THERMODYNAMICS AND STATISTICAL MECHANICS

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This text was compiled on 04/15/2025

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CHAPTER OVERVIEW

1: Basic Concepts

Thermodynamics is the description of thermal properties of matter in bulk. The study of phenomena involving the transfer of heat energy and allied processes form the subject matter. The fundamental description of the properties of matter in bulk, such as temperature, heat energy, etc., are given by statistical mechanics. For equilibrium states of a system the results of statistical mechanics give us the laws of thermodynamics. These laws were empirically enunciated before the development of statistical mechanics. Taking these laws as axioms, a logical buildup of the subject of thermodynamics is possible.

1.1: Definitions

Thermodynamic Coordinates

The macroscopically and directly observable quantities for any state of a physical system are the thermodynamic coordinates of that state. As an example, the pressure p and volume V of a gas can be taken as thermodynamic coordinates. In more general situations, other coordinates, such as magnetization and magnetic field, surface tension and area, may be necessary. The point is that the thermodynamic coordinates uniquely characterize the macroscopic state of the system.

Thermal Contact

Two bodies are in thermal contact if there can be free flow of heat between the two bodies.

Adiabatic Isolation

A body is said to be in adiabatic isolation if there can be no flow of heat energy into the body or out of the body into the environment. In other words, there is no exchange of heat energy with the environment.

Thermodynamic Equilibrium

A body is said to be in thermodynamic equilibrium if the thermodynamic coordinates of the body do not change with time.

Two bodies are in thermal equilibrium with each other if on placing them in thermal contact, the thermodynamic coordinates do not change with time.

Quasistatic Changes

The thermodynamic coordinates of a physical can change due to any number of reasons, due to compression, magnetization, supply of external heat, work done by the system, etc. A change is said to be quasistatic if the change in going from an initial state of equilibrium to a final state of equilibrium is carried out through a sequence of intermediate states which are all equilibrium states. The expectation is that such quasistatic changes can be achieved by changes which are slow on the time-scale of the molecular interactions.

Since thermodynamics is the description of equilibrium states, the changes considered in thermodynamics are all quasistatic changes.

Work done by a System

It is possible to extract work from a thermodynamic system or work can be done by external agencies on the system, through a series of quasistatic changes. The work done by a system is denoted by W. The amount of work done between two equilibrium states of a system will depend on the process connecting them. For example, for the expansion of a gas, the work done by the system is

$$dW = p\,dV \tag{1.1.1}$$

Exact Differentials

Consider a differential form defined on some neighborhood of an n-dimensional manifold which may be written explicitly as

$$A = \sum_i f_i dx^i \tag{1.1.2}$$

where f_i are functions of the coordinates x^i. A is an exact differential form if we can integrate A along any curve C between two points, say, $\vec{x} = (x^1, x^2, \cdots, x^n)$ and $\overrightarrow{x'} = (x^{1'}, x^{2'}, \cdots, x^{n'})$ and the result depends only on the two end-points and is independent of the path C. This means that there exists a function F in the neighborhood under consideration such that $A = d\,F$. A necessary condition for exactness of A is

$$\frac{\partial f_j}{\partial x^i} - \frac{\partial f_i}{\partial x^j} = 0 \tag{1.1.3}$$

Conversely, if the conditions Equation 1.1.3 are satisfied, then one can find a function F such that $A = dF$ in a star-shaped neighborhood of the points $\vec{x}$ and $\overrightarrow{x'}$.

The differential forms we encounter in thermodynamics are not necessarily exact. For example, the work done by a system, say, dW is not an exact differential. Thus the work done in connecting two states α and β, which is given by $\int_{\alpha}^{\beta} dW$, will depend on the path, i.e., the process involved in going from state α to state β.

1.2: The Zeroth Law of Thermodynamics

This can be stated as follows.

Zeroth Law of Thermodynamics:

If two bodies A and B are in thermal equilibrium with a third body C, then they are in thermal equilibrium with each other.

Consequences of the Zeroth Law

Thermal equilibrium of two bodies will mean a restrictive relation between the thermodynamic coordinates of the first body and those of the second body. In other words, thermal equilibrium means that

$$F(\overrightarrow{x_A}, \overrightarrow{x_B}) = 0 \tag{1.2.1}$$

if A and B are in thermal equilibrium. Thus the zeroth law states that

$$\left.\begin{array}{l} F(\overrightarrow{x_A}, \overrightarrow{x_B}) = 0 \\ F(\overrightarrow{x_B}, \overrightarrow{x_C}) = 0 \end{array}\right\} \Rightarrow F(\overrightarrow{x_A}, \overrightarrow{x_C}) = 0 \tag{1.2.2}$$

This is possible if and only if the relations are of the form

$$F(\overrightarrow{x_A}, \overrightarrow{x_B}) = t(\overrightarrow{x_A}) - t(\overrightarrow{x_B}) = 0 \tag{1.2.3}$$

This means that, for any body, there exists a function $t(\vec{x})$ of the thermodynamic coordinates $\vec{x}$, such that equality of t for two bodies implies that the bodies are in thermal equilibrium. The function t is not uniquely defined. Any single-valued function of t, say, $T(t)$ will also satisfy the conditions for equilibrium, since

$$t_A = t_B \Rightarrow T_A = T_B \tag{1.2.4}$$

The function $t(\vec{x})$ is called the **empirical temperature**. This is the temperature measured by gas thermometers.

The zeroth law defines the notion of temperature. Once it is defined, we can choose $n+1$ variables $(\vec{x}, t)$ as the thermodynamic coordinates of the body, of which only n are independent. The relation $t(\vec{x})$ is an equation of state.

1.3: Equation of State

The Ideal Gas Equation of State

In specifying the equation of state, we will use the absolute temperature, denoted by t. We will introduce this concept later, but for now, we will take it as given. The absolute temperature is always positive, varying from zero (or absolute zero) to infinity. The ideal gas is then characterized by the equation of state

$$pV = nkT \tag{1.3.1}$$

where N denotes the number of molecules of the gas and k is a constant, known as Boltzmann's constant. Another way of writing this is as follows. We define the Avogadro number as 6.02214×10^{23}. This number comes about as follows. The mass of an atom is primarily due to the protons and neutrons in its nucleus. Each proton has a mass of $1.6726 \times 10^{-24} gm$, each neutron has a mass of $1.6749 \times 10^{-24} gm$. If we neglect the mass difference between the proton and the neutron, the mass of an atom of atomic weight A (= number of protons + number of neutrons in the nucleus) is given by $A \times 1.6726 \times 10^{-24} gm$. Thus if we take A grams of the material, the number of atoms is given by $(1.67 \times 10^{-24})^{-1} \approx 6 \times 10^{23}$. This is essentially the Avogadro number. The mass difference between the proton and neutron is not completely negligible and also there are slight variations from one type of nucleus to another due to the varying binding energies of the protons and neutrons. So we standardize the Avogadro number by defining it as 6.02214×10^{23}, which is very close to the number of atoms in $12\, gm$ of the isotope C^{12} of carbon (which was used to standardize the atomic masses).

If we have N molecules of a material, we say that it has$n$ moles of the material, where $n = \frac{N}{\text{Avogadro Number}}$. Thus we can rewrite the ideal gas equation of state as

$$pV = nRT, \quad R = k\,(\text{Avogadro Number}) \tag{1.3.2}$$

Numerically, we have, in joules per kelvin unit of temperature,

$$k \approx 1.38065 \times 10^{-23} \frac{J}{K}, \quad R \approx 8.3145 \frac{J}{\text{mole } K} \tag{1.3.3}$$

The van der Waals Equation of State

The ideal gas law is never obtained for real gases. There are intermolecular forces which change the equation of state, not to mention the quantum nature of the dynamics of the molecules which becomes more important at low temperatures. The equation of state can in principle be calculated or determined from the intermolecular forces in statistical mechanics. The corrections to the ideal gas law can be expressed as series of terms known as the virial expansion, the second virial coefficient being the first such correction. While the method is general, the specifics depend on the nature of the molecules and a simple formula is not easy to write down.

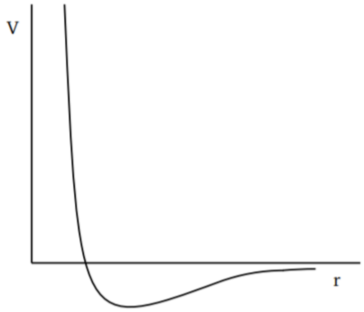


Figure 1.3.1: The general form of the intermolecular potential as a function of distance

An equation of state which captures some very general features of the intermolecular forces was written down by van der Waals, in the 1870s, long before the virial expansion was developed. It is important in that it gives a good working approximation for many gases. The van der Waals equation of state is

$$(p + \frac{aN^2}{V^2})(V - bN) = NkT \tag{1.3.4}$$

The reasoning behind this equation is as follows. In general, intermolecular forces have a short range repulsion, see Fig. 1.3.1. This prevents the molecules from forming bound states. The formation of bound states would be a chemical reaction, so we are really considering gases where there is no further chemical reaction beyond the initial formation of the molecules. For example, if we consider oxygen, two oxygen atoms bind together to form the oxygen molecule O_2, but there is no binding for two oxygen molecules (two O_2's) to form something more complicated. At the potential level, this is due to a short range repulsion keeping them from binding together. In van der Waals' reasoning, such an effect could be incorporated by arguing that the full volume V is not available to the molecules, a certain volume b around each molecule is excluded from being accessible to other molecules. So we must replace V by $(V - bN)$ in the ideal gas law.

Intermolecular forces also have an attractive part at slightly larger separations. This attraction would lead to the molecules coming together, thus reducing the pressure. So the pressure calculated assuming the molecules are noninteracting, which is the kinetic pressure p_{kin}, must be related to the actual pressure p by

$$p = p_{kin} - \frac{aN^2}{V^2} \tag{1.3.5}$$

The interaction is pairwise primarily, so we expect a factor of $\frac{N(N-1)}{2}$ (which is number of pairings one can do) for N molecules. This goes like $\sim N^2$, which explains the second term in Equation 1.3.5. Using the ideal gas law for p_{kin} with the volume $(V - bN)$, we get Equation 1.3.4. In this equation, a and b are parameters specific to the gas under consideration.

CHAPTER OVERVIEW

2: The First Law of Thermodynamics

2.1: The First Law

The first law of thermodynamics is the conservation of energy, including the equivalence of work and energy, and about assigning an internal energy to the system.

First Law of Thermodynamics

When an amount of heat dQ is supplied to the system and an amount of work dW is done by the system, changes are produced in the thermodynamic coordinates of the system such that

$$dU = dQ - dW \tag{2.1.1}$$

where U is a function of the thermodynamic coordinates of the system. (In other words, dU is an exact differential.)

If the system is in adiabatic isolation, $dQ = 0$ and $dU = -dW$. Since dU is an exact differential, this means that

$$W_{adiab} = U_{initial} - U_{final} \tag{2.1.2}$$

Thus the adiabatic work done by the system is independent of the process involved and depends only on the initial and final states of the system. It is the recognition of this fact through careful experiments (by Joule) which led to the first law.

The quantity U is called the **internal energy** of the system. For a gas, where the work done is given by Equation 2.1.2, we may write the first law as

$$dU = dQ - p\,dV \tag{2.1.3}$$

If we put $dQ = 0$, we get a relation between p and V which is valid for adiabatic processes. The curve connecting p and V so obtained is called an adiabatic. Starting with different initial states, we can get a family of adiabatics. In general, when we have more thermodynamic coordinates, adiabatics can be similarly defined, but are higher dimensional surfaces.

Specific Heats

When heat is supplied to a body, the temperature increases. The amount of heat dQ needed to raise the temperature by dT is called the specific heat. This depends on the process, on what parameters are kept constant during the supply of heat. Two useful specific heats for a gas are defined for constant volume and constant pressure. If heat is supplied keeping the volume constant, then the internal energy will increase. From the first law, we find, since $dV = 0$,

$$dU = dQ = C_v dT \tag{2.1.4}$$

Thus the specific heat C_v may be defined as the rate of increase of internal energy with respect to temperature. For supply of heat at constant pressure, we have

$$\begin{aligned} d(U + pV) &= dQ + V\cancel{dp} \\ &= dQ \\ &\equiv C_p dT \end{aligned}$$

Thus the specific heat at constant pressure may be taken as the rate at which the quantity $U + pV$ increases with temperature. The latter quantity is called the enthalpy.

In general, the two specific heats are functions of temperature. The specific heat at constant volume, Cv, can be calculated using statistical mechanics or it can be measured in experiments. C_p can then be evaluated using the equation of state for the material. The ratio $\frac{Cp}{Cv}$ is often denoted by γ.

2.2: Adiabatic and Isothermal Processes

Among the various types of thermodynamic processes possible, there are two very important ones. These are the **adiabatic** and **isothermal** processes. An adiabatic process is one in which there is no supply of heat to the body undergoing change of thermodynamic state. In other words, the body is in adiabatic isolation. An isothermal process is a thermodynamic change where the temperature of the body does not change.

The thermodynamic variables involved in the change can be quite general; for example, we could consider magnetization and the magnetic field, surface tension and area, or pressure and volume. For a gas undergoing thermodynamic change, the relevant variables are pressure and volume. In this case, for an adiabatic process, since $dQ = 0$,

$$\begin{aligned} dU &\equiv C_v dT = -p dV \\ d(U + pV) &\equiv C_p dT = V dp \end{aligned}$$

From these, we find

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \tag{2.2.1}$$

Generally γ can depend on temperature (and hence on pressure), but if we consider a material (such as the ideal gas) for which γ is a constant, the above equation gives

$$pV^{\gamma} = \text{constant} \tag{2.2.2}$$

This is the equation for an adiabatic process for an ideal gas.

If we consider an isothermal process for an ideal gas, the equation of state gives

$$pV = nRT = \text{constant} \tag{2.2.3}$$

2.3: Barometric Formula and the Speed of Sound

Here we consider two simple examples of using the ideal gas law and the formula for adiabatic expansion.First, consider the barometric formula which gives the density (or pressure) of air at a height h above the surface of Earth (also called Pascal's principle). We assume complete equilibrium, mechanical, and thermal. The argument is illustrated in Figure $2.3.1$.

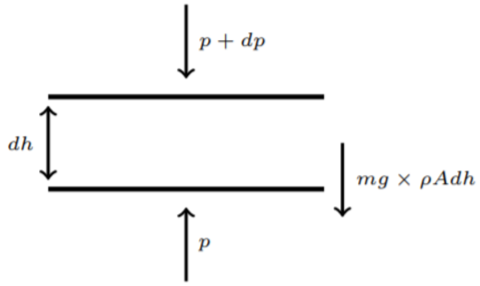


Figure $2.3.1$: Matching of forces for barometric formula

We consider a layer of air, with horizontal cross-sectional area A and height dh. If we take the molecules to have a mass m and the number density of particles to be ρ, then the weight of this layer of air is $mg \times \rho A dh$. This is the force acting downward. It is compensated by the difference of pressure between the upper boundary and the lower boundary for this layer. The latter is thus $dp \times A$, again acting downward, as we have drawn it. The total force being zero for equilibrium, we get

$$dp\ A + mg\rho A dh = 0 \tag{2.3.1}$$

Thus the variation of pressure with height is given by

$$\frac{dp}{dh} = -mg\rho \tag{2.3.2}$$

Let us assume the ideal gas law for air; this is not perfect, but is a reasonably good approximation. Then $p = \frac{NkT}{V} = \rho kT$ and the equation above becomes

$$\frac{dp}{dh} = -\frac{mg}{kT} p \tag{2.3.3}$$

The solution is

$$p = p_0 \exp\left(-\frac{mgh}{kT}\right), \tag{2.3.4}$$

or

$$\rho = \rho_0 \exp\left(-\frac{mgh}{kT}\right) \tag{2.3.5}$$

This argument is admittedly crude. In reality, the temperature also varies with height. Further, there are so many nonequilibrium processes (such as wind, heating due to absorption of solar radiation, variation of temperature between day and night, etc.) in the atmosphere that Equation $2.3.5$ can only be valid for a short range of height and over a small area of local equilibrium.

Our next example is about the speed of sound. For this, we can treat the medium, say, air, as a fluid, characterized by a number density ρ and a flow velocity $\vec{v}$. The equations for the fluid are

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \tag{2.3.6}$$

$$\frac{\partial \vec{v}}{\partial t} + v_i \partial_i \vec{v} = -\frac{\nabla p}{\rho} \tag{2.3.7}$$

Equation $2.3.6$ is the equation of continuity which expresses the conservation of particle number, or mass, if we multiply the equation by the mass of a molecule. Equation $2.3.7$ is the fluid equivalent of Newton’s second law. In the absence of external forces, we still can have force terms; in fact the gradient of the pressure, as seen from the equation, acts as a force term. This may also be re-expressed in terms of the density, since pressure and density are related by the equation of state.

Now consider the medium in equilibrium with no sound waves in it. The equilibrium pressure should be uniform; we denote this by p_0, with the corresponding uniform density as ρ_0. Further, we have $\vec{v} = 0$ in equilibrium. Now we can consider sound waves as perturbations on this background, writing

$$\begin{aligned} \rho &= \rho_0 + \delta\rho \\ p &= p_0 + \delta\rho \left(\frac{\partial p}{\partial \rho}\right)_0 \\ \vec{v} &= 0 + \vec{v} \end{aligned}$$

Treating $\delta\rho$ and $\vec{v}$ as being of the first order in the perturbation, the fluid equations can be approximated as

$$\begin{aligned} \frac{\partial}{\partial t}(\delta\rho) &\approx -\rho_0 \nabla\cdot\vec{v} \\ \frac{\partial \vec{v}}{\partial t} &\approx -\frac{1}{\rho_0}\left(\frac{\partial p}{\partial \rho}\right)_0 \nabla\delta\rho \end{aligned}$$

Taking the derivative of the first equation and using the second, we find

$$\left(\frac{\partial^2}{\partial t^2} - c_s^2\nabla^2\right)\delta\rho = 0 \tag{2.3.8}$$

where

$$c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_0 \tag{2.3.9}$$

Equation 2.3.8 is the wave equation with the speed of propagation given by c_s. This equation shows that density perturbations can travel as waves; these are the sound waves. It is easy to check that the wave equation has wave-like solutions of the form

$$\delta\rho = A\cos(\omega t - \vec{k}\cdot\vec{x}) + B\sin(\omega t - \vec{k}\cdot\vec{x}) \tag{2.3.10}$$

with $\omega^2 = c_s^2 \vec{k}\cdot\vec{k}$. This again identifies c_s as the speed of propagation of the wave.

We can calculate the speed of sound waves more explicitly using the equation of state. If we take air to obey the ideal gas law, we have $p = \rho kT$. If the process of compression and de-compression which constitutes the sound wave is isothermal, then

$$\left(\frac{\partial p}{\partial \rho}\right)_0 = \frac{p_0}{\rho_0}. \tag{2.3.11}$$

Actually, the time-scale for the compression and de-compression in a sound wave is usually very short compared to the time needed for proper thermalization, so that it is more accurate to treat it as an adiabatic process. In this case, we have

$$pV^\gamma = \text{constant} \tag{2.3.12}$$

so that

$$c_s^2 = \left(\frac{\partial p}{\partial \rho}\right)_0 = \gamma\frac{p_0}{\rho_0} \tag{2.3.13}$$

Since $\gamma > 1$, this gives a speed higher than what would be obtained in an isothermal process. Experimentally, one can show that this formula for the speed of sound is what is obtained, showing that sound waves result from an adiabatic process.

CHAPTER OVERVIEW

3: The Second Law of Thermodynamics

3.1: Carnot Cycle

A thermodynamic engine operates by taking in heat from a hot reservoir and performing certain work and then giving up a certain amount of heat into a colder reservoir. If it can be operated in reverse, it can function as a refrigerator. The Carnot cycle is a reversible cyclic process (or engine) made of the following four steps:

1. It starts with an adiabatic process which raises the temperature of the working material of the engine to, say, T_H
2. This is followed by a isothermal process, taking in heat from the reservoir at T_H.
3. The next step is an adiabatic process which does some amount of work and lowers the temperature of the material to T_L.
4. The final step is isothermal, at the lower temperature T_L, dumping some amount of heat into a colder reservoir, with the material returning to the thermodynamic state at the beginning of the cycle.

This is an idealized engine, no real engine can be perfectly reversible. The utility of the Carnot engine is to give the framework and logic of the arguments related to the second law of thermodynamics. We may say it is a *gedanken* engine. The processes involved in the Carnot cycle may refer to compression and expansion if the material is a gas; in this case, the cycle can be illustrated in a $p-V$ diagram as shown in Fig. 3.1.1. But any other pair of thermodynamic variables will do as well. We can think of a Carnot cycle utilizing magnetization and magnetic field, or surface tension and area, or one could consider an electrochemical cell.

Let the amount of heat taken in at temperature T_H be Q_H and let the amount of heat given up at the lower temperature T_L be Q_L. Since this is an idealized case, we assume there is no loss of heat due to anything like friction. Thus the amount of work done, according to the first law is

$$W=Q_H-Q_L \tag{3.1.1}$$

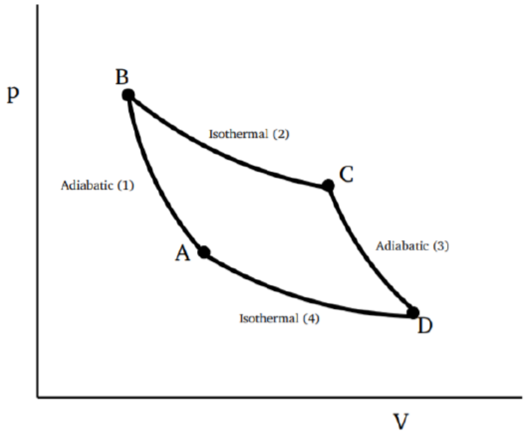


Figure 3.1.1: The Carnot cycle for a gas

The efficiency of the engine is given by the amount of work done when a given amount of heat is supplied, which is $\frac{W}{Q_H}$. (The heat Q_L which is dumped into the reservoir at lower temperature is not usable for work.) The efficiency η for a Carnot cycle is thus

$$\eta=\frac{Q_H-Q_L}{Q_H}=1-\frac{Q_L}{Q_H} \tag{3.1.2}$$

The importance of the Carnot cycle is due to its idealized nature of having no losses and because it is reversible. This immediately leads to some simple but profound consequences.

3.2: The Second Law

The second law of thermodynamics is a statement of what we know by direct experience. It is not something that is derived from more fundamental principles, even though a better understanding of this law has emerged over time. There are several ways to state the second law, the most common ones being the Kelvin statement and the Clausius statement.

> K: Kelvin statement of the second law: There exists no thermodynamics process whose sole effect is to extract an amount of heat from a source and convert it entirely to work.
>
> C: Clausius statement of the second law: There exists no thermodynamics process whose sole effect is to extract an amount of heat from a colder source and deliver it to a hotter source.

The keyword here is “sole". Consider the expansion of a gas and consequent conversion of heat into work. Complete conversion can be achieved but this is not the sole effect, for the state of the system has been changed. The second law does not forbid such a process.

The two statements are equivalent. This can be seen by showing that $\tilde{K} \Rightarrow \tilde{C}$ and $\tilde{C} \Rightarrow \tilde{K}$, where the tildes denote the negation of the statements.

First consider $\tilde{K} \Rightarrow \tilde{C}$. Consider two heat reservoirs at temperatures T_L and T_H, with $T_H > T_L$. Since K is false, we can extract a certain amount of heat from the colder reservoir (at T_L) and convert it entirely to work. Then, we can use this work to deliver a certain amount of heat to the hotter reservoir. For example, work can be converted to heat by processes like friction. So we can have some mechanism like this to heat up the hotter source further. The net result of this operation is to extract a certain amount of heat from a colder source and deliver it to a hotter source, thus contradicting C. Thus $\tilde{K} \Rightarrow \tilde{C}$.

Now consider $\tilde{C} \Rightarrow \tilde{K}$. Since C is presumed false, we can extract an amount of heat, say Q_2, from the colder reservoir (at T_L) and deliver it to the hotter source. Then we can have a thermodynamic engine take this amount of heat Q_2 from the hotter reservoir and do a certain amount of work $W = Q_2 - Q_1$ delivering an amount of heat Q_1 to the colder reservoir. The net result of this cycle is to take the net amount of heat $Q_2 - Q_1$ from the reservoir at T_L and convert it entirely to work. This shows that $\tilde{C} \Rightarrow \tilde{K}$.

The two statements $\tilde{K} \Rightarrow \tilde{C}$ and $\tilde{C} \Rightarrow \tilde{K}$ show the equivalence of the Kelvin and Clausius statements of the second law.

The second law is a statement of experience. Most of the thermodynamic results can be derived from a finer description of materials, in terms of molecules, atoms, etc. However, to date, there is no clear derivation of the second law. Many derivations, such as Boltzmann’s $\mathcal{H}$-theorem, or descriptions in terms of information, have been suggested, which are important in their own ways, but all of them have some additional assumptions built-in. This is not to say that they are not useful. The assumptions made have a more fundamental nature and do clarify many aspects of the second law.

3.3: Consequences of the Second Law

Once we take the second law as an axiom of thermodynamics, there are some important and immediate consequences. The first result is about the efficiency of the Carnot cycle, captured as the following theorem.

Theorem 3.3.1: Carnot Theorem

No engine operating between two specified heat reservoirs can be more efficient than a Carnot engine.

The proof is easy, based on the second law. Consider two engines, say a Carnot engine E_1 and another engine we call E_2, and two reservoirs, at temperatures T_H and T_L. The Carnot engine is reversible, so we can operate it as a refrigerator. So we can arrange for it to take a certain amount of heat Q_1 from the colder reservoir and deliver an amount $Q_2 > Q_1$ to the hotter reservoir. This will, of course, require work $W = Q_2 - Q_1$ to drive the Carnot engine. Now we can arrange for E_2 to take Q_2 from the hotter reservoir, and do an amount of work $W' = Q_2 - Q'_1$, delivering heat Q'_1 to the colder reservoir. The efficiencies are given by

$$\eta_1 = \frac{W}{Q_2}, \qquad \eta_2 = \frac{W'}{Q_2} \tag{3.3.1}$$

Assume E2 is more efficient. Then $\eta_2 > \eta_1$, or $W' > W$. Thus $Q_1 > Q'_1$ The net amount of heat extracted from the hotter reservoir is zero, the net amount of heat extracted from the colder reservoir is $Q_1 - Q'_1$. This is entirely converted to work (equal to $W' - W$) contradicting the Kelvin statement of the second law. Hence our assumption of $\eta_2 > \eta_1$ must be false, proving the Carnot theorem. Thus we must have $\eta_2 \leq \eta_1$.

We also have an immediate corollary to the theorem:

Proposition 1

All perfectly reversible engines operating between two given temperatures have the same efficiency.

This is also easily proved. Consider the engine E_2 to be a Carnot engine. From what we have already shown, we will have $\eta_2 < \eta_1$. Since E_2 is reversible, we can change the roles of E_1 and E_2, running E_2 as a refrigerator and E_1 as the engine producing work. In this case, the previous argument would lead to $\eta_1 \leq \eta_2$. We end up with two statements, $\eta_1 \leq \eta_2$ and $\eta_2 \leq \eta_1$. The only solution is $\eta_1 = \eta_2$. Notice that this applies to any reversible engine, since we have not used any specific properties of the Carnot engine except reversibility.

If an engine is irreversible, the previous arguments hold, showing $\eta_2 \leq \eta_1$, but we cannot get the other inequality because E_2 is not reversible. Thus irreversible engines are less efficient than the Carnot engine.

A second corollary to the theorem is the following:

Proposition 2

The efficiency of a Carnot engine is independent of the working material of the engine.

The arguments so far did not use any specific properties of the material of the Carnot engine, and since all Carnot engines between two given reservoirs have the same efficiency, this clear. We now state another important consequence of the second law

Proposition 3

The adiabatics of a thermodynamic system do not intersect.

We prove again by reductio ad absurdum. Assume the adiabatics can intersect, as shown in Fig. 3.3.1. Then we can consider a process going from A to B which is adiabatic and hence no heat is absorbed or given up, then a process from B to C which absorbs some heat ΔQ, and then goes back to A along another adiabatic. Since the thermodynamic state at A is restored, the temperature and internal energy are the same at the end as at the beginning, so that $\Delta U = 0$. Thus by the first law, $\Delta Q = \Delta W$, which means that a certain amount of heat is absorbed and converted entirely to work with no other change in the system. This contradicts the Kelvin statement of the second law. It follows that adiabatics cannot intersect.

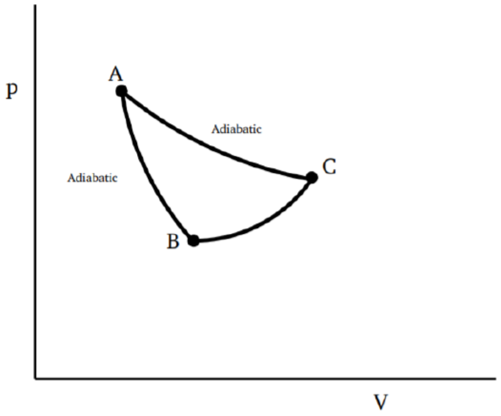


Figure 3.3.1: Argument for no-intersection of adiabatics

3.4: Absolute Temperature and Entropy

Another consequence of the second law is the existence of an absolute temperature. Although we have used the notion of absolute temperature, it was not proven. Now we can show this just from the laws of thermodynamics.

We have already seen that the efficiency of a Carnot cycle is given by

$$\eta = 1 - \frac{Q_2}{Q_3} \tag{3.4.1}$$

where Q_3 is the amount of heat taken from the hotter reservoir and Q_2 is the amount given up to the colder reservoir. The efficiency is independent of the material and is purely a function of the lower and upper temperatures. The system under consideration can be taken to be in thermal contact with the reservoirs, which may be considered very large. There is no exchange of particles or any other physical quantity between the reservoirs and the system, so no parameter other than the temperature can play a role in this. Let θ denote the empirically defined temperature, with θ_3 and θ_2 corresponding to the reservoirs between which the engine is operating. We may thus write

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3) \tag{3.4.2}$$

for some function f of the temperatures. Now consider another Carnot engine operating between θ_2 and θ_1, with corresponding Q's, so that we have

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2) \tag{3.4.3}$$

Now we can couple the two engines and run it together as a single engine, operating between θ_3 and θ_1, with

$$\frac{Q_1}{Q_3} = f(\theta_1, \theta_3) \tag{3.4.4}$$

Evidently

$$\frac{Q_2}{Q_3}\,\frac{Q_1}{Q_2} = \frac{Q_1}{Q_3} \tag{3.4.5}$$

so that we get the relation

$$f(\theta_1, \theta_2)\; f(\theta_2, \theta_3) = f(\theta_1, \theta_3) \tag{3.4.6}$$

This requires that the function f must be of the form

$$f(\theta_1, \theta_2) = \frac{f(\theta_1)}{f(\theta_2)} \tag{3.4.7}$$

for some function $f(\theta)$. Thus there must exist some function of the empirical temperature which can be defined independently of the material. This temperature is called the absolute temperature. Notice that since $Q_1 < Q_2$, we have $|f(\theta_1)| < |f(\theta_2)|$ if $\theta_1 < \theta_2$. Thus $|f|$ should be an increasing function of the empirical temperature. Further, we cannot have $f(\theta_1) = 0$ for some temperature θ_1. This would require $Q_1 = 0$. The corresponding engine would take some heat Q_2 from the hotter reservoir and convert it entirely to work, contradicting the Kelvin statement. This means that we must take f to be either always positive or always negative, for all θ. Conventionally we take this to be positive. The specific form of the function determines the scale of temperature. The simplest is to take a linear function of the empirical temperatures (as defined by conventional thermometers). Today, we take this to be

$$f(\theta) \equiv T = \text{Temperature in Celsius} + 273.16 \tag{3.4.8}$$

The unit of absolute temperature is the kelvin.

