{2} + \frac{m\omega^2 x_2^2}{2} + m\Omega^2 (x_1 - x_2)^2,$$

(5.5)

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

a) $\langle x_1^2 \rangle$ for the case $\Omega = 0$.

b) $\langle x_1^2 \rangle$, however without assuming that $\Omega = 0$.

c) $\langle (x_1 - x_2)^2 \rangle$, again without assuming that $\Omega = 0$.

7. 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 a volume $V = L^3$. In the extreme relativistic limit the dispersion relation $\varepsilon(k)$ is modified: the energy $\varepsilon$ of a single particle quantum state having a wavefunction $\psi$ given by

$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z),$$

(5.6)

is given by

$$\varepsilon(k) = \hbar kc,$$

(5.7)

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 $\varepsilon(k) = \frac{\hbar^2 k^2}{2M}$). The system is in thermal equilibrium at temperature $\tau$. Calculate:
5.2 Solutions

a) the total energy $U$ of the system.
b) the pressure $p$.

8. Consider a system made of two localized spin $1/2$ particles whose energy is given by

$$
\varepsilon_{\sigma_1, \sigma_2} = -\mu_0 H (\sigma_1 + \sigma_2) + J \sigma_1 \sigma_2 ,
$$

(5.8)

where both $\sigma_1$ and $\sigma_2$ can take one of two possible values $\sigma_n = \pm 1$ ($n = 1, 2$). 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

$$
\chi = \lim_{H \to 0} \frac{\partial M}{\partial H} ,
$$

(5.9)

$$
M = -\left( \frac{\partial F}{\partial H} \right)_{\tau} 
$$

(5.10)

is the magnetization of the system, and where $F$ is the Helmholtz free energy.

9. Consider a one dimensional gas containing $N$ non-interacting electrons moving along the $x$ direction. The electrons are confined by a potential given by

$$
V(x) = \frac{1}{2} m \omega^2 x^2 ,
$$

(5.11)

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 $\tau \gg \hbar \omega$.

10. The state equation of a given matter is

$$
p = \frac{A \tau^n}{V} ,
$$

(5.12)

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.

5.2 Solutions

1. The single particle eigen energies are given by

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

(5.13)

where $n = 0, 1, 2, \ldots$. 
Chapter 5. Exercises

a) For Bosons

\[ Z_{c,B} = \frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \exp\left[\beta \left(\epsilon_n + \epsilon_m\right)\right] + \frac{1}{2} \sum_{n=0}^{\infty} \exp\left(-2\beta \epsilon_n\right) \]

\[ = \frac{1}{2} \left( \sum_{n=0}^{\infty} \exp\left(-\beta \epsilon_n\right) \right)^2 + \frac{1}{2} \sum_{n=0}^{\infty} \exp\left(-2\beta \epsilon_n\right) \]

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

Note that the average energy \( U_B \) is given by

\[ U_B = -\frac{\partial \log Z_{c,B}}{\partial \beta} = \hbar \omega \frac{1 + 2e^{-2\beta \hbar \omega} + e^{-\beta \hbar \omega}}{1 - e^{-2\beta \hbar \omega}} . \]  

(5.15)

b) For Fermions

\[ Z_{c,F} = \frac{1}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \exp\left[\beta \left(\epsilon_n + \epsilon_m\right)\right] - \frac{1}{2} \sum_{n=0}^{\infty} \exp\left(-2\beta \epsilon_n\right) \]

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

Note that for this case the average energy \( U_F \) is given by

\[ U_F = -\frac{\partial \log Z_{c,F}}{\partial \beta} = \hbar \omega \frac{2 + e^{-2\beta \hbar \omega} + e^{-\beta \hbar \omega}}{1 - e^{-2\beta \hbar \omega}} . \]  

(5.17)

