The Undergraduate Companion to Theoretical Physics

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Contents

If you are out to describe the truth, leave elegance to the tailor.

— Ludwig Eduard Boltzmann

References

Several textbooks, online courses/resources were referenced heavily (to the extend of making this text completely unoriginal, yet hopefully helpful for revision) throughout the writing of these lecture notes. Using a typical bibliography (research paper style) would be a formidable task.Pinpointing exactly where each reference as been used is quite difficult for such a large and well-referenced subject, and would probably change the writing style to a far too formal one for lecture notes. Therefore we instead list the most relevant below giving a brief comment on which topics they were mostly used for:

- S. Blundell, K. Blundell *Concepts in Thermal Physics*

  Fantastic introduction to thermodynamics. All of part I was typeset referencing this textbook heavily. I particularly enjoyed the extra special topics section with discussions of more contemporary advances in physics based on statistical mechanics.

- W. Greiner, L. Neise, H. Stocker *Thermodynamics and Statistical Mechanics*

  This is a more advanced version of Blundell, covering the same topics but more in-depth. I used this mostly while writing parts III and IV.

- M. Kardar *Statistical Physics of Particles*

  Comprehensive but advanced, good for a second review of the subject. It is supplemented by an equally fantastic lecture series on MIT OCW. It was used mostly in part IV on Quantum statistical physics.

- A. Schekhohichin course notes on *A3 Statistical Physics*

  Discusses kinetic theory and statistical physics from a more mathematical point of view. It was really helpful for part II.

- Course notes by D. Tong on *Part II Statistical Mechanics*

  Excellent notes as usual, particularly recommended for statistical mechanics. It skips through thermodynamics at the beginning (indeed part II students taking the course will have already studied thermodynamics beforehand in part IB), but does dedicate an entire chapter to it later on.

- E. Terentjev *Part II Thermal and Statistical Physics*

  Similar content to the notes by David Tong, but the lecture slides made the content really succint and easy to digest while revising.

Preliminaries

1.1   How much stuff?

The branch of thermal physics often involves the statistical study of macroscopic systems, assemblies of many, many atoms. For example, the number of atoms in an average human is about a staggering 7×10^{27}, that's more than the number of sand particles on Earth (10^9 times more in fact). Therefore, we can't use words like dozen, billion, billion trillion, we must instead invent a name for large quantities of matter, the **mole**.

> **Definition 1: The mole**
>
> A **mole** is the quantity of matter equivalent to the number of atoms in 12 g of ^{12}C. It is equivalent to an **Avogadro number** N_A of atoms:
>
> $$N_A = 6.022 \times 10^{23} \tag{1.1.1}$$
>
> For example a mole of ping pong balls would be 6.022×10^{23} ping pong balls.

The **molar mass** of a substance is the mass of 1 mole of the substance. Carbon-12 therefore has a molar mass of exactly 12g [1]

1.2   The thermodynamic limit

Let us consider the following problem. We have 1 kg of nitrogen gas in a container, which is approximately 2×10^{25} molecules, and we want to model the motion of every single one of these. One year contains 3.2×10^7 seconds, so for a $3\ GHz$ computer counting one molecule per cycle, it would count 9.5×10^16 molecules in one year. So, to count all the molecules in 1kg of N_2, it would take 0.2 billion years. That is just for counting the molecules, imagine what it would take to model their positions and velocities!

It is clear that we need to approach this problem from a more statistical perspective. Instead of making measurements on individual atoms, we can instead consider their average. For an infinitely large sample (10^25 molecules is definitely a good approximation), we can then ignore any fluctuations which get smoothed out for a randomized sample. We refer to this limit of an infinitely large sample as the **thermodynamic limit**.

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[1]this is not the value found in periodic tables, which is around 12.01 g. Indeed, the periodic table provides the **relative atomic mass**, which is the weighted average of the molar masses for all isotopes.

Suppose the container of gas had a volume V, temperature T, pressure p and total kinetic energy U. If we then slice the container, these variables change to V', T', p', U'. How do these relate to their initial values? By definition, slicing the container in half implies its volume is halved:

$$V' = \frac{V}{2} \tag{1.2.1}$$

Since there are half as many particles the total kinetic energy will also be halved (assuming a randomized distribution of particles, which is clearly the case):

$$U' = \frac{U}{2} \tag{1.2.2}$$

The temperature however should not change, nor does pressure as we will see later:

$$p' = p \quad \text{and} \quad T' = T \tag{1.2.3}$$

> **Definition 2:Intensive/Extensive variables**
>
> An **intensive** variable, such as p, T, does not scale with the size of the system.
> An **extensive variable**, such as V, U does scale with the system size.

For example, consider combining 2 volumes of identical gases with state variables N, V, p, T each. The combined system will have state variables $2N, 2V, p, T$. Hence, volume and the number of particles are extensive, whereas pressure and temperature are intensive.

1.3 Approximating large numbers

We will often come across numbers much larger than N_A. Dealing with statistics and probability, we will oten come across factorials, such as $10^{23}!$. In such cases, we may not need an exact value, which would be difficult to calculate, and an approximation would suffice.

To do so, we can use **Stirling's formula**:

$$\ln n! \approx n \ln n - n \tag{1.3.1}$$

In the case of $10^{95}!$, Stirling's formula gives:

$$\ln\left(10^{95}!\right) \approx 10^{95} \ln 10^{95} - 10^{95} \approx 2.2 \times 10^{97} \tag{1.3.2}$$

Therefore:

$$10^{95}! \approx \exp\left(2.2 \times 10^{95}\right) = 10^{9.55 \times 10^{94}} \tag{1.3.3}$$

which is a one followed by more zeros than the number of particles in the universe.

1.4 The ideal gas law

Experiments in the 18th century showed the relation between pressure, temperature and volume. Boyle's law showed that:

$$p \propto \frac{1}{V} \tag{1.4.1}$$

and Charles' law showed that:

$$V \propto T \tag{1.4.2}$$

and finally Gay-Lussac's law showed that:

$$pV \propto T \tag{1.4.3}$$

These three can be combined into the **ideal gas law**.

The Ideal Gas Law

For a system containing N molecules of an **ideal gas**:

$$pV = Nk_BT \tag{1.4.4}$$

where k_B is the **Boltzmann constant**, with value:

$$k_B \approx 1.38 \times 10^{-23} JK^{-1} \tag{1.4.5}$$

This equation makes several assumptions on the properties of the gas. Firstly, it assumes that a gas can be modelled as an assembly of tiny particles which can bounce off of each other and the walls of the container. Secondly, it assumes that the molecules are point-like, and that there are no intermolecular forces. It also models the gas molecules as non-relativistic.

Definition 3: Ideal Gas

An **ideal gas** is made of molecules of point size obeying Newtonian principles. They do not interact through intermolecular forces, and have no potential energy, and do not condense when cooled.

1.5 What is heat

Definition 4: Heat

Heat is defined as thermal energy in transit.

1.6 Probability and statistics

1.7 What is temperature

1.8 Partial differentiation

Suppose we have a set of variables x, y, z related through the constraint:

$$F(x, y, z) = 0 \iff x = x(y, z) \tag{1.8.1}$$

We may express this in differentials as:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{1.8.2}$$

Analogously one may also define:

$$z = z(x, y) \implies dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{1.8.3}$$

and thus substituting (1.8.3) into (1.8.2) we find that:

$$dx = \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x\right) dy \tag{1.8.4}$$

If we choose x, y to be independent then $dy = 0$ yields:

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_y \frac{\partial z}{\partial x}\bigg|_y = 0 \iff \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}} \tag{1.8.5}$$

whereas $dx = 0$ yields:

$$\boxed{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = -1} \tag{1.8.6}$$

Part I

Classical Thermodynamics

The First Law

2.1 Definitions

A **system** is whatever part of the universe we choose to study. The **surroundings** are the regions near the system. A system is:

(i) **Isolated**: if it does not interact with its surroundings. Here the energy, volume and particle number are all conserved.

(ii) **Closed**: if it can only exchange energy with the surroundings. Volume and particle number are still conserved.

(iii) **Open**: if it can interact with the surroundings

(iv) **Homogeneous**: if it has the same properties everywhere throughout it

(v) **Heterogeneous**: if it has discontinuities in its properties

The **phases** of a system are the individual components of it which are homogeneous, and they are separated by **phase boundaries**.

A system is in **thermal equilibrium** when the macroscopic observables have no time dependence, this set of observables form a particular **equilibirum state**. These observables, which have a well-defined value for each equilibrium state of the system are then called **functions of state.**

If we define equilibrium surfaces from equations of state, then every point on these surfaces will represent a state of equilibrium: If we let $\mathbf{x} = (x_1, x_2...)$ specify a state of a system, and let $f(\mathbf{x})$ be a function of state. Allowing the system to change from $\mathbf{x}_i$ to $\mathbf{x}_f$, then:

$$\Delta f = \int_{\mathbf{x}_i}^{\mathbf{x}_f} df = \int_{\mathbf{x}_i}^{\mathbf{x}_f} \nabla f(\mathbf{x}) \cdot d\mathbf{x} = f(\mathbf{x}_f) - f(\mathbf{x}_i) \tag{2.1.1}$$

independent of how the change occurs, it only depends on the end points. We call df an **exact differential**, and a quantity that does not have an exact differential is not a function of state.

For example, if $đg = ydx$, then for a change from $(0,0)$ to $(1,1)$ then along a straight line
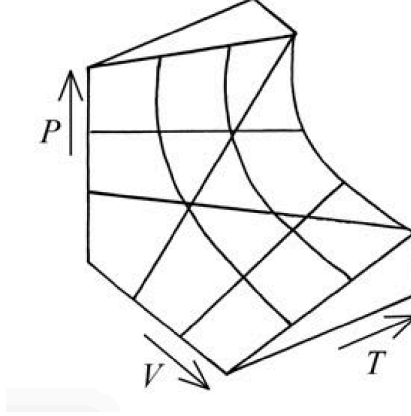
Figure 2.1. pVT surface defines an equilibrium surface for ideal gases which follow the state equation $pV = k_B nT$

path connecting these points:

$$\Delta g = \int_{(0,0)}^{(1,1)} y dx = \int_0^1 x dx = \frac{1}{2} \tag{2.1.2}$$

whereas for a path going to $(1,0)$ and then $(1,1)$ we have:

$$\Delta g = \int_{(0,0)}^{(1,0)} y dx + \int_{(1,0)}^{(1,1)} y dx = 0 \tag{2.1.3}$$

So clearly $đg$ is an inexact differential, which is symbolized by the small cross through the d. Since Δg depends on the path taken, g is not a function of state.

More generally, to test whether $df = \mathbf{F} \cdot d\mathbf{x}$ it is sufficient to check whether or not $\mathbf{F}$ is conservative

$$\nabla \times \mathbf{F} = 0 \tag{2.1.4}$$

2.2 The first law of thermodynamics

In 1789 Lavoisier proposed a model of heat as a weightless, conserved fluid called **caloric**. It could neither be created nor destroyed, but could be released through combustion. This however did not explain other forms of heating, such as friction which was observed by Rumsford in 1798. So in 1842 Mayer proposed the mechanical equivalent of heat by frictionally generating heat in paper. Joule performed similar experiments but more carefully. He let a mass tied to a string descend a certain height, making a paddle immersed in a mass of water turn. This motion heats the water, and after making the mass fall a certain height Joule measured the temperature rise in the water, deducing correctly the mechanical equivalent of heat. He also measured the heat output of a resistor, and showed that for the same energy input, the same amount of heat was produced, thus suggesting that heat was a form of energy.