Once the notion of absolute temperature has been defined, we can simplify the formula for the efficiency of the Carnot engine as

$$\eta = 1 - \frac{T_L}{T_H} \tag{3.4.9}$$

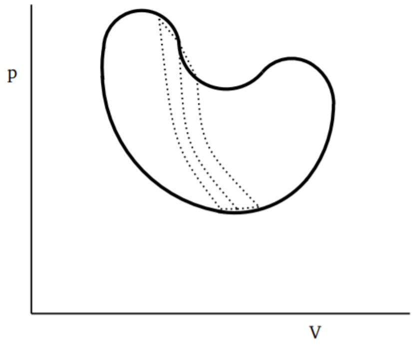


Figure 3.4.1: Illustrating Clausius theorem

Also, we have $\frac{Q1}{Q2} = \frac{T1}{T2}$, which we may rewrite as $\frac{Q1}{T1} = \frac{Q2}{T2}$. Since Q2 is the heat absorbed and Q1 is the heat released into the reservoir, we can assign ± signs to the Q's, + for intake and − for release of heat, and write this equation as

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{3.4.10}$$

In other words, if we sum over various steps (denoted by the index i) of the cycle, with appropriate algebraic signs,

$$\sum_{cycle} \frac{Q_i}{T_i} = 0 \tag{3.4.11}$$

If we consider any closed and reversible cycle, as shown in Fig. 3.4.1, we can divide it into small cycles, each of which is a Carnot cycle. A few of these smaller cycles are shown by dotted lines, say with the long dotted lines being adiabatics and the short dotted lines being isothermals. By taking finer and finer such divisions, the error in approximating the cycle by a series of closed Carnot cycles will go to zero as the number of Carnot cycles goes to infinity. Since along the adiabatics, the change in Q is zero, we can use the result from Equation 3.4.11 above to write

$$\oint_{cycle} \frac{dQ}{T} = 0 \tag{3.4.12}$$

where we denote the heat absorbed or given up during each infinitesimal step as dQ. The statement in Equation 3.4.12 is due to Clausius. The important thing is that this applies to any closed curve in the space of thermodynamic variables, provided the process is reversible.

This equation has another very important consequence. If the integral of a differential around any closed curve is zero, then we can write the differential as the derivative of some function. Thus there must exist a function $S(p, V)$ such that

$$\frac{dQ}{T} = dS, \quad or\ dQ = TdS \tag{3.4.13}$$

This function S is called entropy. It is a function of state, given in terms of the thermodynamic variables.

Clausius' Inequality

Clausius' discovery of entropy is one of most important advances in the physics of material systems. For a reversible process, we have the result,

$$\oint_{cycle} \frac{dQ}{T} = \oint_{cycle} dS = 0 \tag{3.4.14}$$

as we have already seen. There is a further refinement we can make by considering irreversible processes. There are many processes such as diffusion which are not reversible. For such a process, we cannot write $dQ = TdS$. Nevertheless, since entropy is a function of the state of the system, we can still define entropy for each state. For an irreversible process, the heat transferred to a system is less than TdS where dS is the entropy change produced by the irreversible process. This is easily seen from the second law. For assume that a certain amount of heat dQ_{irr} is absorbed by the system in the irreversible process. Consider then a combined process where the system changes from state A to state B in an irreversible manner and then we restore state A by a reversible process. For the latter step, $dQ_{rev} = TdS$. The combination thus absorbs an amount of heat equal to $dQ_{irr} - TdS$ with no change of state. If this is positive, this must be entirely converted to work. However, that would violate the second law. Hence we should have

$$dQ_{irr} - TdS < 0 \tag{3.4.15}$$

If we have a cyclic process, $\oint dS = 0$ since S is a state function, and hence

$$\oint \frac{dQ}{T} \leq 0 \tag{3.4.16}$$

with equality holding for a reversible process. This is known as Clausius' inequality.

For a system in thermal isolation, $dQ = 0$, and the condition $dQ_{irr} < TdS$ becomes

$$dS > 0 \tag{3.4.17}$$

In other words, the entropy of a system left to itself can only increase, equilibrium being achieved when the entropy (for the specified values of internal energy, number of particles, etc.) is a maximum.

The second law has been used to define entropy. But once we have introduced the notion of entropy, the second law is equivalent to the statement that entropy tends to increase. For any process, we can say that

$$\frac{dS}{T} \geq 0 \tag{3.4.18}$$

We can actually see that this is equivalent to the Kelvin statement of the second law as follows. Consider a system which takes up heat ΔQ at temperature T. For the system (labeled 1) together with the heat source (labeled 2), we have $\Delta S_1 + \Delta S_2 \geq 0$. But the source is losing heat at temperature T and if this is reversible, $\Delta S_2 = -\frac{\Delta Q}{T}$. Further if there is no other change in the system, $\Delta S_1 = 0$ and $\Delta U_1 = 0$. Thus

$$\Delta S_1 + \Delta S_2 \geq 0 \Rightarrow -\frac{\Delta Q}{T} \geq 0 \Rightarrow \Delta Q \leq 0 \tag{3.4.19}$$

Since $\Delta U_1 = 0, \Delta Q = \Delta W$ and this equation implies that the work done by the system cannot be positive, if we have $\frac{dS}{dt} \geq 0$. Thus, we have arrived at the Kelvin statement that a system cannot absorb heat from a source and convert it entirely to work without any other change. We may thus restate the second law in the form:

Proposition 4

Second Law of Thermodynamics: The entropy of a system left to itself will tend to increase to a maximum value compatible with the specified values of internal energy, particle number, etc.

Nature of Heat Flow

We can easily see that heat by itself flows from a hotter body to a cooler body. This may seem obvious, but is a crucial result of the second law. In some ways, the second law is the formalization of such statements which are “obvious" from our experience.

Consider two bodies at temperatures T_1 and T_2, thermally isolated from the rest of the universe but in mutual thermal contact. The second law tells us that $dS \geq 0$. This means that

$$\frac{dQ_1}{T1} + \frac{dQ_2}{T2} \geq 0 \tag{3.4.20}$$

Because the bodies are isolated from the rest of the world, $dQ_1 + dQ_2 = 0$, so that we can write the condition above as

$$(\frac{1}{T_1} - \frac{1}{T_2})dQ_1 \geq 0 \tag{3.4.21}$$

If $T_1 > T_2$, we must have $dQ_1 < 0$ and if $T_1 < T_2, dQ_1 > 0$. Either way, heat flows from the hotter body to the colder body.

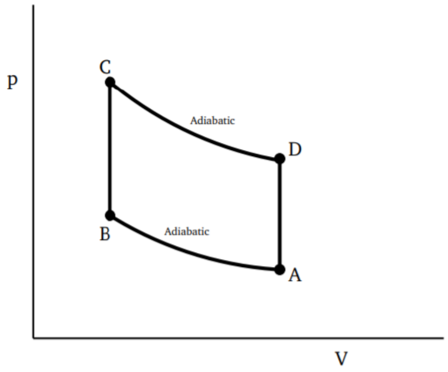


Figure $3.4.2$: The Otto cycle for an automobile engine.

3.5: Some Other Thermodynamic Engines

We will now consider some other thermodynamic engines which are commonly used.

Otto Cycle

The automobile engine operates in four steps, with the injection of the fuel-air mixture into the cylinder. It undergoes compression which can be idealized as being adiabatic. The ignition then raises the pressure to a high value with almost no change of volume. The high pressure mixture rapidly expands, which is again almost adiabatic. This is the power stroke driving the piston down. The final step is the exhaust when the spent fuel is removed from the cylinder. This step happens without much change of volume. This process is shown in Fig. 3.4.2. We will calculate the efficiency of the engine, taking the working material to be an ideal gas.

Heat is taken in during the ignition cycle B to C. The heat comes from the chemical process of burning but we can regard it as heat taken in from a reservoir. Since this is at constant volume, we have

$$Q_H = C_v(T_C - T_B) \tag{3.5.1}$$

Heat is given out during the exhaust process D to A, again at constant volume, so

$$Q_L = C_v(T_D - T_A) \tag{3.5.2}$$

Further, states C and D are connected by an adiabatic process, so are A and B. Thus $pV^\gamma = nRTV^{\gamma-1}$ is preserved for these processes. Also, $V_A = V_D$, $V_B = V_C$, so we have

$$T_D = T_C \left(\frac{V_B}{V_A}\right)^{\gamma-1}, \quad T_A = T_B \left(\frac{V_B}{V_A}\right)^{\gamma-1} \tag{3.5.3}$$

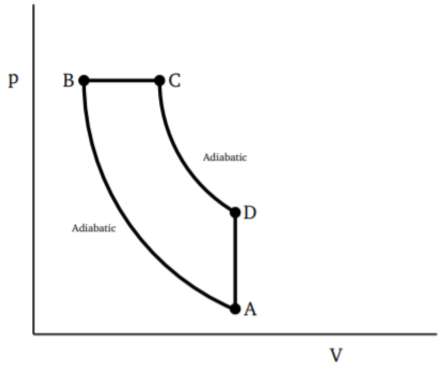


Figure 3.5.1: The idealized Diesel cycle

This gives

$$Q_L = C_v(T_C - T_B)\left(\frac{V_B}{V_A}\right)^{\gamma-1} \tag{3.5.4}$$

The efficiency is then

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \left(\frac{V_B}{V_A}\right)^{\gamma-1} \tag{3.5.5}$$

Diesel Cycle

The idealized operation of a diesel engine is shown in Fig. 3.5.1. Initially, only air is admitted into the cylinder. It is then compressed adiabatically to very high pressure (and hence very high temperature). Fuel is then injected into the cylinder. The temperature in the cylinder is high enough to ignite the fuel. The injection of the fuel is controlled so that the burning happens at essentially constant pressure (B to C in figure). This is the key difference with the automobile engine. At the end of the burning process, the expansion continues adiabatically (part C to D). From D back to A we have the exhaust cycle as in the automobile engine.

Taking the air (and fuel) to be an ideal gas, we can calculate the efficiency of the diesel engine. Heat intake (from burning fuel) is at constant pressure, so that

$$Q_H = C_p(T_C - T_B) \tag{3.5.6}$$

Heat is given out (D to A) at constant volume so that

$$Q_L = C_p(T_D - T_A) \tag{3.5.7}$$

We also have the relations,

$$T_A = T_B\left(\frac{V_B}{V_A}\right)^{\gamma-1}, \quad T_D = T_C\left(\frac{V_C}{V_A}\right)^{\gamma-1} \tag{3.5.8}$$

Further, $p_B = p_C$ implies $T_B = T_C(\frac{V_B}{V_C})$, which, in turn, gives

$$T_A = T_C\left(\frac{V_B}{V_C}\right)\left(\frac{V_B}{V_A}\right)^{\gamma-1} \tag{3.5.9}$$

We can now write

$$\begin{aligned} Q_L &= C_vT_C\left[\left(\frac{V_C}{V_A}\right)^{\gamma-1} - \left(\frac{T_B}{V_C}\right)\left(\frac{V_B}{V_A}\right)^{\gamma-1}\right] \qquad (3.5.10) \\ &= C_vT_C\left(\frac{V_C}{V_A}\right)^{\gamma-1}\left[1 - \left(\frac{V_B}{V_C}\right)^{\gamma}\right] \\ Q_H &= C_pT_C\left[1 - \frac{V_B}{V_C}\right] \qquad (3.5.11) \end{aligned}$$

These two equations give the efficiency of the diesel cycle as

$$\begin{aligned} \eta &= 1 - \frac{1}{\gamma}\left(\frac{V_C}{V_A}\right)^{\gamma-1}\left[\frac{1-\left(\frac{V_B}{V_C}\right)^{\gamma}}{1-\left(\frac{V_B}{V_C}\right)}\right] \qquad (3.5.12) \\ &= 1 - \frac{1}{\gamma}\left(\frac{T_D}{T_C}\right)\left[\frac{1-\left(\frac{V_B}{V_C}\right)^{\gamma}}{1-\left(\frac{V_B}{V_C}\right)}\right] \end{aligned}$$

4: The Third Law of Thermodynamics

The second law defines entropy by the relation $dQ = TdS$. Thus entropy is defined only up to an additive constant. Further, it does not tell us about the behavior of S as a function of T close to absolute zero. This is done by the third law.

Third Law of Thermodynamics

The contribution to the entropy by each set of degrees of freedom in internal thermodynamic equilibrium tends to zero in a differentiable way as the absolute zero of temperature is approached.

The limiting value of S is independent of the process by which $T = 0$ is approached; it does not matter whether the system is in liquid or solid phase, whether it is under pressure, etc. Further, the differentiability condition says that $\left(\frac{\partial S}{\partial T}\right)$ is finite at absolute zero, where the derivative is taken along any process.

Unattainability of Absolute Zero

For different starting points, the variation of entropy with temperature will be as shown in Figure 4.1. A process that reduces the temperature can be viewed as an isothermal decrease of entropy from A to B, followed by an isentropic (adiabatic) decrease of temperature along BC. By continuing the process, one can get closer and closer to absolute zero. But it is obvious that the temperature decreases achieved will become smaller and smaller; after any finite number of steps, there will still be a positive nonzero temperature. Thus we conclude that only an asymptotic approach to absolute zero is possible for any thermodynamic process. Since any thermodynamic process for cooling can be built up as a sum of steps like ABC, the conclusion holds in general.

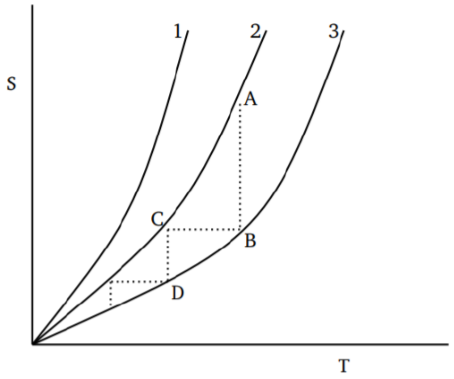


Figure 4.1: Illustrating the unattainability of absolute zero

Vanishing of Specific Heats at Absolute Zero

The specific heat for any process can be written as

$$C_R = \left(\frac{\partial Q}{\partial T}\right)_R = T\left(\frac{\partial S}{\partial T}\right)_R \tag{4.1}$$

where R specifies the quantity held constant. Since, by the third law, $\left(\frac{\partial Q}{\partial T}\right)_R$ is finite as $T \to 0$, we find $C_R \to 0$ as $T \to 0$. In particular, the specific heats at constant volume (C_v) and at constant pressure (C_p) vanish at absolute zero.

CHAPTER OVERVIEW

5: Thermodynamic Potentials and Equilibrium

Extensive and Intensive Variables

All quantities in thermodynamics fall into two types: extensive and intensive. If we consider two independent systems, quantities which add up to give the corresponding quantities for the complete system are characterized as extensive quantities. The volume V, the internal energy U, the enthalpy, and as we will see later on, the entropy S are extensive quantities. If we divide a system into subsystems, those quantities which remain unaltered are called intensive variables. The pressure p, the temperature T, the surface tension are examples of intensive variables.

In any thermodynamic system, there is a natural pairing between extensive and intensive variables. For example, pressure and volume go together as in the formula $dU = dQ - p dV$. Temperature is paired with the entropy, surface tension with the area, etc.

5.1: Thermodynamic Potentials

The second law leads to the result $dQ = TdS$, so that, for a gaseous system, the first law may be written as

$$dU = TdS - pdV \tag{5.1.1}$$

More generally, we have

$$dU = TdS - pdV - \sigma dA - MdB \tag{5.1.2}$$

where σ is the surface tension, A is the area, M is the magnetization, B is the magnetic field, etc.

Returning to the case of a gaseous system, we now define a number of quantities related to U. These are called thermodynamic potentials and are useful when considering different processes. We have already seen that the enthalpy H is useful for considering processes at constant pressure. This follows from

$$dH = d(U + pV) = dQ + Vdp \tag{5.1.3}$$

so that for processes at constant pressure, the inflow or outflow of heat may be seen as changing the enthalpy

The Helmholtz free energy is defined by

$$F = U - TS \tag{5.1.4}$$

Taking differentials and comparing with the formula for dU, we get

$$dF = -SdT - pdV \tag{5.1.5}$$

The Gibbs free energy G is defined by

$$G = F + pV = H - TS = U - TS + pV \tag{5.1.6}$$

Evidently,

$$dG = -SdT + Vdp \tag{5.1.7}$$

Notice that by construction, H, F and G are functions of the state of the system. They may be expressed as functions of p and V, for example. They are obviously extensive quantities.

So far, we have considered the system characterized by pressure and volume. If there are a number of particles, say, N which make up the system, we can also consider the N-dependence of various quantities. Thus we can think of the internal energy U as a function of S, V and N, so that

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \equiv TdS - pdV + \mu dN \tag{5.1.8}$$

The quantity μ which is defined by

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{5.1.9}$$

is called the chemical potential. It is obviously an intensive variable. The corresponding equations for H, F and G are

$$\begin{aligned} dH &= TdS + Vdp + \mu dN \\ dF &= -SdT - pdV + \mu dN \\ dG &= -SdT + Vdp + \mu dN \end{aligned} \tag{5.1.10}$$

Thus the chemical potential μ may also be defined as

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,p} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,p} \tag{5.1.11}$$

Since U is an extensive quantity and so are S and V, the internal energy has the general functional form

$$U=Nu\left(\frac{S}{N},\frac{V}{N}\right) \tag{5.1.12}$$

where u depends only on $\frac{S}{N}$ and $\frac{V}{N}$ which are intensive variables. In a similar way, we can write

$$\begin{gathered} H=N\,h\left(\frac{S}{N},p\right) \\ F=N\,f\left(T,\frac{V}{N}\right) \\ G=N\,g(T,p) \end{gathered} \tag{5.1.13}$$

The last equation is of particular interest. Taking its variation, we find

$$dG=N\left(\frac{\partial g}{\partial T}\right)_p dT+N\left(\frac{\partial g}{\partial p}\right)_T dT+g\,dN \tag{5.1.14}$$

Comparing with Equation 5.1.10, we get

$$S=-N\left(\frac{\partial g}{\partial T}\right)_p, \quad V=N\left(\frac{\partial g}{\partial p}\right)_T, \quad \mu=g \tag{5.1.15}$$

The quantity g is identical to the chemical potential, so that we may write

$$G=\mu N \tag{5.1.16}$$

We may rewrite the other two relations as

$$S=-N\left(\frac{\partial \mu}{\partial T}\right)_p dT, \quad V=N\left(\frac{\partial \mu}{\partial p}\right)_T \tag{5.1.17}$$

Further, using $G=\mu N$, we can rewrite the equation for dG as

$$N d\mu+SdT-V dp=0 \tag{5.1.18}$$

This essentially combines the previous two relations and is known as the Gibbs-Duhem relation. It is important in that it provides a relation among the intensive variables of a thermodynamic system.

5.2: Thermodynamic Equilibrium

The second law of thermodynamics implies that entropy does not decrease in any natural process. The final equilibrium state will thus be the state of maximum possible entropy. After attaining this maximum possible value, the entropy will remain constant. The criterion for equilibrium may thus be written as

$$\delta S = 0 \tag{5.2.1}$$

We can take S to be a function of U, V and N. The system, starting in an arbitrary state, adjusts U, V and N among its different parts and constitutes itself in such a way as to maximize entropy. Consider the system subdivided into various smaller subsystems, say, indexed by $i = 1, \ldots, n$. The thermodynamic quantities for each such unit will be indicated by a subscript i. For an isolated system, the total internal energy, the total volume and the total number of particles will be fixed, so that the changes in the subsystems must be constrained as

$$\sum_i \delta\, U_i \;=\; 0, \quad \sum_i \delta\, V_i \;=\; 0, \quad \sum_i \delta\, N_i \;=\; 0 \tag{5.2.2}$$

Since S is extensive, $S \;=\; \sum_i S_i$ where $S_i = S_i(U_i, V_i, N_i)$. We can now maximize entropy subject to the constraints Equation 5.2.2 by considering the maximization of

$$S \;=\; \sum_i S_i - \lambda_1 (\sum_i U_i - U) - \lambda_2 (\sum_i V_i - V) - \lambda_3 (\sum_i N_i - N) \tag{5.2.3}$$

where the Lagrange multipliers $\lambda_1, \lambda_2, \lambda_3$ enforce the required constraints. The variables U_i, V_i and N_i can now be freely varied. Thus, for the condition of equilibrium, we get

$$dS \;=\; \sum_i \left[\left(\frac{\partial S}{\partial U_i} \right) - \lambda_1 \right] dU_i + \left[\left(\frac{\partial S}{\partial V_i} \right) - \lambda_2 \right] dV_i + \left[\left(\frac{\partial S}{\partial N_i} \right) - \lambda_3 \right] dN_i \;=\; 0 \tag{5.2.4}$$

Since the variations are now independent, this gives, for equilibrium,

$$\left(\frac{\partial S}{\partial U_i} \right) = \lambda_1, \quad \left(\frac{\partial S}{\partial V_i} \right) = \lambda_2, \quad \left(\frac{\partial S}{\partial N_i} \right) = \lambda_3 \tag{5.2.5}$$

This can be rewritten as

$$\frac{1}{T_i} \;=\; \lambda_1, \quad \frac{p_i}{T_i} \;=\; \lambda_2, \quad \frac{\mu_i}{T_i} \;=\; \lambda_3 \tag{5.2.6}$$

where we used

$$dS \;=\; \frac{dU}{T} \;+\; \frac{p}{T} dV \;-\; \frac{\mu}{T} dN \tag{5.2.7}$$

Equation 5.2.6 tells us that, for equilibrium, the temperature of all subsystems must be the same, the pressure in different subsystems must be the same and the chemical potential for different subsystems must be the same.

Reaction Equilibrium

Suppose we have a number of constituents $A_1, A_2, \ldots, B_1, B_2, \ldots$, at constant temperature and pressure which undergo a reaction of the form

$$\nu_{A_1} A_1 \;+\; \nu_{A_2} A_2 + \ldots \rightleftharpoons \nu_{B_1} B_1 \;+\; \nu_{B_2} B_2 + \ldots \tag{5.2.8}$$

The entropy of the system is of the form

$$S \;=\; \sum_k S_k(N_k) \tag{5.2.9}$$

where the summation covers all A's and B's. Since the temperature and pressure are constant, reaction equilibrium is obtained when the N_k change so as to maximize the entropy. This gives

$$dS = \frac{1}{T}\sum_{k}\mu_k dN_k = 0 \tag{5.2.10}$$

The quantities dN_k are not independent, but are restricted by the reaction. When the reaction happens, ν_{A_1} of A_1-particles must be destroyed, ν_{A_2} of A_2-particles must be destroyed, etc., while ν_{B_1} of B_1 particles are produced, etc. Thus we can write

$$dN_{A_1} = -\nu_{A_1}dN_0, \quad dN_{A_2} = -\nu_{A_2}dN_0, \ldots, \; dN_{B_1} = -\nu_{B_1}dN_0, \quad dN_{B_2} = -\nu_{B_2}dN_0, \ldots, \quad etc. \tag{5.2.11}$$

where d_{N_0} is arbitrary. The condition of equilibrium thus reduces to

$$-\sum_{A}\nu_{A_i}\mu_{A_i} + \sum_{B}\nu_{B_i}\mu_{B_i} = 0 \tag{5.2.12}$$

With the understanding that the ν's for the reactants will carry a minus sign while those for the products have a plus sign, we can rewrite this as

$$\sum_{k}\nu_k\mu_k = 0 \tag{5.2.13}$$

This condition of reaction equilibrium can be applied to chemical reactions, ionization and dissociation processes, nuclear reactions, etc.

5.3: Phase Transitions

If we have a single constituent, for thermodynamic equilibrium, we should have equality of T, p and μ for different subparts of the system. If we have different phases of the system, such as gas, liquid, or solid, in equilibrium, we have

$$\begin{aligned} T_1 &= T_2 = T_3 = \ldots = T \\ p_1 &= p_2 = p_3 = \ldots = p \\ \mu_1 &= \mu_2 = \mu_3 = \ldots \end{aligned} \tag{5.3.1}$$

where the subscripts refer to various phases.

We will consider the equilibrium of the two phases in more detail. In this case, we have

$$\mu_1(p,\ T) = \mu_2(p,\ T) \tag{5.3.2}$$

If equilibrium is also obtained for a state defined by $(p+dp\,, T+dT)$, then we have

$$\mu_1(p+dp\ ,\ T+dT) = \mu_2(p+dp\ ,\ T+dT) \tag{5.3.3}$$

These two equations yield

$$\Delta\mu_1 = \Delta\mu_2, \quad \Delta\mu = \mu(p+dp\ ,\ T+dT) - \mu(p\ ,\ T) \tag{5.3.4}$$

This equation will tell us how p should change when T is altered (or vice versa) so as to preserve equilibrium. Expanding to first order in the variations, we find

$$-s_1 d_T + v_1 d_p = -s_2 d_T + v_2 d_p \tag{5.3.5}$$

where we have used

$$\frac{\partial\mu}{\partial T} = -\frac{S}{N} \equiv s, \quad \frac{\partial\mu}{\partial p} = -\frac{V}{N} \equiv v \tag{5.3.6}$$

Equation 5.3.5 reduces to

$$\frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{L}{T(v_1 - v_2)} \tag{5.3.7}$$

where $L = T(s_1 - s_2)$ is the latent heat of the transition. This equation is known as the Clausius-Clapeyron equation. It can be used to study the variation of saturated vapor pressure with temperature (or, conversely, the variation of boiling point with pressure). As an example, consider the variation of boiling point with pressure, when a liquid boils to form gaseous vapor. In this case, we can take $v_1 = v_g \gg v_2 = v_l$. Further, if we assume, for the sake of the argument, that the gaseous phase obeys the ideal gas law, $v_g = \frac{kT}{p}$, then the Clausius-Clapeyron Equation 5.3.7 becomes

$$\frac{dp}{dT} \approx p\frac{L}{kT^2} \tag{5.3.8}$$

Integrating this from one value of T to another,

$$\log\left(\frac{p}{p_0}\right) = \frac{L}{k}\left(\frac{1}{T_0} - \frac{1}{T}\right) \tag{5.3.9}$$

Thus for $p > p_0$, T must be larger than T_0; this explains the increase of boiling point with pressure.

If $\frac{\partial\mu}{\partial T}$ and $\frac{\partial\mu}{\partial p}$ are continuous at the transition, $s_1 = s_2$ and $v_1 = v_2$. In this case, we have to expand μ to second order in the variations. Such a transition is called a second order phase transition. In general, if the first $(n-1)$ derivatives of μ are continuous, and the n-th derivatives are discontinuous at the transition, the transition is said to be of the n-th order. Clausius-Clapeyron equation, as we have written it, applies to the first order phase transitions. These have a latent heat of transition.

CHAPTER OVERVIEW

6: Thermodynamic Relations and Processes

6.1: Maxwell Relations

For a system with one constituent with fixed number of particles, from the first and second laws, and from Equation 5.1.10, we have the basic relations

$$\begin{aligned} dU &= TdS - pdV \\ dH &= TdS - Vdp \\ dF &= -SdT - pdV \\ dG &= -SdT - Vdp \end{aligned} \tag{6.1.1}$$

The quantities on the left are all **perfect differentials**. For a general differential dR of the form

$$dR = Xdx + Ydy \tag{6.1.2}$$

to be a perfect differential, the necessary and sufficient condition is

$$\left(\frac{\partial X}{\partial y}\right)_x = \left(\frac{\partial Y}{\partial x}\right)_y \tag{6.1.3}$$

Applying this to the four differentials in 6.1.1, we get

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \tag{6.1.4}$$

These four relations are called the Maxwell relations.

A Mathematical Result

Let X, Y, Z be three variables, of which only two are independent. Taking Z to be a function of X and Y, we can write

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \tag{6.1.5}$$

If now we take X and Z as the independent variables, we can write

$$dY = \left(\frac{\partial Y}{\partial X}\right)_Y dX + \left(\frac{\partial Y}{\partial Z}\right)_X dZ \tag{6.1.6}$$

Upon substituting this result into 6.1.5, we get

$$dZ = \left[\left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z\right] dX + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial Z}\right)_X dZ \tag{6.1.7}$$

Since we are considering X and Z as independent variables now, this equation immediately yields the relations

$$\begin{aligned} \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial Z}\right)_X dZ &= 1 \\ \left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z &= 0 \end{aligned} \tag{6.1.8}$$

These relations can be rewritten as

$$\begin{aligned} \left(\frac{\partial Z}{\partial Y}\right)_X &= \frac{1}{\left(\frac{dY}{dZ}\right)_X} \\ \left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z &= -1 \end{aligned} \tag{6.1.9}$$

6.2: Other Relations

The TdS Equations

The entropy S is a function of the state of the system. We can take it to be a function of any two of the three variables (p, T, V). Taking S to be a function of p and T, we write

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp \tag{6.2.1}$$

For the first term on the right hand side, we can use

$$T\left(\frac{\partial S}{\partial T}\right)_p dT = \left(\frac{\partial Q}{\partial T}\right)_p dT = C_p \tag{6.2.2}$$

where C_p is the specific heat at constant pressure. Further, using the last of the Maxwell relations, we can now write Equation 6.2.2 as

$$Tds = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \tag{6.2.3}$$

The **coefficient of volumetric expansion** (due to heating) is defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{6.2.4}$$

Equation 6.2.3 can thus be rewritten as

$$TdS = C_p dT - \alpha TV dp \tag{6.2.5}$$

If we take S to be a function of V and T,

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \tag{6.2.6}$$

Again the first term on the right hand side can be expressed in terms of Cv, the specific heat at constant volume, using

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_v \tag{6.2.7}$$

Further using the Maxwell relations, we get

$$TdS = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \tag{6.2.8}$$

Equations 6.2.3 (or 6.2.5 and 6.2.8) are known as the TdS equations.

Equations for Specific Heats

Equating the two expressions for TdS, we get

$$(C_p - C_v)dT = T\left[\left(\frac{\partial p}{\partial T}\right)_V dV + \left(\frac{\partial V}{\partial T}\right)_p dp\right] \tag{6.2.9}$$

By the equation of state, we can write p as a function of V and T, so that

$$dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV \tag{6.2.10}$$

Using this in Equation 6.2.9, we find

$$(C_p - C_v)dT = T\left[\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T\right]dV + T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V dT \tag{6.2.11}$$

However, using Equation 6.1.9, taking $X = V$, $Y = p$ and $Z = T$, we have

$$\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T = 0 \tag{6.2.12}$$

Thus the coefficient of dV in Equation 6.2.11 vanishes and we can simplify it as

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V = -T\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2 \left(\frac{\partial p}{\partial V}\right)_T \tag{6.2.13}$$

where we have used Equation 6.2.12 again. We have already defined the **coefficient of volumetric expansion** α. The **isothermal compressibility** κ_T is defined by

$$\frac{1}{\kappa_T} = -V\left(\frac{\partial p}{\partial V}\right)_T \tag{6.2.14}$$

In terms of these we can express $C_p - C_v$ as

$$C_p - C_v = V\frac{\alpha^2 T}{\kappa_T} \tag{6.2.15}$$

This equation is very useful in calculating C_v from measurements of C_p and α and κ_T. Further, for all substances, $\kappa_T > 0$. Thus, we see from this equation that $C_p \geq C_v$. (The result $\kappa_T > 0$ can be proved in statistical mechanics.)