2. The orbital eigenenergies are given by

\[ \epsilon_n = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 n^2 , \]

where \( n = 1, 2, 3, \ldots \). The grandcanonical partition function of the gas is given by

\[ Z_{gc} = \prod_n \zeta_n , \]

where

\[ \zeta_n = \prod_1 \left(1 + \lambda \exp(-\beta \epsilon_n) \exp(-\beta E_l)\right) \]

(5.20)

is the orbital grandcanonical Fermionic partition function where,

\[ \lambda = \exp(\beta \mu) = e^{-\eta} , \]

(5.21)

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

$$\log Z_{gc} = \sum_{n=1}^{\infty} \log \zeta_n$$

$$= 2 \sum_{n=1}^{\infty} \log (1 + \lambda \exp (-\beta \varepsilon_n))$$

$$\simeq 2 \int_{0}^{\infty} d\varepsilon \log \left( 1 + \lambda \exp \left( -\beta \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2 \right) \right).$$

(5.22)

By employing the variable transformation

$$\varepsilon = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} \right)^2 n^2,$$

(5.23)

one has

$$\log Z_{gc} = \frac{1}{2} \int_{0}^{\infty} d\varepsilon D(\varepsilon) \log (1 + \lambda \exp (-\beta \varepsilon)),$$

(5.24)

where

$$D(\varepsilon) = \begin{cases} \frac{2L}{\pi} \sqrt{\frac{2m}{\varepsilon}} \varepsilon^{-1/2} & \varepsilon \geq 0 \\ 0 & \varepsilon < 0 \end{cases}$$

(5.25)

is the 1D density of states. Using Eqs. (1.80) and (1.94) for the energy $U$ and the number of particles $N$, namely using

$$U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_{\eta},$$

(5.26)

$$N = \lambda \left( \frac{\partial \log Z_{gc}}{\partial \lambda} \right),$$

(5.27)

one finds that

$$U = \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) \varepsilon f_{FD}(\varepsilon),$$

(5.28)

$$N = \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) f_{FD}(\varepsilon),$$

(5.29)

where $f_{FD}$ is the Fermi-Dirac distribution function [see Eq. (2.35)]

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}.$$
At zero temperature, where $\mu = \varepsilon_F$ one has
\begin{align*}
U &= D(\varepsilon_F) \frac{\varepsilon_F}{\varepsilon_F^{-1/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} = \frac{2D(\varepsilon_F)}{3} \varepsilon_F^2, \\
N &= D(\varepsilon_F) \frac{\varepsilon_F}{\varepsilon_F^{-1/2}} \int_0^{\varepsilon_F} d\varepsilon \varepsilon^{-1/2} = 2D(\varepsilon_F) \varepsilon_F,
\end{align*}
(5.31)
(5.32)
thus
\begin{equation}
\frac{U}{\varepsilon_F} = \frac{N}{3}.
\end{equation}
(5.33)

3. The Helmholtz free energy is given by
\begin{equation}
F = N\tau \left( \log \frac{n}{nQ} - \log Z_{\text{int}} - 1 \right),
\end{equation}
(5.34)
where
\begin{equation}
Z_{\text{int}} = \exp(\beta \mu_0 H) + \exp(-\beta \mu_0 H) = 2 \cosh(\beta \mu_0 H)
\end{equation}
(5.35)
is the internal partition function. Thus the magnetization is given by
\begin{equation}
M = -\left( \frac{\partial F}{\partial H} \right)_\tau = N\mu_0 \tanh(\beta \mu_0 H).
\end{equation}
(5.36)

4. The grandcanonical partition function of the gas is given by
\begin{equation}
Z_{\text{gc}} = \prod_n \zeta_n,
\end{equation}
(5.37)
where
\begin{equation}
\zeta_n = \prod_l (1 + \lambda \exp(-\beta \varepsilon_n) \exp(-\beta E_l))
\end{equation}
(5.38)
is a grandcanonical Fermionic partition function of an orbital having energy $\varepsilon_n$ given by
\begin{equation}
\varepsilon_n = \pi \hbar c n \sqrt{n_x^2 + n_y^2 + n_z^2},
\end{equation}
(5.39)
where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, $n_x, n_y, n_z = 1, 2, 3, \cdots$,
\begin{equation}
\lambda = \exp(\beta \mu) = e^{-\eta}
\end{equation}
(5.40)
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

\[
\log Z_{gc} = \sum_l \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \log (1 + \lambda \exp (-\beta \varepsilon_n) \exp (-\beta E_l)) . \tag{5.41}
\]