> **The first law of thermodynamics**
>
> Energy is conserved, and heat and work are forms of energy, but not functions of state. If U is the **internal energy** of the system, the sum of the energy of all its degrees of freedom, then:
> $$dU = đQ + đW \qquad (2.2.1)$$
> where $đQ$ is the heat supplied to the system, and $đW$ is the work done on the system.

A **thermally isolated system** cannot exchange heat with its surroundings so that:

$$dU = đW \qquad (2.2.2)$$

Consider the work done by compressing gas of pressure p and volume V:

$$đW = Fdx = pAdx = -pdV \qquad (2.2.3)$$

since decreasing the volume requires positive work. It is important to note that this equation is only true for reversible changes, as we will see in the following chapter.

2.3 Heat capacity

Generally the internal energy will be a function of temperature and volume, so we may set $U = U(T, V)$ and:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad (2.3.1)$$

Inserting this into $đQ = dU + pdV$ we find:

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV \qquad (2.3.2)$$

and dividing by dT we find:

$$\frac{đQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{dV}{dT} \qquad (2.3.3)$$

Using this we can now calculate the amount of heat we must add to have a change in temperature. If we keep the volume constant:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (2.3.4)$$

since the second term in 2.3.3 vanishes at constant volume. If we keep the pressure constant:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \qquad (2.3.5)$$

We then define the specific heat capacities as the heat capacity per mass of gas:

$$c_V = \frac{C_V}{M} \tag{2.3.6}$$

$$c_p = \frac{C_p}{M} \tag{2.3.7}$$

where M is the mass of the material. We can also define the ratio of C_p to C_V, called the **adiabatic index** γ:

$$\gamma = \frac{C_p}{C_V} \tag{2.3.8}$$

Example (5.1.1 Sh)

For an ideal monoatomic gas, the internal energy is all due to the kinetic energy, and can be shown (see kinetic theory of gases) to be $U = \frac{3}{2}RT$ per mole, where $R = N_A k_B$ is a constant. Therefore:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}R \tag{2.3.9}$$

per mole. Also:

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{2.3.10}$$

but $\left(\frac{\partial U}{\partial V}\right)_T = 0$, and using the ideal gas law for one mole of gas:

$$pV = RT \implies \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \tag{2.3.11}$$

so that:

$$C_p = C_V + R = \frac{5}{2}R \tag{2.3.12}$$

per mole. Therefore the adiabatic index is given by:

$$\gamma = \frac{5}{3} \tag{2.3.13}$$

It follows that for an ideal gas:

$$đQ = C_V dT + pdV \implies dU = C_V dT \tag{2.3.14}$$

We can also use the result that for an ideal gas $C_p = C_V + R$ to write that:

$$đQ = C_V dT + pdV = (C_p - R)dT + pdV \tag{2.3.15}$$

Hence using the ideal gas law $pV = RT \ pdV + V dp = RdT$ we find that:

$$đQ = C_p dT - V dp \tag{2.3.16}$$

First Law for Ideal Gases

For an ideal gas undergoing a reversible process, we have that:

$$dU = C_V\,dT, \ dW = -p\,dV \qquad (2.3.17)$$

and consequently:

$$đQ = C_V\,dT + p\,dV \qquad (2.3.18)$$
$$đQ = C_p\,dT - V\,dp \qquad (2.3.19)$$

2.4 Reversible processes

Pretty much all processes in the universe are governed by time-reversible laws of physics. This is given by the fact that if we looked at a video of the entire universe, we would not be able to realize whether it is in reverse or not. The reason we don't see a broken egg reassemble itself and float on top of a table is due to energy dissipation. When an egg falls off a table and breaks, part of its potential energy is dissipated into its surroundings as heat. This **dissipation** can't be traced back exactly (this has to do with entropy). Similarly, when we delete a file on our computers, we're not truly deleting any information, but converting it into other forms of energy (mostly heat). Tracing back the heat to the original 1s and 0s that encoded the information is impossible, the process is thus irreversible.

For a process to be reversible we require that it be:

1. **Quasistatic**: the system is always in an equilibrium state or infinitesimally close to one (so that any changes in the state variables are infinitesimal). Suppose for example that we push a piston down a column of gas. If we do this slowly enough, the gas will have enough time to adjust to the moving piston, and hence it will always be in an equilibrium state. If instead we introduce a rapid perturbation, this will send shock waves through the gas, exciting its constituent atoms and creating regions of higher temperature. There is no way to extract the sound waves from these regions of high temperature by moving the piston back.

2. **No hysteresis**: hysteresis occurs when a systems time evolution depends on its history. The most common example is the magnetization of iron, where if we remove the magnetizing field slowly, the iron won't go back to its original state, but will instead follow a hysteresis loop as shown below.

Reversibility and dissipation

A process involving dissipation is **irreversible**. A reversible process, called **quasistatic** is a process whose direction can be reversed by an infinitesimal change. A reversible process is therefore **quasistatic** and without **hysteresis** or heat dissipation.
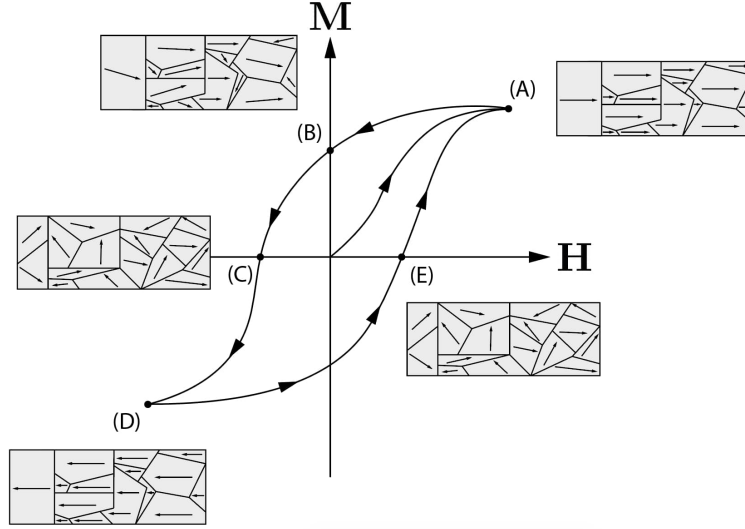
Figure 2.2. Hysteresis loop for the magnetization of iron

The property that the system is always in an equilibrium state or infinitesimally close to one is analogous to a ball free to roll on a smooth table. If we want to maintain the ball in an equilibrium state, so that it does not slip, we must move the table very, very, very slowly. In real life forces such as friction make it so that it doesn't take an infinite amount of time, but in an idealized world this process would take infinitely long.

Since we may define equilibrium as the set of points on an equilibrium surface defined by an equation of state, reversible processes may be defined as processes on this surface. Irreversible processes on the other hand leave this surface.

Hence when systems approach equilibrium, their trajectory is outside of the equilibrium surface and intersects it once equilibrium has been reached. This process is therefore irreversible, as expected from the second law of thermodynamics.

2.5 Isothermal expansion

Consider the heat change in a reversible **isothermal** expansion of an ideal gas, where the temperature remains constant. For an ideal gas we have that $dU = C_V dT = 0$. Inserting this into the first law of thermodynamics:

$$\dbar W = -pdV = -\dbar Q \tag{2.5.1}$$

Therefore for an isothermal expansion from V_1 to V_2, the heat that must be added is:

$$\Delta Q = \int \dbar Q = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln \frac{V_2}{V_1} \tag{2.5.2}$$

Hence, for an expansion, $V_2 > V_1$, and $\Delta Q > 0$, and heat must therefore be added to the system, whereas for a compression ΔQ heat must be taken from the system.

2.6 Adiabatic expansion

An **adiathermal** process involves no flow of heat, so a system bounded by adiathermal walls is said to be thermally isolated. A process is further classified as **adiabatic** if it is also reversible. In such a case we have that for an ideal gas:

$$đQ = 0 \quad \text{and} \quad dU = C_V dT \tag{2.6.1}$$

Hence, using the first law of thermodynamics:

$$C_V dT = -pdV = -\frac{RT}{V}dV \implies \ln\frac{T_2}{T_1} = -\frac{R}{C_V}\ln\frac{V_2}{V_1} \tag{2.6.2}$$

but using the adiabatic index:

$$\gamma = 1 + \frac{R}{C_V} \tag{2.6.3}$$

we can write:

$$TV^{\gamma-1} = \text{cnst.} \tag{2.6.4}$$

or alternatively:

$$pV^{\gamma} = \text{cnst.} \tag{2.6.5}$$

The work done on the system is given by:

$$W = \Delta U = c_v \Delta T = c_v \left(\frac{p_2 V_2}{R} - \frac{p_1 V_1}{R}\right) = \frac{1}{\gamma - 1}(p_2 V_2 - p_1 V_1) \tag{2.6.6}$$

Using $pV^{\gamma} = cnst.$ we then find that:

$$\Delta U = W = \frac{p_1 V_1^{\gamma}}{\gamma - 1}\left(V_2^{1-\gamma} - V_1^{\gamma-1}\right) \tag{2.6.7}$$

Therefore during an adiabatic process, reducing the internal energy of a system allows for work to be done on the surrounding environment.

Example. Adiabatic atmosphere The pressure due to a thickness dz of atmosphere (which we model as nitrogen gas) with density ρ is given by:

$$dp = -\rho g dz \implies \frac{dp}{dz} = -\rho g \tag{2.6.8}$$

and since $\rho = \frac{mN}{V}$ and $p = \frac{Nk_B T}{V}$ where m is the mass of one molecule, n is the number of nitrogen molecules, we can write:

$$\frac{dp}{dz} = -\frac{mgp}{k_B T} \implies T\frac{dp}{p} = -\frac{mg}{k_B}dz \tag{2.6.9}$$

If we model the atmosphere to be adiabatic, so that each parcel of air does not exchange heat with its surrounding, then we can use:

$$p^{1-\gamma}T^{\gamma} = \text{cnst.} \tag{2.6.10}$$

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to find differentiating:

$$(1 - \gamma)p^{-\gamma}T^{\gamma}\frac{dp}{dT} + \gamma p^{1-\gamma}T^{\gamma-1} = 0 \implies (1 - \gamma)\frac{dp}{p} + \gamma\frac{dT}{T} = 0 \tag{2.6.11}$$

Combining this with 2.6.7 we can finally find:

$$\frac{dT}{dz} = -\left(\frac{\gamma - 1}{\gamma}\right)\frac{mg}{k_B} \tag{2.6.12}$$

but using the relation $R = N_A k_B = C_p - C_V$ we quickly find that:

$$\frac{dT}{dz} = -\frac{Mg}{C_p} = -\frac{g}{c_p} \tag{2.6.13}$$

where $c_p = \frac{C_p}{M}$ is the specific heat capacity and M is the molar mass of nitrogen.