In the TdS equations, if dT, dV and dp are related adiabatically, $dS = 0$ and we get

$$C_p = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S, \quad C_v = -T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S \tag{6.2.16}$$

This gives

$$\frac{C_p}{C_v} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S \left[\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S\right]^{-1} \tag{6.2.17}$$

We have the following relations among the terms involved in this expression,

$$\begin{gathered}\left(\frac{\partial p}{\partial T}\right)_S = \left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial p}{\partial V}\right)_S = \left(\frac{\partial V}{\partial T}\right)_S \frac{1}{V\kappa_S} \\ \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} = \left(\frac{\partial p}{\partial T}\right)_V V\kappa_T\end{gathered} \tag{6.2.18}$$

Using these we find

$$\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S} \tag{6.2.19}$$

Going back to the Maxwell relations and using the expressions for TdS, we find

$$\begin{aligned} dU &= C_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \\ dH &= C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \end{aligned} \tag{6.2.20}$$

these immediately yield the relations

$$\begin{gathered} C_v = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p \\ \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \end{gathered} \tag{6.2.21}$$

Gibbs-Helmholtz Relation

Since the Helmholtz free energy is defined as $F = U - TS$,

$$dF = dU - TdS - SdT = -SdT - pdV \tag{6.2.22}$$

This gives immediately

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T \tag{6.2.23}$$

Using this equation for entropy, we find

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V \tag{6.2.24}$$

This is known as the Gibbs-Helmholtz relation. If F is known as a function of T and V, we can use these to obtain S, p and U. Thus, all thermodynamic variables can be obtained from F as a function of T and V.

6.3: Joule-Kelvin Expansion

The expansion of a gas through a small opening or a porous plug with the pressure on either side being maintained is called Joule-Kelvin expansion. It is sometimes referred to as the Joule-Thomson expansion since Thomson was Lord Kelvin's original name. The pressures are maintained by the flow of gases but for the theoretical discussion, we may think of them as being maintained by pistons which move in or out to keep the pressure the same. The values of the pressures on the two sides of the plug are not the same. The gas undergoes a decrease in volume on one side as the molecules move through the opening to the other side. The volume on the other side increases as molecules move in. The whole system is adiabatically sealed so that the net flow of heat in or out is zero.

Since $dQ = 0$, we can write, from the first law,

$$dU + pdV = 0 \tag{6.3.1}$$

Consider the gas on one side starting with volume V_1 going down to zero while on the other side the volume increases from zero to V_2. Integrating Equation 6.3.1, we find

$$\int_{p_1,V_1,U_1}^{0} (dU + pdV) + \int_{0}^{p_2,V_2,U_2} (dU + pdV) = 0 \tag{6.3.2}$$

This yields the relation

$$U_1 + p_1 V_1 = U_2 + p_2 V_2 \tag{6.3.3}$$

Thus the enthalpy on either side of the opening is the same. It is isenthalpic expansion. The change in the temperature of the gas is given by

$$\Delta T = \int_{p_1}^{p_2} dp \left(\frac{\partial T}{\partial p}\right)_H = \int_{p_1}^{p_2} dp\, \mu_{JK} \tag{6.3.4}$$

The quantity

$$\mu_{JK} = \left(\frac{\partial T}{\partial p}\right)_H \tag{6.3.5}$$

is called the **Joule-Kelvin coefficient**. From the variation of H we have

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \tag{6.3.6}$$

so that, considering an isenthalpic process we get

$$\mu_{JK} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] \tag{6.3.7}$$

This gives a convenient formula for μ_{JK}. Depending on whether this coefficient is positive or negative, there will be heating or cooling of the gas upon expansion by this process. By choosing a range of pressures for which μ_{JK} is negative, this process can be used for cooling and eventual liquifaction of gases.

CHAPTER OVERVIEW

7: Classical Statistical Mechanics

Dynamics of particles is given by Newton’s laws or, if we include quantum effects, the quantum mechanics of point-particles. Thus, if we have a large number of particles such as molecules or atoms which constitute a macroscopic system, then, in principle, the dynamics is determined. Classically, we just have to work out solutions to Newton’s laws. But for systems with large numbers of particles, such as the Avogadro number which may be necessary in some cases, this is a wholly impractical task. We do not have general solutions for the three-body problem in mechanics, let alone for 10^{23} particles. What we can attempt to do is a statistical approach, where one focuses on certain averages of interest, which can be calculated with some simplifying assumptions. This is the province of Statistical Mechanics.

If we have N particles, in principle, we can calculate the future of the system if we are given the initial data, namely, the initial positions and velocities or momenta. Thus we need $6\,N$ input numbers. Already, as a practical matter, this is impossible, since $N \sim 10^{23}$ and we do not, in fact, cannot measure the initial positions and momenta for all the molecules in a gas at any time. So generally we can make the assumption that a probabilistic treatment is possible. The number of molecules is so large that we can take the initial data to be a set of random numbers, distributed according to some probability distribution. This is the basic working hypothesis of statistical mechanics. To get some feeling for how large numbers lead to simplification, we start with the binomial distribution.

7.1: The Binomial Distribution

This is exemplified by the tossing of a coin. For a fair coin, we expect that if we toss it a very large number of times, then roughly half the time we will get heads and half the time we will get tails. We can say that the probability of getting heads is $\frac{1}{2}$ and the probability of getting tails is $1-\frac{1}{2}=\frac{1}{2}$. Thus the two possibilities have equal *a priori* probabilities.

Now consider the simultaneous tossing of N coins. What are the probabilities? For example, if $N=2$, the possibilities are HH, HT, TH and TT. There are two ways we can get one head and one tail, so the probabilities are $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$ for two heads, one head and no heads respectively. The probability for one head (and one tail) is higher because there are many (two in this case) ways to get that result. So we can ask: How many ways can we get n_1 heads (and $(N-n_1)$ tails)? This is given by the number of ways we can choose n_1 out of N, to which we can assign the heads. In other words, it is given by

$$W(n_1,n_2)=\frac{N!}{n_1!(N-n_1)!}=\frac{N!}{n_1!n_2!},\quad n_1+n_2=N \tag{7.1.1}$$

The probability for any arrangement n_1, n_2 will be given by

$$p(n_1,n_2)=\frac{W(n_1,n_2)}{\sum_{n_1',n_2'}W(n_1',n_2')}=\frac{W(n_1,n_2)}{2^N} \tag{7.1.2}$$

where we have used the binomial theorem to write the denominator as 2^N. This probability as a function of $x=\frac{n_1}{N}$ for large values of N, n_1 is shown in Figure $7.1.1$. Notice that already for $N=8$, the distribution is sharply peaked around the middle value of $n_1 = 4$. This becomes more and more pronounced as N becomes large. We can check the place where the maximum occurs by noting that the values $\frac{n_1}{N}$ and $\frac{(n_1+1)}{N}$ are very close to each other, infinitesimally different for $N\to\infty$, so that $x=\frac{n_1}{N}$ may be taken to be continuous as $N\to\infty$. Further, for large numbers, we can use the **Stirling formula**

$$\log N! \approx N\log N - N \tag{7.1.3}$$

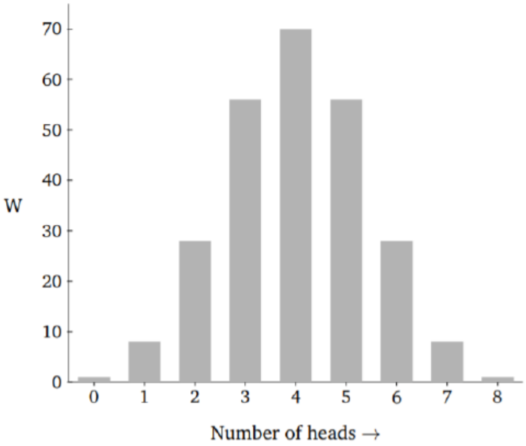


Figure $7.1.1$: The binomial distribution showing $W(n_1,n_2)$ as a function of n_1 = the number of heads for $N=8$

Then we get

$$\begin{aligned}\log p &= \log W(n_1,n_2)-N\log 2\\ &\approx N\log N-N-(n_1\log n_1 - n_1)-(N-n_1)\log(N-n_1)+(N-n_1)-N\log 2\\ &\approx -N[x\log x+(1-x)\log(1-x)]-N\log 2\end{aligned}$$

This has a maximum at $x=x_*=\frac{1}{2}$. Expanding $\log p$ around this value, we get

$$\log p \approx -2N(x-x_*)^2 + O((x-x_*)^3),\quad or\ p \approx exp(-2N(x-x*)^2) \tag{7.1.4}$$

We see that the distribution is peaked around x_* with a width given by $\Delta x^2 \sim (\frac{1}{4}N)$. The probability of deviation from the mean value is very very small as $N\to\infty$. This means that many quantities can be approximated by their mean values or values at the maximum of the distribution.

We have considered equal a priori probabilities. If we did not have equal probabilities then the result will be different. For example, suppose we had a coin with a probability of q, $0 < q < 1$ for heads and probability $(1-q)$ for tails. Then the probability for N coins would go like

$$p(n_1, n_2) = q^{n_1}(1-q)^{n_2} W(n_1, n_2) \tag{7.1.5}$$

(Note that $q = \frac{1}{2}$ reproduces Equation 7.1.2.) The maximum is now at $x = x_* = q$. The standard deviation from the maximum value is unchanged.

Here we considered coins for each of which there are only two outcomes, head or tail. If we have a die with 6 outcomes possible, we must consider splitting N into $n_1, n_2, \cdots, n_6$. Thus we can first choose n_1 out of N in $\frac{N!}{(n_1!(N-n_1)!)}$ ways, then choose n_2 out of the remaining $N-n_1$ in $\frac{(N-n_1)!}{(n_2!(N-n_1-n_2)!)}$ ways and so on, so that the number of ways we can get a particular assignment $n_1, n_2, \cdots, n_6$ is

$$W(\{n_i\}) = \frac{N!}{(n_1!(N-n_1)!)} \frac{(N-n_1)!}{(n_2!(N-n_1-n_2)!)} \cdots = \frac{N!}{n_1, n_2, \cdots, n_6}, \qquad \sum_i n_i = N \tag{7.1.6}$$

More generally, the number of ways we can distribute N particles into K boxes is

$$W(\{n_i\}) = N_i \prod_i^K \frac{1}{n_i!}, \qquad \sum_{i=1}^K n_1 = N \tag{7.1.7}$$

Basically, this gives the multinomial distribution.

7.2: Maxwell-Boltzmann Statistics

Now we can see how all this applies to the particles in a gas. The analog of heads or tails would be the momenta and other numbers which characterize the particle properties. Thus, we can consider N particles distributed into different cells, each of the cells standing for a collection of observables or quantum numbers which can characterize the particle. The number of ways in which N particles can be distributed into these cells, say K of them, would be given by Equation 7.1.8. The question is then about a priori probabilities. The basic assumption which is made is that there is nothing to prefer one set of values of observables over another, so we assume equal a priori probabilities. This is a key assumption of statistical mechanics. So we want to find the distribution of particles into different possible values of momenta or other observables by maximizing the probability

$$p(n_i) \;=\; C\;N_i \prod_i^K \frac{1}{n_i!} \tag{7.2.1}$$

Here C is a normalization constant given by $C = P\sum_{\{n_i\}} W$, the analog of 2^N in Equation 7.1.2. Now the maximization has to be done obviously keeping in mind that $\sum_i n_i = N$, since we have a total of N particles. But this is not the only condition. For example, energy is a conserved quantity and if we have a system with a certain energy U, no matter how we distribute the particles into different choices of momenta and so on, the energy should be the same. Thus the maximization of probability should be done subject to this condition. Any other conserved quantity should also be preserved. Thus our condition for the equilibrium distribution should read

$$\delta_{n_i} p(\{n_i\}) \;=\; 0, \qquad \textit{subject to} \sum_i n_i O_i^{(\alpha)} \;=\; \textit{fixed} \tag{7.2.2}$$

where $O^{(\alpha)}$ (for various values of α) give the conserved quantities, the total particle number and energy being two such observables.

The maximization of probability seems very much like what is given by the second law of thermodynamics, wherein equilibrium is characterized by maximization of entropy. In fact this suggests that we can define entropy in terms of probability or W, so that the condition of maximization of probability is the same as the condition of maximization of entropy. This identification was made by Boltzmann who defined entropy corresponding to a distribution $\{n_i\}$ of particles among various values of momenta and other observables by

$$S \;=\; k \log W(\{n_i\}) \tag{7.2.3}$$

where k is the Boltzmann constant. For two completely independent systems A, B, we need $S = S_A + S_B$, while $W = W_A W_B$. Thus the relation should be in terms of $\log W$. This equation is one of the most important formulae in physics. It is true even for quantum statistics, where the counting of the number of ways of distributing particles is different from what is given by Equation 7.1.8. We will calculate entropy using this and show that it agrees with the thermodynamic properties expected of entropy. We can restate Boltzmann's hypothesis as

$$p(\{n_i\}) = C\;W(\{n_i\}) = Ce^{\frac{S}{k}} \tag{7.2.4}$$

With this identification, we can write

$$S = k\log\left[N_i \prod_i \frac{1}{n_i!}\right] \tag{7.2.5}$$

$$\approx\; k\left[N\log N - N - \sum_i (n_i \log n_i - n_i)\right] \tag{7.2.6}$$

We will consider a simple case where the single particle energy values are ϵ_i (where i may be interpreted as momentum label) and we have only two conserved quantities to keep fixed, the particle number and the energy. To carry out the variation subject to the conditions we want to impose, we can use Lagrange multipliers. We add terms $\lambda(\sum_i n_i - N) - \beta(\sum_i n_i\epsilon_i - U)$, and vary the parameters (or multipliers) β, λ to get the two conditions

$$\sum_i n_i = N, \qquad \sum_i n_i\epsilon_i = U \tag{7.2.7}$$

Since these are anyway obtained as variational conditions, we can vary n_i freely without worrying about the constraints, when we try to maximize the entropy. Usually we use μ instead of λ, where $\lambda = \beta$μ, so we will use this way of writing the Lagrange multiplier. The equilibrium condition now becomes

$$\delta\left[\frac{S}{k} - \beta(\sum_i n_i\epsilon_i - U) + \lambda(\sum_i n_i - N)\right] = 0 \tag{7.2.8}$$

This simplifies to

$$\sum_i \delta n_i(\log n_i + \beta\epsilon_i - \beta\mu) = 0 \tag{7.2.9}$$

Since n_i are not constrained, this means that the quantity in brackets should vanish, giving the solution

$$n_i \;=\; e^{-\beta(\epsilon_i-\mu)} \tag{7.2.10}$$

This is the value at which the probability and entropy are a maximum. It is known as the **Maxwell-Boltzmann distribution**. As in the case of the binomial distribution, the variation around this value is very very small for large values of n_i) , so that observable values can be obtained by using just the solution in Equation 7.2.10. We still have the conditions from Equation 7.2.7 obtained as maximization conditions (for variation of β, λ), which means that

$$\begin{aligned}\sum_i e^{-\beta(\epsilon_i-\mu)} \;&=\; N \\ \sum_i \epsilon_i e^{-\beta(\epsilon_i-\mu)} &= U\end{aligned} \tag{7.2.11}$$

The first of these conditions will determine μ in terms of N and the second will determine β in terms of the total energy U.

In order to complete the calculation, we need to identify the summation over the index i. This should cover all possible states of each particle. For a free particle, this would include all momenta and all possible positions. This means that we can replace the summation by an integration over $d^3p\; d^3x$. Further the single-particle energy is given by

$$\epsilon \;=\; \frac{p^2}{2m} \tag{7.2.12}$$

Since

$$\int d^3x\; d^3p\exp\left(-\frac{\beta p^2}{2m}\right) \;=\; V\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \tag{7.2.13}$$

we find from 7.2.11

$$\begin{aligned}\beta \;&=\; \frac{3N}{2U} \\ \beta\mu \;&=\; \log\left[\frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}}\right] \;=\; \log\left[\frac{N}{V}\left(\frac{3N}{4\pi mU}\right)^{\frac{3}{2}}\right]\end{aligned} \tag{7.2.14}$$

The value of the entropy at the maximum can now be expressed as

$$S \;=\; k\left[\frac{5}{2}N - N\log N + N\log V - \frac{3}{2}N\log\left(\frac{3N}{4\pi mU}\right)\right] \tag{7.2.15}$$

From this, we find the relations

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = k\frac{3N}{2U} = k\ \beta \tag{7.2.16}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,U} = -\log\left[\frac{N}{V}\left(\frac{3N}{4\pi mU}\right)^{\frac{3}{2}}\right] = -k\ \beta\mu \tag{7.2.17}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = k\frac{N}{V} \tag{7.2.18}$$

Comparing these with

$$dU = T\ dS - p\ dV + \mu\ dN \tag{7.2.19}$$

which is the same as Equation 5.1.8, we identify

$$\beta\ =\ \frac{1}{kT} \tag{7.2.20}$$

Further, μ is the chemical potential and U is the internal energy. The last relation in Equation 7.2.18 tells us that

$$p\ =\ \frac{N\ k\ T}{V} \tag{7.2.21}$$

which is the ideal gas equation of state.

Once we have the identification from Equation 7.2.20, we can also express the chemical potential and internal energy as functions of the temperature:

$$\mu\ =\ kT\log\left[\frac{N}{V}\left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}\right] \tag{7.2.22}$$

$$U\ =\ \frac{3}{2}NkT$$

The last relation also gives the specific heats for a monatomic ideal gas as

$$C_v = \frac{3}{2}Nk, \quad C_p = \frac{5}{2}Nk \tag{7.2.23}$$

These specific heats do not vanish as $T \rightarrow 0$, so clearly we are not consistent with the third law of thermodynamics. This is because of the classical statistics we have used. The third law is a consequence of quantum dynamics. So, apart from the third law, we see that with Boltzmann's identification of entropy as $S = k\log W$, we get all the expected thermodynamic relations and explicit formulae for the thermodynamic quantities.

We have not addressed the normalization of the entropy carefully so far. There are two factors of importance. In arriving at Equation 7.2.15, we omitted the $N!$ in W, using $\frac{W}{N!}$ in Boltzmann's formula rather than W itself. This division by $N!$ is called the Gibbs factor and helps to avoid a paradox about the entropy of mixing, as explained below. Further, the number of states cannot be just given by $d^3x\ d^3p$ since this is, among other reasons, a dimensionful quantity. The correct prescription comes from quantum mechanics which gives the semiclassical formula for the number of states as

$$\text{Number of states}\ =\ \frac{d^3x d^3p}{(2\pi h)^3} \tag{7.2.24}$$

where h is Planck's constant. Including this factor, the entropy can be expressed as

$$S\ =\ N\ k\ \left[\frac{5}{2} + \log\left(\frac{V}{N}\right) + \frac{3}{2}\log\left(\frac{U}{N}\right) + \frac{3}{2}\log\left(\frac{4\pi m}{3(2\pi\hbar)^2}\right)\right] \tag{7.2.25}$$

This is known as the Sackur-Tetrode formula for the entropy of a classical ideal gas.

Gibbs Paradox

Our expression for entropy has omitted the factor $N!$. The original formula for the entropy in terms of W includes the factor of $N!$ in W. This corresponds to an additional factor of $N \log N - N$ in the formula from Equation ???. The question of whether we should keep it or not was considered immaterial since the entropy contained an additive undetermined term anyway. However, Gibbs pointed out a paradox that arises with such a result. Consider two ideal gases at the same temperature, originally with volumes V_1 and V_2 and number of particles N_1 and N_2. Assume they are mixed together, this creates some additional entropy which can be calculated as $S - S_1 - S_2$. Since $U = \frac{3}{2}NkT$, if we use the formula from Equation ??? without the factors due to $\frac{1}{N!}$ (which means with an additional $N \log N - N$), we find

$$S - S_1 - S_2 = k[N \log V - N_1 \log V_1 - N_2 \log V_2] \tag{7.2.26}$$

(We have also ignored the constants depending on m for now.) This entropy of mixing can be tested experimentally and is indeed correct for monatomic nearly ideal gases. The paradox arises when we think of making the gases more and more similar, taking a limit when they are identical. In this case, we should not get any entropy of mixing, but the above formula gives

$$S - S_1 - S_2 = k\left[N_1 \log\left(\frac{V}{V_1}\right) + N_2 \log\left(\frac{V}{V_2}\right)\right] \tag{7.2.27}$$

(In this limit, the constants depending on m are the same, which is why we did not have to worry about it in posing this question.) This is the paradox. Gibbs suggested dividing out the factor of $N!$, which leads to the formula in Equation ???. If we use that formula, there is no change for identical gases because the specific volume $\frac{V}{N}$ is the same before and after mixing. For dissimilar gases, the formula of mixing is still obtained. The Gibbs factor of $N!$ arises naturally in quantum statistics.

Equipartition

The formula for the energy of a single particle is given by

$$\epsilon = \frac{p^2}{2m} = \frac{p_1^2 + p_2^2 + p_3^2}{2m} \tag{7.2.28}$$

If we consider the integral in Equation 7.2.13 for each direction of p, we have

$$\int dx\ dp\ \exp\left(-\frac{\beta p_1^2}{2m}\right) = L_1\left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}} \tag{7.2.29}$$

The corresponding contribution to the internal energy is $\frac{1}{2}kT$, so that for the three degrees of freedom we get $\frac{3}{2}kT$, per particle. We have considered the translational degrees of freedom corresponding to the movement of the particle in 3-dimensional space. For more complicated molecules, one has to include rotational and vibrational degrees of freedom. In general, in classical statistical mechanics, we will find that for each degree of freedom we get $\frac{1}{2}kT$. This is known as the equipartition theorem. The specific heat is thus given by

$$C_v = \frac{1}{2}k \times \text{number of degrees of freedom} \tag{7.2.30}$$

Quantum mechanically, equipartition does not hold, at least in this simple form, which is as it should be, since we know the specific heats must go to zero as $T \to 0$.

7.3: The Maxwell Distribution For Velocities

The most probable distribution of velocities of particles in a gas is given by Equation 7.2.9 with $\epsilon = \frac{p^2}{2m} = \frac{1}{2}mv^2$. Thus we expect the distribution function for velocities to be

$$f(v)d^3v = C\ \exp\left(-\frac{mv^2}{2kT}\right)d^3v \tag{7.3.1}$$

This is known as the **Maxwell distribution**. Maxwell arrived at this by an ingenious argument many years before the derivation we gave in the last section was worked out. He considered the probability of a particle having velocity components (v_1, v_2, v_3). If the probability of a particle having the x-component of velocity between v_1 and $v_1 + dv_1$ is $f(v_1)dv_1$, then the probability for (v_1, v_2, v_3) would be

$$\text{Probability of } (v_1, v_2, v_3) \ = \ f(v_1)f(v_2)f(v_3)dv_1dv_2dv_3 \tag{7.3.2}$$

Since the dynamics along the three dimensions are independent, the probability should be the product of the individual ones. Further, there is nothing to single out any particular Cartesian component, they are all equivalent, so the function f should be the same for each direction. This leads to 7.3.2. Finally, we have rotational invariance in a free gas with no external potentials, so the probability should be a function only of the speed $v = \sqrt{v_1^2 + v_2^2 + v_3^2}$. Thus we need a function $f(v)$ such that $f(v_1)f(v_2)f(v_3)$ depends only on v. The only solution is for $f(v)$ to be of the form

$$f(v_1) \ \propto \ \exp -(\alpha v_1^2) \tag{7.3.3}$$

for some constant α. The distribution of velocities is thus

$$f d^3v \ = \ C \exp(-\alpha v_1^2) d^3v \tag{7.3.4}$$

Since the total probability $\int f d^3v$ must be one, we can identify the constant C as $(\frac{\alpha}{\pi})^{\frac{3}{2}}$.

We now consider particles colliding with the wall of the container, say the face at $x = L_1$, as shown in Fig. 7.3.1. The momentum imparted to the wall in an elastic collision is $\Delta p_1 = 2mv_1$. At any given instant roughly half of the molecules will have a component v_1 towards the wall. All of them in a volume $A \times v_1$ (where A is the area of the face) will reach the wall in one second, so that the force on the wall due to collisions is

$$F \ = \ \frac{1}{2}\left(\frac{N}{V}\right) A \ \times \ v_1 \ \times \ (2mv_1) \ = \ \left(\frac{N}{V}\right) Amv_1^2 \tag{7.3.5}$$

Averaging over v_1^2 using Equation 7.3.4, we get the pressure

$$p \ = \ \frac{\langle F \rangle}{A} = \left(\frac{N}{V}\right) m\langle v_1^2 \rangle \ = \ \left(\frac{N\ m}{2\alpha V}\right) \tag{7.3.6}$$

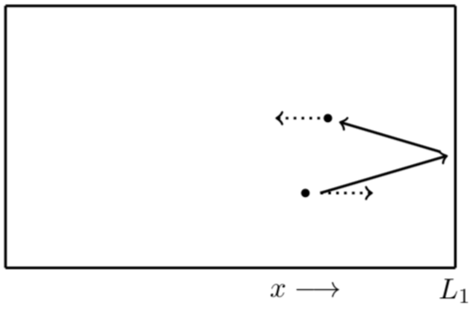


Figure 7.3.1: A typical collision with the wall of the container at $x = L_1$. The velocity component v_1 before and after collision is shown by the dotted line.

Comparing with the ideal gas law, we can identify α as $\frac{m}{2kT}$. Thus the distribution of velocities is

$$
\begin{aligned}
f(v)d^3v &= \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\exp\left(-\frac{mv^2}{2kT}\right)d^3v \\
f(v)d^3v &= \left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}\exp\left(-\frac{\epsilon}{kT}\right)d^3p
\end{aligned}
\tag{7.3.7}
$$

This is in agreement with Equation 7.2.9.

Adapting Maxwell's Argument to a Relativistic Gas

Maxwell's argument leading to Equation 7.3.7 is so simple and elegant that it is tempting to see if there are other situations to which such a symmetry-based reasoning might be applied. The most obvious case would be a gas of free particles for which relativistic effects are taken into account. In this case, $\epsilon=\sqrt{p_2+m_2}$ and it is clear that $e^{-\beta\epsilon}$ cannot be obtained from a product of the form $f(p_1)f(p_2)f(p_3)$. So, at first glance, Maxwell's reasoning seems to fail. But this is not quite so, as the following line of reasoning will show.

As a first step, notice that the distribution in Equation 7.3.7 is for a gas which has no overall drift motion. This is seen by noting that

$$
\langle v_i\rangle \;=\; \int d^3p\,\frac{p_i}{m}\left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}\exp\left(-\frac{\epsilon}{kT}\right) \;=\; 0 \tag{7.3.8}
$$

We can include an overall velocity $\vec{u}$ by changing the distribution to

$$
f(p)=\left(\frac{1}{2\pi mkT}\right)^{\frac{3}{2}}\exp\left(-\frac{(\vec{p}-m\vec{u})^2}{2mkT}\right) \tag{7.3.9}
$$

It is easily verified that $\langle v_i\rangle=u_i$. It is important to include the overall motion in the reasoning since the symmetry is the full set of Lorentz transformations in the relativistic case and they include velocity-transformations.

Secondly, we note that in the relativistic case where we have the 4-momentum p_μ, $\mu=0,\ 1,\ 2,\ 3$ and what is needed to sum over all states is not the integration over all p_μ, rather we must integrate with the invariant measure

$$
d\mu=d^4p\,\delta(p^2-m^2)\Theta(p_0) \tag{7.3.10}
$$

where Θ is the step function,

$$
\Theta(x)=\begin{cases}1 & \text{for x>0}\\ 0 & \text{for x<0}\end{cases} \tag{7.3.11}
$$

Further the δ-function can be expanded as

$$
\delta(p^2-m^2)=\delta(p_0^2-\vec{p}^2-m^2)=\frac{1}{2p_0}\left[\delta(p_0-\sqrt{\vec{p}^2+m^2})+\delta(p_0+\sqrt{\vec{p}^2+m^2})\right] \tag{7.3.12}
$$

The integration over p_0 is trivial because of these equations and we find that

$$
\int d\mu f(p_\mu) \;=\; \int\frac{d^3p}{2\sqrt{\vec{p}^2+m^2}}f(\sqrt{\vec{p}^2+m^2},\ \vec{p}) \tag{7.3.13}
$$

Now we seek a function which can be written in the form $f(p_0)f(p_1)f(p_2)f(p_3)$ involving the four components of p_μ and integrate it with the measured Equation 7.3.10. The function f must also involve the drift velocity in general. In the relativistic case, this is the 4-velocity U^μ, whose components are

$$
U_0=\frac{1}{\sqrt{1-\vec{u}^2}},\qquad U_i=\frac{u_i}{\sqrt{1-\vec{u}^2}} \tag{7.3.14}
$$

The solution is again an exponential

$$
f(p)=C\exp(-\beta\, p_\mu U^\mu) \;=\; C\exp\left(-\beta(p_0U_0-\vec{p}\cdot\vec{U})\right) \tag{7.3.15}
$$

With the measure from Equation 7.3.10, we find

$$\int d\mu\ f(p)\ B(p) = C\ \int \frac{d^3p}{2\epsilon_p} \exp\Big(-\beta(\epsilon_p U_0 - \vec{p}\cdot\vec{U})\Big)\ B(\epsilon_p, \vec{p}) \tag{7.3.16}$$

for any observable $B(p)$ and where $\epsilon_p = \sqrt{p_2 + m_2}$. At this stage, if we wish to, we can consider a gas with no overall motion, setting $\vec{u} = 0$, to get

$$\langle B\rangle\ =\ C\ \int \frac{d^3p}{2\epsilon_p} \exp(-\beta\epsilon_p)\ B(\epsilon_p, \vec{p}) \tag{7.3.17}$$

This brings us back to a form similar to Equation 7.2.9, even for the relativistic case.

7.4: The Gibbsian Ensembles

The distribution which was obtained in Equation 7.17 gives the most probable number of particles with momentum p as $n_p = \exp(-\beta(\epsilon_p - \mu))$. This was obtained by considering the number of ways in which free particles can be distributed among possible momentum values subject to the constraints of fixed total number of particles and total energy. We want to consider some generalizations of this now. First of all, one can ask whether a similar formula holds if we have an external potential. The barometric formula (2.13) has a similar form since mgh is the potential energy of a molecule or atom in that context. So, for external potentials, one can make a similar argument.

Interatomic or intermolecular forces are not so straightforward. In principle, if we have intermolecular forces, single particle energy values are not easily identified. Further, in some cases, one may even have new molecules formed by combinations or bound states of old ones. Should they be counted as one particle or two or more? So, one needs to understand the distribution from a more general perspective. The idea is to consider the physical system of interest as part of a larger system, with exchange of energy with the larger system. This certainly is closer to what is really obtained in most situations. When we study or do experiments with a gas at some given temperature, it is maintained at this temperature by being part of a larger system with which it can exchange energy. Likewise, one could also consider a case where exchange of particles is possible. The important point is that, if equilibrium is being maintained, the exchange of energy or particles with a larger system will not change the distribution in the system under study significantly. Imagine high energy particles get scattered into the volume of gas under study from the environment. This can raise the temperature slightly. But there will be roughly equal number of particles of similar energy being scattered out of the volume under study as well. Thus while we will have fluctuations in energy and particle number, these will be very small compared to the average values, in the limit of large numbers of particles. So this approach should be a good way to analyze systems statistically.

Arguing along these lines one can define three standard ensembles for statistical mechanics: the micro-canonical, the canonical and the grand canonical ensembles. The canonical ensemble is the case where we consider the system under study (of fixed volume V) as one of a large number of similar systems which are all in equilibrium with larger systems with free exchange of energy possible. For the grand canonical ensemble, we also allow free exchange of particles, so that only the average value of the number of particles in the system under study is fixed. The micro-canonical ensemble is the case where we consider a system with fixed energy and fixed number of particles. (One could also consider fixing the values of other conserved quantities, either at the average level (for grand canonical case) or as rigidly fixed values (for the micro-canonical case)).