For a macroscopic system the sum over \( n \) can be approximately replaced by an integral

\[
\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow 4\pi \int_0^\infty d n^2 , \tag{5.42}
\]

thus, one has

\[
\log Z_{gc} = 2 \frac{4\pi}{8} \int_0^\infty d n^2 \log (1 + \lambda \exp \left(-\beta \frac{\pi \hbar n}{L}\right)) . \tag{5.43}
\]

By employing the variable transformation

\[
\varepsilon = \frac{\pi \hbar n}{L} , \tag{5.44}
\]

one has

\[
\log Z_{gc} = \int_0^\infty d\varepsilon \frac{V \varepsilon^2}{\pi^2 \hbar^3 c^3} \log (1 + \lambda \exp (-\beta \varepsilon)) . \tag{5.45}
\]

The energy \( U \) and the number of particles \( N \) are given by

\[
U = -\left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \int_0^\infty d\varepsilon \frac{V \varepsilon^3}{\pi^2 \hbar^3 c^3} f_{FD}(\varepsilon) , \tag{5.46}
\]

\[
N = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda} = \int_0^\infty d\varepsilon \frac{V \varepsilon^2}{\pi^2 \hbar^3 c^3} f_{FD}(\varepsilon) , \tag{5.47}
\]

where \( f_{FD} \) is the Fermi-Dirac distribution function [see Eq. (2.35)]

\[
f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1} . \tag{5.48}
\]

At zero temperature

\[
U = \int_0^{\varepsilon_F} d\varepsilon \frac{V \varepsilon^3}{\pi^2 \hbar^3 c^3} = \frac{V \varepsilon_F^4}{\pi^2 \hbar^3 c^3} , \tag{5.49}
\]

\[
N = \int_0^{\varepsilon_F} d\varepsilon \frac{V \varepsilon^2}{\pi^2 \hbar^3 c^3} = \frac{V \varepsilon_F^3}{\pi^2 \hbar^3 c^3} , \tag{5.50}
\]
and therefore

\[ U = \frac{3N}{4} \varepsilon_F . \] (5.51)

The energy \( U \) can be expressed as a function of \( V \) and \( N \) as

\[ U = \frac{(3N)^{4/3} \left( \pi^2 h^3 c^3 \right)^{1/3} V^{-1/3}}{4} . \]

At zero temperature the Helmholtz free energy \( F \) equals the energy \( U \), thus the pressure \( p \) is given by

\[ p = -\left( \frac{\partial F}{\partial V} \right)_{\tau,N} = -\left( \frac{\partial U}{\partial V} \right)_{\tau,N} = \frac{1}{3} \frac{(3N)^{4/3} \left( \pi^2 h^3 c^3 \right)^{1/3}}{4} , \] (5.52)

thus

\[ \frac{p}{U} = \frac{1}{3V} . \] (5.53)

5. First, consider the case of an ideal gas made of a unique type of particles. Recall that the entropy \( \sigma \), \( c_V \) and \( c_p \) are given by [see Eqs. (2.87), (2.88) and (2.89)]

\[ \sigma = N \left( \frac{5}{2} + \log \frac{n_Q}{n} + \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right) , \] (5.54)

\[ c_V = N \left( \frac{3}{2} + h_{\text{int}} \right) , \] (5.55)

\[ c_p = c_V + N , \] (5.56)

where \( n = N/V \) is the density,

\[ n_Q = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} \] (5.57)

is the quantum density, \( M \) is the mass of a particle in the gas, and

\[ h_{\text{int}} = \tau \frac{\partial^2 (\tau \log Z_{\text{int}})}{\partial \tau^2} = \frac{c_V}{N} - \frac{3}{2} . \] (5.58)