2.7   Isochoric and Isobaric expansions

In an **Isochoric process**, the gas has a constant volume throughout. Therefore, the work done on the system is null, because $dW = pdV = 0$. Therefore, we find that the heat released is:

$$Q = C_V \Delta T \tag{2.7.1}$$

and from the first law of thermodynamics:

$$\Delta U = Q = C_V \delta T \tag{2.7.2}$$

So in an isochoric process, heat enters (leaves) the system thus increasing (decreasing) the internal energy. No work is done on the system, and no work is therefore obtainable from the process.

Instead, in an **Isobaric process**, the gas is kept at a constant pressure throughout. Therefore, the work done on the system is:

$$W = -\int_{V_1}^{V_2} pdV = -p\Delta V \tag{2.7.3}$$

The heat supplied is then equal to:

$$Q = C_p \Delta T = (C_V + R)\Delta T \tag{2.7.4}$$

and from the first law of thermodynamics we find that:

$$\Delta U = \Delta Q + \Delta W = (C_V + R)\Delta T - p\Delta V \tag{2.7.5}$$

In an isobaric process, heat enters (leaves) the system. Part of the heat is used by the system to increase (decrease the internal energy) and the rest is used to do work on the surrounding environment.

Thermodynamic quasi-static processes

Process	Condition	ΔU	ΔQ	ΔW
isothermal	$dT = 0$	$\Delta U = 0$	$\Delta Q = -\Delta W$	$W = RT \ln \frac{V_1}{V_2}$
adiabatic	$dQ = 0$	$\Delta U = \Delta W$	$\Delta Q = 0$	$W = \frac{1}{\gamma - 1}(p_2 V_2 - p_1 V_1)$
isochoric	$dV = 0$	$\Delta U = Q$	$\Delta Q = C_V \Delta T$	$\Delta W = 0$
isobaric	$dp = 0$	$\Delta U = \Delta Q + \Delta W$	$\Delta Q = C_p \Delta T$	$\Delta W = -p \Delta V$

The Second Law

This chapter will introduce the second law of thermodynamics and its applications in the study of engines, machines operating between two reservoirs of different temperatures.

3.1 Perpetual motion machine

Throughout history several attempts have been made to construct a **perpetual motion machine**. Mainly two types of such machines have been though of:

(i) machine that produces more energy than it uses

(ii) machine that produces exactly the same amount of energy as it uses, but continues running indefinitely by converting its waste heat into work

Clearly, the first type violates the first law of thermodynamics. The second type of machine however, is not in violation of this principle, and would theoretically be possible given the thermal physics we have studied.

We are clearly missing a fundamental principle that forbids the "re-usability" of energy, so that no machine is able to convert heat purely into work indefinitely. This principle is the second law of thermodynamics.

3.2 The second law of thermodynamics

Empirical evidence seem to show that heat always flow from hot bodies to cold bodies, and the reverse process never occurs in thermodynamic isolation. This formulation leads to the **Clausius' statement** of the second law of thermodynamics:

> **Clausius' statement of the second law of thermodynamics**
>
> No process can have the sole net result of transferring heat from a colder to a hotter body.

A second, seemingly unrelated statement of the same law can be made, regarding how easy energy can be converted in different forms. This is called **Kelvin's statement of the second law of thermodynamics**

> **Kelvin's statement of the second law of thermodynamics**
>
> No process can have the sole net result of converting heat into work completely.

To see the relation between these two statements, we must first look at **engines**.

3.3 The Carnot Engine

An **engine** is a machine operating between two reservoirs that converts some heat into work by operating through a **Carnot cycle**. The cycle consists of:
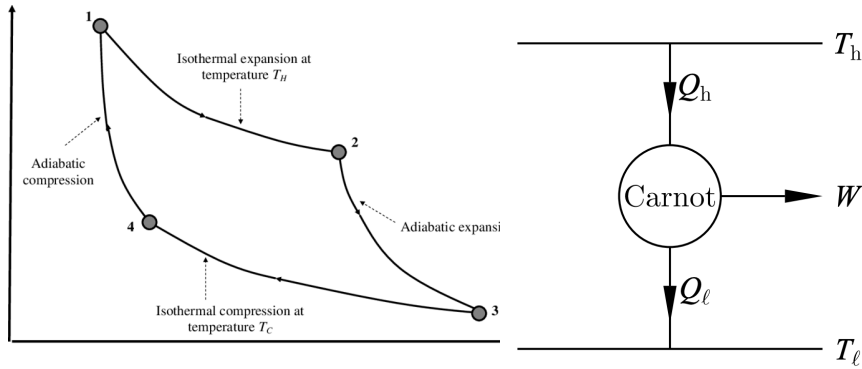
Figure 3.1. Carnot cycle and engine

$1 \to 2$ is an isothermal expansion of the gas operating at a higher temperature T_h in which heat Q_h enters from the hot reservoir.

$2 \to 3$ is an isentropic (which means adiabatic and reversible) expansion in which the gas is isolated from the reservoirs, but continues expanding by sacrificing its internal energy. The temperature therefore drops to T_l.

$3 \to 4$ is an isothermal compression of the gas operating at a lower temperature T_l in which heat Q_l exits into the cold reservoir.

$4 \to 1$ is an isentropic (which means adiabatic and reversible) compression in which the gas is isolated from the reservoirs, but continues compressing increasing its internal energy, and thus temperature to T_h.

Note that the process is cyclic, and therefore in one cycle the total internal energy U does not change overall. The first law of thermodynamics then tells us that the work output by the engine is:

$$W = Q_h - Q_l \tag{3.3.1}$$

Using the results from the previous chapter on isothermal and isentropic processes:

$$1 \to 2: \; Q_h = RT_h \ln \frac{V_2}{V_1} \tag{3.3.2}$$

$$2 \to 3: \; \frac{T_h}{T_l} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \tag{3.3.3}$$

$$3 \to 4: \; -Q_l = RT_l \ln \frac{V_4}{V_3} \tag{3.3.4}$$

$$4 \to 1: \; \frac{T_l}{T_h} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \tag{3.3.5}$$

where the negative sign in the third equation is due to the fact that the change in energy is negative, whereas the heat transfer Q_l is positive. The first and second equations give:

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \tag{3.3.6}$$

and dividing the second equation by the fourth, and substituting 3.2.6 we find:

$$\frac{Q_h}{Q_l} = \frac{T_h}{T_l} \tag{3.3.7}$$

The **efficiency** η of an engine can be seen as the ratio of the output energy and the input energy, how much work must be done to obtain a certain energy output. For the Carnot engine, we find that this efficiency is the ratio of the work output W by the machine, and the heat Q_h provided by the reservoirs (which must be kept at the same temperature). Therefore:

$$\eta_C = \frac{W}{Q_h} = 1 - \frac{T_l}{T_h} \tag{3.3.8}$$

> **Carnot's Engine**
>
> A Carnot engine is a machine operating between two reservoirs of temperature T_l and T_h through a Carnot cycle, and has efficiency $\eta_C = 1 - \frac{T_l}{T_h}$.

Since, by equation 3.2.1 $W < Q_h$, the efficiency of the Carnot machine is always lower than 100%, and as we will see soon, no machine can be more efficient than the Carnot engine.

It is now evident how the second law of thermodynamics can explain the impossibility of a *perpetuum mobile* of the second type.

3.4 Carnot's theorem

It turns out that the efficiency of the Carnot engine is maximized, as encapsulated in the **Carnot's theorem**.

> **Carnot's Theorem**
>
> Of all the heat engines working between two temperatures, the most efficient one is the Carnot engine. Thus all reversible engines working between two temperatures have the same efficiency η_C.

Proof. Suppose that there does exist an engine E more efficient than the Carnot engine. Because all the processes in a Carnot cycle are reversible, we run the Carnot engine in reverse and connect it to engine E as shown below.
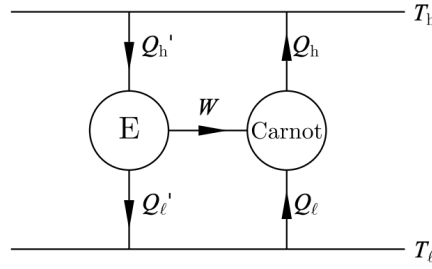
Figure 3.2. Engine E connected to Carnot engine run in reverse

From the first law of thermodynamics we have:

$$W = Q_h' - Q_l' = Q_h - Q_l \implies Q_h - Q_h' = Q_l - Q_l' \tag{3.4.1}$$

Now because $\eta_C > \eta_E$, we must have that $\frac{W}{Q_h'} < \frac{W}{Q_h}$ and thus $Q_h > Q_h'$.

So $Q_h - Q_h' > 0 \implies Q_l - Q_l' > 0$. Since $Q_h - Q_h'$, the amount of heat dumped into the reservoir T_h is positive and equal to $Q_l - Q_l'$, the amount of heat extracted from reservoir T_l, this engine has the sole purpose of transferring heat from a cold body to a hotter body, and therefore violates Clausius's statement of the second law of thermodynamics.

To prove that all reversible engines have the same efficiency, consider a reversible engine R connected to a Carnot engine as shown below:
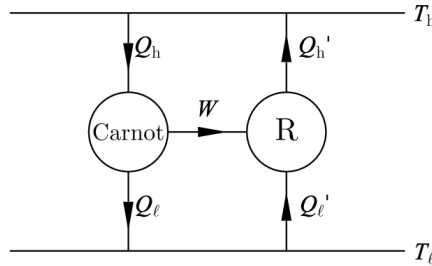
Figure 3.3. Reversible engine R connected to a Carnot engine.

Then its efficiency, by Carnot's theorem, is $\eta_E \leq \eta_C$. Using the same logic as before, we find that the system only dumps heat from the cold reservoir to the hot reservoir for

$\eta_E < \eta_C$, thus violating the Clausius' statement. The only possibility is therefore to have $\eta_E = \eta_C = 1 - \frac{T_l}{T_h}$. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ □

3.5 The equivalence of Clausius' and Kelvin's statements

To prove that the two are equivalent, it suffices to prove that:

(i) if a system violates Kelvin's statement then it violates Clausius' statement.

(ii) if a system violates Clausius' statement violates Kelvin's statement

Proof.   (i) If an engine violates Kelvin's statement (so that all the heat is converted to work), then we can connect it to a Carnot engine as shown below: From the first law:
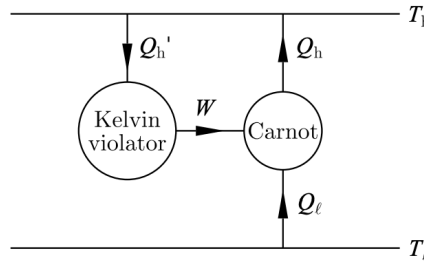
Figure 3.4. Kelvin violator is connected to a Carnot engine

$$Q'_h = W, \quad Q_h = W + Q_l \qquad\qquad (3.5.1)$$

So the heat dumped into the reservoir T_h is $Q_h - Q'_h = Q_l$ which is the heat extracted from the reservoir T_l. Hence this system is transferring heat from a colder body to a warmer body.