We still need a formula for the probability for a given distribution of particles in various states. In accordance with the assumption of equal *a priori* probabilities, we expect the probability to be proportional to the number of states $\mathcal{N}$ available to the system subject to the constraints on the conserved quantities. In classical mechanics, the set of possible trajectories for a system of particles is given by the phase space since the latter constitutes the set of possible initial data. Thus the number of states for a system of N particles would be proportional to the volume of the subspace of the phase space defined by the conserved quantities. In quantum mechanics, the number of states would be given in terms of the dimension of the Hilbert space. The semiclassical formula for the counting of states is then

$$d\mathcal{N} = \prod_{i=1}^{N} \frac{d^3x_i d^3p_i}{(2\pi\hbar)^3} \tag{7.4.1}$$

In other words, a cell of volume $(2\pi h)^{3N}$ in phase space corresponds to a state in the quantum theory. (This holds for large numbers of states; in other words, it is semiclassical.) This gives a more precise meaning to the counting of states via the phase volume. In the microcanonical ensemble, the total number of states with total energy between E and $E+\delta E$ would be

$$\mathcal{N} = \int_{H=E}^{H=E+\delta E} \prod_{i=1}^{N} \frac{d^3x_i d^3p_i}{(2\pi\hbar)^3} \equiv W(E) \tag{7.4.2}$$

where $H(\{x\},\{p\})$ is the Hamiltonian of the N-particle system. The entropy is then defined by Boltzmann's formula as $S(E) = k\log W(E)$. For a Hamiltonian $H = \sum_i \frac{p_i^2}{2m}$, this can be explicitly calculated and leads to the formulae we have already obtained. However, as explained earlier, this is not easy to do explicitly when the particles are interacting. Nevertheless, the key idea is that the required phase volume is proportional to the exponential of the entropy,

$$\text{Probability} \propto \exp\left(\frac{S}{k}\right) \tag{7.4.3}$$

This idea can be carried over to the canonical and grand canonical ensembles.

In the canonical ensemble, we consider the system of interest as part of a much larger system, with, say, $N+M$ particles. The total number of available states is then

$$d\mathcal{N}=\prod_{i=1}^{N+M}\frac{d^3x_id^3p_i}{(2\pi\hbar)^3} \tag{7.4.4}$$

The idea is then to consider integrating over the M particles to obtain the phase volume for the remaining, viewed as a subsystem. We refer to this subsystem of interest as system 1 while the M particles which are integrated out will be called system 2. If the total energy is E, we take the system 1 to have energy E_1, with system 2 having energy $E-E_1$. Of course, E_1 is not fixed, but can vary as there can be some amount of exchange of energy between the two systems. Integrating out the system 2 leads to

$$\delta\mathcal{N}=\prod_{i=1}^{N}\frac{d^3x_id^3p_i}{(2\pi\hbar)^3}W(E-E_1)=\prod_{i=1}^{N}\frac{d^3x_id^3p_i}{(2\pi\hbar)^3}e^{\frac{S(E-E_1)}{k}} \tag{7.4.5}$$

We then expand $S(E)$ as

$$\begin{aligned}S(E-E_1)&=S(E)-E_1\left(\frac{\partial S}{\partial E}\right)_{V,N}+\dots\\&=S(E)-\frac{1}{T}E_1+\dots\\&=S(E)-\frac{H_N}{T}+\dots\end{aligned} \tag{7.4.6}$$

where have used the thermodynamic formula for the temperature. The temperature is the same for system 1 and the larger system (system 1 + system 2) of which it is a part. H_N is the Hamiltonian of the N particles in system 1. This shows that, as far as the system under study is concerned, we can take the probability as

$$\text{Probability}=C\prod_{i=1}^{N}\frac{d^3x_id^3p_i}{(2\pi\hbar)^3}\exp\left(-\frac{H_n(x,p)}{T}\right) \tag{7.4.7}$$

Here C is a proportionality factor which can be set by the normalization requirement that the total probability (after integration over all remaining variables) is 1. (The factor $e^{\frac{S(E)}{k}}$ from Equation 7.4.6 can be absorbed into the normalization as it is a constant independent of the phase space variables for the particles in system 1. Also, the subscript 1 referring to the system under study is now redundant and has been removed.)

There are higher powers in the Taylor expansion in Equation 7.4.6 which have been neglected. The idea is that these are very small as E_1 is small compared to the energy of the total system. In doing the integration over the remaining phase space variables, in principle, one could have regions with H_N comparable to E, and the neglect of terms of order E_1^2 may not seem justified. However, the formula 7.4.7 in terms of the energy is sharply peaked around a certain average value with fluctuations being very small, so that the regions with E_1 comparable to E will have exponentially vanishing probability. This is the ultimate justification for neglecting the higher terms in the expansion from Equation 7.4.6. We can *a posteriori* verify this by calculating the mean square fluctuation in the energy value which is given by the probability distribution in Equation 7.4.7. This will be taken up shortly.

Turning to the grand canonical case, when we allow exchange of particles as well, we get

$$\begin{aligned}S(E-E_1,(N+M)-N))&=S(E,N+M)-E_1\left(\frac{\partial S}{\partial U}\right)_{V,N+M}-N\left(\frac{\partial S}{\partial N}\right)_{U,V}+\dots\\&=S(E,N+M)-\frac{1}{T}E_1+\frac{\mu}{T}N+\dots\\&=S(E,N+M)-\frac{1}{T}(H_N-\mu_N)+\dots\end{aligned} \tag{7.4.8}$$

By a similar reasoning as in the case of the canonical ensemble, we find, for the grand canonical ensemble,

$$\text{Probability} \equiv dp_N = C \prod_{i=1}^{N} \frac{d^3x_i d^3p_i}{(2\pi\hbar)^3} \exp\left(-\frac{H(x,p)-\mu_N}{kT}\right) \tag{7.4.9}$$

More generally, let us denote by $\mathcal{O}_\alpha$ an additively conserved quantum number or observable other than energy. The general formula for the probability distribution is then

$$dp_N = C \prod_{i=1}^{N} \frac{d^3x_i d^3p_i}{(2\pi\hbar)^3} \exp\left(-\frac{H(x,p)-\sum_\alpha \mu_\alpha \mathcal{O}_\alpha}{kT}\right) \tag{7.4.10}$$

Even though we write the expression for N particles, it should be kept in mind that averages involve a summation over N as well. Thus the average of some observable $B(x,p)$ is given by

$$\langle B\rangle = \sum_{N=0}^{\infty} \int dp_N \; B_N(x,p) \tag{7.4.11}$$

Since the normalization factor C is fixed by the requirement that the total probability is 1, it is convenient to define the “partition function". In the canonical case, it is given by

$$Q_N = \int \frac{1}{N!} \prod_{i=1}^{N} \left[\frac{d^3x_i d^3p_i}{(2\pi\hbar)^3}\right] \exp\left(-\frac{H(x,p)}{kT}\right) \tag{7.4.12}$$

We have introduced an extra factor of $\frac{1}{N!}$. This is the Gibbs factor needed for resolving the Gibbs paradox; it is natural in the quantum counting of states. Effectively, because the particles are identical, permutation of particles should not be counted as a new configuration, so the phase volume must be divided by $N!$ to get the “correct" counting of states. We will see that even this is not entirely adequate when full quantum effects are taken into account. In the grand canonical case, the partition function is defined by

$$Z = \sum_N \int \frac{1}{N!} \prod_{i=1}^{N} \left[\frac{d^3x_i d^3p_i}{(2\pi\hbar)^3}\right] \exp\left(-\frac{H(x,p)-\sum_\alpha \mu_\alpha \mathcal{O}_\alpha}{kT}\right) \tag{7.4.13}$$

Using the partition functions in place of $\frac{1}{C}$, and including the Gibbs factor, we find the probability of a given configuration as

$$dp_N = \frac{1}{Q_N} \frac{1}{N!} \prod_{i=1}^{N} \left[\frac{d^3x_i d^3p_i}{(2\pi\hbar)^3}\right] \exp\left(-\frac{H(x,p)}{kT}\right) \tag{7.4.14}$$

while for the grand canonical case we have

$$dp_N = \frac{1}{Z} \frac{1}{N!} \prod_{i=1}^{N} \left[\frac{d^3x_i d^3p_i}{(2\pi\hbar)^3}\right] \exp\left(-\frac{H(x,p)-\sum_\alpha \mu_\alpha \mathcal{O}_\alpha}{kT}\right) \tag{7.4.15}$$

The partition function contains information about the thermodynamic quantities. Notice that, in particular,

$$\frac{1}{\beta}\frac{\partial}{\partial \mu_\alpha} \log Z = \langle \mathcal{O}_\alpha \rangle \tag{7.4.16}$$

$$-\frac{\partial}{\partial \beta} \log Z = \langle H - \sum_\alpha \mu_\alpha \mathcal{O}_\alpha \rangle = U - \sum_\alpha \mu_\alpha \langle \mathcal{O}_\alpha \rangle$$

We can also define the average value of the entropy (not the entropy of the configuration corresponding to particular way of distributing particles among states, but the average over the distribution) as

$$\bar{S} = k \left[\log Z + \beta(U - \sum_\alpha \mu_\alpha \langle \mathcal{O}_\alpha \rangle)\right] \tag{7.4.17}$$

While the averages $U = \langle H \rangle$ and $\langle \mathcal{O}_\alpha \rangle$ do not depend on the factors of $N!$ and $(2\pi h)^{3N}$, the entropy does. This is why we chose the normalization factors in Equation 7.4.12to be what they are.

Consider the case when we have only one conserved quantity, the particle number, in addition to the energy. In this case, Equation 7.4.17 can be written as

$$\mu N = U - TS + kT \log Z \tag{7.4.18}$$

Comparing this with the definition of the Gibbs free energy in Equation 5.6 and its expression in terms of μ in Equation 5.16, we find that we can identify

$$pV = kT \log Z \tag{7.4.19}$$

This gives the equation of state in terms of the partition function.

These equations (7.4.13), (7.4.16 - 7.4.19) are very powerful. Almost all of the thermodynamics we have discussed before is contained in them. Further, they can be used to calculate various quantities, including corrections due to interactions among particles, etc. As an example, we can consider the calculation of corrections to the equation of state in terms of the intermolecular potential.

7.5: Equation of State

The equation of state, as given by Equation 7.4.19, requires the computation of the grand canonical partition function. We will consider the case where the only conserved quantities are the Hamiltonian and the number of particles. The grand canonical partition function can then be written as

$$Z=\sum_{N=0}^{\infty} z^N Q_N=1+\sum_{N=1}^{\infty} z^N Q_N \qquad z=e^{\beta\mu} \tag{7.5.1}$$

where Q_N is the canonical partition for a fixed number of particles, given in Equation 7.4.12. The variable $z=e^{\beta\mu}$ is called the fugacity. The easiest way to proceed to the equation of state is to consider an expansion of $\log Z$ in powers of z. This is known as the cumulant expansion and, explicitly, it takes the form

$$\log\left[1+\sum_{N=1}^{\infty} z^N Q_N\right]=1+\sum_{n=1}^{\infty} z^N a_n \tag{7.5.2}$$

where the first few coefficients are easily worked out as

$$\begin{aligned} a_1 &= Q_1 \\ a_2 &= Q_2-\frac{1}{2}Q_1^2 \\ a_3 &= Q_3-Q_2Q_1+\frac{1}{3}Q_1^2 \end{aligned} \tag{7.5.3}$$

The Hamiltonian, for N particles, has the form

$$H_N=\sum_i \frac{p_i^2}{2m}+\sum_{i<j} V(x_i,x_j)+\dots \tag{7.5.4}$$

where we have included a general two-particle interaction and the ellipsis stands for possible 3-particle and higher interactions. For $N=1$ we just have the first term. The p-integrations factorize and, if $V(x_i,x_j)=0$, we get $Q_N=\frac{Q_1^N}{N!}$. All cumulants a_n vanish except for a_1. We can explicitly obtain

$$a_1=Q_1=\int \frac{d^3x_i d^3p_i}{(2\pi\hbar)^3}\exp\left(-\frac{\beta p^2}{2m}\right)=V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3}{2}} \tag{7.5.5}$$

For Q_2, we find

$$\begin{aligned} Q_2 &= \frac{1}{2!}\frac{Q_1^2}{V^2}\int d^3x_1 d^3x_2\; e^{-\beta V(x_1,x_2)} \\ &= \frac{Q_1^2}{2V}\int d^3x\; e^{-\beta V(x)} \end{aligned} \tag{7.5.6}$$

where, in the second line, we have taken the potential to depend only on the difference $\vec{x}_1-\vec{x}_2$ and carried out the integration over the center of mass coordinate. Thus

$$a_2=\frac{Q_1^2}{2V}\int d^3x\left(1-e^{-\beta V(x)}\right) \tag{7.5.7}$$

Using the cumulant expansion to this order, we find $\log Z\approx zQ_1+z^2a_2$ and the average number of particles in the volume V is given by

$$\bar{N}=\frac{1}{\beta}\frac{\partial}{\partial\mu}\log Z\approx zQ_1+z^2a_2 \tag{7.5.8}$$

which can be solved for z as

$$zQ_1 \approx \bar{N} - 2a_2 \frac{\bar{N}^2}{Q_1^2} + \ldots \tag{7.5.9}$$

If we ignore the a_2-term, this relation is the same as what we found in Equation 7.2.14, with the addition of the $(2\pi\hbar)^3$ correction,

$$\beta\mu = \log\left[\frac{\bar{N}}{V}\left(\frac{2\pi\hbar^2}{mkT}\right)\right] \tag{7.5.10}$$

Using Equation 7.5.9 (with the a_2-term) back in $\log Z$ and the expression 7.5.7 for a_2, we get

$$\frac{pV}{\bar{N}kT} \approx \left[1 + \frac{\bar{N}}{V} B_2 + \ldots\right] \tag{7.5.11}$$
$$B_2 = \frac{1}{2}\int d^3x \, \left(1 - e^{-\beta V(x)}\right)$$

These formulae show explicitly the first correction to the ideal gas equation of state. The quantity B_2 is a function of temperature; it is called the **second virial coefficient** and can be calculated, once a potential is known, by carrying out the integration. Even for complicated potentials it can be done, at least, numerically. As a simple example, consider a hard sphere approximation to the interatomic potential,

$$V(r) = \begin{cases} \infty & r < r_0 \\ 0 & r > r_0 \end{cases} \tag{7.5.12}$$

In this case the integral is easily done to obtain $B_2 = \left(\frac{2\pi r_0^3}{3}\right)$ This is independent of the temperature. One can consider more realistic potentials for better approximations to the equation of state.

The van der Waals equation, which we considered earlier, is, at best, a model for the equation of state incorporating some features of the interatomic forces. Here we have a more systematic way to calculate with realistic interatomic potentials. Nevertheless, there is a point of comparison which is interesting. If we expand the van der Waals equation in the form in Equation 7.5.11, it has $B_2 = b - \left(\frac{a}{kT}\right)$; the term b is independent of the temperature. Comparing with the hard sphere repulsion at short distances, we see how something like the excluded volume effect can arise.

We have considered the first corrections due to the interatomic forces. More generally, the equation of state takes the form

$$\frac{pV}{\bar{N}kT} = \left[1 + \sum_{n=2}^{\infty}\left(\frac{\bar{N}}{V}\right)^{n-1} B_n\right] \tag{7.5.13}$$

This is known as the **virial expansion**, with B_n referred to as the n-th virial coefficient. These are in general functions of the temperature; they can be calculated by continuing the cumulant expansion to higher order and doing the integrations needed for Q_N. In practice such a calculation becomes more and more difficult as N increases. This virial expansion in Equation 7.5.13 is in powers of the density $\frac{\bar{N}}{V}$ and integrations involving powers of $e^{-\beta V_{int}}$, where V_{int} is the potential energy of the interaction. Thus for low densities and interaction strengths small compared to kT, truncation of the series at some finite order is a good approximation. So only a few of the virial coefficients are usually calculated.

It is useful to calculate corrections to some of the other quantities as well. From the identification of $\bar{N}$ in Equation 7.5.8 and from Equation 7.4.16, we can find the internal energy as

$$U = \frac{3}{2}\bar{N}kT + \frac{\bar{N}^2}{2V}\int d^3x V(x) e^{-\beta V(x)} + \ldots \tag{7.5.14}$$

In a similar way, the entropy is found to be

$$\bar{S} = \bar{N}\, k\left[\frac{5}{2} + \log\frac{V}{\bar{N}} + \frac{3}{2}\log\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{\bar{N}}{2V}\int d^3x \left(\beta V(x) e^{-\beta V(x)} - 1 + e^{-\beta V(x)}\right)\right] \tag{7.5.15}$$

Since the number of pairs of particles is $\approx \frac{N_2}{2}$, the correction to the internal energy is easily understood as an average of the potential energy. Also the first set of terms in the entropy reproduces the Sackur-Tetrode formula (7.2.25) for an ideal gas.

7.6: Fluctuations

We will now calculate the fluctuations in the values of energy and the number of particles as given by the canonical and grand canonical ensembles. First consider N. From the definition, we have

$$\begin{gathered} \frac{1}{\beta}\frac{\partial Z}{\partial \mu} = Z\langle N\rangle = Z\,\bar{N} \\ \frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \mu^2} = Z\langle N^2\rangle \end{gathered} \tag{7.6.1}$$

If we calculate $\bar{N}$ from the partition function as a function of β and μ, we can differentiate it with respect to μ to get

$$\frac{1}{\beta}\frac{\partial \bar{N}}{\partial \mu} = -\frac{1}{Z^2\beta^2}\left(\frac{\partial Z}{\partial \mu}\right)^2 + \frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \mu^2} = \langle N^2\rangle - \langle N\rangle^2 = \Delta N^2 \tag{7.6.2}$$

The Gibbs free energy is given by $G = \mu\bar{N}$ and it also obeys

$$dG = -SdT + Vdp + \mu d\bar{N} \tag{7.6.3}$$

These follow from Equation 5.1.16 and Equation 5.1.10. Since T is fixed in the differentiations we are considering, this gives

$$\frac{\partial \mu}{\partial \bar{N}} = \frac{V}{\bar{N}}\frac{\partial p}{\partial \bar{N}} \tag{7.6.4}$$

The equation of state gives p as a function of the number density $\rho \equiv \frac{\bar{N}}{V}$, at fixed temperature. Thus

$$\frac{\partial p}{\partial \bar{N}} = \frac{1}{V}\frac{\partial p}{\partial \rho} \tag{7.6.5}$$

Using this in Equation 7.6.4, we get

$$\frac{1}{\beta}\frac{\partial \bar{N}}{\partial \mu} = \bar{N}\frac{kT}{\frac{\partial p}{\partial \rho}} \tag{7.6.6}$$

From Equation 7.6.2, we now see that the mean square fluctuation in the number is given by

$$\frac{\Delta N^2}{N^2} = \frac{1}{\bar{N}}\frac{kT}{\frac{\partial p}{\partial \rho}} \tag{7.6.7}$$

This goes to zero as $\bar{N}$ becomes large, in the thermodynamic limit. An exception could occur if $\left(\frac{\partial p}{\partial \rho}\right)$ becomes very small. This can happen at a second order phase transition point. The result is that fluctuations in numbers become very large at the transition. The theoretical treatment of such a situation needs more specialized techniques.

We now turn to energy fluctuations in the canonical ensemble. For this we consider N to be fixed and write

$$\begin{aligned} \frac{\partial U}{\partial \beta} &= \frac{\partial}{\partial \beta}\left[-\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta}\right] = \left[\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta}\right]^2 - \left[\frac{1}{Q_N}\frac{\partial^2 Q_N}{\partial \beta^2}\right] \\ &= \langle H\rangle^2 - \langle H^2\rangle \equiv -\Delta U^2 \end{aligned} \tag{7.6.8}$$

The derivative of $U = \langle H\rangle$ with respect to $\bar{T}$ gives the specific heat, so we find

$$\Delta U^2 = kC_vT^2, \quad \frac{\Delta U^2}{U^2} = \frac{kC_vT^2}{U^2} \sim \frac{1}{N} \tag{7.6.9}$$

Once again, the fluctuations are small compared to the average value as N becomes large.

7.7: Internal Degrees of Freedom

Many particles, such as atoms, molecules have internal degrees of freedom. This can be due to atomic energy levels, due to vibrational and rotational states for molecules, etc. Very often one has to consider mixtures of particles where they can be in different internal states as well. For example, in a sodium lamp where the atoms are at a high temperature, some of the atoms are in an electronic excited state while some are in the ground state. Of course, the translational degrees of freedom are important as well. In principle, at the classical level, the internal dynamics has its own phase space and by including it in the integration measure for the partition function, we can have a purely classical statistical mechanics of such systems. However, this can be grossly inadequate. Even though in many situations, the translational degrees of freedom can be treated classically, it is necessary to take account of the discreteness of states and energy levels for the internal degrees of freedom. The question is: How do we do this?

The simplest strategy is to consider the particles in different internal states as different species of particles. For example, consider a gas of, say, argon atoms which can be in the ground state (call them A) and in an excited state (call them A∗). The partition function would thus be

$$Z = \sum_{N_A, N_{A^*}} z_A^{N_A} z_{A^*}^{N_A} Q_{N_A, N_{A^*}} \tag{7.7.1}$$

If we ignore interatomic forces, considering a gas of free particles, $Q_N = \frac{(Q_1)^N}{N}!$, so that

$$Z = \exp\left(Z_A Q_{1_A}\right) + \left(Z_{A^*} Q_{1^*_A}\right) \tag{7.7.2}$$

The single particle partition function which we have used so far is of the for

$$Q_1 = \int \frac{d^3x d^3p}{(2\pi h)^3} \exp\left(-\beta \frac{p^2}{2m}\right) \tag{7.7.3}$$

This is no longer good enough since A and A^* have difference in energies for the internal degrees of freedom and this is not reflected in using just $\frac{p^2}{2m}$. Because of the equivalence of mass and energy, this means that m_A and m_{A^*} are different. From the relativistic formula

$$E_p = \sqrt{m^2c^4 + C^2p^2} \approx mc^2 + \frac{p^2}{2m} + \dots \tag{7.7.4}$$

we see that this difference is taken account of if we include the rest energy in Q_1. (Here c is the speed of light in vacuum.) Thus we should use the modified formula

$$\begin{aligned} Q_1 &= \int \frac{d^3x d^3p}{(2\pi h)^3} \exp\left(-\beta\left[mc^2 + \frac{p^2}{2m}\right]\right) \\ &= e^{-\beta mc^2} V \frac{mkT}{2\pi\hbar^2}^{\frac{3}{2}} \end{aligned} \tag{7.7.5}$$

even for nonrelativistic calculations. If there are degenerate internal states, the mass would be the same, so in log Z we could get a multiplicity factor. To see how this arises, consider a gas of particles each of which can have g internal states of the same energy (or mass). Such a situation is realized, for example, by a particle of spin s with $g = 2s + 1$. If we treat each internal state as a separate species of particle, the partition function would be

$$Z = \sum_{\{N_i\}} z_1^{N_1} z_2^{N_2} \cdots z_g^{N_g} Q_{N_1, N_2, \dots N_g} \tag{7.7.6}$$

Each of the μ_i will specify the average number in the distribution for each internal state. However, in many cases, we do not specify the numbers for each state, only the total average number is macroscopically fixed for the gas. Thus all z_i are the same giving a single factor z^N, $N = \sum N_i$, in Equation 7.7.6. Correspondingly, if we have no interparticle interactions, we get

$$Z = \exp\left(z \sum Q_i\right) = \exp(z\, g\, Q_1) \tag{7.7.7}$$

where we used the fact that all masses are the same. We see the degeneracy factor g explicitly.

7.8: Examples

7.8.1: Osmotic Pressure

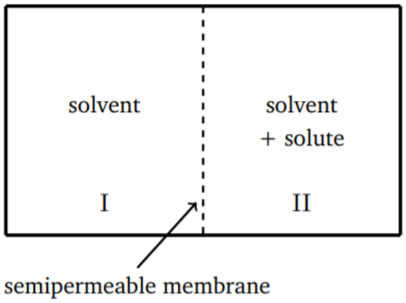


Figure 7.8.1: Illustrating the set-up for calculating osmotic pressure

An example of the use of the idea of the partition function in a very simple way is provided by the osmotic pressure. Here one considers a vessel partitioned into two regions, say, I and II, with a solvent (labeled A) on one side and a solution of the solvent plus a solute (labeled B) on the other side. The separation is via a semipermeable membrane which allows the solvent molecules to pass through either way, but does not allow the solute molecules to pass through. Thus the solute molecules stay in region II, as the Fig. 7.8.1. When such a situation is set up, the solvent molecules pass back and forth and eventually achieve equilibrium with the average number of solvent molecules on each side not changing any further. What is observed is that the pressure in the solution pII is higher than the pressure pI in the solvent in region I. Once equilibrium is achieved, there is no further change of volume or temperature either, so we can write the equilibrium condition for the solvent as

$$\mu_A^{(I)} = \mu_A^{(II)} \tag{7.8.1}$$

Correspondingly, we have $z_A^{(I)} = z_A^{(II)}$, for the fugacities. The partition function has the form

$$\begin{aligned} Z &= \sum_{N_A,N_B} z_A^{N_A} z_B^{N_B}\, Q_{N_A,N_B} \\ &= \sum_{N_A} z_A^{N_A} Q_{N_A,0} + \sum_{N_A} z_A^{N_A} z_B\, Q_{N_A,1} + \cdots \\ &= Z_A\left(1 + \frac{1}{Z_A}\sum_{N_A} z_A^{N_A} z_B\, Q_{N_A,1} + \cdots\right) \end{aligned} \tag{7.8.2}$$

Here Z_A is the partition function for just the solvent. For simplicity, let us take the volumes of the two regions to be the same. Then we may write

$$\log Z_A = \frac{p_I\, V}{kT} \tag{7.8.3}$$

even though this occurs in the formula for the full partition function in region II, since z_A is the same for regions I and II. Going back to Z, we expand log in powers of z_B, keeping only the lowest order term, which is adequate for dilute solutions. Thus

$$\log Z \approx \log Z_A + z_B\left(\frac{1}{Z_A}\sum_{N_A} z_A^{N_A}\, Q_{N_A,1}\right) \tag{7.8.4}$$

The derivative of the partition function with respect to μ_B is related to N_B, as in Equation 7.4.16, so that

$$\left(\frac{1}{Z_A}\sum_{N_A} z_A^{N_A}\, Q_{N_A,1}\right) = N_B \tag{7.8.5}$$

Further, log Z is given by $\frac{p_{II}V}{kT}$. Using these results, Equation 7.8.4 gives

$$p_{II} = p_I + \frac{N_B}{V}kT = p_I + n_B kT \tag{7.8.6}$$

where n_B is the number density of the solute. The pressure difference $p_{II} - p_I$ is called the osmotic pressure.

7.8.2: Equilibrium of a Chemical Reaction

Here we consider a general chemical reaction of the form

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{7.8.7}$$

If the substances A, B, C, D can be approximated as ideal gases, the partition function is given by

$$\log Z = z_A Q_{1A} + z_B Q_{1B} + z_C Q_{1C} + z_D Q_{1D} \tag{7.8.8}$$

For the individual chemical potentials, we can use the general formula in 7.5.10 but with the correction due to the βmc^2 factor as in Equation 7.7.5, since we have different species of particles here. Thus

$$\beta\mu = \log n + \beta\, mc^2 - \log\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{7.8.9}$$

The condition of equilibrium of the reaction is given as $\nu_A\mu_A + \nu_B\mu_B - \nu_C\mu_C - \nu_D\mu_D$. Using Equation 7.8.9, this becomes

$$\begin{aligned} \log\left(\frac{n_A^{\nu_A} n_B^{\nu_B}}{n_C^{\nu_C} n_D^{\nu_D}}\right) &= -\beta c^2(\nu_A\mu_A + \nu_B\mu_B - \nu_C\mu_C - \nu_D\mu_D) + \nu_A f_A + \nu_B f_B - \nu_C f_C - \nu_D f_D \\ f &= \log\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \end{aligned} \tag{7.8.10}$$

The total pressure of the mixture of the substances is given from $pV = kT\log Z$ as

$$p = (n_A + n_B + n_C + n_D)kT \tag{7.8.11}$$

So if we define the concentrations,

$$x_i = \frac{n_i}{\sum_j n_j}, \qquad i = A, B, C, D \tag{7.8.12}$$

then we can rewrite Equation 7.8.10 as

$$\begin{aligned} \frac{x_A^{\nu_A} x_B^{\nu_B}}{x_C^{\nu_C} x_D^{\nu_D}} p^{\nu_A+\nu_B-\nu_C-\nu_D} &= \exp(-\beta\,\epsilon + \nu_A\phi_A + \nu_B\phi_B - \nu_C\phi_C - \nu_D\phi_D) \equiv K \\ \epsilon &= (\nu_A m_A + \nu_B m_B - \nu_C m_C - \nu_D m_D)c^2 \\ \phi &= f + \log kT \end{aligned} \tag{7.8.13}$$

With our interpretation of the masses as rest energy, we see that ϵ is the heat of reaction, i.e., the total energy released by the reaction. ϵ is positive for an exothermic reaction and negative for an endothermic reaction. K, in Equation 7.8.13, is known as the reaction constant and is a function only of the temperature (and the masses of the molecules involved, but these are fixed once a reaction is chosen). The condition in Equation 7.8.13 on the concentrations of the reactants is called the law of mass action.

7.8.3 Ionization Equilibrium

Another interesting example is provided by ionization equilibrium, which is of interest in plasmas and in astrophysical contexts. Consider the ionization reaction of an atom X

$$X \rightleftharpoons X^+ + e^- \tag{7.8.14}$$

There is a certain amount of energy ϵ_I needed to ionize the atom X. Treating the particles involved as different species with possible internal states, we can use Equation 7.7.7 to write

$$\log Z = z_X g_X Q_{1X} + z_e g_e Q_{1e} + Z_{X^+} g_{X^+} Q_{1X^+} \tag{7.8.15}$$

By differentiation with respect to μ, we find, for each species,

$$z = \frac{n}{g} e^{\beta mc^2} \left(\frac{2\pi\hbar^2}{mkT}\right)^{\frac{3}{2}} \tag{7.8.16}$$

The condition for equilibrium $\mu_X - \mu_{X^+} - \mu_e = 0$ is the same as $\left(\frac{z_X}{z_{X^+} z_e}\right) = 1$. Using Equation 7.8.16, this becomes

$$1 = \frac{n_X}{g_X} \frac{g_{X^+}}{n_{X^+}} \frac{g_e}{n_e} e^{\beta(m_X - m_{X^+} + - m_e)c^2} \left(\frac{m_X + m_e}{m_X}\right)^{\frac{3}{2}} \left(\frac{kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{7.8.17}$$

The mass of the atom X is almost equal to the mass of X^+ and the electron; the difference is the binding energy of the electron in X. This is the ionization energy ϵ_I, $(m_X - m_{X^+} - m_e)c^2 = -\epsilon_I$. Using this, Equation 7.8.17 can be rewritten as

$$\left(\frac{n_X + n_e}{n_X}\right) = \left(\frac{g_X + g_e}{g_X}\right) e^{\beta\epsilon_I} \left(\frac{m_X + m_e}{m_X}\right)^{\frac{3}{2}} \left(\frac{kT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \tag{7.8.18}$$

This is known as Saha's equation for ionization equilibrium. It relates the number density of the ionized atom to that of the neutral atom. (While the mass difference is important for the exponent, it is generally a good approximation to take $m_X \approx m_{X^+}$ in the factor $\left(\frac{m_{X^+}}{m_X}\right)^{\frac{3}{2}}$. So it is often omitted.) The degeneracy for the electron states, namely g_e, is due to the spin degrees of freedom, so $g_e = 2$. The degeneracies g_X and g_{X^+} will depend on the atom and the energy levels involved.