The requirement that \( h_{\text{int}} \) is temperature independent leads to

\[ \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} = g_{\text{int}} + h_{\text{int}} \log \frac{\tau}{\tau_0} , \] (5.59)

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
\[ \Delta \sigma = \sigma_2 - \sigma_1 = N \left( \log \frac{V_2 \tau_2^{3/2}}{V_1 \tau_1^{3/2}} + \left( \frac{c_V}{N} - \frac{3}{2} \right) \log \frac{\tau_2}{\tau_1} \right) \]
\[ = N \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_V}{N}} \right). \tag{5.60} \]

Thus the total change in the entropy of the mixture is given by
\[ \Delta \sigma = \Delta \sigma_A + \Delta \sigma_B \]
\[ = N_A \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V_A}}{N_A}} \right) + N_B \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V_B}}{N_B}} \right) \tag{5.61} \]
\[ = (N_A + N_B) \log \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V_A+V_B}}{N_A+N_B}} \right), \tag{5.62} \]
and the requirement \( \Delta \sigma = 0 \) leads to
\[ \left( \frac{V_2}{V_1} \left( \frac{\tau_2}{\tau_1} \right)^{\frac{c_{V_A+V_B}}{N_A+N_B}} \right) = 1. \tag{5.63} \]

Alternatively, by employing the equation of state
\[ pV = N \tau, \tag{5.64} \]
this can be rewritten as
\[ \left( \frac{V_2}{V_1} \right)^{\frac{c_{V_A+V_B}}{N_A+N_B}+1} \left( \frac{p_2}{p_1} \right)^{\frac{c_{V_A+V_B}}{N_A+N_B}} = 1, \tag{5.65} \]
or with the help of Eq. (5.56) as
\[ p_2 = p_1 \left( \frac{V_2}{V_1} \right)^{-\frac{c_{p_A+p_B}}{N_A+N_B}+1} \]
\[ = p_1 \left( \frac{V_1}{V_2} \right)^{\frac{c_{p_A+p_B}}{N_A+N_B}}. \tag{5.66} \]

6. It is convenient to employ the coordinate transformation
\[ x_+ = \frac{x_1 + x_2}{\sqrt{2}}, \tag{5.67} \]
\[ x_- = \frac{x_1 - x_2}{\sqrt{2}}. \tag{5.68} \]

The inverse transformation is given by
\[ x_1 = \frac{x_+ + x_-}{\sqrt{2}}, \quad \text{(5.69)} \]
\[ x_2 = \frac{x_+ - x_-}{\sqrt{2}}. \quad \text{(5.70)} \]

The following holds
\[ x_1^2 + x_2^2 = x_+^2 + x_-^2, \quad \text{(5.71)} \]
and
\[ \dot{x}_1^2 + \dot{x}_2^2 = \dot{x}_+^2 + \dot{x}_-^2. \quad \text{(5.72)} \]

Thus, the kinetic energy \( T \) of the system is given by
\[ T = \frac{m}{2} \left( \dot{x}_1^2 + \dot{x}_2^2 \right) = \frac{m}{2} \left( \dot{x}_+^2 + \dot{x}_-^2 \right), \quad \text{(5.73)} \]
and the potential energy \( V \) is given by
\[ V(x_1, x_2) = \frac{m\omega^2 x_1^2}{2} + \frac{m\omega^2 x_2^2}{2} + m\Omega^2 (x_1 - x_2)^2 \]
\[ = \frac{m\omega^2 x_+^2}{2} + \frac{m}{2} \left( \omega^2 + 4\Omega^2 \right) x_-^2. \quad \text{(5.74)} \]