(ii) If a system violates Clausius' statement, then its only effect is to transfer heat from the reservoir at T_l to the reservoir at T_h. We can then connect it to a Carnot engine as shown:
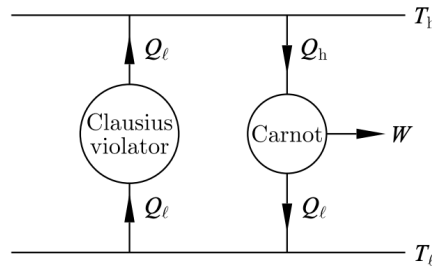
Figure 3.5. Clausius violator is connected to a Carnot engine

From the first law $Q_h - Q_l = W$, so the sole effect of the system is to convert heat into work, thus violating Kelvin's statement.
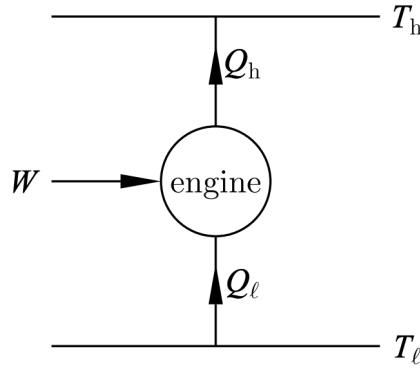
Figure 3.6. Refrigerator/heat pump designs

Example.

(a) **Refrigerator**

The refrigerator is a heat engine run in reverse. The cold reservoir is the cold food inside the refrigerator, and the hot reservoir is the kitchen. Therefore the efficiency here will be the heat sucked out of the contents (which is what we wish to get) divided by the work required to achieve this:

$$\eta = \frac{Q_l}{W} \tag{3.5.2}$$

For a refrigerator with a Carnot engine, we can show:

$$\eta_C = \frac{T_l}{T_h - T_l} \tag{3.5.3}$$

which is sometimes greater than 100%

(b) **Heat pump**

A heat pump is a refrigerator, used to pump heat from a reservoir to another place. The effect we want is to add heat Q_h to this place, and W is the work that must be done, so that the efficiency is:

$$\eta = \frac{Q_h}{W} \tag{3.5.4}$$

So for a heat pump with a Carnot engine we have that:

$$\eta_C = \frac{T_h}{T_h - T_l} \tag{3.5.5}$$

which is always greater than 100%.

3.6 Clausius' theorem

Consider a general cycle where in an infinitesimal step i heat $đQ_i$ enters at some point connected to a reservoir at temperature T_i. The total work extracted is:

$$\Delta W = \sum_{cycle} đQ_i \tag{3.6.1}$$

We now let each point be supplied with heat via a Carnot engine as shown in (b), operating between a reservoir at temperature T providing heat $đQ_i + đW_i$, and a reservoir T_i. Each engine produces work $đW_i$ such that:

$$\frac{\text{heat to } T_i}{T_i} = \frac{\text{heat from } T}{T} \tag{3.6.2}$$

and so:

$$\frac{đQ_i}{T_i} = \frac{đQ_i + đW}{T} \implies đW_i = đQ_i\left(\frac{T}{T_i} - 1\right) \tag{3.6.3}$$

Because we can't heat completely into work, we must have that the total work in the entire cycle is negative or zero, otherwise we would have converted heat to work.
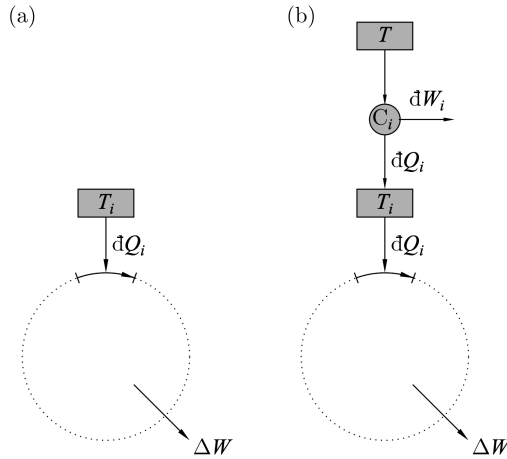
Figure 3.7. (a) A general cycle in which heat $đQ_i$ enters (b) Same cycle, but with heat entering through a carnot engine

Therefore:

$$\Delta W + \sum_{cycle} đW_i \leq 0 \implies \sum_{cycle} đQ_i + đW_i \leq 0 \tag{3.6.4}$$

and therefore:

$$T \sum_{cycle} \frac{đQ_i}{T_i} \leq 0 \implies \frac{đQ_i}{T_i} \leq 0 \tag{3.6.5}$$

since temperature is positive. Turning the sum into an integral:

$$\oint \frac{đQ}{T} \leq 0 \tag{3.6.6}$$

which is the **Clausius inequality**.

If the cycle is reversible, then running it in reverse $đQ$ turns into $-đQ$ and we find:

$$\oint \frac{-đQ}{T} \leq 0 \implies \oint \frac{đQ}{T} = 0 \tag{3.6.7}$$

Clausius' Theorem

For any closed cycle:

$$\oint \frac{đQ}{T} \leq 0 \tag{3.6.8}$$

where equality only holds for reversible cycles.

In essence, Clausius' theorem emphasizes the fact that the heat available to do work in a closed cycle must always decrease or remain constant.

Example. Consider two bodies with heat capacities C_h and C_l used as reservoirs for a Carnot heat engine. We wish to find the total work obtainable. We have that:

$$đQ_h = -C_h dT_h \tag{3.6.9}$$
$$đQ_l = -C_l dT_l \tag{3.6.10}$$

For a Carnot engine we also have:

$$\frac{đQ_l}{T_l} = \frac{đQ_h}{T_h} \tag{3.6.11}$$

Integrating directly we find:

$$C_l \ln \frac{T_f}{T_l} = -C_h \ln \frac{T_f}{T_h} \implies T_f^{C_h + C_l} = T_h^{C_h} T_l^{C_l} \tag{3.6.12}$$

where T_f is the final temperature of the reservoirs. Thus:

$$\Delta Q_h = C_h (T_f - T_f) \tag{3.6.13}$$
$$\Delta Q_l = C_l (T_f - T_l) \tag{3.6.14}$$

so that the work obtainable is:

$$\Delta W = \Delta Q_h - \Delta Q_l = C_h (T_f - T_f) - C_l (T_f - T_l) \tag{3.6.15}$$

Entropy

4.1 Definition of Entropy

Recall that for a reversible process, we have:

$$\oint \frac{đQ_{rev}}{T} = 0 \qquad (4.1.1)$$

This implies that $\frac{đQ_{rev}}{T}$ is a function of state defined as **entropy** S as:

> **Definition: Entropy**
>
> The entropy S is a function of state:
>
> $$dS = \frac{đQ_{rev}}{T} \qquad (4.1.2)$$
>
> so that the change in entropy between two points A,B is:
>
> $$\Delta S = \int_A^B \frac{đQ_{rev}}{T} \qquad (4.1.3)$$

For an irreversible change $A \rightarrow B$, and let us form a closed loop by joining it with a reversible change $B \rightarrow A$. Then the Clausius' inequality reads:

$$\oint \frac{đQ}{T} = \int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{rev}}{T} \leq 0 \qquad (4.1.4)$$

and rearranging gives:

$$\int_A^B \frac{đQ}{T} \leq \int_A^B \frac{đQ_{rev}}{T} \qquad (4.1.5)$$

Therefore:

$$dS \geq \frac{đQ}{T} \qquad (4.1.6)$$

For a thermally isolated system $đQ = 0$ always and thus:

$$\boxed{dS \geq 0} \qquad (4.1.7)$$

If we assume that the universe is isolated, then we can write that the total entropy tends

to a maximum.

> **Entropic statement of the second law**
>
> For a thermally isolated system, the entropy must always increase for an irreversible change and stay the same for a reversible change.

Example.

A large reservoir at constant temperature T_R is placed in thermal contact with a small system at temperature T_S, and both end up with temperature T_R.

The heat transferred to the system is therefore equal to $\Delta Q = C(T_R - T_S)$. The entropy change in the reservoir can then be calculated as:

$$\Delta S_{res} = \int \frac{dQ}{T_R} \tag{4.1.8}$$

$$= -\frac{\Delta Q}{T_R} \tag{4.1.9}$$

$$= \frac{C(T_S - T_R)}{T_R} \tag{4.1.10}$$

Instead, the entropy change of the system is :

$$\Delta S_s ys = \int_{T_S}^{T_R} \frac{CdT}{T} = C \ln \frac{T_R}{T_S} \tag{4.1.11}$$

Therefore, the total change in entropy is:

$$\Delta S = C\left(C \ln \frac{T_R}{T_S} + \frac{T_S}{T_R} - 1\right) \tag{4.1.12}$$

From the plot below, we can see that the entropy is always non-negative, and equal to zero when $T_S = T_R$, which intuitively makes sense since there would be no heat flow.
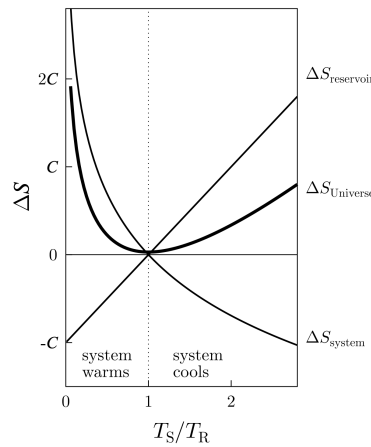
4.2 Reformulating the First Law

For a reversible change, we can write $đQ = TdS$, $đW = -pdV$. We can then write:

$$dU = TdS - pdV \tag{4.2.1}$$

Luckily, this equation actually holds for irreversible processes as well! This is fundamental equation of thermodynamics:

Fundamental equation of thermodynamics

$$\boxed{dU = TdS - pdV}$$

Note that we may write dU using the chain rule as:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{4.2.2}$$

from which it follows that:

$$\begin{cases} T &= \left(\frac{\partial U}{\partial S}\right)_V \\ p &= \left(\frac{\partial U}{\partial V}\right)_S \end{cases} \implies \frac{p}{T} = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V \tag{4.2.3}$$

Now, from the reciprocity theorem we must have that $\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial V}{\partial S}\right)_S \left(\frac{\partial V}{\partial S}\right)_U = 1$ and thus:

$$\boxed{\frac{p}{T} = -\left(\frac{\partial S}{\partial V}\right)_U} \tag{4.2.4}$$

In summary.

$$\begin{cases} dU = đQ + đW & \text{is always true} \\ đQ = TdS & \text{is only true for reversible changes} \\ đW = -pdV & \text{is only true for reversible changes} \\ dU = TdS - pdV & \text{is always true} \end{cases} \tag{4.2.5}$$

4.3 Joule Expansion

We now go back to the problem of expanding a gas freely and quasistatically in a container, and try to answer the question of why the particles do not reassemble themselves.

Indeed, if this were to happen, then the second law of thermodynamics, $dS \geq 0$, would be violated. We see this by noting that since the system is thermally isolated, $dU = 0$, and if the particles reassemble themselves into their original volume, $dV \leq 0$. Then, using the fundamental equation of thermodynamics we get $dS < 0$, a contradiction.

Physically, this means that the particles reassembling themselves does not satisfy the maximum entropy principle. This explains why, if we let a gas expand freely in a container, this process is irreversible, and we do not observe the gas particles neatly reassemble themselves in the smaller volume they were initially contained within.

The expansion of the gas is therefore irreversible, because $\Delta S > 0$.

Let us calculate the entropy change, we consider one mole of an ideal gas confined to a container of volume V_0, which freely expands isothermally, upon the opening of a tap, into a container of volume V_1 [1].