The number densities can be related to the pressure by the equation of state; they are also important in determining the intensities of spectral lines. Thus by observation of spectral lines from the photospheres of stars, one can estimate the pressures involved.

CHAPTER OVERVIEW

8: Quantum Statistical Mechanics

One of the important lessons of quantum mechanics is that there is no a priori meaning to qualities of any system, no independent reality, aside from what can be defined operationally in terms of observations. Thus we cannot speak of this electron (or photon, or any other particle) versus that electron (or photon, or any other particle). We can only say that there is one particle with a certain set of values for observables and there is another, perhaps with a different set of values for observables. This basic identity of particles affects the counting of states and hence leads to distributions different from the Maxwell-Boltzmann distribution we have discussed. This is the essential refinement due to quantum statistics.

8.1: Prelude to Quantum Statistical Mechanics

There are two kinds of particles from the point of view of statistics, bosons and fermions. The corresponding statistical distributions are called the **Bose-Einstein distribution** and the **Fermi-Dirac distribution**. Bosons have the property that one can have any number of particles in a given quantum state, while fermions obey the Pauli exclusion principle which allows a maximum of only one particle per quantum state. Any species of particles can be put into one of these two categories. The natural question is, of course, how do we know which category a given species belongs to; is there an a priori way to know this? The answer to this question is yes, and it constitutes one of the deep theorems in quantum field theory, the so-called spin-statistics theorem. The essence of the theorem, although this is not the precise statement, is given as follows.

Theorem 8.1.1: Spin-Statistics Theorem

Identical particles with integer values for spin (or intrinsic angular momentum) are bosons, they obey Bose-Einstein statistics.

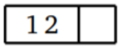
$$\text{Identical particles with spin (or intrinsic angular momentum)} = \left(n + \frac{1}{2}\right) \tag{8.1.1}$$

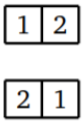
where n is an integer, obey the Pauli exclusion principle and hence they are fermions and obey Fermi-Dirac statistics.

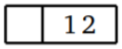
Thus, among familiar examples of particles, photons (which have spin = 1), phonons (quantized version of elastic vibrations in a solid), atoms of He^4, etc. are bosons, while the electron (spin = $\frac{1}{2}$), proton (also spin $-\frac{1}{2}$), atoms of He^3, etc. are fermions. In all cases, particles of the same species are identical.

8.2: Bose-Einstein Distribution

We will now consider the derivation of the distribution function for free bosons carrying out the counting of states along the lines of what we did for the Maxwell-Boltzmann distribution. Let us start by considering how we obtained the binomial distribution. We considered a number of particles and how they can be distributed among, say, K boxes. As the simplest case of this, consider two particles and two boxes. The ways in which we can distribute them are as shown below. The boxes may correspond to different values of momenta, say $\vec{p_1}$ and $\vec{p_2}$, which have







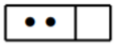
the same energy. There is one way to get the first or last arrangement, with both particles in one box; this corresponds to

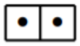
$$W(2,0)=\frac{2!}{2!0!}=\frac{2!}{0!2!}=W(0,2) \tag{8.2.1}$$

There are two ways to get the arrangement of one particle in each box, corresponding to

$$W(1,1)=\frac{2!}{1!1!} \tag{8.2.2}$$

The generalization of this counting is what led us to the Maxwell-Boltzmann statistics. But if particles are identical with no intrinsic attributes distinguishing the particles we have labeled 1 and 2, this result is incorrect. The possible arrangements are just





Counting the arrangement of one particle per box twice is incorrect; the correct counting should give $W(2,0)=W(0,2)=1$ and $W(1,1)=1$, giving a total of 3 distinct arrangements or states. To generalize this, we first consider n particles to be distributed in 2 boxes. The possible arrangements are n in box 1, 0 in box 2; $n-1$ in box 1, 1 in box 2; $\cdots$; 0 in box 1, n in box 2, giving $n+1$ distinct arrangements or states in all. If we have n particles and 3 boxes, we can take $n-k$ particles in the first two boxes (with $n-k+1$ possible states) and k particles in the third box. But k can be anything from zero to n, so that the total number of states is

$$\sum_{k=0}^{n}(n-k+1)=\frac{(n+2)(n+1)}{2}=\frac{(n+3-1)!}{n!(3-1)!} \tag{8.2.3}$$

We may arrive at this in another way as well. Represent the particles as dots and use 3 − 1 = 2 partitions to separate them into three groups. Any arrangement then looks like

$$\bullet\,\bullet\cdots\bullet \;|\; \bullet\,\bullet\cdots\bullet \;|\; \bullet\,\bullet\,\bullet\cdots\bullet$$

Clearly any permutation of the $n+2$ entities (dots or partitions) gives an acceptable arrangement. There are $(n+2)!$ such permutations. However, the permutations of the two partitions do not change the arrangement, neither do the permutations of the dots among themselves. Thus, the number of distinct arrangements or states is

$$\frac{(n+2)!}{n!2!}=\frac{(n+2)(n+1)}{2} \tag{8.2.4}$$

Generalizing this argument, for g boxes and n particles, the number of distinct arrangements is given by

$$W=\frac{(n+g-1)!}{n!(g-1)!} \tag{8.2.5}$$

We now consider N particles, with n_1 of them having energy ϵ_1 each, n_2 of them with energy ϵ_2 each, etc. Further, let g_1 be the number of states with energy ϵ_1, g_2 the number of states with energy ϵ_2, etc. The degeneracy g_α may be due to different values of momentum (e.g., different directions of $\vec{p}$ with the same energy $\epsilon=\frac{p^2}{2m}$) or other quantum numbers, such as spin. The total number of distinct arrangements for this configuration is

$$W(\{n_\alpha\}) = \prod_\alpha \frac{(n_\alpha + g_\alpha - 1)}{n_\alpha!(g_\alpha - 1)!} \tag{8.2.6}$$

The corresponding entropy is $k \log W$ and we must maximize this subject to $\sum_\alpha n_\alpha = N$ and $\sum_\alpha n_\alpha \epsilon_\alpha = U$. With the Stirling formula for the factorials, the function to be extremized is thus

$$\begin{gathered} \frac{S}{k} - \beta U + \beta\mu N = \sum_\alpha \left[(n_\alpha + g_\alpha - 1)\log(n_\alpha + g_\alpha - 1) - (n_\alpha + g_\alpha - 1) - n_\alpha \log n_\alpha + n_\alpha - \beta\epsilon_\alpha n_\alpha + \beta\mu n_\alpha \right] \\ + \text{terms independent of } n_\alpha \end{gathered} \tag{8.2.7}$$

The extremization condition is

$$\log\left[\frac{n_\alpha + g_\alpha - 1}{n_\alpha}\right] \tag{8.2.8}$$

with the solution

$$n_\alpha = \frac{g_\alpha}{e^{\beta(\epsilon_\alpha - \mu)} - 1} \tag{8.2.9}$$

where we have approximated $g_\alpha - 1 \approx g_\alpha$, since the use of the Stirling formula needs large numbers. As the occupation number per state, we can take the result as

$$n = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1} \tag{8.2.10}$$

with the degeneracy factors arising from the summation over states of the same energy. This is the Bose-Einstein distribution. For a free particle, the number of states in terms of the momenta can be taken as the single-particle $d\mathcal{N}$, which, from Equation 7.4.1, is

$$d\mathcal{N} = \frac{d^3x d^3p}{(2\pi\hbar)^3} \tag{8.2.11}$$

Thus the normalization conditions on the Bose-Einstein distribution are

$$\begin{aligned} \sum \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1} &= N \\ \sum \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{\epsilon}{e^{\beta(\epsilon_\alpha - \mu)} - 1} &= U \end{aligned} \tag{8.2.12}$$

The remaining sum in this formula is over the internal states of the particle, such as spin states. It is also useful to write down the partition function Z. Notice that we may write the occupation number n in Equation 8.2.10 as

$$n = \frac{1}{\beta} \frac{\partial}{\partial\mu} \left[-\log\left(1 - e^{-\beta(\epsilon_\alpha - \mu)}\right) \right] \tag{8.2.13}$$

This result holds for each state for which we are calculating n. But recall that the total number N should be given by

$$N = \frac{1}{\beta} \frac{\partial}{\partial\mu} \log Z \tag{8.2.14}$$

Therefore, we expect the partition function to be given by

$$\begin{aligned} \log Z &= -\sum \log\left(1 - e^{-\beta(\epsilon_\alpha - \mu)}\right) \\ Z &= \prod \frac{1}{1 - e^{-\beta(\epsilon_\alpha - \mu)}} \end{aligned} \tag{8.2.15}$$

For each state with fixed quantum numbers, we can write

$$\begin{aligned}\frac{1}{1-e^{-\beta(\epsilon_\alpha-\mu)}} &= 1+e^{-\beta(\epsilon-\mu)}+e^{-2\beta(\epsilon-\mu)}+e^{-3\beta(\epsilon-\mu)} \\ &= \sum_n e^{-n\beta(\epsilon-\mu)}\end{aligned} \tag{8.2.16}$$

This shows that the partition function is the sum over states of possible occupation numbers of the Boltzmann factor $e^{-beta(\epsilon-\mu)}$. This is obtained in a clearer way in the full quantum theory where

$$Z=\mathrm{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})}) \tag{8.2.17}$$

where $\hat{H}$ and $\hat{N}$ are the Hamiltonian operator and the number operator, respectively, and Tr denotes the trace over a complete set of states of the system.

8.3: Fermi-Dirac Distribution

The counting of distinct arrangements for fermions is even simpler than for the Bose-Einstein case, since each state can have an occupation number of either zero or 1. Thus consider g states with n particles to be distributed among them. There are n states which are singly occupied and these can be chosen in $\frac{g!}{(n!(g-n)!)}$ ways. The total number of distinct arrangements is thus given by

$$W(\{n_\alpha\}) = \prod_\alpha \frac{g_\alpha}{n_\alpha!(g_\alpha - n_\alpha)} \tag{8.3.1}$$

The function to be maximized to identify the equilibrium distribution is therefore given by

$$\frac{S}{k} - \beta U + \beta \mu N = -n_\alpha \log n_\alpha - (g_\alpha - n_\alpha)\log(g_\alpha - n_\alpha) - \beta(\epsilon_\alpha - \mu)n_\alpha + \text{constant} \tag{8.3.2}$$

The extremization condition reads

$$\log\left[\frac{(g_\alpha - n_\alpha)}{n_\alpha}\right] = \beta(\epsilon_\alpha - \mu) \tag{8.3.3}$$

with the solution

$$n_\alpha = \frac{g_\alpha}{e^{\beta(\epsilon_\alpha - \mu)} + 1} \tag{8.3.4}$$

So, for fermions in equilibrium, we can take the occupation number to be given by

$$n = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \tag{8.3.5}$$

with the degeneracy factor arising from summation over states of the same energy. This is the **Fermi-Dirac distribution**. The normalization conditions are again,

$$\begin{aligned} \sum \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} &= N \\ \sum \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{\epsilon}{e^{\beta(\epsilon-\mu)} + 1} &= U \end{aligned} \tag{8.3.6}$$

As in the case of the Bose-Einstein distribution, we can write down the partition function for free fermions as

$$\begin{aligned} \log Z &= \sum \log\left(1 + e^{-\beta(\epsilon-\mu)}\right) \\ Z &= \prod \frac{1}{1 + e^{-\beta(\epsilon-\mu)}} \end{aligned} \tag{8.3.7}$$

Notice that, here too, the partition function for each state is $\sum_n e^{-n\beta(\epsilon-\mu)}$; it is just that, in the present case, n can only be zero or 1.

8.4: Applications of the Bose-Einstein Distribution

We shall now consider some simple applications of quantum statistics, focusing in this section on the Bose-Einstein distribution.

8.3.1: The Planck Distribution for Black Body Radiation

Any material body at a finite nonzero temperature emits electromagnetic radiation, or photons in the language of the quantum theory. The detailed features of this radiation will depend on the nature of the source, its atomic composition, emissivity, etc. However, if the source has a sufficiently complex structure, the spectrum of radiation is essentially universal. We want to derive this universal distribution, which is also known as the Planck distribution.

Since a black body absorbs all radiation falling on it, treating all wavelengths the same, a black body may be taken as a perfect absorber. (Black bodies in reality do this only for a small part of the spectrum, but here we are considering the idealized case.) By the same token, black bodies are also perfect emitters and hence the formula for the universal thermal radiation is called the black body radiation formula.

The black body radiation formula was obtained by Max Planck by fitting to the observed spectrum. He also spelled out some of the theoretical assumptions needed to derive such a result and this was, as is well known, the beginning of the quantum theory. Planck's derivation of this formula is fairly simple once certain assumptions, radical for his time, are made; from the modern point of view it is even simpler. Photons are particles of zero rest mass, the energy and momentum of a photon are given as

$$\epsilon=\hbar\omega, \qquad \vec{p}=\hbar\vec{k} \tag{8.4.1}$$

where the frequency of the radiation ω and the wave number $\vec{k}$ are related to each other in the usual way, $\omega=c\,|\vec{k}|$. Further photons are spin-1 particles, so we know that they are bosons. Because they are massless, they have only two polarization states, even though they have spin equal to 1. (For a massive particle we should expect $(2s+1)=3$ polarization states for a spin-1 particle.) We can apply the Bose-Einstein distribution Equation 8.1.10 directly, with one caveat. The number of photons is not a well-defined concept. Since long-wavelength photons carry very little energy, the number of photons for a state of given energy could have an ambiguity of a large number of soft or long-wavelength photons. This is also seen more theoretically; there is no conservation law in electromagnetic theory beyond the usual ones of energy and momentum. This means that we should not have a chemical potential which is used to fix the number of photons. Thus the Bose-Einstein distribution simplifies to

$$n=\frac{1}{e^{\beta\epsilon}-1} \tag{8.4.2}$$

We now consider a box of volume V in which we have photons in thermal equilibrium with material particles such as atoms and molecules. The distribution of the internal energy as a function of momentum is given by

$$dU=2\frac{d^3x\,d^3p}{(2\pi\hbar)^3}\frac{\epsilon}{e^{\beta\epsilon}-1} \tag{8.4.3}$$

where the factor of 2 is from the two polarization states. Using Equation 8.4.1, for the energy density, we find

$$d\,u=2\frac{d^3k}{(2\pi)^3}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1} \tag{8.4.4}$$

This is Planck's radiation formula. If we use $\omega=c\,|\vec{k}|$ and carry out the integration over angular directions of $\vec{k}$, it reduces to

$$d\,u=\frac{\hbar}{\pi^2c^3}\frac{d\omega\,\omega^3}{e^{\frac{\hbar\omega}{kT}}-1} \tag{8.4.5}$$

This distribution function vanishes at $\omega=0$ and as $\omega\to\infty$. It peaks at a certain value which is a function of the temperature. In Fig. 8.3.1, we show the distribution for some sample values of temperature. Note that the value of ω at the maximum increases with temperature; in addition, the total amount of radiation (corresponding to the area under the curve) also increases with temperature.

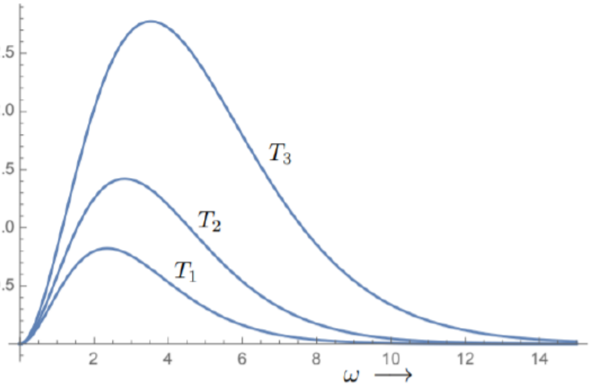


Figure 8.4.1: The Planck distribution as a function of frequency for three sample values of temperature, with $T_3 > T_2 > T_1$; units are arbitrary

If we integrate 8.4.5 over all frequencies, the total energy density comes out to be

$$u = \frac{\pi^2}{15(\hbar c)^3}(kT)^4 \tag{8.4.6}$$

where we have used the result

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = 3!\zeta(4) = \frac{\pi^4}{15} \tag{8.4.7}$$

Rate of Radiation from a Black Body

We can convert the formula for the energy density to the intensity of the radiation by considering the conservation of energy in electrodynamics. The energy density of the electromagnetic field is given by

$$u = \frac{1}{2}(E^2 + B^2) \tag{8.4.8}$$

Using the Maxwell equations in free space, we find

$$\begin{aligned} \frac{\partial u}{\partial t} &= E_i \dot{E}_i + B_i \dot{B}_i = c[E_i(\nabla \times B)_i - B_i(\nabla \times E)_i] \\ &= -c\nabla \cdot (\vec{E} \times \vec{B}) = -\nabla \cdot \vec{P} \\ \vec{P} &= c(\vec{E} \times \vec{B}) \end{aligned} \tag{8.4.9}$$

Integrating over a volume V, we find

$$\frac{\partial}{\partial t} = \int d^3x \; u = \oint_{\partial V} \vec{P} \cdot d\vec{S} \tag{8.4.10}$$

Thus the energy flux per unit area or the intensity is given by the Poynting vector $\vec{P} = c(\vec{E} \times \vec{B})$. For electromagnetic waves, $|E| = |B|$, $\vec{E}$ and $\vec{B}$ are orthogonal to each other and both are orthogonal to $\vec{k}$, the wave vector which gives the direction of propagation, i.e., the direction of propagation of the photon. In this case we find

$$u = E^2, \quad \vec{P} = cu\,\hat{k} \tag{8.4.11}$$

Using the Planck formula 8.4.4, the magnitude of the intensity of blackbody radiation is given by

$$d\ I = 2c\frac{d^3k}{(2\pi)^3}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \tag{8.4.12}$$

We have considered radiation in a box of volume V in equilibrium. To get the rate of radiation per unit area of a blackbody, note that, because of equilibrium, the radiation rate from the body must equal the energy flux falling on area under consideration (which is all taken to be absorbed since it is a blackbody); thus emission rate equals absorption rate as expected for equilibrium. The flux is given by

$$\vec{P}\cdot d\vec{S}=\vec{P}\cdot\hat{n}dS=cu\hat{k}\cdot\hat{n}dS=cu\cos\theta dS \tag{8.4.13}$$

where $\hat{n}$ is the normal to the surface and θ is the angle between $\hat{k}$ and $\hat{n}$. Further, in the equilibrium situation, there are photons going to and away from the surface under consideration, so we must only consider positive values of $\hat{k}\cdot\hat{n}=\cos\theta$, or $0\leq\theta\leq\frac{\pi}{2}$. Thus the radiation rate over all wavelengths per unit area of the emitter is given by

$$\begin{aligned} R &= 2c\int\frac{d^3k}{(2\pi)^3}\frac{\hbar\omega cos\theta}{e^{\frac{\hbar\omega}{kT}}-1} \\ &= 2c\int\frac{dk\,k^2}{4\pi^2}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}\int_0^{\frac{\pi}{2}}d\theta\sin\theta\cos\theta \\ &= \frac{\hbar}{4\pi^2c^2}\int_0^\infty d\omega\frac{\omega^3}{e^{\frac{\hbar\omega}{kT}}-1} \\ &= \sigma\,T^4 \\ \sigma &= \frac{\pi^2k^4}{60\hbar^3c^2} \end{aligned} \tag{8.4.14}$$

This result is known as the **Stefan-Boltzmann law**.

Radiation Pressure

Another interesting result concerning thermal radiation is the pressure of radiation. For this, it is convenient to use one of the relations in Equation 6.2.21, namely,

$$\left(\frac{\partial U}{\partial V}\right)_T=T\left(\frac{\partial p}{\partial T}\right)_V-p \tag{8.4.15}$$

From Equation 8.4.6, we have

$$U=V\frac{\pi^2}{15(\hbar c)^3}k^4T^4 \tag{8.4.16}$$

Equations 8.4.15 and 8.4.16 immediately lead to

$$p=\frac{\pi^2}{45(\hbar c)^3}k^4T^4=\frac{1}{3}u \tag{8.4.17}$$

Radiation pressure is significant and important in astrophysics. Stars can be viewed as a gas or fluid held together by gravity. The gas has pressure and the pressure gradient between the interior of the star and the exterior region tends to create a radial outflow of the material. This is counteracted by gravity which tends to contract or collapse the material. The hydrostatic balance in the star is thus between gravity and pressure gradients. The normal fluid pressure is not adequate to prevent collapse. The radiation produced by nuclear fusion in the interior creates an outward pressure and this is a significant component in the hydrostatic equilibrium of the star. Without this pressure a normal star would rapidly collapse.

Maximum of Planck Distribution

We have seen that the Planck distribution has a maximum at a certain value of ω. It is interesting to consider the wavelength λ_* at which the distribution has a maximum. This can be done in terms of frequency or wavelength, but we will use the wavelength here as this is more appropriate for the application we consider later. (The peak for frequency and wavelength occur at different places since these variables are not linearly related, but rather are reciprocally related.) Using $d\omega=-(2\pi c)\frac{d\lambda}{\lambda^2}$, we can write down the Planck distribution (Equation 8.4.12) in terms of the wavelength λ as

$$d\,I = \frac{2(2\pi\hbar)}{c^2}\frac{1}{\lambda^5(e^{\frac{\hbar\omega}{kT}}-1)}d\lambda d\Omega \tag{8.4.18}$$

(The minus sign in $d\omega$ only serves to show that when the intensity increases with frequency, it should decrease with λ and vice versa. So we have dropped the minus sign. Ω is the solid angle for the angular directions.) Extremization with respect to λ gives the condition

$$(x-5)e^x+5=0 \tag{8.4.19}$$

where $x=\beta\hbar\omega$. The solution of this transcendental equation is

$$\lambda_* \approx \frac{(2\pi\hbar)c}{k}\frac{1}{4.96511}\frac{1}{T} \tag{8.4.20}$$

This relation is extremely useful in determining the temperature of the outer layer of stars, called the photosphere, from which we receive radiation. By spectroscopically resolving the radiation and working out the distribution as a function of wavelength, we can see where the maximum is, and this gives, via Equation 8.4.20, the temperature of the photosphere. Notice that higher temperatures correspond to smaller wavelengths; thus blue stars are hotter than red stars. For the Sun, the temperature of the photosphere is about $5777K$, corresponding to a wavelength $\lambda_* \approx 502nm$. Thus the maximum for radiation from the Sun is in the visible region, around the color green.

Another case of the importance in which the radiation pressure and the λ_* we calculated are important is in the early history of the universe. Shortly after the Big Bang, the universe was in a very hot phase with all particles having an average energy so high that their masses could be neglected. The radiation pressure from all these particles, including the photon, is an important ingredient in solving the Einstein equations for gravity to work out how the universe was expanding. As the universe cooled by expansion, the unstable massive particles decayed away, since there was not enough average energy in collisions to sustain the reverse process. Photons continued to dominate the evolution of the universe. This phase of the universe is referred to as the radiation-dominated era.

Later, the universe cooled enough for electrons and nuclei to combine to form neutral atoms, a phase known as the recombination era. Once this happened, since neutral particles couple only weakly (through dipole and higher multipole moments) to radiation, the existing radiation decoupled and continued to cool down independently of matter. This is the matter dominated era in which we now live. The radiation obeyed the Planck spectrum at the time of recombination, and apart from cooling would continue to do so in the expanding universe. Thus the existence of this background relic radiation is evidence for the Big Bang theory. This cosmic microwave background radiation was predicted to be a consequence of the Big Bang theory, by Gamow, Dicke and others in the 1940s. The temperature was estimated in calculations by Alpher and Herman and by Gamow in the 1940s and 1950s. The radiation was observed by Penzias and Wilson in 1964. The temperature of this background can be measured in the same way as for stars, by comparing the maximum of the distribution with the formula 8.4.20. It is found to be approximately $2.7K$. (Actually this has been measured with great accuracy by now, the latest value being $2.72548 \pm 0.00057K$). The corresponding λ_* is in the microwave region, which is why this is called the cosmic microwave background.

8.3.2: Bose-Einstein Condensation

We will now work out some features of an ideal gas of bosons with a conserved particle number; in this case, we do have a chemical potential. There are many atoms which are bosons and, if we can neglect the interatomic forces as a first approximation, this discussion can apply to gases made of such atoms. The partition function Z for gas of bosons was given in Equation 8.1.15. Since log Z is related to pressure as in Equation 7.4.19, this gives immediately

$$\begin{aligned}\frac{pV}{kT} &= \log Z = -\int \frac{d^3x d^3p}{(2\pi\hbar)^3 \log\left(1-e^{-\beta(\epsilon-\mu)}\right)} \\ &= V\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\left[z+\frac{z^2}{2^{\frac{5}{2}}}+\frac{z^3}{3^{\frac{5}{2}}}+\cdots\right] \\ &= V\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\mathrm{Li}_{\frac{5}{2}}(z)\end{aligned} \tag{8.4.21}$$

where $z = e\beta\mu$ is the fugacity and $\text{Li}_s(z)$ denotes the polylogarithm defined by

$$\text{Li}_s(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^s} \tag{8.4.22}$$

The total number of particles N is given by the normalization condition (Equation 8.1.12) and works out to

$$\begin{aligned} \frac{N}{V} &= \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \left[z + \frac{z^2}{2^{\frac{3}{2}}} + \frac{z^3}{3^{\frac{3}{2}}} + \cdots\right] \\ &= \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \text{Li}_{\frac{3}{2}}(z) = \frac{1}{\lambda^3} \text{Li}_{\frac{3}{2}(z)} \end{aligned} \tag{8.4.23}$$

We have defined the thermal wavelength λ by

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}} \tag{8.4.24}$$

Apart from some numerical factors of order 1, this is the de Broglie wavelength for a particle of energy kT.

If we eliminate z in favor of $\frac{N}{V}$ from this equation and use it in Equation 8.4.21, we get the equation of state for the ideal gas of bosons. For high temperatures, this can be done by keeping the terms up to order z^2 in the polylogarithms. This gives

$$p = \frac{N}{V} kT \left[1 - \frac{N}{V} \frac{\lambda^3}{2^{\frac{5}{2}}} + \cdots\right] \tag{8.4.25}$$

This equation shows that even the perfect gas of bosons does not follow the classical ideal gas law. In fact, we may read off the second virial coefficient as

$$B_2 = -\frac{\lambda^3}{2^{\frac{5}{2}}} \tag{8.4.26}$$

The thermal wavelength is small for large T, so this correction is small at high temperatures, which is why the ideal gas was a good approximation for many of the early experiments in thermal physics. If we compare this with the second virial coefficient of a classical gas with interatomic potential $V(x)$ as given in Equation 7.5.11, namely,

$$B_2 = \frac{1}{2} \int d^3x \left(1 - e^{-\beta V(x)}\right) \tag{8.4.27}$$

we see that we can mimic Equation ref{8.3.26} by an attractive $(V(x) < 0)$ interatomic potential. Thus bosons exhibit a tendency to cluster together.

We can now consider what happens when we lower the temperature. It is useful to calculate a typical value of λ. Putting in the constants,

$$\lambda = \sqrt{\left(\frac{300}{T}\right)\left(\frac{m_p}{m}\right)} \times 6.3 \times 10^{-10} \text{ meters} \tag{8.4.28}$$

(m_p is the mass of the proton $\approx$ the mass of the hydrogen atom.) Thus for hydrogen at room temperature, λ is of atomic size. Since $\frac{V}{N}$ is approximately the free volume available to a molecule, we find from Equation 8.4.23that z must be very small under normal conditions. The function $Li_{\frac{3}{2}}(z)$ starts from zero at $z = 0$ and rises to about 2.61238 at $z = 1$, see Fig. 8.3.2. Beyond that, even though the function can be defined by analytic continuation, it is imaginary. In fact, there is a branch cut from $z = 1$ to ∞. Thus for $z < 1$, we can solve Equation 8.4.23for $z$in terms of $\frac{N}{V}$. As the temperature is lowered, λ decreases and eventually we get to the point where $z = 1$. This happens at a temperature

$$T_c = \frac{1}{k}\left(\frac{N}{V\ 2.61238}\right)^{\frac{2}{3}} \left(\frac{2\pi\hbar^2}{m}\right) \tag{8.4.29}$$

If we lower the temperature further, it becomes impossible to satisfy Equation 8.4.23. We can see the problem at $z=1$ more clearly by considering the partition function, where we separate the contribution due to the zero energy state,

$$Z=\frac{1}{1-z}\prod_{p\neq 0}\frac{1}{1-ze^{-\beta\epsilon_p}} \tag{8.4.30}$$

We see that the partition function has a singularity at $z=1$. This is indicative of a phase transition. The system avoids the singularity by having a large number of particles making a transition to the state of zero energy and momentum. Recall that the factor $\frac{1}{(1-z})$ may be viewed as $\sum_n z^n$, as a sum over different possible occupation numbers for the ground state. The idea here is that, instead of various possible occupation numbers for the ground state, what happens below T_c is that there is a certain occupation number for the ground state, say, N_0, so that the partition function should read

$$Z=z^{N_0}\prod_{p\neq 0}\frac{1}{1-ze^{-\beta\epsilon_p}} \tag{8.4.31}$$

Thus, rather than having different probabilities for the occupation numbers for the ground state, with correspondingly different probabilities as given by the Boltzmann factor, we have a single multiparticle quantum state, with occupation number N_0, for the ground state. The normalization condition Equation 8.4.23 is then changed to

$$\frac{N}{V}=\frac{N_0}{V}+\frac{1}{\lambda^3}\text{Li}_{\frac{3}{2}}(z) \tag{8.4.32}$$

Below T_c, this equation is satisfied, with $z=1$, and with N_0 compensating for the second term on the right hand side as λ increases. This means that a macroscopically large number of particles have to be in the ground state. This is known as Bose-Einstein condensation. In terms of T_c, we can rewrite Equation 8.4.32 as

$$\frac{N_0}{V}=\frac{N}{V}+\left[1-\left(\frac{T}{T_C}\right)^{\frac{3}{2}}\right] \tag{8.4.33}$$

which gives the fraction of particles which are in the ground state.

Since $z=1$ for temperatures below T_c, we have $\mu=0$. This is then reminiscent of the case of photons where we do not have a conserved particle number. The proper treatment of this condensation effect requires quantum field theory, using the concept of spontaneous symmetry breaking. In such a description, it will be seen that the particle number is still a conserved operator but that the condensed state cannot be an eigenstate of the particle number.