The equipartition theorem yields
\[ \frac{m\omega^2 \langle x_+^2 \rangle}{2} = \frac{m}{2} \left( \omega^2 + 4\Omega^2 \right) \langle x_-^2 \rangle = \frac{\tau}{2}, \quad \text{(5.75)} \]
thus
\[ \langle (x_1 + x_2)^2 \rangle = \frac{2\tau}{m\omega^2}, \quad \text{(5.76)} \]
and
\[ \langle (x_1 - x_2)^2 \rangle = \frac{2\tau}{m(\omega^2 + 4\Omega^2)}. \quad \text{(5.77)} \]

Furthermore, since by symmetry \( \langle x_+ x_- \rangle = 0 \) one has
\[ \langle x_1^2 \rangle = \frac{1}{2} \langle (x_+ + x_-)^2 \rangle \]
\[ = \frac{1}{2} \left( \langle x_+^2 \rangle + \langle x_-^2 \rangle \right) \]
\[ = \frac{\tau}{m\omega^2} \left( 1 - \frac{1}{2} \frac{4\Omega^2}{\omega^2} \right). \quad \text{(5.78)} \]
7. The $k$ vector is restricted due to boundary conditions to the values

$$ k = \frac{\pi n}{L}, \quad (5.79) $$

where

$$ n = (n_x, n_y, n_z), \quad (5.80) $$

and $n_x, n_y, n_z = 1, 2, 3, \cdots$. The single particle partition function is given by

$$ Z_1 = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left( -\frac{\varepsilon(k)}{\tau} \right). \quad (5.81) $$

Approximating the discrete sum by a continuous integral according to

$$ \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \rightarrow \frac{4\pi}{8} \int_0^{\infty} \frac{d n}{n^2}, \quad (5.82) $$

one has

$$ Z_1 = \frac{4\pi}{8} \int_0^{\infty} \frac{d n}{n^2} \exp \left( -\frac{\hbar \pi c}{L \tau} \right) $$

$$ = \frac{4V\tau^3}{8\pi^2\hbar^3c^3} \int_0^{\infty} \frac{d x}{x^2} \exp (-x) $$

$$ = \frac{V\tau^3}{\pi^2\hbar^3c^3}. \quad (5.83) $$

In the classical limit the grandcanonical partition function $Z_{gc}$ is given by [see Eq. (2.44)]

$$ \log Z_{gc} = \lambda Z_1, \quad (5.84) $$

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

$$ \log Z_{gc} = e^{-\eta} \frac{V}{\pi^2\hbar^3c^3\beta^3}. \quad (5.85) $$

a) The average energy $U$ and average number of particle $N$ are calculated using Eqs. (1.80) and (1.81) respectively.

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\[ U = - \left( \frac{\partial \log Z_{gc}}{\partial \beta} \right)_\eta = \frac{3}{\beta} \log Z_{gc}, \quad (5.86) \]

\[ N = - \left( \frac{\partial \log Z_{gc}}{\partial \eta} \right)_\beta = \log Z_{gc}, \quad (5.87) \]

thus

\[ U = 3N\tau, \quad (5.88) \]

and

\[ \eta = \log \left( \frac{V\tau^3}{\pi^2 N\hbar^3 c^3} \right), \quad (5.89) \]

b) The entropy is evaluate using Eq. (1.86)

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

\[ = N (1 + 3 + \eta) \]

\[ = N \left[ 4 + \log \left( \frac{V\tau^3}{\pi^2 N\hbar^3 c^3} \right) \right], \quad (5.90) \]

and the Helmholtz free energy by the definition (1.116)

\[ F = U - \tau \sigma = -N\tau \left[ 1 + \log \left( \frac{V\tau^3}{\pi^2 N\hbar^3 c^3} \right) \right]. \quad (5.91) \]

Thus the pressure \( p \) is given by

\[ p = - \left( \frac{\partial F}{\partial V} \right)_{\tau,N} = \frac{N\tau}{V}. \quad (5.92) \]