The system is thermally isolated, so $\Delta U = 0$ and since $C_V \Delta T = \Delta U = 0 \implies \Delta T = 0$ so the initial and final temperatures are the same, T. Also, $dU = 0 = TdS - pdV$.

Now using the ideal gas law, $p_i V_0 = RT = p_f V_1 \implies p_f = \frac{V_0}{V_1} p_i$. Now we can write:

$$\Delta S = \int \frac{dQ}{T} = \int_{V_0}^{V_1} \frac{p(V)dV}{T} = \int_{V_0}^{V_1} \frac{RdV}{V} = R \ln \frac{V_1}{V_0} \tag{4.3.1}$$

We now write that $\Delta S = \Delta S_{universe} > 0$ since there can be no heat transfer to the surroundings. Hence, the Joule expansion is irreversible.

4.4 Entropy change for ideal gas

For an ideal gas we have that:

$$dQ = dU - dW = C_V dT + pdV = C_V dT + \frac{nRT}{V} dV \tag{4.4.1}$$

We cannot integrate this without knowing how the volume changes with temperature, however, if we divide by T we find that:

$$\frac{dQ}{T} = \frac{C_V dT}{T} + \frac{nR}{V} dV \tag{4.4.2}$$

which upon integration gives:

$$\boxed{\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}} \tag{4.4.3}$$

---

[1] the fact that the process is isothermal is irrelevant, since dS is a function of state and is independent of path

4.5 Statistical interpretation of entropy

In the Statistical Mechanics part of these lectures we will see that entropy may alternatively be defined as

$$S = k_B \ln \Omega \qquad (4.5.1)$$

called the **Boltzmann-Planck equation**, where Ω is the number of microstates consistent with the given macrostate.

Example.

Consider two ideal gases, separated in two containers of volumes xV and $(1-x)V$ at pressure p, temperature T. From the ideal gas law, $p = \frac{Nk_BT}{V}$, so there are xN moles of gas 1 and $(1-x)N$ moles of gas 2.

If we now open the tap between the two containers, the gases will mix resulting in an increasing entropy. If we assume an isothermal expansion, $\Delta U = 0$ so $TdS = pdV \implies dS = \frac{pdV}{T}$ and thus:

$$\Delta S = xNk_B \int_{xV}^{V} \frac{dV_1}{V_1} + (1-x)Nk_B \int_{(1-x)V}^{V} \frac{dV_2}{V_2} \qquad (4.5.2)$$

$$= -Nk_B(x \ln x + (1-x) \ln(1-x)) \qquad (4.5.3)$$

We plot the entropy of mixing below:
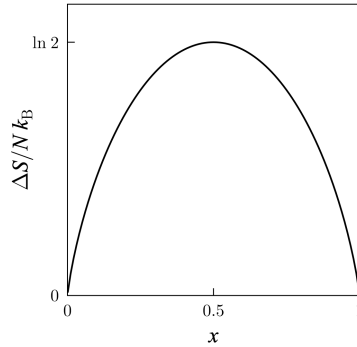
We see that entropy is maximum when $x = \frac{1}{2}$ with value $Nk_B \ln 2$, and is lowest when $x = 0, 1$ obviously. The plot is symmetric about $x = \frac{1}{2}$, since the system too is symmetric (we can exchange the two containers, switch $x \leftrightarrow (1-x)$).

In the case where $x = \frac{1}{2}$, the two containers have equal volume. So, when the tap is opened, Ω, the number of microstates that can exist must be multiplied by 2^N, since every molecule can be in either container 1 or container 2, and not only in its original container. So, the change in entropy is $k_B \ln 2^N = Nk_b \ln 2$ as required.

4.5.1 Gibb's paradox

But what if the two gases were identical? In this previous example we assumed that the gases had some distinctive quality that allowed us to say that each molecule could be in

either one container or the other. However, with indistinguishable molecules, it does not make sense anymore in the case where $x = \frac{1}{2}$ that the number of microstates is multiplied by 2^N. The change in entropy would therefore be: $\Delta S = 0$, and not $\Delta S = Nk_b \ln 2$.

We see that the results for distinguishable particles cannot be used for identical particles.

4.5.2 Maxwell's demon

Another paradox that attempts to contradict the second law of thermodynamics is **Maxwell's demon**. A gas is initially in a chamber, and performs a Joule expansion into a second connected chamber. This process, as we explained earlier through the maximum entropy principle, must be irreversible. However, Maxwell came up with the idea of inserting an intelligent valve (the so-called demon), that upon sensing a particle directed towards the initial container, opens only allowing that particle to return to its original vessel. If we repeat this process for long enough, we should get all the particles back to the original container, thus reversing the Joule expansion and reducing the entropy of the system.

The same demon could be used to partition fast gas molecules into one container, and slower gas molecules into the other, thereby transferring heat without doing work.

It turns out that to function properly, the demon must store information to understand where the molecules are going. This leads to an increase in entropy, called the **Shannon entropy**.

4.6 Gibbs expression for entropy

Consider a system with N different microstates. Each ith microstate has n_i contained within it, all identical to each other, and not directly measurable. The probability of observing the system in the ith microstate is $P_i = \frac{n_i}{N}$, with $N = \sum_i n_i$.

The total entropy is, of course, $S_{tot} = k_B \ln N$. However, we may express this total entropy as the sum of the entropy S due to the freedom of choice of each microstate, and the entropy S_{micro} due to the different sub-microstates. So:

$$S_{tot} = S + S_{micro} \tag{4.6.1}$$

We cannot measure S_{micro} directly, we can take the expectation value:

$$S_{micro} = \sum_i P_i S_i = \sum_i k_B \ln n_i \tag{4.6.2}$$

so that:

$$S = k_B \left(\ln N - \sum_i P_i \ln n_i \right) \tag{4.6.3}$$

and since $\ln \frac{n_i}{N} = \ln P_i$ we find that:

$$\boxed{S = -k_B \sum_i P_i \ln P_i} \tag{4.6.4}$$

It follows that the configuration with the most possible microstates will also maximize the entropy, and lead to equilibria. Systems approaching a state of equilibrium will therefore maximize the number of microstates they can occupy.

Thermodynamic potentials

5.1 Definitions

We have seen that the internal energy of a system is a very useful function of state. It turns out that there are several other such quantities with units of energy, called **thermodynamic potentials**. They can all be found by adding to U several combinations of p, V, T, S. We define them below:

> **Definition: Thermodynamic potentials**
>
> We define the following thermodynamic potentials:
>
> $$\begin{cases} \text{Internal energy}: & U \\ \text{Enthalpy}: & H = U + pV \\ \text{Hemholtz function}: & F = U - TS \\ \text{Gibbs function}: & G = U + pV - TS \end{cases} \tag{5.1.1}$$

5.2 Differentials

Internal energy

The internal energy may be interpreted as the energy needed to create a system, with all its internal degrees of freedom. We find that:

$$dU = TdS - pdV \tag{5.2.1}$$

$$= \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{5.2.2}$$

which implies:

$$\begin{cases} T = \left(\frac{\partial U}{\partial S}\right)_V \\ p = -\left(\frac{\partial U}{\partial V}\right)_S \end{cases} \tag{5.2.3}$$

This suggests that we use S, V as the pair of independent thermodynamic variables to define the internal energy. Such pairs will be known as **natural variables**.

> **Definition: Natural variables**
>
> The natural variables of a quantity are a set of independent thermodynamic variables that fully specify it through partial differentiation.

Enthalpy

Enthalpy is interpreted as the energy needed to create a system and the work needed to make space for it, at constant pressure. It is therefore the heat released/absorbed by a system undergoing reversible isobaric processes. It is particularly useful in laboratories, where pressure is almost always held constant. We find that:

$$dH = TdS - pdV + pdV + Vdp \tag{5.2.4}$$
$$= TdS + Vdp \tag{5.2.5}$$
$$= \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \tag{5.2.6}$$

which implies:

$$\begin{cases} T = \left(\frac{\partial H}{\partial S}\right)_p \\ V = -\left(\frac{\partial H}{\partial p}\right)_S \end{cases} \tag{5.2.7}$$

Hemholtz function

The Hemholtz function may be interpreted as the maximum amount of work you can get out of a system at constant temperature and volume. Alternatively, it is the energy needed to create a system, minus the energy that can be supplied by the environment.

We find that:

$$dF = TdS - pdV - TdS - SdT \tag{5.2.8}$$
$$= -SdT - pdV \tag{5.2.9}$$
$$= \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial V}\right)_T dV \tag{5.2.10}$$

which implies:

$$\begin{cases} S = -\left(\frac{\partial F}{\partial T}\right)_V \\ p = -\left(\frac{\partial F}{\partial V}\right)_T \end{cases} \tag{5.2.11}$$

Gibb's function

Finally, we may interpret the Gibb's function as the energy needed to make a system and make room for it, minus the amount of work available from the surroundings. It is alternatively the maximum amount of work that may be performed at constant temperature

and pressure. We find that:

$$dG = TdS + Vdp - TdS - SdT \tag{5.2.12}$$

$$= Vdp - SdT \tag{5.2.13}$$

$$= \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \tag{5.2.14}$$

which implies:

$$\begin{cases} S = -\left(\frac{\partial G}{\partial T}\right)_p \\ V = \left(\frac{\partial G}{\partial p}\right)_T \end{cases} \tag{5.2.15}$$

In summary:

Potential	First law	Other fundamental variables
$U(S,V) = TS - pV$	$dU = TdS - pdV$	$\begin{cases} T = \left(\frac{\partial U}{\partial S}\right)_V \\ p = -\left(\frac{\partial U}{\partial V}\right)_S \end{cases}$
$H(S,p) = U + pV$	$dH = TdS + Vdp$	$\begin{cases} T = \left(\frac{\partial H}{\partial S}\right)_p \\ V = -\left(\frac{\partial H}{\partial p}\right)_S \end{cases}$
$F(T,V) = U - TS$	$dF = -SdT - pdV$	$\begin{cases} S = -\left(\frac{\partial F}{\partial T}\right)_V \\ p = -\left(\frac{\partial F}{\partial V}\right)_T \end{cases}$
$G(T,p) = U - TS + pV$	$dG = -SdT + Vdp$	$\begin{cases} S = -\left(\frac{\partial G}{\partial T}\right)_p \\ V = \left(\frac{\partial G}{\partial p}\right)_T \end{cases}$

5.3 Integrals under constant variable

Isochoric processes

At constant volume, we have an isochoric process. Here the internal energy U is the most useful, since the expression for U simplifies to:

$$dU = TdS \tag{5.3.1}$$

and

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q_{rev}}{\partial T}\right)_V \equiv C_V \tag{5.3.2}$$

. Therefore the internal energy change:

$$\Delta U = \int_{T_1}^{T_2} C_V dT \tag{5.3.3}$$

represents the heat reversibly absorbed by the system.

Isobaric processes

At constant pressure, we have an isobaric process. Here the enthalpy is the most useful, since the expression for H simplifies to:

$$dH = TdS \tag{5.3.4}$$

and

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial Q_{rev}}{\partial T}\right)_p \equiv C_p \tag{5.3.5}$$

so

$$\Delta H = \int_{T_1}^{T_2} C_p dT \tag{5.3.6}$$

is the heat reversibly absorbed by the system.

   (i) If heat enters the system, $\Delta H > 0$ and we have an **endothermic** reaction.