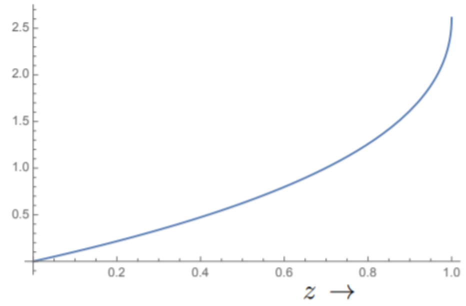


Figure 8.4.2: The polylogarithm \text{Li}_{\frac{3}{2}} (z)

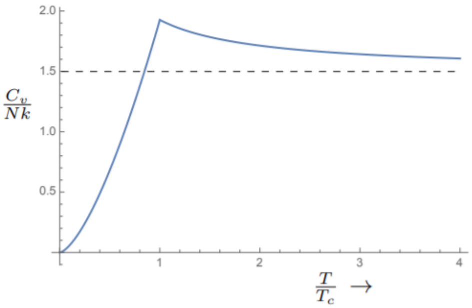


Figure 8.4.3: Qualitative behavior of the specific heat of a gas of bosons

There are many other properties of the condensation phenomenon we can calculate. Here we will focus on just the specific heat. The internal energy for the gas is given by

$$\begin{aligned} U &= \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \frac{\epsilon}{e^{\beta(\epsilon-\mu)}-1} \\ &= V \frac{3}{2} kT \frac{1}{\lambda^3} \mathrm{Li}_{\frac{5}{2}}(z) \end{aligned} \tag{8.4.34}$$

At high temperatures, z is small and $\mathrm{Li}_{\frac{5}{2}}(z) \approx z$ and Equation 8.4.23 gives $\frac{z}{\lambda^3} = \frac{N}{V}$. Thus $U = \frac{3}{2} NkT$ in agreement with the classical ideal gas. This gives $C_v = \left(\frac{3}{2}\right) Nk$.

For low temperatures below T_c, $z = 1$ and we can set $\mathrm{Li}_{\frac{5}{2}}(z) = \mathrm{Li}_{\frac{5}{2}}(1) \approx 1.3415$. The specific heat becomes

$$C_v = V\, k \frac{15}{4} \frac{\mathrm{Li}_{\frac{5}{2}}(1)}{\lambda^3} = N\, k \frac{15}{4} \frac{\mathrm{Li}_{\frac{5}{2}}(1)}{\mathrm{Li}_{\frac{3}{2}}(1)} \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \approx 1.926\, N\, k \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \tag{8.4.35}$$

We see that the specific heat goes to zero at absolute zero, in agreement with the third law of thermodynamics. It rises to a value which is somewhat above $\frac{3}{2}$ at $T = T_c$. Above T_c, we must solve for z in terms of N and substitute back into the formula for U. But qualitatively, we can see that the specific heat has to decrease for $T > T_c$ reaching the ideal gas value of $\frac{3}{2}$ at very high temperatures. A plot of the specific heat is shown in Fig. 8.3.3.

There are many examples of Bose-Einstein condensation by now. The formula for the thermal wavelength in Equation 8.4.28 shows that smaller atomic masses will have larger λ and one may expect them to undergo condensation at higher temperatures. While molecular hydrogen (which is a boson) may seem to be the best candidate, it turns to a solid at around $14\ K$. The best candidate is thus liquid Helium. The atoms of the isotope He^4 are bosons. Helium becomes a liquid below $4.2K$ and it has a density of about $125 \frac{kg}{m^3}$ (under normal atmospheric pressure) and if this value is used in the formula 8.4.29, we find T_c to be about $3\ K$. What is remarkable is that liquid Helium undergoes a phase change at $2.17\ K$. Below this temperature, it becomes a superfluid, exhibiting essentially zero viscosity. (He3 atoms are fermions, there is superfluidity here too, at a much lower temperature, and the mechanism is very different.) This transition can be considered as an example of Bose-Einstein condensation. Helium is not an ideal gas of bosons, interatomic forces (particularly a short-range repulsion) are important and this may explain the discrepancy in the value of T_c. The specific heat of liquid He_4 is shown in Fig. 8.3.4. There is a clear transition point, with the specific heat showing a discontinuity in addition to the peaking at this point. Because of the similarity of the graph to the Greek letter λ, this is often referred to as the λ-transition. The graph is very similar, in a broad qualitative sense, to the behavior we found for Bose-Einstein condensation in Fig. 8.3.3; however, the Bose-Einstein condensation in the noninteracting gas is a first-order transition, while the λ-transition is a second-order transition, so there are differences with the Bose-Einstein condensation of perfect gas of bosons.

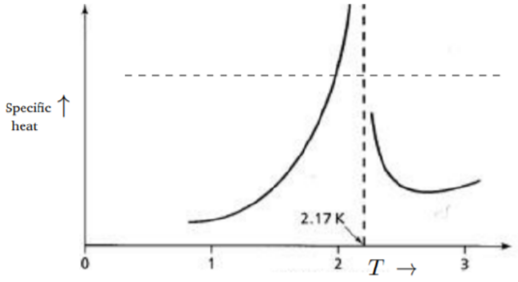


Figure 8.4.4: Specific heat of liquid Helium near the λ-transition

The treatment of superfluid Helium along the lines we have used for a perfect gas is very inadequate. A more sophisticated treatment has to take account of interatomic forces and incorporate the idea of spontaneous symmetry breaking. By now, there is a fairly comprehensive theory of liquid Helium.

Recently, Bose-Einstein condensation has been achieved in many other atomic systems such as a gas of Rb^87 atoms, Na^23 atoms, and a number of others, mostly alkaline and alkaline earth elements.

8.3.3: Specific Heats of Solids

We now turn to the specific heats of solids, along the lines of work done by Einstein and Debye. In a solid, atoms are not free to move around and hence we do not have the usual translational degrees of freedom. Hence the natural question which arises is: When a solid is heated, what are the degrees of freedom in which the energy which is supplied can be stored? As a first approximation, atoms in a solid may be taken to be at the sites of a regular lattice. Interatomic forces keep each atom at its site, but some oscillation around the lattice site is possible. This is the dynamics behind the elasticity of the material. These oscillations, called lattice vibrations, constitute the degrees of freedom which can be excited by the supplied energy and are thus the primary agents for the specific heat capacity of solids. In a conductor, translational motion of electrons is also possible. There is thus an electronic contribution to the specific heat as well. This will be taken up later; here we concentrate on the contribution from the lattice vibrations. In an amorphous solid, a regular lattice structure is not obtained throughout the solid, but domains with regular structure exist, and so, the elastic modes of interest are still present.

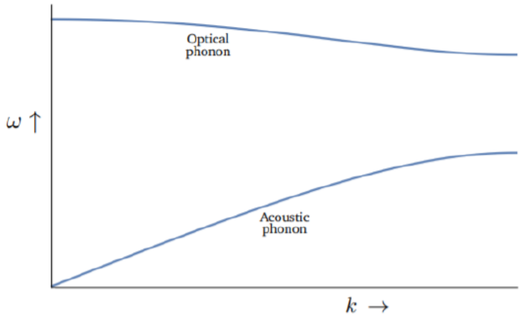


Figure 8.4.5: Typical phonon dispersion curves

Turning to the details of the lattice vibrations, for N atoms on a lattice, we expect $3N$ modes, since each atom can oscillate along any of the three dimensions. Since the atoms are like beads on an elastic string, the oscillations can be transferred from one atom to the next and so we get traveling waves. We may characterize these by a frequency ω and a wave number $\vec{k}$. The dispersion relation between ω and $\vec{k}$ can be obtained by solving the equations of motion for N coupled particles. There are distinct modes corresponding to different $\omega - k$ relations; the typical qualitative behavior is shown in Fig. 8.3.5. There are three acoustic modes for which $\omega \approx c_s|\vec{k}|$, for low $|\vec{k}|$, $c_s$being the speed of sound in the material. The three polarizations correspond to oscillations in the three possible directions. The long-wavelength part of these modes can also be obtained by solving for elastic waves (in terms of the elastic moduli) in the continuum approximation to the lattice. They are basically sound waves, hence the name acoustic modes. The highest value for $|\vec{k}|$ is limited by the fact that we do not really have a continuum; the shortest wavelength is of the order of the lattice spacing.

There are also the so-called optical modes for which $\omega \neq 0$ for any $\vec{k}$. The minimal energy needed to excite these is typically in the range of 30-60 meV or so; in terms of photon energy, this corresponds to the infrared and visible optical frequencies, hence the name. Since $1\text{eV} \approx 10^4\ K$, the optical modes are not important for the specific heat at low temperatures.

Just as electromagnetic waves, upon quantization, can be viewed as particles, the photons, the elastic waves in the solid can be described as particles in the quantum theory. These particles are called phonons and obey the expected energy and momentum relations

$$E = \hbar\omega, \qquad \vec{p} = \hbar\vec{k} \tag{8.4.36}$$

The relation between ω and $\vec{k}$ may be approximated for the two cases rather well by

$$w \approx \begin{cases} c_s|\vec{k}| & \text{(Acoustic)} \\ \omega_0 & \text{(Optical)} \end{cases} \tag{8.4.37}$$

where ω_0 is a constant independent of $\vec{k}$. If there are several optical modes, the corresponding ω_0's may be different. Here we consider just one for simplicity. The polarizations correspond to the three Cartesian axes and hence they transform as vectors under rotations; i.e., they have spin = 1 and hence are bosons. The thermodynamics of these can now be worked out easily.

First, consider the acoustic modes. The total internal energy due to these modes is

$$U = 3\int \frac{d^3x d^3k}{(2\pi)^3} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \tag{8.4.38}$$

The factor of 3 is for the three polarizations. For most of the region of integration which contributes significantly, we are considering modes of wavelengths long compared to the lattice spacing and so we can assume isotropy and carry out the angular integration. For high k, the specific crystal structure and anisotropy will matter, but the corresponding ω's are high and the $e^{-\beta\hbar\omega}$ factor will diminish their contributions to the integral. Thus

$$U = V\int \frac{3\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{8.4.39}$$

Here ω_D is the Debye frequency which is the highest frequency possible for the acoustic modes. The value of this frequency will depend on the solid under consideration. We also define a Debye temperature T_D by $\hbar\omega_D = kT_D$. We then find

$$U = 3\left(\frac{V}{2\pi^2\hbar^3 c_s^3}\right)(kT)^4 \int_0^{\frac{T_D}{T}} du \frac{u^3}{e^u - 1} \tag{8.4.40}$$

For low temperatures, $\frac{T_D}{T}$ is so large that one can effectively replace it by ∞ in a first approximation to the integral. For high $T >> T_D$, we can expand the integrand in powers of u to carry out the integration. This way we find

$$\int_0^{\frac{T_D}{T}} du \frac{u^3}{e^u - 1} = \begin{cases} \frac{\pi^4}{15} + \mathcal{O}(e^{-\frac{T_D}{T}}) & T << T_D \\ \frac{1}{3}\left(\frac{T_D}{T}\right)^3 - \frac{1}{8}\left(\frac{T_D}{T}\right)^4 + \cdots & T >> T_D \end{cases} \tag{8.4.41}$$

The internal energy for $T << T_D$ is thus

$$U = \left(\frac{V}{2\pi^2\hbar^3 c_s^3}\right)\frac{\pi^4(kT)^4}{5} + \mathcal{O}(e^{-\frac{T_D}{T}}) \tag{8.4.42}$$

The specific heat at low temperatures is thus given by

$$U \approx \left(\frac{V}{2\pi^2\hbar^3 c_s^3}\right)\frac{4\ k}{5}\pi^4(kT)^3 \tag{8.4.43}$$

We can relate this to the total number of atoms in the material as follows. Recall that the total number of vibrational modes for N atoms is $3N$. Thus

$$3\int^{\omega_D} \frac{d^3x d^3k}{(2\pi)^3} + \text{Total number of optical modes} = 3N \tag{8.4.44}$$

If we ignore the optical modes, we get

$$\left(\frac{V}{2\pi^2 c_s^3}\right) = \frac{3N}{\omega_D^3} \tag{8.4.45}$$

This formula will hold even with optical modes if N is interpreted as the number of unit cells rather than the number of atoms. In terms of N, we get, for $T << T_D$,

$$\begin{aligned} U &= \frac{3Nk\pi^4}{5}\frac{T^4}{T_D^3} + \mathcal{O}(e^{-\frac{T_D}{T}}) \\ C_v &= \frac{12Nk\pi^4}{5}\frac{T^3}{T_D^3} + \mathcal{O}(e^{-\frac{T_D}{T}}) \end{aligned} \tag{8.4.46}$$

The expression for C_v in Equation 8.4.43 and 8.4.46 is the famous T^3 law for specific heats of solids at low temperatures derived by Debye in 1912. There is a universality to it. The derivation relies only on having modes with $\omega \sim k$ at low k. There are always three such modes for any elastic solid. These are the sound waves in the solid. (The existence of these modes can also be understood from the point of view of spontaneous symmetry breaking, but that is another matter.) The power 3 is of course related to the fact that we have three spatial dimensions. So any elastic solid will exhibit this behavior for the contribution from the lattice vibrations. As we shall see shortly, the optical modes will not alter this result. Some sample values of the Debye temperature are given in Table 8.3.1. This will give an idea of when the low temperature approximation is applicable.

Table 8.3.1: Some Sample Debye Temperatures

Solid	**T_D in K**	**Solid**	**T_D in K**
Gold	170	Aluminum	428
Silver	215	Iron	470
Platinum	240	Silicon	645
Copper	343.5	Carbon	2230

For $T >> T_D$, we find

$$\begin{aligned} U &= \left(\frac{V}{2\pi^2 c_s^3}\right)\left[kT(\hbar\omega_D)^4 - \frac{3}{8}(\hbar\omega_D)^3 + \mathcal{O}\left(\frac{T_D}{T}\right)\right] \\ &= 3N\left[kT - \frac{3}{8}\hbar\omega_D + \mathcal{O}\left(\frac{T_D}{T}\right)\right] \end{aligned} \tag{8.4.47}$$

The specific heat is then given by

$$C_v = k\left(\frac{V}{2\pi^2 c_s^3}\right)(\hbar\omega_D)^3 + \mathcal{O}\left(\frac{1}{T^2}\right) = 3Nk + \mathcal{O}\left(\frac{1}{T^2}\right) \tag{8.4.48}$$

Turning to the optical modes, we note that the frequency ω is almost independent of k, for the whole range of k. So it is a good approximation to consider just one frequency ω_0, for each optical mode. Let N_{opt} be the total number of degrees of freedom in the optical mode of frequency ω_0. Then the corresponding internal energy is given by

$$U_{opt} = N_{opt}\frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} \tag{8.4.49}$$

The specific heat contribution is given by

$$\begin{aligned} U &= Nk \frac{(\beta\hbar\omega_0)^2}{(e^{\beta\hbar\omega_0}-1)(1-e^{\beta\hbar\omega_0})} \\ &\approx Nk\left[1-\frac{1}{12}\left(\frac{\hbar\omega_0}{kT}\right)^2+\cdots\right] \qquad \text{for } T >> \hbar\omega_0 \\ &\approx Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \exp\left(-\frac{\hbar\omega_0}{kT}\right) \qquad \text{for } T << \hbar\omega_0 \end{aligned} \tag{8.4.50}$$

8.5: Applications of the Fermi-Dirac Distribution

We now consider some applications of the Fermi-Dirac distribution (8.2.5). It is useful to start by examining the behavior of this function as the temperature goes to zero. This is given by

$$n \to \begin{cases} 1 & \epsilon < \mu \\ 0 & \epsilon > \mu \end{cases} \tag{8.5.1}$$

Thus all states below a certain value, which is the zero-temperature value of the chemical potential, are filled with one fermion each. All states above this value are empty. This is a highly quantum state. The value of ϵ for the highest filled state is called the Fermi level. Given the behavior in Equation 8.5.1, it is easy to calculate the Fermi level in terms of the number of particles. Let p_F correspond to the magnitude of the momentum of the highest filled level. Then

$$N = g_s \int_F^p \frac{d^3x d^3p}{(2\pi\hbar)^3} = g_s V \frac{p_F^3}{6\pi^2\hbar^3} \tag{8.5.2}$$

where g_s is the number of polarizations for spin, $g_s = 2s+1$. Denoting $\frac{N}{V} = \bar{n}$, the Fermi level is thus given by

$$\epsilon_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{6\pi^2\bar{n}}{g_s}\right)^{\frac{2}{3}} \tag{8.5.3}$$

The ground state energy is given by

$$\begin{aligned} U &= g_s \int_F^p \frac{d^3x d^3p}{(2\pi\hbar)^3}\frac{p^2}{2m} \\ &= V g_s \frac{p_F^5}{20\pi^2 m\hbar^3} = \frac{3}{10}\frac{h^2}{2m}\left(\frac{6\pi^2}{g_s}\right)^{\frac{2}{3}}\frac{N^{\frac{5}{3}}}{V^{\frac{2}{3}}} \end{aligned} \tag{8.5.4}$$

$$= V\frac{3}{5}\epsilon_F\bar{n} \tag{8.5.5}$$

The pressure is then easily calculated as

$$p = \frac{h^2}{5m}\left(\frac{6\pi^2}{g_s}\right)^{\frac{2}{3}}\bar{n}^{\frac{5}{3}} \tag{8.5.6}$$

(Since ϵ_F depends on $\bar{n}$, it is easier to use Equation 8.5.4 for this.) The multiparticle state here is said to be highly degenerate as particles try to go to the single quantum state of the lowest energy possible subject to the constraints of the exclusion principle. The pressure from Equation 8.5.6 is referred to as the degeneracy pressure. Since fermions try to exclude each other, it is as if there is some repulsion between them and this is the reason for this pressure. It is entirely quantum mechanical in origin, due to the needed correlation between the electrons. As we will see, it plays an important role in astrophysics.

The Fermi energy ϵ_F determines what temperatures can be considered as high or low. For electrons in a metal, ϵ_F is of the order of eV, corresponding to temperatures around $10^4 K$. Thus, for most of the physics considerations, electrons in a metal are at low temperatures. For atomic gases, the Fermi level is much smaller due to the $\frac{1}{m}$ factor in Equation 8.5.3, and room temperature is high compared to ϵ_F. We will first consider the high temperature case, where we expect small deviations from the classical physics.

The expression for N, given by the normalization condition (8.2.6) is

$$\begin{aligned} \bar{n} = \frac{N}{V} &= g_s \int \frac{d^3k}{(2\pi)^3}\frac{1}{e^{\beta(\epsilon-\mu)}+1} = g_s \int \frac{d^3k}{(2\pi)^3}\frac{ze^{\beta\epsilon}}{1+ze^{\beta\epsilon}} \\ &= g_s \frac{4}{\lambda^3\sqrt{\pi}}\int_0^\infty du\ u^2\ e^{-u}\left[z - z^2 e^{-u^2} z^3 e^{-2u^2} + \cdots\right] \\ &= \frac{g_s}{\lambda^3}\left(-\mathrm{Li}_{\frac{3}{2}}(-z)\right) \end{aligned} \tag{8.5.7}$$

where λ is the thermal wavelength, defined as before, by $\lambda=\sqrt{\frac{2\pi\hbar^2}{mkT}}$. The partition function Z, from (8.2.7), is given by

$$\log Z=g_s\int\frac{d^3xd^3p}{(2\pi\hbar)^3}\log\left(1+e^{-\beta(\epsilon-\mu)}\right)\tag{8.5.8}$$

This being \frac{pV}{kT}, the equation of state is given by

$$\begin{aligned}\frac{p}{kT}&=\frac{g_s}{V}\int\frac{d^3xd^3p}{(2\pi\hbar)^3}\log\left(1+e^{-\beta(\epsilon-\mu)}\right)\\&=\frac{g_s}{\lambda^3}\left(-\mathrm{Li}_{\frac{5}{2}}(-z)\right)\end{aligned}\tag{8.5.9}$$

At low densities and high temperatures, we see from the power series expansion of the polylogarithms that it is consistent to take z to be small. Keeping terms up to the quadratic order in z, we get

$$\begin{aligned}z&\approx\frac{\bar{n}\lambda^3}{g_s}+\frac{1}{2^{\frac{3}{2}}}\left(\frac{\bar{n}\lambda^3}{g_s}\right)^2+\cdots\\\frac{p}{kT}&=\bar{n}\left[1+\bar{n}\frac{\lambda^3}{g_s2^{\frac{5}{2}}}+\cdots\right]\end{aligned}\tag{8.5.10}$$

So, as in the bosonic case, we are not far from the ideal gas law. The correction may be identified in terms of the second virial coefficient as

$$B_2=\frac{\lambda^3}{g_s2^{\frac{5}{2}}}\tag{8.5.11}$$

This is positive; so, unlike the bosonic case, we would need a repulsive potential between classical particles to mimic this effect via the classical expression (8.3.27) for $B2$.

8.4.1: Electrons in a Metal

Consider a two-state system in quantum mechanics and, to begin with, we take the states to be degenerate. Thus the Hamiltonian is just a diagonal 2×2 matrix,

$$H_0=\begin{pmatrix}E_0&0\\0&E_0\end{pmatrix}\tag{8.5.12}$$

If we consider a perturbation to this system such that the Hamiltonian becomes

$$H=H_0+V=H_0+\begin{pmatrix}0&v\\v&0\end{pmatrix}=\begin{pmatrix}E_0&v\\v&E_0\end{pmatrix}\tag{8.5.13}$$

then the degeneracy between the two eigenstates of H_0 is lifted and we have two eigenstates with eigenvalues

$$E_{\pm}=E_0\pm v\tag{8.5.14}$$

Now consider a system with N states, with the Hamiltonian as an $N\times N$ matrix. Starting with all states degenerate, a perturbation would split the levels by an amount depending on the perturbing term. We would still have N eigenstates, of different energies which will be close to each other if the perturbation is not large. As N becomes very large, the eigenvalues will be almost continuous; we get a band of states as the new eigenstates. This is basically what happens in a solid. Consider N atoms on a lattice. The electronic states, for each atom by itself, is identical to the electronic states of any other atom by itself. Thus we have a Hamiltonian with a very large degeneracy for any of the atomic levels. The interatomic forces act as a perturbation to these levels. The result is that, instead of each atomic level, the solid has a band of energy levels corresponding to each unperturbed single-atom state. Since typically $N\sim$ the Avogadro number, it is a very good approximation to treat the band as having continuous energy eigenvalues between two fixed values. There are gaps between different bands, reflecting the energy gaps in the single-atom case. Thus the structure of electronic states in a solid is a series of well-separated bands with the energy levels within each band so close together as to be practically continuous. Many of these eigenstates will have wave functions localized around individual nuclei.

These correspond to the original single-atom energy states which are not perturbed very much by the neighboring atoms. Typically, inner shell electrons in a multi-electron atom would reside in such states. However, for the outer shell electrons, the perturbations can be significant enough that they can hop from one atomic nucleus to a neighbor, to another neighbor, and so on, giving essentially free electrons subject to a periodic potential due to the nuclei. In fact, for the calculation of these bands, it is a better approximation to start from free electrons in a periodic potential rather than perturbing individual atomic states. These nonlocalized bands are crucial for electrical conductivity. The actual calculation of the band structure of a solid is a formidable problem, but for understanding many physical phenomena, we only need the general structure.

Consider now a solid with the electronic states being a set of bands. We then consider filling in these bands with the available electrons. Assume that the number of electrons is such that a certain number of bands are completely filled, at zero temperature. Such a material is an insulator, because if an electric field is applied, then the electrons cannot respond to the field because of the exclusion principle, as there are no unoccupied states of nearby energy.

Table 8.4.1: Some Sample Fermi levels

Metal	$\boldsymbol{\epsilon_F}$ **in** $\boldsymbol{eV}$	**Metal**	$\boldsymbol{\epsilon_F}$ **in** $\boldsymbol{eV}$
Gold	5.53	Aluminum	11.7
Silver	5.49	Iron	11.1
Copper	7.00	Zinc	9.47

The only available unoccupied states are in the next higher band separated by an energy gap. As a result, the electrical conductivity is zero. If the field is strong enough to overcome the gap, then, of course, there can be conduction; this amounts to a dielectric breakdown.

However, when all the available electrons have been assigned to states, if there is a band of nonlocalized states which is not entirely filled, it would mean that there are unoccupied states very close to the occupied ones. Electrons can move into these when an electric field is applied, even if the amount of energy given by the potential is very small. This will lead to nonzero electrical conductivity. This is the case for conductors; they have bands which are not fully filled. Such bands are called conducting bands, while the filled ones are called valence bands.

The nonlocalized states of the conducting band can be labeled by the electron momentum $\vec{k}$ with energy $\epsilon(k)$. The latter is, in general, not a simple function like $\frac{\hbar^2 k^2}{2m}$, because of interactions with the lattice of atoms and between electrons. In general, it is not isotropic either but will depend on the crystalline symmetry of the lattice. But for most metals, we can approximate it by the simple form

$$\epsilon = \frac{\hbar^2 k^2}{2m^*} \tag{8.5.15}$$

The effect of interactions can be absorbed into an effective electron mass m^*. (Showing that this can actually be done is a fairly complicated task; it goes by the name of fermi liquid theory, originally guessed, with supporting arguments, by Landau and proved to some extent by Migdal, Luttinger and others. We will not consider it here.) At zero temperature, when we have a partially filled band, the highest occupied energy level within the band is the Fermi level ϵ_F. The value of ϵ_F can be calculated from (8.5.3), knowing $\bar{n}$, the number of electrons (not bound to sites); this is shown in Table 8.4.1. Since 1 eV is of the order $10^4\ K$ in terms of temperature, we see that, for phenomena at normal temperatures, we must consider the low temperature regime of the Fermi-Dirac distribution. The fugacity $z = e^{\beta\mu}$ is very large and we need a large fugacity asymptotic expansion for various averages. This is done using a method due to Sommerfeld.

Consider the expression for$\bar{n}$ from (8.5.7), which we can write as

$$\begin{aligned} \bar{n} &= g_s \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(\epsilon-\mu)}+1} \\ &= \frac{g_s}{\lambda^3} \frac{4}{\sqrt{\pi}} \int_0^\infty du \frac{u^2}{e^{u^2-\beta\mu}+1} = \frac{g_s}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty dw \frac{\sqrt{w}}{e^{w-\beta\mu}+1} \end{aligned} \tag{8.5.16}$$

where $u = k\sqrt{\frac{\hbar^2}{2mkT}}$ and $w = u^2$. The idea is to change the variable of integration to $w - \beta\mu$. The lower limit of integration will then be $-\beta\mu$, which may be replaced by $-\infty$ as a first approximation. But in doing so, we need to ensure that the integrand vanishes at $-\infty$. For this one needs to do a partial integration first. Explicitly, we rewrite Equation 8.5.16 as

$$\begin{aligned} \frac{\bar{n}\lambda^3}{g_s} &= \frac{4}{3\sqrt{\pi}} \int_{-\beta\mu}^{\infty} dw \frac{(w+\beta\mu)^{\frac{3}{2}}}{(e^w+1)(e^{-w}+1)} \\ &= \frac{4}{3\sqrt{\pi}} \int_{-\infty}^{\infty} dw \frac{(w+\beta\mu)^{\frac{3}{2}}}{(e^w+1)(e^{-w}+1)} + \mathcal{O}(e^{-\beta\mu}) \end{aligned} \tag{8.5.17}$$

In the first line, we have done a partial integration of the expression from Equation 8.5.16; in the second line, we replaced the lower limit by $-\infty$. The discrepancy in doing this is at least of order $e^{-\beta\mu}$ due to the e^{-w} in the denominator of the integrand. This is why we needed a partial integration. We can now expand $(w+\beta\mu)^{\frac{3}{2}}$ in powers of w; the contribution from large values of $|w|$ will be small because the denominator ensures the integrand is sharply peaked around $w = 0$. Odd powers of w give zero since integrand would be odd under $w \to -w$. Thus

$$\begin{aligned} \int_{-\infty}^{\infty} dw \frac{(w+\beta\mu)^{\frac{3}{2}}}{(e^w+1)(e^{-w}+1)} &= \int_{-\infty}^{\infty} \frac{dw}{(e^w+1)(e^{-w}+1)} \left[(\beta\mu)^{\frac{3}{2}} + \frac{3}{8}(\beta\mu)^{-\frac{1}{2}} w^2 + \cdots\right] \\ &= (\beta\mu)^{\frac{3}{2}} + (\beta\mu)^{-\frac{1}{2}} \frac{\pi^2}{8} + \cdots \end{aligned} \tag{8.5.18}$$

This gives us the equation for μ as

$$\frac{\bar{n}\lambda^3 3\sqrt{\pi}}{4\ g_s} = (\beta\mu)^{\frac{3}{2}} + \frac{\pi^2}{8}(\beta\mu)^{-\frac{1}{2}} \tag{8.5.19}$$

By writing $\mu = \mu_0 + \mu_1 + \cdots$, we can solve this to first order as

$$\beta\mu \approx \beta\epsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right] \tag{8.5.20}$$

where we have used the expression for ϵ_F in terms of $\bar{n}$. As expected, the value of μ at zero temperature is ϵ_F. Turning to the internal energy, by a similar procedure, we find

$$\begin{aligned} \frac{U}{V} &= g_s kT \frac{4}{5\sqrt{\pi}} \int_{-\infty}^{\infty} dw \frac{(w+\beta\mu)^{\frac{5}{2}}}{(e^w+1)(e^{-w}+1)} + \mathcal{O}(e^{-\beta\mu}) \\ &= g_s kT \frac{4}{5\sqrt{\pi}} \left[(\beta\mu)^{\frac{5}{2}} + \frac{5\ \pi^2}{8}(\beta\mu)^{\frac{1}{2}} + \cdots\right] \end{aligned} \tag{8.5.21}$$

Using the result (8.5.20) for μ, this becomes

$$\frac{U}{V} = \frac{3}{5}\epsilon_F \bar{n} \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right] \tag{8.5.22}$$

The most interesting result of this calculation is that there is an electronic contribution to the specific heat which, at low temperatures, is given by

$$C_v = N\ k \frac{\pi^2}{2} \frac{kT}{\epsilon_F} + \mathcal{O}(T^3) \tag{8.5.23}$$

As expected from the third law, this too vanishes as $T \to 0$.

8.4.2: White Dwarf Stars

A gas of fermions which is degenerate is also important in many other physical phenomena, including astrophysics. Here we will briefly consider its role in white dwarf stars.

The absolute magnitude of a star which is proportional to its luminosity or total output of energy per unit time is related to its spectral characteristic, which is in turn related to the temperature of its photosphere. Thus a plot of luminosity versus spectral classification, known as a Hertsprung-Russell diagram, is a useful guide to classifying stars. Generally, bluer stars or hotter stars have a higher luminosity compared to stars in the red part of the spectrum. They roughly fall into a fairly well-defined curve. Stars in this category are called main sequence stars. Our own star, the Sun, is a main sequence star. There are two main exceptions, white dwarfs which tend to have low luminosity even though they are white and red giants which have a higher luminosity than expected for the red part of the spectrum. White dwarfs have lower luminosity because they have basically run of hydrogen for fusion and usually are not massive enough to pass the threshold for the fusion of higher nuclei. They are thus mostly made of helium. The radiation is primarily from gravitational contraction. (Red giants are rather low mass stars which have exhausted the hydrogen in their cores. But then the cores contract, hydrogen from outer layers get pulled in somewhat and compressed enough to sustain fusion outside the core. Because the star has a large radius, the total output is very high even though the photosphere is not very hot, only around 4000 K.)