8. The partition function is given by

\[ Z = \sum_{\sigma_1,\sigma_2 = \pm 1} \exp (-\beta \varepsilon_{\sigma_1,\sigma_2}) \]

\[ = \exp (-\beta J) [\exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H)] + 2 \exp (\beta J), \quad (5.93) \]

where \( \beta = 1/\tau \). The free energy is given by

\[ F = -\tau \log Z, \quad (5.94) \]

thus the magnetization is given by

\[ M = - \left( \frac{\partial F}{\partial H} \right)_{\tau} = \frac{2\mu_0 \exp (-\beta J) [- \exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H)]}{\exp (-\beta J) [\exp (-2\beta \mu_0 H) + \exp (2\beta \mu_0 H)] + 2 \exp (\beta J)}, \quad (5.95) \]
and the magnetic susceptibility is given by
\[ \chi = \frac{4\beta\mu_0^2}{1 + e^{2\beta J}}. \] (5.96)

Note that in the high temperature limit \( \beta J \ll 1 \)
\[ \chi \simeq \frac{2\mu_0^2}{\tau + J}. \] (5.97)

9. The orbital eigenenergies in this case are given by
\[ \varepsilon_n = \hbar\omega \left( n + \frac{1}{2} \right), \] (5.98)
where \( n = 0, 1, 2, \cdots \). The grandcanonical partition function of the gas is given by
\[ Z_{gc} = \prod_n \zeta_n, \] (5.99)
where
\[ \zeta_n = \prod_l (1 + \lambda \exp(-\beta\varepsilon_n) \exp(-\beta E_l)) \] (5.100)
is the orbital grandcanonical Fermionic partition function where,
\[ \lambda = \exp(\beta\mu) = e^{-\eta} \] (5.101)
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
\[ \log Z_{gc} = \sum_{n=0}^{\infty} \log \zeta_n = 2 \sum_{n=0}^{\infty} \log (1 + \lambda \exp(-\beta\varepsilon_n)). \] (5.102)
The number of particles \( N \) is given by
\[ N = \lambda \frac{\partial \log Z_{gc}}{\partial \lambda} = 2 \sum_{n=0}^{\infty} f_{FD}(\varepsilon_n), \] (5.103)
where \( f_{FD} \) is the Fermi-Dirac distribution function
\[ f_{FD}(\varepsilon) = \frac{1}{\exp[\beta (\varepsilon - \mu)] + 1}. \] (5.104)
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. (5.103) one finds that

$$N = \frac{2\varepsilon_F}{\hbar \omega}, \quad (5.105)$$

thus

$$\mu = \varepsilon_F = \frac{N \hbar \omega}{2}. \quad (5.106)$$

b) Using the approximation

$$f_{FD}(\varepsilon) \simeq \exp\left[-\beta (\varepsilon - \mu)\right], \quad (5.107)$$

for the the limit of high temperatures and approximating the sum by an integral one has

$$N = 2 \sum_{n=0}^{\infty} \exp\left[-\beta \left(\hbar \omega \left(n + \frac{1}{2}\right) - \mu\right)\right]$$

$$= 2 \exp\left(\beta \left(\mu - \frac{\hbar \omega}{2}\right)\right) \int_0^{\infty} dn \exp(-\beta \hbar \omega n)$$

$$= 2 \exp\left(\frac{\beta(\mu - \frac{\hbar \omega}{2})}{\beta \hbar \omega}\right), \quad (5.108)$$

thus

$$\mu = \tau \left(\log\left(\frac{N \beta \hbar \omega}{2}\right) + \frac{\beta \hbar \omega}{2}\right)$$

$$\simeq \tau \log\left(\frac{N \beta \hbar \omega}{2}\right). \quad (5.109)$$

10. Using Eq. (2.239), which is given by

$$c_p - c_V = \tau \left(\frac{\partial p}{\partial \tau}\right)_{V,N} \left(\frac{\partial V}{\partial \tau}\right)_{p,N}, \quad (5.110)$$

one finds that

$$c_p - c_V = \frac{A^2 \tau}{pV} n^2 T^{-2(n-1)} = n^2 A T^{n-1}. \quad (5.111)$$
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