   (ii) If heat leaves the system, $\Delta H < 0$ and we have an **exothermic** reaction.

Isothermal processes

At constant temperature, we have an isothermal process. Here the hemholtz function is the most useful, since the expression for F simplifies to:

$$dF = -pdV \tag{5.3.7}$$

so:

$$\Delta F = \int_{V_1}^{V_2} -pdV \tag{5.3.8}$$

is the work done reversibly on the system (remember $dW = -pdV$ only for reversible processes).

Isothermal and isobaric processes

If we keep both pressure and temperature constant, then $dG = 0$ so that:

$$\Delta G = 0 \tag{5.3.9}$$

so the Gibbs function is a conserved quantity.

Note that if we know any one of the thermodynamic potentials, we get the other free for free. Consider for example the case where the Hemholtz free energy $F(T,V)$ is known. Then we have found that:

$$\begin{cases} S = -\left(\frac{\partial F}{\partial T}\right)_V \\ p = -\left(\frac{\partial F}{\partial V}\right)_T \end{cases} \tag{5.3.10}$$

The internal energy is then:

$$U(S,V) = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V \tag{5.3.11}$$

and similarly the enthalpy will be:

$$H(S,p) = U + pV = F - T\left(\frac{\partial F}{\partial T}\right)_V - \left(\frac{\partial F}{\partial V}\right)_T \tag{5.3.12}$$

Finally the Gibbs free energy will be:

$$G(T,p) = F + pV = F - V\left(\frac{\partial F}{\partial V}\right)_T = -V^2\frac{\partial}{\partial V}\left(\frac{F}{V}\right)_T \tag{5.3.13}$$

5.4 Legendre transformations

The Legendre Transformations

Consider a function $f(x)$ such that $\frac{df}{dx} = u(x)$ with $u(x)$ invertible. Let us then define:

$$g(u) = f(x(u)) - u \cdot x(u) \implies \frac{dg}{du} = x(u) \tag{5.4.1}$$

One calls f and g **Legendre transforms** of each other, and to transform from one to the other we simply exchange $x \longleftrightarrow u$. Legendre transforms are such that their derivatives are inverses of each other.

Let us take for example $f(x) = x^3$. Then $f'(x) = u(x) = 3x^2 \implies x(u) = \sqrt{\frac{u}{3}}$ and hence $g(u) = \left(\sqrt{\frac{u}{3}}\right)^3 - u\sqrt{\frac{u}{3}} = \left(\frac{u}{3}\right)^{3/2}$. Hence the Legendre transform of f will be $g(x) = \left(\frac{x}{3}\right)^{3/2}$, which is indeed $f(x(u))$.

Legendre transformations are particularly relevant when discussing thermodynamic potentials, which are all Legendre transforms of each other.

Indeed, starting from $dU = TdS - pdV$ suppose we wish to instead find some potential H with natural variables S, p rather than S, V. Then we clearly must interchange p, V, and we may do so by applying the Legendre transformation with $x = -p$ and $u = V$. We find that:

$$dH = dU + d(pV) = TdS - pdV + pdV + Vdp = TdS + VdP \tag{5.4.2}$$

as we found earlier. This process can be repeated to find the other potentials.

Not only, suppose we had a system with more than two degrees of freedom, such as a rod. In the next chapter we will see that the first law reads:

$$dU = TdS + fdL - pdV \tag{5.4.3}$$

Suppose we want a new potential X with natural variables T, L, p rather than S, L, V.

Then we must write that:

$$dX = TdS + fdL - pdV - d(TS) + d(pV) = -SdT + fdL + Vdp \tag{5.4.4}$$

implying that we use:

$$X = U - TS + pV \tag{5.4.5}$$

5.5 Equilibrium conditions

It is still unclear how these quantities may be put to use effectively. We will see however that the thermodynamic potentials provide an effective way to define how equilibrium may be reached in different conditions.

Consider a system with T, p absorbing heat $đQ$. The entropy of the surroundings changes by $dS_0 = -\frac{đQ}{T}$, where all the heat exchange is reversible since the surroundings are in thermal equilibrium. Since $dS_{tot} = dS_0 + dS \geq 0$, where dS is the change in entropy of the system, we must have that $TdS \geq đQ$. Using the first law:

$$đW \geq dU - TdS \tag{5.5.1}$$

Now notice that $đW = -p_0 dV + đW_{mech}$ where $đW_{mech}$ is any mechanical work that can be done on the system, and $-p_0 dV$ is the work done by the surroundings on the system as its volume changes.

So, we find that:

$$đW_{mech} \geq dU + p_0 dV - T_0 dS = d(U + p_0 V - T_0 S) \tag{5.5.2}$$

since p_0, T_0 are constants (the surroundings are in thermodynamic equilibrium).

Definition: Availability

We define the availability as:

$$\boxed{A \equiv U + p_0 V - T_0 S} \tag{5.5.3}$$

which is the maximum amount of work which we can extract from a system in surroundings with temperature T_0 and pressure p_0.

To see why we can interpret the avialability as such, suppose we have a system with temperature T and pressure p fitted with a piston, in surroundings with temperature T_0 and pressure p_0. The maximum amount of work is extracted when the process is reversible, hence when:

$$dU = TdS - pdV \tag{5.5.4}$$

and thus

$$dA = (T - T_0)dS - (p - p_0)dV \tag{5.5.5}$$

The second term is the net mechanical work done on the piston through a change of volume. To see the significance of the first term, suppose we run a reversible Carnot engine between

the system and the surroundings. We must have that the work done by the engine be:

$$dW_e = T_0 dS - T dS = -(T - T_0) dS \tag{5.5.6}$$

Therefore the first term represents the maximum work we may extract from the system through a change of entropy.

We can finally write:

$$\boxed{dW \geq dA} \tag{5.5.7}$$

so the mechanical work done on a system must always be greater than or equal to the available work the system can do. Normally, the system is mechanically isolated, so we may write:

$$dA \leq 0 \tag{5.5.8}$$

Equilibrium is reached when $dA = 0$, that is, when we minimize A, as a direct result of maximizing the global entropy (we started with the inequality $dS_{tot} \geq 0$).

In the following we consider mechanically isolated systems, so that we may assert $dA \leq 0$.

Thermally isolated system at constant volume

No heat can leave, and the volume can't change so that no work can be done by the system. Therefore $dU = 0$ and so $dA = -T_0 dS$, the availability is minimized when the system's **entropy is maximum**.

Thermally isolated system at constant pressure

Since no heat can leave we have that $dS = 0$, as well as $dp = 0$ due to the constant pressure constraint. Hence $dA = dU + p_0 dV = dU + p dV + V dp = dH$. Consequently, the availability is minimized when the system's **Enthalpy is minimum**.

Constant volume and temperature

Since $dV = 0$ and $dT = 0$ we have that $dA = dU - T_0 dS = dU - T dS = dF$. Consequently the availability is minimized when the system's **Helmholtz function is minimum**

5.5.1 Constant pressure and temperature

We have that $dp = dT = 0$ so $dA = dU + p_0 dV - T_0 dS = dU + p dV + T dS = dG$, the availability is minimized when the system's **Gibb's function is mimimum**.

Note that these conditions are all equivalent formulations of the maximum *global* entropy principle, but are more or less useful in different situations where different constraints are imposed.

Our set of equilibrium conditions therefore reads:

$$dS = 0, \ dV = 0, \ dU = 0 \tag{5.5.9}$$

$$dS = 0, \ dp = 0, \ dH = 0 \tag{5.5.10}$$

$$dT = 0, \ dV = 0, \ dF = 0 \tag{5.5.11}$$

$$dT = 0, \ dp = 0, \ dG = 0 \tag{5.5.12}$$

If any two of the quantities in an above row is specified and kept constant, then the third must be minimized (or maximized for entropy). We therefore get the following conditions (only the most useful) for equilibria:

Variables	Equilibrium condition
T, p	G minimized
T, V	F minimized
U, V	S maximized
S, p	H minimized

5.6 Connecting the potentials: Maxwell's relations

Consider a state function $f(x, y)$, then we may write that:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = F_x dx + F_y dy \tag{5.6.1}$$

where $F_x = \left(\frac{\partial f}{\partial x}\right)_y$ and $F_y = \left(\frac{\partial f}{\partial y}\right)_x$. Also, by symmetry of the second derivative:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{5.6.2}$$

so that:

$$\left(\frac{\partial F_x}{\partial y}\right)_x = \left(\frac{\partial F_y}{\partial x}\right)_y \tag{5.6.3}$$

We can apply this idea to the thermodynamic potentials to obtain Maxwell's relations.

For example, the Maxwell relation based on G, the Gibb's function, can be found as follows. Firstly, we write down the exact differential equation:

$$dG = -SdT + V\,dp \tag{5.6.4}$$

Hence:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \tag{5.6.5}$$

Repeating this for the other three potentials, we find that:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \qquad (5.6.6\text{a})$$

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad (5.6.6\text{b})$$

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \qquad (5.6.6\text{c})$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (5.6.6\text{d})$$

To remember these, the following mnemonic may be used:

(i) Cross mutliplication of the variables gives $(TS) = (pV)$.

(ii) Opposite pairs of variables (both in numerator or both in denominator) are set as constants.

(iii) The sign is positive when T appears with p in the derivative.

The Maxwell's equations are supremely powerful, because they relate partial differentials that are easy to measure, shown to the right of the equality, with partial differentials that are very difficult to measure shown to the left of the equality.

Example. Find expressions for $\left(\frac{\partial C_p}{\partial p}\right)_T$ and $\left(\frac{\partial C_V}{\partial V}\right)_T$.

Solution   Firstly, note that:

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \qquad (5.6.7)$$

Also:

$$dU = đQ + dW = TdS - pdV \qquad (5.6.8)$$

Taking the volume to be constant and differentiating with respect to temperature

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad (5.6.9)$$

Since in a reversible process $dU = dQ$, we find that:

$$\left(\frac{\partial Q}{\partial T}\right)_V = C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad (5.6.10)$$

and similarly:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad (5.6.11)$$

Therefore:

$$\left(\frac{\partial C_p}{\partial V}\right)_T = \left[\frac{\partial}{\partial p}T\left(\frac{\partial S}{\partial T}\right)_p\right]_T \tag{5.6.12}$$

$$= T\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial p}\right)_T\right]_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{5.6.13}$$

Similarly:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V \tag{5.6.14}$$

◀

In general, the following strategies may help in solving problems regarding Maxwell's relations:

(i) write down the differential of a thermodynamic potential:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{5.6.15}$$

(ii) use the reciprocal theorem:

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} \tag{5.6.16}$$

(iii) Use the reciprocity theorem:

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{5.6.17}$$

(iv) Use the heat capacities:

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V, \ \ \frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p \tag{5.6.18}$$

(v) Define a generalized susceptibility as how a variable changes when a generalized force, a variable which is a partial derivative of the internal energy, such as T or p.

$$\begin{cases} \text{Isobaric expansivity :} & \beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\[2mm] \text{Adiabatic expansivity :} & \beta_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \\[2mm] \text{Isothermal compressibility :} & \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \\[2mm] \text{Adiabatic compressibility :} & \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \end{cases} \tag{5.6.19}$$

Note the expansivities express fractional change in volume as temperature varies, whereas compressibilities fractional change in volume as pressure varies.