Returning to white dwarfs, what keeps them from completely collapsing is the degeneracy pressure due to electrons. The stars are hot enough for most of the helium to be ionized and so there is a gas of electrons. The Fermi level is around 20 MeV or so, while the temperature in the core is of the order of $10^7\ K \sim 10^3\ eV$. Thus the electron gas is degenerate and the pressure due to this is important in maintaining equilibrium. Electron mass being $\sim 0.5\ MeV$, the gas is relativistic. If we use the extreme relativistic formula, the energy-momentum relation is

$$\epsilon \sim c|\vec{p}| \tag{8.5.24}$$

Calculating the Fermi level and energy density, we find

$$\begin{aligned} \frac{N}{V} &\equiv \bar{n} = g_s \int_0^{k_F} dw \frac{d^3k}{(2\pi)^3} = g_s \frac{k_F^3}{6\pi^2} \\ \frac{U}{V} &= g_s \hbar c \int_0^{k_F} dw \frac{d^3k}{(2\pi)^3} k = \frac{g_s \hbar c}{8\pi^2} \left(\frac{6\pi^2 \bar{n}}{g_s}\right)^{\frac{4}{3}} \equiv K\ \bar{n}^{\frac{4}{3}} \\ p &= \frac{K}{3} \bar{n}^{\frac{4}{3}} \end{aligned} \tag{8.5.25}$$

For the condition for hydrostatic equilibrium, consider a spherical shell of material in the star, of thickness dr at a radius r from the center. If the density (which is a function of the radius) is $\rho(r)$, then the mass of this shell is $\rho 4\pi r^2 dr$. The attractive force pulling this towards the center is $-(\frac{Gm\rho}{r^2})4\pi r^2 dr$, where $m(r)$ is the mass enclosed inside the sphere of radius r. The pressure difference between the inside and outside of the shell under consideration is $p(r) - p(r+dr)$, with an outward force $(\frac{dp}{dr})4\pi r^2 dr$ Thus equilibrium requires

$$\frac{dp}{dr} = -\frac{G\,m\,\rho}{r^2} \tag{8.5.26}$$

Further, the mass enclosed can be written as

$$m(r) = \int_0^r dr 4\pi r^2 \rho \tag{8.5.27}$$

These two equations, along with the equation of state, give a second order equation for $\rho(r)$. The radius R of the star is defined by $p(R) = 0$.

What contributes to the pressure? This is the key issue in solving these equations. For a main sequence star which is still burning hydrogen, the kinetic pressure (due to the random movements of the material particles) and the radiation pressure contribute. For a white dwarf, it is basically the degeneracy pressure. Thus we must solve these equations, using the pressure from Equation 8.5.25. The result is then striking. If the mass of the star is beyond a certain value, then the electron degeneracy pressure is not enough to counterbalance it, and hence the star cannot continue as a white dwarf. This upper limit on the mass of a white dwarf is approximately 1.4 times the mass of the Sun. This limit is known as the Chandrasekhar limit.

What happens to white dwarfs with higher masses? They can collapse and ignite other fusion processes, usually resulting in a supernova. They could end up as a neutron star, where the electrons, despite the degeneracy pressure, have been squeezed to a point where they combine with the protons and we get a star made of neutrons. This (very dense) star is held up by neutron degeneracy pressure. (The remnant from the Crab Nebula supernova explosion is such a neutron star.) There is an upper limit to the mass of neutron stars as well, by reasoning very similar to what led to the Chandrasekhar limit; this is known as the Tolman-Oppenheimer-Volkov limit. What happens for higher masses? They may become quark stars, and for even higher masses, beyond the stability limit of quark stars, they may completely collapse to form a black hole.

8.4.3: Diamagnetism and Paramagnetism

Diamagnetism and paramagnetism refer to the response of a material system to an external magnetic field B_i. To quantify this, we look at the internal energy U of the material, considered as a function of the magnetic field. The magnetization M_i of the material is then defined by

$$M_i = \frac{1}{V}\left(-\frac{\partial U}{\partial B_i}\right)_{S,V,N} \tag{8.5.28}$$

The magnetization is the average magnetic dipole moment (per unit volume) which the material develops in response to the field and, in general, is itself a function of the field B_i. For ferromagnetic materials, the magnetization can be nonzero even when we turn off the external field, but for other materials, for small values of the field, we can expect a series expansion in powers of B_i, so that

$$M_i = \chi_{ij} B_j + \mathcal{O}(B^2) \tag{8.5.29}$$

χ_{ij} is the magnetic susceptibility of the material. In cases where the linear approximation (8.5.29) is not adequate, we define

$$\chi_{ij} = \left(\frac{\partial M_i}{\partial B_j}\right) = \left(-\frac{1}{V}\right)\left(\frac{\partial^2 U}{\partial B_i \partial B_j}\right)_{S,V,N} \tag{8.5.30}$$

In general χ_{ij} is a tensor, but for materials which are isotropic to a good approximation, we can take $\chi_{ij} = \chi\delta_{ij}$, defining a scalar susceptibility χ. Materials for which $\chi < 0$ are said to be diamagnetic while materials for which $\chi > 0$ are said to be paramagnetic. The field $\vec{H}$, which appears in the Maxwell equation which has the free current $\vec{J}$ as the source, is related to the field $\vec{B}$ by $\vec{H} = \vec{B}(1-\chi) = \frac{\vec{B}}{\mu}$; μ is the magnetic permeability.

Regarding magnetization and susceptibility, there is a theorem which is very simple but deep in its implications. It is originally due to Niels Bohr and later rediscovered by H.J. van Leeuwen. The theorem can be rephrased as follows.

Theorem 8.5.1 — Bohr-van Leeuwen Theorem

The equilibrium partition function of a system of charged particles obeying classical statistics in an external magnetic field is independent of the magnetic field.

It is very easy to prove this theorem. Consider the Hamiltonian of a system of N charged particles in an external magnetic field. It is given by

$$H = \sum_{\alpha=1}^{N} \frac{(p_{\alpha i} - q_\alpha A_i(x_{\alpha i}))}{2\, m_\alpha} + V(x) \tag{8.5.31}$$

where α refers to the particle, $i = 1, 2, 3$, as usual, and V is the potential energy. It could include the electrostatic potential energy for the particles as well as the contribution from any other source. $A_i(x_{\alpha i})$ is the vector potential which is evaluated at the position of the α-th particle. The classical canonical partition function is given by

$$Q_N = \frac{1}{N!}\int \prod_\alpha \frac{d^3x_\alpha d^3p_\alpha}{2\pi\hbar^3} e^{-\beta H} \tag{8.5.32}$$

The strategy is to change the variables of integration to

$$\Pi_{\alpha i} = p_{\alpha i} - q_\alpha A_i(x_{\alpha i}) \tag{8.5.33}$$

The Hamiltonian becomes

$$H=\sum_{\alpha=1}^{N}\frac{\Pi_{\alpha i}\Pi_{\alpha i}}{2\,m_{\alpha}}+V(x) \tag{8.5.34}$$

Although this eliminates the external potential A_i from the Hamiltonian, we have to be careful about the Jacobian of the transformation. But in this case, we can see that the Jacobian is 1. For the phase space variables of one particle, we find

$$\begin{pmatrix} d\Pi_i \\ dx_i \end{pmatrix}=\begin{bmatrix} \delta_{ij} & -q\frac{\partial A_i}{\partial x_j} \\ 0 & \delta_{ij} \end{bmatrix}\begin{pmatrix} dp_j \\ dx_j \end{pmatrix} \tag{8.5.35}$$

The determinant of the matrix in this equation is easily verified to be the identity and the argument generalizes to N particles. Hence

$$Q_N=\frac{1}{N!}\int\prod_{\alpha}\frac{d^3x_\alpha d^3\Pi_\alpha}{2\pi\hbar^3}e^{-\beta H(\{\Pi,x\})} \tag{8.5.36}$$

We see that A_i has disappeared from the integral, proving the theorem. Notice that any mutual binding of the particles via electrostatic interactions, which is contained in $V(x)$, does not change this conclusion. The argument extends to the grand canonical partition since it is $\sum_n z^n Q_N$.

Note

For the cognoscenti, what we are saying is that one can describe the dynamics of charged particles in a magnetic field in two ways. We can use the Hamiltonian (8.5.31) with the symplectic form $\omega=dp_i\wedge dx_i$ or one can use the Hamiltonian (8.5.34) with the symplectic form $\Omega=d\Pi_i\wedge dx_i+q\frac{\partial A_j}{\partial x_i}dx_i\wedge dx_j$. The equations of motion will be identical. But in the second form, the Hamiltonian does not involve the vector potential. The phase volume defined by Ω is also independent of A_i. Thus the partition function is independent of A_i.

This theorem shows that the explanation for diamagnetism and paramagnetism must come from the quantum theory. We will consider these briefly, starting with diamagnetism. The full treatment for an actual material has to take account of the proper wave functions of the charged particles involved, for both the localized states and the extended states. We will consider a gas of charged particles, each of charge e and mass m, for simplicity. We take the magnetic field to be along the third axis. The energy eigenstates of a charged particle in an external uniform magnetic field are the so-called Landau levels, and these are labeled by p, k, λ. The energy eigenvalues are

$$E_{k,p}=\frac{p^2}{2m}+\hbar\omega(k+\frac{1}{2}),\qquad k=0,1,\cdots \tag{8.5.37}$$

where $\omega=\frac{eB}{m}$. p is the momentum along the third axis and k labels the Landau level. Each of these levels has a degeneracy equal to

$$\text{Degeneracy }=\frac{eB}{(2\pi\hbar)}\times\text{ Area of Sample} \tag{8.5.38}$$

The states with the same energy eigenvalue are labeled by λ. The particles are fermions (electrons) and hence the occupation number of each state can be zero or one. Thus the partition function Z is given by

$$\begin{aligned}\log Z&=\sum_{\lambda,k,p}\log\left(1+e^{-\beta E_{k,p}+\beta\mu}\right)\\&=\int d^2x\frac{eB}{(2\pi\hbar)}\frac{dp\,dx_3}{(2\pi\hbar)}\sum_k\log\left(1+ze^{-\beta E_{k,p}}\right)\end{aligned} \tag{8.5.39}$$

where z is the fugacity as usual. For high temperatures, we can consider a small z-expansion. Retaining only the leading term,

$$\log Z=V\frac{eB}{(2\pi\hbar)^2}(2\pi mkT)^{\frac{1}{2}}z\frac{e^{-\frac{x}{2}}}{1-e^{-x}}+\cdots,\qquad x=\frac{\hbar\omega}{kT} \tag{8.5.40}$$

For high temperatures, we can also use a small x-expansion,

$$\frac{e^{-\frac{x}{2}}}{1-e^{-x}} \approx \frac{1}{x}\left(1-\frac{x^2}{24}+\cdots\right) \tag{8.5.41}$$

This leads to

$$\log Z = V\left(\frac{2\pi mkT}{(2\pi\hbar)^2}\right)^{\frac{3}{2}} z\left(1-\frac{x^2}{24}+\cdots\right) \tag{8.5.42}$$

The definition (8.5.28) is equivalent to $dU = TdS - pdV + \mu dN - MVdB$. From $pV = kT\log Z$, we have $G - F = \mu N - F = kT\log Z$, so that

$$d(kT\ \log Z) = dG - dF = Nd\mu + SdT + pdV + MVdB \tag{8.5.43}$$

which shows that

$$M = \frac{kT}{V}\left(\frac{\partial \log Z}{\partial B}\right)_{T,V,\mu} = \frac{kT}{V}\left(\frac{\partial \log Z}{\partial B}\right)_{T,V,z} \tag{8.5.44}$$

Using Equation (8.5.28) and (8.5.43), we see that

$$M = \left(\frac{2\pi mkT}{(2\pi\hbar)^2}\right)^{\frac{3}{2}} z\left[-\frac{1}{12}\left(\frac{e\hbar}{m}\right)^2\frac{B}{kT}+\cdots\right] \tag{8.5.45}$$

Further, the average particle number is given by

$$N \equiv z\left(\frac{\partial \log Z}{\partial z}\right)_{T,V,B} = V\left(\frac{2\pi mkT}{(2\pi\hbar)^2}\right)^{\frac{3}{2}} z\left(1-\frac{x^2}{24}+\cdots\right) \tag{8.5.46}$$

Using this to eliminate z, we find from Equation 8.5.45,

$$\begin{aligned} M &= \frac{N}{V}\left[-\frac{1}{12}\left(\frac{e\hbar}{m}\right)^2\frac{B}{kT}+\cdots\right]\left(1-\frac{x^2}{24}\right)^{-1} \\ &\approx \frac{N}{V}\left[-\frac{1}{12}\left(\frac{e\hbar}{m}\right)^2\frac{B}{kT}\right] \end{aligned} \tag{8.5.47}$$

The diamagnetic susceptibility is thus

$$\chi \approx -\frac{N}{V}\left(\frac{e\hbar}{m}\right)^2\frac{1}{12kT} \tag{8.5.48}$$

Although the quantum mechanical formula for the energy levels is important in this derivation, we have not really used the Fermi-Dirac distribution, since only the high temperature case was considered. At low temperatures, the Fermi-Dirac distribution will be important. The problem also becomes closely tied in with the quantum Hall effect, which is somewhat outside the scope of what we want to discuss here. So we will not consider the low temperature case for diamagnetism here. Instead we shall turn to a discussion of paramagnetism.

Paramagnetism can arise for the spin magnetic moment of the electron. Thus this is also very much a quantum effect. The Hamiltonian for a charged point particle including the spin-magnetic field coupling is

$$H = \frac{(p-eA)^2}{2\ m} - \frac{e}{2\ m}\gamma\vec{S}\cdot\vec{B} \tag{8.5.49}$$

Here $\vec{S}$ is the spin vector and γ is the gyromagnetic ratio. For the electron $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$, $\vec{\sigma}$ being the Pauli matrices, and γ is very close to 2; we will take $\gamma = 2$. Since we want to show how a positive χ can arise from the spin magnetic moment, we will, for this argument, ignore the vector potential A in the first term of the Hamiltonian. The energy eigenvalues are thus

$$E_{p,\pm} = \frac{p^2}{2m} \mp \mu_0 B, \qquad \mu_0 = \frac{e\hbar}{2m} \tag{8.5.50}$$

The partition function Z is thus given by

$$\log Z = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} \left[\log\left(1 + z_+ e^{-\frac{\beta p^2}{2m}}\right) + \log\left(1 + z_- e^{-\frac{\beta p^2}{2m}}\right)\right] \tag{8.5.51}$$

where $Z_\pm = \exp(\beta\mu_\pm)$ with

$$\mu_\pm = \mu \pm \mu_0 B \tag{8.5.52}$$

From log Z, we get

$$\begin{aligned} M &= \frac{1}{V}(kT)\left(\frac{\partial \log Z}{\partial B}\right)_z = \mu_0 (n_+ - n_-) \\ n_\pm &= \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\frac{p^2}{2m} - \mu_\pm)} + 1} \end{aligned} \tag{8.5.53}$$

By taking $z(\frac{\partial \log Z}{\partial z})$, we see that the number density of electrons for both spin states together is $n = n_+ + n_-$. For high temperatures, we can approximate the integral in Equation 8.5.53 by

$$n_\pm \approx \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta\frac{p^2}{2m}} e^{\beta\mu_\pm} = \left[\frac{2\pi mkT}{(2\pi\hbar)^2}\right]^{\frac{3}{2}} e^{\beta\mu_\pm} \tag{8.5.54}$$

Using this, the magnetization becomes,

$$\begin{aligned} M &= \mu_0 \; n \tanh\left(\frac{\mu_0 B}{kT}\right) \\ &\approx \frac{\mu_0^2 n}{kT} B, \qquad \text{for } \mu_0 B << kT \end{aligned} \tag{8.5.55}$$

The susceptibility at high temperatures is thus given as

$$\chi = \frac{\mu_0^2 n}{kT} \tag{8.5.56}$$

Turning to low temperatures, notice that we have already obtained the required expansion for the integral in Equation 8.5.53; this is what we have done following Equation 8.5.16, so we can use the formula Equation 8.5.20 for μ, along with Equation 8.5.3 for the Fermi level in terms of $\bar{n}$, applied in the present case to $\mu_\pm$ separately. Thus

$$\begin{aligned} \mu_\pm &= \epsilon_F(n_\pm)\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F(n_\pm)}\right)^2 + \cdots\right] \\ \epsilon_F(n_\pm) &= \frac{\hbar^2}{2m}(6\pi^2 n_\pm)^{\frac{2}{3}} \end{aligned} \tag{8.5.57}$$

Defining $\Delta = n_+ - n_-$, we can write

$$\epsilon_F(n_\pm) = \epsilon_F(n)\Big]_{n=(1\pm\frac{\Delta}{n})}, \qquad \epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{\frac{2}{3}} \tag{8.5.58}$$

The fact that $\mu_+ - \mu_- = 2\mu_0 B$ from Equation 8.5.52 now can be written as

$$2\mu_0 B = \epsilon_F\left[\left(1 + \frac{\Delta}{n}\right)^{\frac{2}{3}} - \left(1 - \frac{\Delta}{n}\right)^{\frac{2}{3}}\right] - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 \left[\frac{1}{(1+\frac{\Delta}{n})^{\frac{2}{3}}} - \frac{1}{(1-\frac{\Delta}{n})^{\frac{2}{3}}}\right] + \cdots \tag{8.5.59}$$

After solving this for $\frac{\Delta}{n}$, we can get the magnetization as $M = \mu_0 \Delta$ or $\chi = \frac{\mu_0 \Delta}{B}$. Since $\Delta = 0$ for $B = 0$, to linear order in the magnetic field, we find

$$\frac{\Delta}{n} = \frac{3}{2}\frac{\mu_0 B}{\epsilon_F}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right] \tag{8.5.60}$$

The susceptibility at low temperatures is then

$$\chi = \frac{3}{2}\frac{\mu_0 n}{\epsilon_F}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{\epsilon_F}\right)^2 + \cdots\right] \tag{8.5.61}$$

The susceptibility from spin magnetic moment shows paramagnetic behavior both at high and low temperatures, as seen from Equation 8.5.56 and 8.5.61.

CHAPTER OVERVIEW

9: The Carathéodory Principle

The formulation of the second law from thermodynamics used the concept of heat engines, at least indirectly. But the law is very general and one could ask whether there is another formulation which does not invoke heat engines but leads to the notion of absolute temperature and the principle that entropy cannot spontaneously decrease. Such a version of the second law is obtained in an axiomatization of thermodynamics due to C. Carathéodory.

9.1: Mathematical Preliminaries

We will start with a theorem on differential forms which is needed to formulate Carathéodory’s version of the second law.

Before proving Carathéodory’s theorem, we will need the following result.

Theorem 9.1.1 — Integrating Factor Theorem

Let $A = A_i dx^i$ denote a differential one-form. If $A \wedge dA = 0$, then at least locally, one can find an integrating factor for A; i.e., there exist functions τ and φ such that $A = \tau\, d\varphi$.

The proof of this result is most easily done inductively in the dimension of the space. First, we consider the two-dimensional case, so that $i = 1, 2$. In this case, the condition $A \wedge dA = 0$ is vacuous. Write $A = A_1 dx^1 + A_2 dx^2$. We make a coordinate transformation to λ, φ where

$$\begin{aligned} \frac{dx^1}{d\lambda} &= -f(x^1, x^2) A_2 \\ \frac{dx^2}{d\lambda} &= f(x^1, x^2) A_1 \end{aligned} \tag{9.1.1}$$

where $f(x^1, x^2)$ is an arbitrary function which can be chosen in any convenient way. This equation shows that

$$A_1 \frac{\partial x^1}{\partial \lambda} + A_2 \frac{\partial x^2}{\partial \lambda} = 0 \tag{9.1.2}$$

Equations 9.1.1 define a set of nonintersecting trajectories, λ being the parameter along the trajectory. We choose ϕ as the coordinate on transverse sections of the flow generated by (9.1.1). Making the coordinate transformation from x^1, x^2 to λ, ϕ, we can now write the one-form A as

$$\begin{aligned} A &= \left(A_1 \frac{\partial x^1}{\partial \lambda} + A_2 \frac{\partial x^2}{\partial \lambda} \right) d\lambda + \left(A_1 \frac{\partial x^1}{\partial \phi} + A_2 \frac{\partial x^2}{\partial \phi} \right) d\phi \\ &= \tau\, d\phi \\ \tau &= A_i \frac{\partial x^i}{\partial \phi} \end{aligned} \tag{9.1.3}$$

This proves the theorem for two dimensions. In three dimensions, we have

$$A = A_1 dx^1 + A_2 dx^2 + A_3 dx^3 \tag{9.1.4}$$

The strategy is to start by determining τ, ϕ for the A_1, A_2 subsystem. We choose the new coordinates as λ, ϕ, x^3 and impose Equation 9.1.1. Solving these, we will find x^1 and x^2 as functions of λ and x^3. The trajectories will also depend on the staring points which may be taken as points on the transverse section and hence labeled by ϕ. Thus we get

$$x^1 = x^1(\lambda, \phi, x^3), x^2 = x^2(\lambda, \phi, x^3) \tag{9.1.5}$$

The one-form A in Equation 9.1.4 now becomes

$$\begin{aligned} A &= \left(A_1 \frac{\partial x^1}{\partial \lambda} + A_2 \frac{\partial x^2}{\partial \lambda} \right) d\lambda + \left(A_1 \frac{\partial x^1}{\partial \phi} + A_2 \frac{\partial x^2}{\partial \phi} \right) d\phi + A_3 dx^3 + \left(A_1 \frac{\partial x^1}{\partial x^3} + A_2 \frac{\partial x^2}{\partial x^3} \right) dx^3 \\ &= \tau\, d\phi + \widetilde{A}_3 dx^3 \\ \widetilde{A}_3 &= A_3 \left(A_1 \frac{\partial x^1}{\partial x^3} + A_2 \frac{\partial x^2}{\partial x^3} \right) \end{aligned} \tag{9.1.6}$$

We now consider imposing the equations $A \wedge dA = 0$,

$$\begin{aligned} A \wedge dA &= \left[\widetilde{A}_3 (\partial_\lambda A_\phi - \partial_\phi A_\lambda) + A_\lambda (\partial_\phi \widetilde{A}_3 - \partial_3 A_\phi) + A_\phi (\partial_3 A_\lambda - \partial_\lambda \widetilde{A}_3) \right] dx^3 \wedge d\lambda \wedge d\phi \\ &= 0 \end{aligned} \tag{9.1.7}$$

Since $A_\lambda = 0$ and $A_\phi = \tau$ from Equation 9.1.6, this equation becomes

$$\widetilde{A}_3 \frac{\partial \tau}{\partial \lambda} - \tau \frac{\partial \widetilde{A}_3}{\partial \lambda} = 0 \tag{9.1.8}$$

Writing $\widetilde{A}_3 = \tau\, h$, this becomes

$$\tau^2 \frac{\partial h}{\partial \lambda} = 0 \tag{9.1.9}$$

Since τ is not identically zero for us, we get $\frac{\partial h}{\partial \lambda} = 0$ and, going back to Equation 9.1.6, we can write

$$A = \tau \left[d\phi + h(\phi, x^3) dx^3 \right] \tag{9.1.10}$$

The quantity in the square brackets is a one-form on the two-dimensional space defined by ϕ, x^3. For this we can use the two-dimensional result and write it as $\tilde{\tau} d\widetilde{\phi}$, so that

$$A = \tau \tau [d\phi + h(\phi, x^3) dx^3] = \tau \tilde{\tau} d\widetilde{\phi} \equiv T d\widetilde{\phi} \tag{9.1.11}$$

$T = \tau\tilde{\tau}$ This proves the theorem for the three-dimensional case.

The extension to four dimensions follows a similar pattern. The solutions to Equation 9.1.1 become

$$x^1 = x^1(\lambda, \phi, x^3, x^4), \qquad x^2 = x^2(\lambda, \phi, x^3, x^4) \tag{9.1.12}$$

so that we can bring A to the form

$$\begin{aligned} A \; &= \left(A_1 \frac{\partial x^1}{\partial \phi} + A_2 \frac{\partial x^2}{\partial \phi} \right) d\phi + \left(A_3 + A_1 \frac{\partial x^1}{\partial x^3} + A_2 \frac{\partial x^2}{\partial x^3} \right) dx^3 + \left(A_4 + A_1 \frac{\partial x^1}{\partial x^4} + A_2 \frac{\partial x^2}{\partial x^4} \right) dx^4 \\ &= \tau\, d\phi + \widetilde{A}_3 dx^3 + \widetilde{A}_4 dx^4 \end{aligned} \tag{9.1.13}$$

We now turn to imposing the condition $A \wedge dA = 0$. In local coordinates this becomes

$$A_\alpha (\partial_\mu A_\nu - \partial_\nu A_\mu) + A_\mu (\partial_\nu A_\alpha - \partial_\alpha A_\nu) + A_\nu (\partial_\alpha A_\mu - \partial_\mu A_\alpha) = 0 \tag{9.1.14}$$

There are four independent conditions here corresponding to $(\alpha, \mu, \nu) = (1,2,3), (4,1,2), (3,4,1), (3,2,4)$ Using $A_\lambda = 0$ and $A_\phi = \tau$, these four equations become

$$\widetilde{A}_3 \frac{\partial \tau}{\partial \lambda} - \tau \frac{\partial \widetilde{A}_3}{\partial \lambda} = 0 \tag{9.1.15}$$

$$\widetilde{A}_4 \frac{\partial \tau}{\partial \lambda} - \tau \frac{\partial \widetilde{A}_4}{\partial \lambda} = 0 \tag{9.1.16}$$

$$\widetilde{A}_4 \frac{\partial \widetilde{A}_3}{\partial \lambda} - \widetilde{A}_3 \frac{\partial \widetilde{A}_4}{\partial \lambda} = 0 \tag{9.1.17}$$

$$\widetilde{A}_3 \frac{\partial \widetilde{A}_4}{\partial \phi} - \widetilde{A}_4 \frac{\partial \widetilde{A}_3}{\partial \phi} + \tau \frac{\partial \widetilde{A}_3}{\partial x^4} - \widetilde{A}_3 \frac{\partial \tau}{\partial x^4} + \widetilde{A}_4 \frac{\partial \tau}{\partial x^3} - \tau \frac{\partial \widetilde{A}_4}{\partial x^3} = 0 \tag{9.1.18}$$

Again, we introduce h and g by \widetilde{A}_3 = τ h\), $\widetilde{A}_4 = \tau g$. Then, equations (9.1.15) and (9.1.16) become

$$\frac{\partial h}{\partial \lambda} = 0, \qquad \frac{\partial g}{\partial \lambda} = 0 \tag{9.1.19}$$

Equation 9.1.17 is then identically satisfied. The last equation, namely, 9.1.18, simplifies to

$$h \frac{\partial g}{\partial \phi} - g \frac{\partial h}{\partial \phi} + \frac{\partial h}{\partial x^4} - \frac{\partial g}{\partial x^3} = 0 \tag{9.1.20}$$

Using these results, Equation 9.1.13 becomes

$$A == [\tau d\phi + h dx^3 + g dx^4] \tag{9.1.21}$$

The quantity in the square brackets is a one-form on the three-dimensional space of ϕ, x^3, x^4 and we can use the previous result for an integrating factor for this. The condition for the existence of an integrating factor for $d\phi + h dx^3 + g dx^4$ is precisely 9.1.20. Thus if we have Equation 9.1.20, we can write $d\phi + h dx^3 + g dx^4$ as tds for some functions t and s, so that finally A takes the form $A = TdS$.

Thus the theorem is proved for four dimensions. The procedure can be extended to higher dimensions recursively, establishing the theorem for all dimensions.

Now we turn to the basic theorem needed for the Carathéodory formulation. Consider an n-dimensional manifold M with a one-form A on it. A solution curve to A is defined by $A = 0$ along the curve. Explicitly, the curve may be taken as given by a set of function $x^i = \xi^i(t)$ where t is the parameter along the curve and

$$A_i \frac{dx^i}{dt} = A_i \dot{\xi}^i = 0 \tag{9.1.22}$$

In other words, the tangent vector to the curve is orthogonal to A_i. The curve therefore lies on an $(n-1)$-dimensional surface. Two points, say, P and P' on M are said to be A accessible if there is a solution curve which contains P and P'. Carathéodory's theorem is the following:

Theorem 9.1.2 — Carathéodory's Theorem.

If in the neighborhood of a point P there are A-inaccessible points, then A admits an integrating factor; i.e., $A = TdS$ where T and S are well defined functions in the neighborhood.

The proof of the theorem involves a *reductio ad absurdum* argument which constructs paths connecting P to any other point in the neighborhood. (This proof is due to H.A. Buchdahl, Proc. Camb. Phil. Soc. **76**, 529 (1979).) For this, define

$$C_{ijk} = A_i(\partial_j A_k - \partial_k A_j) + A_k(\partial_i A_j - \partial_j A_i) + A_j(\partial_k A_i - \partial_i A_k) \tag{9.1.23}$$

Now consider a point P' near P We have a displacement vector $\epsilon\eta^i$ for the coordinates of P' (from P). η^i can in general have a component along A_i and some components orthogonal to A_i. The idea is to solve for these from the equation $A = 0$. Let $\xi^i(t)$ be a path which begins and ends at P, i.e., $\xi^i(0) = \xi^i(1) = 0$, $0 \leq t \leq 1$, and which is orthogonal to A_i. Thus it is a solution curve. Any closed curve starting at P and lying in the $(n-1)$-dimensional space orthogonal to A_i can be chosen. Consider now a nearby path given by $x^i(t) = \xi^i(t) + \epsilon\eta^i(t)$. This will also be a solution curve if $A_I(\xi + \epsilon\eta)(\dot{\xi} + \epsilon\dot{\eta})^i = 0$. Expanding to first order in ϵ, this is equivalent to

$$A_i \dot{\eta}^i + \dot{\xi}^i \left(\frac{\partial A_i}{\partial x^j}\right) \eta^j = 0 \tag{9.1.24}$$

where we also used $A_i \dot{\xi}^i = 0$. We may choose $\dot{\xi}^i$ to be of the form $\dot{\xi}^i = f^{ij} A_j$ where f^{ij} is antisymmetric, to be consistent with $A_i \dot{\xi}^i = 0$. We can find quantities f^{ij} such that this is true; in any case, it is sufficient to show one path which makes P' accessible. So we may consider $\dot{\xi}^i$'s of this form. Thus Equation 9.1.24becomes

$$A_i \dot{\eta}^i + \eta^j (\partial_j A_i) f^{ik} A_k = 0 \tag{9.1.25}$$

This is one equation for the n components of the displacement η^i. We can choose the $n-1$ components of η^i which are orthogonal to A_i as we like and view this equation as determining the remaining component, the one along A_i. So we rewrite this equation as an equation for $A_i \eta^i$ as follows.

$$\begin{aligned}
\frac{d}{dt}(A_i \eta^i) &= \dot{A}_i \eta^i + A_i \dot{\eta}^i \\
&= (\partial_j A_i) \dot{\xi}^j \eta^i - \eta^j (\partial_j A_i) f^{ik} A_k) \\
&= -\eta^i f^{jk} (\partial_i A_j - \partial_j A_i) A_k \\
&= \frac{1}{2} \eta^i f^{jk} [A_k(\partial_i A_j - \partial_j A_i) + A_j(\partial_k A_i - \partial_i A_k) + A_i(\partial_j A_k - \partial_k A_j)] + \frac{1}{2}(A \cdot \eta) f^{jk} (\partial_j A_k - \partial_k A_j) \\
&= \frac{1}{2} \eta^i f^{jk} C_{kij} + \frac{1}{2}(A \cdot \eta) f^{ij} (\partial_i A_j - \partial_j A_i)
\end{aligned} \tag{9.1.26}$$

This can be rewritten as

$$\frac{d}{dt}(A \cdot \eta) - F(A \cdot \eta) = -\frac{1}{2}(C_{kij} \eta^i f^{jk}) \tag{9.1.27}$$

where $F=\frac{1}{2}f^{ij}(\partial_i A_j-\partial_j A_i)$. The important point is that we can choose f^{ij}, along with a coordinate transformation if needed, such that $C_{kij}\eta^i f^{jk}$ has no component along A_i. For this, notice that

$$C_{kij}\eta^i f^{jk}A_i=A^2F_{ij}-A_iA_kF_{kj}+A_jA_kF_{ki}f^{ij} \tag{9.1.28}$$

where $F_{ij}=\partial_i A_j-\partial_j A_i$. There are $\frac{1}{2}n(n-1)$ components for f^{ij}, for which we have one equation if we set $C_{kij}\eta^i f^{jk}A_i$ to zero. We can always find a solution; in fact, there are many solutions. Making this choice, $C_{kij}\eta^i f^{jk}$ has no component along A_i, so the components of η on the right hand side of Equation 9.1.27 are orthogonal to A_i. As mentioned earlier, there is a lot of freedom in how these components of η are chosen. Once they are chosen, we can integrate Equation 9.1.27 to get $(A\cdot\eta)$, the component along A_i. Integrating Equation 9.1.27, we get

$$A\cdot\eta(1)=\int_0^1 dt\,\exp\left(\int_t^1 dt'\,F(t')\right)\left(\frac{1}{2}C_{kij}\eta^i f^{jk}\right) \tag{9.1.29}$$

We have chosen $\eta(0)=0$. It is important that the right-hand side of Equation 9.1.27 does not involve $(A\cdot\eta)$ for us to be able to integrate like this. We choose all components of η^i orthogonal to A_i to be such that

$$\epsilon\eta^i = \text{coordinates of } P' \text{ orthogonal to } A \tag{9.1.30}$$

We then choose f^{jk}, if needed by scaling it, such that $A\cdot\eta(1)$ in Equation 9.1.30 gives $A_i(x_{P'}-x_P)^i$. We have thus shown that we can always access P' along a solution curve. The only case where the argument would fail is when $C_{ijk}=0$. In this case, $A\cdot\eta(1)$ as calculated is zero and we have no guarantee of matching the component of the displacement of P' along the direction of A_i. Thus if there are inaccessible points in the neighborhood of P, then we must have $C_{ijk}=0$. In this case, by the previous theorem, A admits an integrating factor and we can write $A=TdS$ for some functions T and S in the neighborhood of P. This completes the proof of the Carathéodory theorem.