Example. Show that $C_p - C_V = \frac{VT\beta_p^2}{\kappa_T}$ by considering $S = S(T, V)$.

Solution We begin by writing the differential entropy as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad (5.6.20)$$

so that:

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad (5.6.21)$$

Using Maxwell's relations and the reciprocity theorem:

$$\left(\frac{\partial S}{\partial V}\right)_T = +\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad (5.6.22)$$

so that:

$$\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = \frac{(V\beta_p)^2}{V\kappa_T} = \frac{V\beta_p^2}{\kappa_T} \qquad (5.6.23)$$

Finally we find that:

$$C_p - C_V = T\left[\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] = \frac{VT\beta_p^2}{\kappa_T} \qquad (5.6.24)$$

as desired. ◀

Example. Find the entropy of 1 mole of ideal gas.

Solution For this quantity of an ideal gas, the state equation is $pV = RT$. Hence, we may write $S = S(T, V)$, or, in differential form:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad (5.6.25)$$

$$= \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV \qquad (5.6.26)$$

Also:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\partial}{\partial T} \frac{RT}{V} = \frac{R}{V} \qquad (5.6.27)$$

so that:

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV \qquad (5.6.28)$$

which upon integration gives:

$$S = C_V \ln T + R \ln V + cnst \qquad (5.6.29)$$

◀

Rods, bubbles and gases

6.1 Elastic materials

We look at a rod of cross-section A and length L, held at a constant temperature T. If the rod is made of elastic material, then it can be placed under tension df. We then define the isothermal Young's modulus E_T as the ratio of stress $\sigma = df/A$ and strain $\epsilon = dL/L$, so:

$$E_T = \frac{L}{A}\left(\frac{\partial f}{\partial L}\right)_T \tag{6.1.1}$$

We also define the linear expansivity as:

$$\alpha_f = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_f \tag{6.1.2}$$

It follows that a wire held at constant length is characterized by a tension-temperature relation:

$$\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial f}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_f = -AE_T\alpha_f \tag{6.1.3}$$

So, for a material with positive linear expansivity, tension decreases as tempearture increases. This effect is particularly familiar to stringed-instrument players, where the metal strings slacken when placed in hot environments.

Rubber bands, on the other hands, have negative expansivity, so that as we increase the temperature, the tension too increases. Consequently, if we hang a weight at the end of a rubber band, and subsequently heat it up, the increase in tension will cause the weight to rise.

Further, we may work with the Hemholtz potential and write:

$$dF = -SdT + fdL = -\left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial f}{\partial L}\right)_T dL \tag{6.1.4}$$

implying that:

$$S = -\left(\frac{\partial S}{\partial T}\right)_L \tag{6.1.5}$$

$$f = \left(\frac{\partial f}{\partial L}\right)_T \tag{6.1.6}$$

Following the derivation of the Maxwell relations, we may then write:

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L = AE_T\alpha_f \tag{6.1.7}$$

Therefore, for materials such as a metal wire, the act of stretching it isothermally results in an increase in entropy. Indeed, the expansion distorts the crystallites which were previously carefully aligned in a steady state.

More specifically, in the case of an isothermal, reversible extension, the heat absorbed is:

$$\Delta Q = T\Delta S = AE_T T\alpha_f \Delta L \tag{6.1.8}$$

However, in the case of a rubber band, $\alpha_f < 0$, so that an isothermal extension results in entropy decrease. Indeed, unlike the case of metal wires, the rubber molecules are initially coiled up, and stretching it aligns these molecules introducing more order to the system and reducing entropy.

One can indeed show that increasing the link distance between rubber molecules decreases the entropy.

One final consideration that must be made is what happens to the internal energy of the rod when it is extended isothermally?

We can write the first law of thermodynamics as:

$$dU = TdS + fdL \implies \left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + f = ATE_T\alpha_f + f \tag{6.1.9}$$

This term is the sum of the work done on the rod by the tension force, and the heat flowing into the rod due to the change of length.

6.2 Surface tension

Consider the surface of some liquid surface of area A. To change the area of the surface by dA, work must be done against the cohesive forces of the interface. This work can be quantified as:

$$dW = \gamma dA \tag{6.2.1}$$

where γ is known as the surface tension. Now consider the set up shown below, with a piston pushing down and doing work $dW = pdV$ on an incompressible liquid.
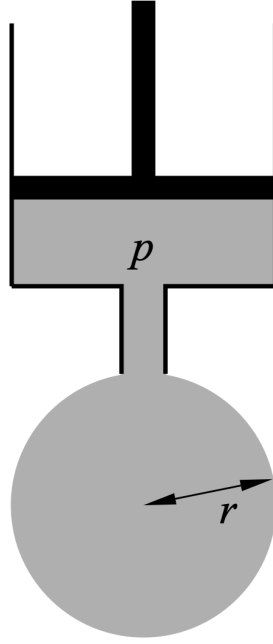
Figure 6.1. Piston pushing on spherical droplet held by surface tension

The liquid forms a spherical droplet suspended from the end of a thin pipe connected to the piston, whose change in volume is $dV = 4\pi r^2 dr$. Then:

$$dA = 4\pi(r + dr)^2 - 4\pi r^2 \approx 8\pi r dr \implies dW = 8\pi\gamma r dr \tag{6.2.2}$$

At the same time, $dW = pdV = 4\pi p r^2 dr$, and equating the two expressions for the work done we find that:

$$8\pi\gamma r dr = 4\pi p r^2 dr \implies p = \frac{2\gamma}{r} \tag{6.2.3}$$

This is the pressure difference between inside and outside the droplet.

For the case of a spherical bubble, then the surface tension acts on two surfaces. Hence, $da = 16\pi\gamma r dr$ and thus the pressure difference is $p = \frac{4\gamma}{r}$.

The first law of thermodynamics for our surface takes the following form:

$$dU = TdS + \gamma dA \tag{6.2.4}$$

so that:

$$\left(\frac{\partial U}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T + \gamma \tag{6.2.5}$$

The Hemholtz function can be written as:

$$dF = -SdT + \gamma dA \tag{6.2.6}$$

The Maxwell's relation deriving from these expressions is:

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_A \tag{6.2.7}$$

Therefore, (6.2.5) can be written as:

$$\left(\frac{\partial U}{\partial A}\right)_T = \gamma - \left(\frac{\partial \gamma}{\partial T}\right)_A \tag{6.2.8}$$

Note that usually, surface tension decreases as we increase temperature, so that both terms in the above expression are positive. The first term describing the energy flowing in the surface due to the external work, and the second expressing the heat flow into the surface.

For an isothermal stretching of a surface, the heat absorbed by the surface is:

$$\Delta Q = T\left(\frac{\partial S}{\partial A}\right)_T \Delta A = -T\Delta A\left(\frac{\partial \gamma}{\partial T}\right)_A > 0 \tag{6.2.9}$$

6.3 Magnetization

We know from the electromagnetism course that the work supplied to a magnetic dipole immersed in a magnetic field $d\mathbf{B}$ is:

$$dW = -\mathbf{m} \cdot d\mathbf{B} \tag{6.3.1}$$

A system of non-interacting magnetic moments is called a paramagnet. When we apply a magnetic field in the vicinity of a paramagnet, these magnetic moments line up exhibiting paramagnetism.

The first law of thermodynamics can then be written as:

$$dU = TdS - mdB \tag{6.3.2}$$

where $m = MV$ is the magnetic moment, M the magnetization and V the volume. B, the magnetic field is expressed as $B = \mu_0(H + M)$. The magnetic susceptibility is defined as:

$$\chi = \lim_{H\to 0} \frac{M}{H} \tag{6.3.3}$$

and is usually much much smaller than 1. Consequently $B \approx \mu_0 H$, and the suscepbility may be approximated as:

$$\chi \approx \frac{\mu_0 M}{B} \tag{6.3.4}$$

Now the Hemholtz differential may be expressed as:

$$dF = -SdT - mdB \tag{6.3.5}$$

yielding:

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \approx \frac{VB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B \qquad (6.3.6)$$

Therefore for an isothermal change of the magnetic field:

$$\Delta Q = T\left(\frac{\partial S}{\partial B}\right)_T \Delta B = \frac{TVB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B \qquad (6.3.7)$$

Now, paramagnetic systems obey Curie's law $\chi \propto \frac{1}{T}$ as shall be shown later. It follows that $\left(\frac{\partial \chi}{\partial T}\right)_B < 0$ and that consequently $\Delta Q < 0$, heat is emitted by the paramagnet.

The change in temperature in an adiabatic change, instead, is:

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_B\left(\frac{\partial S}{\partial B}\right)_T \qquad (6.3.8)$$

where we used the reciprocity theorem. Since by definition:

$$C_B = T\left(\frac{\partial S}{\partial T}\right)_B \qquad (6.3.9)$$

we may finally write:

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{TVB}{\mu_0 C_B}\left(\frac{\partial \chi}{\partial T}\right)_B > 0 \qquad (6.3.10)$$

It follows that adiabatic demagnetization leads to a drop in temperature. This method may be used in experiments requiring temperatures as low as mK or even μK

Our physica intuition backs up this result. Indeed, consider a sample of paramagnetic material. Before applying a magnetic field, all the magnetic moments have a stochastic distribution (assuming there is no interaction between them). As we apply a magnetic field, the moments will tend to line up, decreasing the entropy of the system. However, as we raise the temperature, the thermal energy $k_B T$ begins to contrast the magnetic energy, until at some point we reach a random distribution again. This state is characterized by a very high entropy.

At a low temperature instead, all the magnetic moments align. The ways we can arrange the system is therefore unique, and hence:

$$S = k_B \ln \Omega = k_B \ln 1 = 0 \qquad (6.3.11)$$

as required.

How does this magnetic cooling occur? The typical process is depicted below:

Firstly, $(a \to b)$ isothermal magnetization is initiated. At constant temperature, the paramagnetic material is subjected to an increasing magnetic field. This leads to a decrease in entropy.
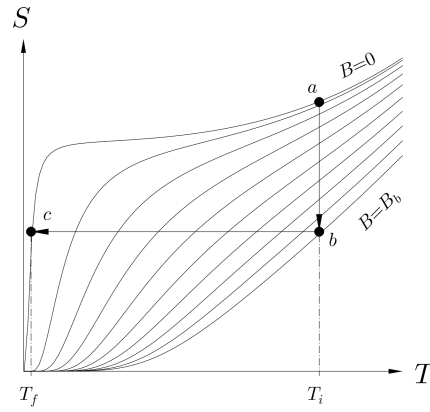
Then, $(b \rightarrow c)$ adiabatic demagnetization occurs. The sample is thermally isolated and the magnetic field is slowly reduced to zero. This lowers the temperature of the paramagnet, while keeping the entropy constant.

How does this entropy remain the same? In truth, there is an entropy exchange between the phonons holding together the lattice and the spins of the magnetic moments. As we lower the magnetic field the phonons, the so-called "spring forces" holding together the molecules in the lattice, lose entropy, and exchange it to the magnetic moments, the spin, of the paramagnet, which randomize their orientation.