9.2: Carathéodory Statement of the Second Law

The statement of the second law due to Carathéodory is:

Definition: Carathéodory Principle

In the neighborhood of any equilibrium state of a physical system with any number of thermodynamic coordinates, there exist states which are inaccessible by adiabatic processes.

The adiabatic processes can be quite general, not necessarily quasi-static. It is easy to see that this leads immediately to the notion of absolute temperature and entropy. This has been discussed in a concise and elegant manner in Chandrasekhar's book on stellar structure. We briefly repeat his argument for completeness. For simplicity, consider a gas characterized by pressure p and volume V, and (empirical) temperature t, only two of which are adequate to specify the thermodynamic state, the third being given by an equation of state. Since these are the only variables, dQ has an integrating factor and we may write

$$dQ = \tau d\sigma \tag{9.2.1}$$

where σ and τ will be functions of the variables p, V, t. The power of Carathéodory's formulation becomes clear when we consider two such systems brought into thermal contact and come to equilibrium. We then have a common temperature t and the thermodynamic variables can now be taken as V_1, V_2, t (or t and one variable from each of $(p_1, V_1), (p_2, V_2)$). We also have $dQ = dQ_1 + dQ_2$. The number of variables is now three; nevertheless, the Carathéodory principle tells us that we can write

$$\tau d_\sigma = \tau_1 d\sigma_1 + \tau_2 d\sigma_2 \tag{9.2.2}$$

We now choose t, σ_1, σ_2 as the independent variables. Equation 9.2.2 then leads to

$$\frac{\partial\sigma}{\partial\sigma_1} = \frac{\tau_1}{\tau}, \qquad \frac{\partial\sigma}{\partial\sigma_2} = \frac{\tau_2}{\tau}, \qquad frac\partial\sigma\partial t = 0 \tag{9.2.3}$$

The last of these equations tells us that σ is only a function of σ_1 and σ_2, $\sigma = \sigma(\sigma_1, \sigma_2)$. Further, since σ is a well-defined function of the various variables, derivatives on σ commute and so

$$\frac{\partial}{\partial t}\frac{\partial\sigma}{\partial\sigma_1} - \frac{\partial\sigma}{\partial\sigma_1}\frac{\partial\sigma}{\partial t} = 0 \tag{9.2.4}$$

with a similar relation for derivatives with respect to σ_2 as well. Thus we have the result

$$\frac{\partial}{\partial t}\left(\frac{\tau_1}{\tau}\right) = 0, \qquad \frac{\partial}{\partial t}\left(\frac{\tau_2}{\tau}\right) = 0 \tag{9.2.5}$$

Equivalently, we can write

$$\frac{1}{\tau_1}\frac{\partial\tau_1}{\partial t} = \frac{1}{\tau_2}\frac{\partial\tau_2}{\partial t} = \frac{1}{\tau}\frac{\partial\tau}{\partial t} \tag{9.2.6}$$

This shows that the combination $\left(\frac{1}{\tau}\right)\left(\frac{\partial\tau}{\partial t}\right)$ is independent of the system and is a universal function of the common variable t. Taking this function as $g(t)$ and integrating, we get

$$\begin{gathered}\tau = \Sigma(\sigma_1, \sigma_2) C \exp\left(\int_{t_0}^{t} dt\ g(t)\right) \\ \tau_1 = \Sigma_1(\sigma_1) C \exp\left(\int_{t_0}^{t} dt\ g(t)\right) \\ \tau_2 = \Sigma_2(\sigma_2) C \exp\left(\int_{t_0}^{t} dt\ g(t)\right)\end{gathered} \tag{9.2.7}$$

The τ's are determined up to a function of the σ's; we take this arbitrariness as $C\Sigma$, where C is a constant and Σ is a function of the σ's involved. We can now define the absolute temperature as

$$T \equiv C\,\exp\left(\int_{t_0}^{t} dt\; g(t)\right) \tag{9.2.8}$$

Notice that, in the case under consideration, $T_1 = T_2 = T$ as expected for equilibrium. This gives $dQ_1 = T\Sigma_1 d\sigma_1$, etc. The relation $dQ = dQ_1 + dQ_2$ now reduces to

$$\Sigma d\sigma = \Sigma_1 d\sigma_1 + \Sigma_2 d\sigma_2 \tag{9.2.9}$$

In the two-dimensional space with coordinates σ_1, σ_2, the vector (Σ_1, Σ_2) has vanishing curl, i.e., $\partial_1\Sigma_2 - \partial_2\Sigma_1 = 0$, since Σ_1 only depends on σ_1 and similarly for Σ_2. Thus Equation 9.2.9 shows that Σd_σ is a perfect differential. This means that there exists a function S such that $\Sigma d_\sigma = dS$; this also means that Σ can depend on σ_1 and σ_2 only through the combination $\sigma(\sigma_1, \sigma_2)$. Thus finally we have

$$dQ = T\; dS \tag{9.2.10}$$

In this way, the Carathéodory principle leads to the definition of entropy S.

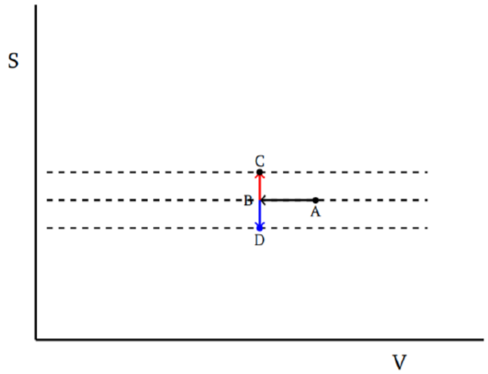


Figure 9.2.1: Illustrating the Carathéodory principle and increase of entropy

One can also see how this leads to the principle of increase of entropy. For this, consider a system with n thermodynamic variables. The entropy will be a function of these. We can alternatively choose $n-1$ of the given variables and the entropy S to characterize states of the system. Now we ask the question: Given a state A, can we find a path which takes us via adiabatic processes to another state C? It is useful to visualize this in a diagram, with S as one of the axes, as in Fig. 9.2.1. We show one of the other axes, but there could be many. To get to C, we can start from A and go along a quasi-static reversible adiabatic to B and then, via some nonquasi-static process such as stirring, mixing, etc., get to C, keeping the system in adiabatic isolation. This second process can be irreversible. The idea is that the first part does not change the entropy, but brings the other variables to their desired final value. Then we move to the required value of S by some irreversible process. As shown $SC > SB = SA$. Suppose the second process can also decrease the entropy in some cases so that we can go from B to D by some similar process. Then we see that all states close to B are accessible. Starting from any point, we can move along the surface of constant S to get to the desired value of the variables, except for S and then jump to the required value of S by the second process. This contradicts the Carathéodory principle. Thus, if we postulate this principle, then we have to conclude that in all irreversible processes in adiabatic isolation the entropy has to either decrease or increase; we cannot have it increase in some processes and decrease in some other processes. So S should be either a nondecreasing quantity or a nonincreasing quantity. The choice of the sign of the absolute temperature, via the choice of the sign of the constant C in Equation 9.2.8, is related to which case we choose for entropy. The conventional choice, of course, is to take $T \geq 0$ and entropy to be nondecreasing. In other words

$$\Delta S \geq 0 \tag{9.2.11}$$

Thus effectively, we have obtained the version of the second law as given in Proposition 4 in Chapter 3.

CHAPTER OVERVIEW

10: Entropy and Information

The concept of entropy is one of the more difficult concepts in physics. Historically, it emerged as a consequence of the second law of thermodynamics, as in Equation 3.4.13. Later, Boltzmann gave a general definition for it in terms of the number of ways of distributing a given number of particles, as in Equation 7.2.3. But a clearer understanding of entropy is related to its interpretation in terms of information. We will briefly discuss this point of view here.

10.1: Information

We want to give a quantification of the idea of information. This is originally due to C. Shannon.

Consider a random variable x with probability distribution with $p(x)$. For simplicity, initially, we take x to be a discrete random variable, with N possible values $x_1, x_2, \cdots, x_N$, with $p_i \equiv p(x_i)$ being the probability for x_i. We may think of an experiment for which the outcomes are the x_i, and the probability for x_i being p_i in a trial run of the experiment. We want to define a concept of information $I(p)$ associated with $p(x)$. The key idea is to note that if an outcome has probability 1, the occurrence of that outcome carries no information since it was clear that it would definitely happen. If an outcome has a probability less than 1, then its occurrence can carry information. If the probability is very small, and the outcome occurs, it is unlikely to be a random event and so it makes sense to consider it as carrying information. Based on this intuitive idea, we expect information to be a function of the probability. By convention, we choose $I(p)$ to be positive. Further from what we said, $I(1)=0$. Now consider two completely independent events, with probabilities p and $\tilde{p}$. The probability for both to occur is $p\,\tilde{p}$, and will carry information $I(p\,\tilde{p})$. Since the occurrence of each event separately carries information $I(p)$ and $I(\tilde{p})$, we expect

$$I(p\,\tilde{p}) = I(p) + I(\tilde{p}) \tag{10.1.1}$$

Finally, if the probability of some event is changed by a small amount, we expect the information for the event to be changed by a small amount as well. This means that we would like $I(p)$ to be a continuous and differentiable function of p. Thus we need a continuous and differentiable function $I(p)$ obeying the requirements $I(p) \geq 0$, $I(1)=0$ and $I(p\,\tilde{p}) = I(p) + I(\tilde{p})$. The only function which obeys these conditions is given by

$$I(p) = -\log p \tag{10.1.2}$$

This is basically Shannon’s definition of information. The base used for this logarithm is not specified by what has been said so far; it is a matter of choosing a unit for information. Conventionally, for systems using binary codes, we use $\log_2 p$, while for most statistical systems we use the natural logarithms.

Consider now the outcome xi which has a probability p_i. The amount of information for x_i is $-\log p_i$. Suppose now that we do N trials of the experiment, where N is very large. Then the number of times xi will be realized is $N\,p_i$. Thus it makes sense to define an average or expectation value for information as

$$S = \sum_i p_i\, I(p_i) = -\sum_i p_i\, \log p_i \tag{10.1.3}$$

This expected value for information is **Shannon’s definition of entropy**.

This definition of entropy requires some clarification. It stands for the amount of information which can be coded using the available outcomes. This can be made clearer by considering an example, say, of N tosses of a coin, or equivalently a stream of 0s and 1s, N units long. Each outcome is then a string of 0s and 1s; we will refer to this as a word, since we may think of it as the binary coding of a word. We take these to be ordered so that permutations of 0s and 1s in a given word will be counted as distinct. The total number of possibilities for this is 2^N, and each occurs with equal probability. Thus the amount of information in realizing a particular outcome is $I = N\,\log 2$, or N bits if we use logarithm to base 2. The entropy of the distribution is

$$S = \sum \frac{1}{2^N} \log 2^N = N\,\log 2 \tag{10.1.4}$$

Now consider a situation where we specify or fix some of the words. For example, let us say that all words start with 0, Then the probability of any word among this restricted set is now $\frac{1}{2^{N-1}}$, and entropy becomes $S = (N-1)\log 2$. Thus entropy has decreased because we have made a choice; we have used some information. Thus entropy is the amount of information which can be potentially coded using a probability distribution.

This definition of entropy is essentially the same as Boltzmann’s definition or what we have used in arriving at various distribution functions for particles. For this consider the formula for entropy which we used in chapter 7, Equation 7.2.5,

$$S \approx k\left[N\log N - N - \sum_i (n_i \log n_i - n_i)\right] \tag{10.1.5}$$

Here the n_i is the occupation number for the state i. In limit of large N, $\frac{n_i}{N}$ may be interpreted as the probability for the state i. Using the symbol p_i for this, we can rewrite Equation 10.1.5 as

$$\frac{S}{k} = -\sum_i p_i \log p_i \tag{10.1.6}$$

showing that the entropy as defined by Boltzmann in statistical physics is the same as Shannon's information-theoretic definition. (In thermodynamics, we measure S in $\frac{J}{K}$; we can regard Boltzmann's constant k as a unit conversion factor. Thus $\frac{S}{k}$ from thermodynamics is the quantity to be compared to the Shannon definition.) The states in thermodynamics are specified by the values of positions and momenta for the particles, so the outcomes are continuous. A continuum generalization of Equation 10.1.6 is then

$$\frac{S}{k} = d\mathcal{N} p \log p \tag{10.1.7}$$

where $d\mathcal{N}$ is an appropriate measure, like the phase space measure in Equation 7.4.1.

Normally, we maximize entropy subject to certain averages such as the average energy and average number of particles being specified. This means that the observer has, by observations, determined these values, and hence the number of available states is restricted. Only those states which are compatible with the given average energy and number of particles are allowed. This constrains the probability distribution which maximizes the entropy. If we specify more averages, then the maximal entropy is lower. The argument is similar to what was given after Equation 10.1.4, but we can see this more directly as well. Let $A_\alpha, \alpha = 1, 2, \cdots, n$ be a set of observables. The maximization of entropy subject to specifying the average values of these is given by maximizing

$$\frac{S}{k} = \int \left[-p \log p - \sum_\alpha^n \lambda_\alpha A_\alpha p \right] + \sum_\alpha^n \lambda_\alpha \langle A_\alpha \rangle \tag{10.1.8}$$

Here $\langle A_\alpha \rangle$ are the average values which have been specified and λ_α are Lagrange multipliers. Variation with respect to the λs give the required constraint

$$\langle A_\alpha \rangle = \int A_\alpha \, p \tag{10.1.9}$$

The distribution p which extremizes Equation 10.1.8 is given by

$$\bar{p}_n = \frac{1}{Z_n} e^{-\sum_\alpha^n \lambda_\alpha A_\alpha}, \qquad Z_n = \int e^{-\sum_\alpha^n \lambda_\alpha A_\alpha} \tag{10.1.10}$$

The corresponding entropy is given by

$$\frac{\bar{S}_n}{k} = \log Z_n + \sum_\alpha^n \lambda_\alpha \langle A_\alpha \rangle \tag{10.1.11}$$

Now let us consider specifying $n+1$ averages. In this case, we have

$$\begin{aligned} \bar{p}_{n+1} &= \frac{1}{Z_{n+1}} e^{-\sum_\alpha^{n+1} \lambda_\alpha A_\alpha}, \qquad Z_{n+1} = \int e^{-\sum_\alpha^{n+1} \lambda_\alpha A_\alpha} \\ \frac{\bar{S}_{n+1}}{k} &= \log Z_{n+1} + \sum_\alpha^{n+1} \lambda_\alpha \langle A_\alpha \rangle \end{aligned} \tag{10.1.12}$$

This distribution reverts to $\bar{p}_n$, and likewise $\bar{S}_{n+1} \to \bar{S}_n$, if we set λ_{n+1} to zero.

If we calculate $\langle A_{n+1} \rangle$ using the distribution $\bar{p}_n$ and the answer comes out to be the specified value, then there is no information in going to $\bar{p}_{n+1}$. Thus it is only if the distribution which realizes the specified value $\langle A_{n+1} \rangle$ differs from $\bar{p}_n$ that there is additional information in the choice of $\langle A_{n+1} \rangle$. This happens if $\lambda_{n+1} \neq 0$. It is therefore useful to consider how $\bar{S}$ changes with λ_α. We find, directly from Equation 10.1.11,

$$\begin{aligned}\frac{\partial \bar{S}}{\partial \lambda_\alpha} &= \sum_\beta \lambda_\beta \frac{\partial}{\partial \lambda_\alpha} \langle A_\beta \rangle = \sum_\beta \lambda_\beta [-\langle A_\alpha A_\beta \rangle + \langle A_\alpha \rangle \langle A_\beta \rangle] \\ &= -\sum_\beta M_{\alpha\beta} \lambda_\beta \\ M_{\alpha\beta} &= \langle A_\alpha A_\beta \rangle - \langle A_\alpha \rangle \langle A_\beta \rangle \end{aligned} \tag{10.1.13}$$

The change of the maximal entropy with the λs is given by a set of correlation functions designated as $M_{\alpha\beta}$. We can easily see that this matrix is positive semi-definite. For this, we use the Schwarz inequality

$$\left[\int B^* B\right] \left[\int C^* C\right] \geq \left[\int B^* C\right] \left[\int C^* B\right] \tag{10.1.14}$$

For any set of complex numbers γ_α, we take $B = \gamma_\alpha A_\alpha$ and $C = 1$. We then see from (10.14) that $\gamma_\alpha \gamma^*_\beta M_{\alpha\beta} \geq 0$. (The integrals in Equation 10.1.14should be finite for the inequality to make sense. We will assume that at least one of the λs, say corresponding to the Hamiltonian. is always included so that the averages are finite.) Equation 10.1.13then tells us that $\bar{S}$ decreases as more and more λs pick up nonzero values. Thus we must interpret entropy as a measure of the information in the states which are still freely available for coding after the constraints imposed by the averages of the observables already measured. This also means that the increase of entropy in a system left to itself means that the system tends towards the probability distribution which is completely random except for specified values of the conserved quantities. The averages of all other observables tend towards the values given by such a random distribution. In such a state, the observer has minimum knowledge about observables other than the conserved quantities.

10.2: Maxwell’s Demon

There is a very interesting thought experiment due to Maxwell which is perhaps best phrased as a potential violation of the second law of thermodynamics. The resolution of this problem highlights the role of entropy as information.

We consider a gas of particles in equilibrium in a box at some temperature T. The velocities of the particles follow the Maxwell distribution from Equation 7.3.7,

$$f(v)d^3v = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv}{2kT}\right)\ d^3v \tag{10.2.1}$$

The mean square speed given by

$$\langle v^2\rangle = \frac{3kT}{m} \tag{10.2.2}$$

may be used as a measure of the temperature. Now we consider a partition which divides the box into two parts. Further, we consider a small gate in the partition which can be opened and closed and requires a very small amount of energy, which can be taken to be zero in an idealized limit. Further, we assume there is a creature (“Maxwell’s demon") with a large brain capacity to store a lot of data sitting next to this box. Now the demon is supposed to do the following. Every time he sees a molecule of high speed coming towards the gate from the left side, he opens the gate and lets it through to the right side. If he sees a slowly moving molecule coming towards the gate from the right side, he opens it and lets the molecule through to the left side. If he sees a slow-moving molecule on the left side, or a fast-moving one on the right side, he does nothing. Now after a while, the mean square speed on the left will be smaller than what it was originally, showing that the temperature on the left side is lower than T. Correspondingly, the mean square speed on the right side is higher and so the temperature there is larger than T. Effectively, heat is being transferred from a cold body (left side of the box) to a hot body (the right side of the box). Since the demon imparts essentially zero energy to the system via opening and closing the gate, this transfer is done with no other change, thus seemingly providing a violation of the second law. This is the problem.

We can rephrase this in terms of entropy change. To illustrate the point, it is sufficient to consider the simple case of N particles in the volume V forming an ideal gas with the demon separating them into two groups of $\frac{N}{2}$ particles in volume $\frac{V}{2}$ each. If the initial temperature is T and the final temperatures are T_1 and T_2, then the conservation of energy gives $T = \frac{1}{2}(T_1 + T_2)$. Further, we can use the the Sackur-Tetrode formula (7.2.25) for the entropies,

$$S \ = \ N\ k\ \left[\frac{5}{2} + \log\left(\frac{V}{N}\right) + \frac{3}{2}\log\left(\frac{U}{N}\right) + \frac{3}{2}\log\left(\frac{4\pi m}{3(2\pi\hbar)^2}\right)\right] \tag{10.2.3}$$

The change in entropy when the demon separates the molecules is then obtained as

$$\Delta S = S_1 + S_2 - S = \frac{3N}{2}\log\left(\frac{\sqrt{T_1T_2}}{T}\right) \tag{10.2.4}$$

Since

$$\left(\frac{T_1+T_2}{2}\right)^2 = T_1T_2 + \left(\frac{T_1-T_2}{2}\right)^2 \geq T_1T_2 \tag{10.2.5}$$

we see that $\Delta S \leq 0$. Thus the process ends up decreasing the entropy in contradiction to the second law.

The resolution of this problem is in the fact that the demon must have information about the speeds of molecules to be able to let the fast ones to the right side and the slow ones to the left side. This means that using the Sackur-Tetrode formula for the entropy of the gas in the initial state is not right. We are starting off with a state of entropy (of gas and demon combined) which is less than what is given by Equation 10.2.3, once we include the information carried by (or obtained via the observation of velocities by) the demon, since the specification of more observables decreases the entropy as we have seen in the last section. While it is difficult to estimate quantitatively this entropy, the expectation is that with this smaller value of S to begin with, ΔS will come out to be positive and that there will be no contradiction with the second law. Of course, this means that we are considering a generalization of the second law, namely that the entropy of an isolated system does not decrease over time, provided all sources of entropy in the information-theoretic sense are taken into account.

10.3: Entropy and Gravity

There is something deep about the concept of entropy which is related to gravity. This is far from being well understood, and is a topic of ongoing research, but there are good reasons to think that the Einstein field equations for gravity may actually emerge as some some sort of entropy maximization condition. A point of contact between gravity and entropy is for spacetimes with a horizon, an example being a black hole. In an ultimate theory of quantum gravity, spacetimes with a horizon may turn out to be nothing special, but for now, they may be the only window to the connection between entropy and gravity. To see something of the connection, we look at a spherical solution to the Einstein equations, corresponding to the metric around a point (or spherical distribution of) mass. This is the **Schwarzschild metric** given as

$$ds^2 = c^2 dt^2 \left(1 - \frac{2GM}{c^2 r}\right) - \frac{dr^2}{\left(1 - \frac{2GM}{c^2 r}\right)} - r^2 d\theta^2 - r^2 \sin^2\theta d\varphi^2 \tag{10.3.1}$$

We are writing this in the usual spherical coordinates (r, θ, φ) for the spatial dimensions. G is Newton's gravitational constant and c is the speed of light in vacuum. We can immediately see that there are two singularities in this expression. The first is obviously at $r = 0$, similar to what occurs in Newton's theory for the gravitational potential, and the second is at $r = \frac{2GM}{c^2}$. This second singularity is a two-sphere since it occurs at finite radius. Now, one can show that $r = 0$ is a genuine singularity of the theory, in the sense that it cannot be removed by a coordinate transformation. The singularity at $r = \frac{2GM}{c^2}$ is a coordinate singularity. It is like the singularity at $\theta = 0, \pi$ when we use spherical coordinates and can be eliminated by choosing a different set of coordinates. Nevertheless, the radius $\frac{2GM}{c^2}$ does have an important role. The propagation of light, in the ray optics approximation, is described by $ds = 0$. As a result, one can see that nothing can escape from $r < \frac{2GM}{c^2}$ to larger values of the radius, to be detected by observers far away. An observer far away who is watching an object falling to the center will see the light coming from it being redshifted due to the $(1 - \frac{2GM}{c^2 r})$ factor, eventually being redshifted to zero frequency as it crosses $r = \frac{2GM}{c^2}$; the object fades out. For this reason, and because it is not a real singularity, we say that the sphere at $r = \frac{2GM}{c^2}$ is a horizon. Because nothing can escape from inside the horizon, the region inside is a black hole. The value $\frac{2GM}{c^2}$ is called the **Schwarzschild radius**.

Are there examples of black holes in nature? The metric (10.3.1) can be used to describe the spacetime outside of a nearly spherical matter distribution such as a star or the Sun. For the Sun, with a mass of about $2 \times 10^{30} kg$, the Schwarzschild radius is about $1.4 km$. The form of the metric in (10.3.1) ceases to be valid once we pass inside the surface of the Sun, and so there is no horizon physically realized for the Sun (and for most stars). (Outside of the gravitating mass, one can use (10.3.1) which is how observable predictions of Einstein's theory such as the precession of the perihelion of Mercury are obtained.) But consider a star which is more massive than the **Chandrasekhar** and **Tolman-Oppenheimer-Volkov limits**. If it is massive enough to contract gravitationally overcoming even the quark degeneracy pressure, its radius can shrink below its Schwarzschild radius and we can get an black hole. The belief is that there is such a black hole at the center of our galaxy, and most other galaxies as well.

Returning to the physical properties of black holes, although classical theory tells us that nothing can escape a black hole, a most interesting effect is that black holes radiate. This is a quantum process. A full calculation of this process cannot be done without a quantum theory of gravity (which we do not yet have). So, while the fact that black holes must radiate can be argued in generality, the nature of the radiation can only be calculated in a semiclassical way. The result of such a semiclassical calculation is that irrespective of the nature of the matter which went into the formation of the black hole, the radiation which comes out is thermal, following the Planck spectrum, corresponding to a certain temperature

$$T_H = \frac{\hbar c^3}{8\pi k G M} \tag{10.3.2}$$

Although related processes were understood by many scientists, the general argument for radiation from black holes was due to Hawking and hence the radiation from any spacetime horizon and the corresponding temperature are referred to as the **Hawking radiation** and **Hawking temperature**, respectively.

Because there is a temperature associated with a black hole, we can think of it as a thermodynamic system obeying

$$dU = T\, dS \tag{10.3.3}$$

The internal energy can be taken as Mc^2 following the Einstein mass-energy equivalence. We can then use Equation 10.3.3 to calculate the entropy of a black hole as

$$S_{B-H} = \frac{c^3}{\hbar}\,\frac{A}{4\,G} \tag{10.3.4}$$

(This formula for the entropy is known as the Bekenstein-Hawking formula.) Here A is the area of the horizon, \(A = 4πR_S^2 , R_S = \frac{2GM}{c^2} being the Schwarzschild radius.

These results immediately bring up a number of puzzles.

1. *A priori*, there is nothing thermodynamic about the Schwarzschild metric or the radiation process. The radiation can obtained from the quantized version of the Maxwell equations in the background spacetime (10.3.1). So how do thermodynamic concepts arise in this case?
2. One could envisage forming a black hole from a very ordered state of very low entropy. Yet once the black hole forms, the entropy is given by (10.3.4). There is nothing wrong with generating more entropy, but how did we lose the information coded into the low entropy state? Further, the radiation coming out is thermal and hence carries no information. So is there any way to understand what happened to it? These questions can be sharpened further. First of all, we can see that the Schwarzschild black hole can evaporate away by Hawking radiation in a finite time. This is because the radiation follows the Planck spectrum and so we can use the Stefan-Boltzmann law (8.3.14) to calculate the rate of energy loss. Then from
$$\frac{d(M\,c^2)}{dt} = -\sigma T_H^4 A \tag{10.3.5}$$
we can obtain the evaporation time. Now, there is a problem with the radiation being thermal. Time-evolution in the quantum theory is by unitary transformations and these do not generate any entropy. So if we make a black hole from a very low entropy state and then it evaporates into thermal radiation which is a high entropy state, how is this compatible with unitary time-evolution? Do we need to modify quantum theory, or do we need to modify the theory of gravity?
3. Usually, when we have nonzero entropy, we can understand that in terms of microscopic counting of states. Are the number of states of a black hole proportional to S_{B-H}? Is there a quantitative way to show this?
4. The entropy is proportional to the area of the horizon. Usually, entropy is extensive and the number of states is proportional to the volume (via things like $\frac{d^3x d^3p}{(2\pi\hbar)^3}$). How can all the states needed for a system be realized in terms of a lower dimensional surface?

There are some tentative answers to some of these questions. Although seemingly there is a problem with unitary time-evolution, this may be because we cannot do a full calculation. The semiclassical approximation breaks down for very small black holes. So we cannot reliably calculate the late stages of black hole evaporation. Example calculations with black holes in lower dimensions can be done using string theory and this suggests that time-evolution is indeed unitary and that information is recovered in the correlations in the radiation which develop in later stages.

For most black hole solutions, there is no reliable counting of microstates which lead to the formula (10.3.4). But there are some supersymmetric black holes in string theory for which such a counting can be done using techniques special to string theory. For those cases, one does indeed get the formula (10.3.4). This suggests that string theory could provide a consistent quantum theory of black holes and, more generally, of spacetimes with horizons. It could also be that the formula (10.3.4) has such universality (as many things in thermodynamics do) that the microscopic theory may not matter and that if we learn to do the counting of states correctly, any theory which has quantum gravity will lead to (10.3.4), with perhaps, calculable additional corrections (which are subleading, i.e., less extensive than area).

The idea that a lower dimensional surface can encode enough information to reconstruct dynamics in a higher dimensional space is similar to what happens in a hologram. So perhaps to understand the entropy formula (10.3.4), one needs a holographic formulation of physical laws. Such a formulation is realized, at least for a restricted class of theories, in the so-called **AdS/CFT correspondence** (or **holographic correspondence**) and its later developments. The original conjecture for this is due to J. Maldacena and states that string theory on an anti-de Sitter(AdS) spacetime background in five dimensions (with an additional 5-sphere) is dual to the maximally supersymmetric Yang-Mills gauge theory (which is a conformal field theory (CFT)) on the boundary of the AdS space. One can, in principle, go back and forth, calculating quantities in one using the other. Although still a conjecture, this does seem to hold for all cases where calculations have been possible.

It is clear that this is far from a finished story. But from what has been said so far, there is good reason to believe that research over the next few years will discover some deep connection between gravity and entropy.

Bibliography

Some useful reference books are:

1. H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (John Wiley & Sons, 1985)
2. D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, 1987)
3. W.Greiner, L. Neise and H. Stöcker, *Thermodynamics and Statistical Mechanics* (Springer, 1995)
4. K. Huang, *Statistical Mechanics* (Joh Wiley & Sons, Inc. 1987)
5. R. Kubo, *Thermodynamics* (North-Holland Publishing Co., 1968)
6. F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill Book Co., 1965)
7. D.V. Schroeder, *An Introduction to Thermal Physics* (Addison Wesley Longman, 2000)
8. M.W. Zemansky and R.H. Dittman, *Heat and Thermodynamics* (7th Ed.) (The McGrawHill Book Companies, Inc., 1997)

The book by Chandrasekhar, referred to in chapter 9, is S. Chandrasekhar, *An Introduction to the Study of Stellar Structure* (Dover Publications, Inc., 1967)

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