Part II

Kinetic Theory of Gases

Speed distribution

7.1 Energetic considerations

Consider a sample of gas, constituted by N molecules which we shall model as particles of mass m moving with velocity $\boldsymbol{v} = (v_x, v_y, v_z)$. Ignoring rotational and vibrational degrees of freedom, the mean energy of is due only to the mean kinetic energy, thus:

$$\langle E \rangle = N \langle \frac{mv^2}{2} \rangle \tag{7.1.1}$$

Suppose the gas overall is moving with velocity $\langle \boldsymbol{v} \rangle = \boldsymbol{u}$. Then, we define the individual velocity of a molecule in this gas as $\boldsymbol{w} = \boldsymbol{v} - \boldsymbol{u}$, that is, the velocity of the molecule as viewed in the frame moving with the gas. Then, since $\langle \boldsymbol{w} \rangle = 0$ by definition, we find that:

$$\langle E \rangle = \frac{Nm}{2} \langle |\boldsymbol{u} + \boldsymbol{w}|^2 \rangle = \frac{Mu^2}{2} + N \langle \frac{mw^2}{2} \rangle \tag{7.1.2}$$

where $M = Nm$ is the mass of the entire gas. The first term is clearly the kinetic energy of the entire system, this is the one we commonly associate with energy. However, there is an additional energy due to the particle's random motion. This is the internal energy we studied in classical thermodynamics, which is only visible when studying the gas at a microscopic scale.

If we assume that $\boldsymbol{u} = 0$ by changing frame of reference, then:

$$\langle E \rangle = U = N \langle \frac{mw^2}{2} \rangle \tag{7.1.3}$$

How does this compare with the exact energy of the gas? The exact energy is just the sum of the kinetic energy of each molecule, hence:

$$E = \sum_i \frac{mv_i^2}{2} \tag{7.1.4}$$

so that:

$$N \langle \frac{mw^2}{2} \rangle = \sum_i \langle \frac{mv_i^2}{2} \rangle \tag{7.1.5}$$

Now, since v_i and v_j are independent for different particles, $\langle f(v_i)g(v_j)\rangle = \langle f(v_i)\rangle \langle g(v_j)\rangle$. Note that:

$$E^2 = \left(\sum_i \frac{mv_i^2}{2}\right)^2 = \sum_{i,j} \frac{m^2 v_i^2 v_j^2}{4} \neq \sum_i \left(\frac{mv_i^2}{2}\right)^2 \tag{7.1.6}$$

Keeping this in mind, we get that:

$$\langle E^2\rangle - U^2 = \sum_{i,j}\left\langle \frac{m^2 v_i^2 v_j^2}{4}\right\rangle - \left(\sum_i \left\langle \frac{mv_i^2}{2}\right\rangle\right)^2 \tag{7.1.7}$$

$$= \sum_i \left\langle \frac{m^2 v_i^4}{4}\right\rangle + \sum_{i\neq j}\left\langle \frac{mv_i^2}{2}\right\rangle\left\langle \frac{mv_j^2}{2}\right\rangle - \left(\sum_i \left\langle \frac{mv_i^2}{2}\right\rangle\right)^2 \tag{7.1.8}$$

$$= N\left\langle \frac{m^2 v^4}{4}\right\rangle + N(N-1)\left\langle \frac{mv^2}{2}\right\rangle^2 - \left(N\left\langle \frac{mv^2}{2}\right\rangle\right)^2 \tag{7.1.9}$$

$$= \frac{Nm^2}{4}(\langle v^4\rangle - \langle v^2\rangle^2) \tag{7.1.10}$$

Hence the standard deviation in the energy is:

$$\sigma_E = \sqrt{\langle E^2\rangle - \langle E\rangle^2} = \sqrt{\frac{Nm^2}{4}(\langle v^4\rangle - \langle v^2\rangle^2)} \tag{7.1.11}$$

The relative error is then:

$$\frac{\sigma_E}{U} = \frac{\sqrt{\frac{Nm^2}{4}(\langle v^4\rangle - \langle v^2\rangle^2)}}{N\left\langle \frac{mv^2}{2}\right\rangle} = \frac{1}{\sqrt{N}}\sqrt{\frac{\langle v^4\rangle}{\langle v^2\rangle^2} - 1} \tag{7.1.12}$$

For large numbers of particles, this relative error is very very small. Hence, we can indeed regard large distributions of particles as sharply peaked near $\langle E\rangle$. In other words, as the number of particles increases, the relative amount that each individual particle's properties varies from the averaged value of the property decreases. This is exactly the prediction made by taking the thermodynamic limit.

7.2 Pressure

Consider a container immersed in a gas, how can we model the pressure exerted on the walls of the container?

Let's assume that the particles hitting the wall are colliding elastically, and let the z-axis be aligned with the normal to one of the container walls. Then, the velocity components of any given particle before and after the collision are given by:

$$v_z^{\text{after}} = -v_z^{\text{before}} \implies \Delta p_m = 2mv_z \tag{7.2.1}$$

where Δp_m, not to be confused with pressure, is the change in momentum. For the sample of $N(v_z)$ particles whose v_z lie in the infinitesimal interval $[v_z, v_z + dz]$, we define the

differential particle flux as:

$$d\Phi(v_z) = \frac{dN(v_z)}{At} \tag{7.2.2}$$

that is, the number of particles with such speeds hitting the box per unit time per unit area. Their contribution to the pressure is:

$$dp(v_z) = \underbrace{\frac{\Delta p_m N(v_z)}{t}}_{\text{force on wall}} \frac{1}{A} = 2mv_z d\Phi(v_z) \tag{7.2.3}$$

Suppose the ratio of particles with speed in the interval $[v_z, v_z + dv_z]$ is given by $f(v_z)dv_z$, so that:

$$N(v_1, v_2) = \int_{v_1}^{v_2} f(v_z)dv_z \tag{7.2.4}$$

is the number of particles with speed between v_1 and v_2. It is the probability density function of velocities, also known as the **velocity distribution**. Then, $dN(v_z)$ is the density of particles in the gas, $n = \frac{N}{V}$, times the volume in which the particles must reside for them to hit the container in time t, Av_zt, times the ratio of particles with speed in the interval $[v_z, v_z + dv_z]$, $f(v_z)dv_z$:

$$dN(v_z) = Av_zt \cdot n \cdot f(v_z)dv_z \tag{7.2.5}$$

Inserting this into (7.2.2) we find:

$$dp(v_z) = 2mnv_z^2 f(v_z)dv_z \tag{7.2.6}$$

and integrating for all particles (so with v_z ranging from 0, still particles, to ∞):

$$p = \int_0^\infty 2mnv_z^2 f(v_z)dv_z = \int_{-\infty}^\infty mnv_z^2 f(v_z)dv_z = mn \langle v_z \rangle^2 \tag{7.2.7}$$

where we assumed that the velocity distribution is symmetrical, $f(v_z) = -f(v_z)$. This is justified by the fact that there should be no preferred motion for the particles to move. Alternatively, one could also consider a rotation in frame of reference, observing a particle hitting the container's wall from two opposite points of view makes no change physically.

In three dimensions, we can introduce the velocity distribution $f(\boldsymbol{v})$. The derivation is exactly the same, and we find that:

$$\boxed{p = mn \int v_z^2 f(\boldsymbol{v})d^3\boldsymbol{v} = mn \langle v_z^2 \rangle} \tag{7.2.8}$$

Furthermore, for isotropic distributions, where, in addition to orientations, no directions are preferred, then:

$$\langle v_z^2 \rangle = \langle v_x^2 \rangle = \langle v_y^2 \rangle = \frac{1}{3} \langle v^2 \rangle \tag{7.2.9}$$

so the pressure is:

$$p = \frac{1}{3}mn \langle v^2 \rangle \tag{7.2.10}$$

The internal energy is:

$$U = \frac{1}{2}mN\langle v^2\rangle = \frac{3pV}{2} \iff \boxed{p = \frac{2U}{3V} = \frac{2}{3}u} \qquad (7.2.11)$$

where u is the energy density.

Moreover, isotropy forces the velocity distribution to be independent of direction. Using spherical coordinates in the (v_x, v_y, v_z)-space:

$$f(\boldsymbol{v}) \to f(v, \theta, \phi) \qquad (7.2.12)$$

and thus:

$$f(\boldsymbol{v})dv_x dv_y dv_z = f(\boldsymbol{v})\left|\frac{\partial(v_x, v_y, v_z)}{\partial(v, \theta, \phi)}\right|dv d\theta d\phi \qquad (7.2.13)$$

$$= f(\boldsymbol{v})v^2 \sin\theta \, dv d\theta d\phi = f(v, \theta, \phi)dv d\theta d\phi \qquad (7.2.14)$$

implying that:

$$f(v, \theta, \phi) = f(\boldsymbol{v})v^2 \sin\theta \qquad (7.2.15)$$

The particle speed distribution is then:

$$\boxed{g(v) = \int_0^\pi \int_0^{2\pi} f(v, \theta, \phi)d\phi d\theta = 4\pi v^2 f(\boldsymbol{v})} \qquad (7.2.16)$$

We can use some geometric insight to get to the same result. In the velocity space, the ratio of particles with speed between v and $v + dv$ is given by the volume of the spherical shell of width dv:

$$g(v)dv = 4\pi v^2 dv \cdot f(\boldsymbol{v}) \qquad (7.2.17)$$

coinciding with the results found above.

Example. Let us consider an anisotropic system, where there exists one special direction in space (call it z), which affects the distribution of particle velocities.
   a) What is the expression for pressure $p_{\parallel}$ on the wall perpendicular to the z-axis?
      What is the expression for pressure $p_{\perp}$ on a wall parallel to the z-axis?
   b) What is a pressure normal to z at an angle θ?

Solution   a) Since we now have a special direction z, we may use cylindrical coordinates- The velocity distribution will depend on v_s and v_z. Then:

$$f(\boldsymbol{v}) = dv_x dv_y dv_z = f(\boldsymbol{v})v_s d\phi dv_s dv_z \qquad (7.2.18)$$

The pressure on a wall with normal along z evaluates to:

$$P = mn\langle v_z^2\rangle \qquad (7.2.19)$$

For a wall whose normal is parallel to z instead, we need to repeat our calcula-

tions, but this time with $v_z \mapsto v_s$. We find that:

$$\Delta p = 2mv_s \implies dP(v_s) = 2mv_s d\Phi(v_s) \tag{7.2.20}$$

Since $d\Phi(v_s) = v_s n f(v_s) dv_s$ we get $dP(v_s) = 2mv_s^2 n f(v_s) dv_s$. Finally, using the fact that the distribution in xy plane is isotropic, $f(v_s) = f(-v_s)$:

$$P = mn \int_{-\infty}^{\infty} v_s^2 f(v_s) dv_s = mn \langle v_s^2 \rangle \tag{7.2.21}$$

b) Consequently, for a wall at an angle θ to z.

$$P = P_\parallel \cos\theta + P_\perp \sin\theta \tag{7.2.22}$$
$$= mn(\langle v_z^2 \rangle \cos\theta + \langle v_s^2 \rangle \sin\theta) \tag{7.2.23}$$

where we decomposed the pressure on the wall into a component along z and perpendicular to z.

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7.3   Deriving the Boltzmann velocity distribution

We now face the task of determining what form $f(\boldsymbol{v})$ takes. We will assume that:

(i) particle-particle interactions are negligible, except for ideal elastic collisions

(ii) they are point particles

(iii) classical, non-relativistic particles

Suppose then that we have taken this gas in a container of volume V, and we have waited for macroscopic equilibrium to occur, so that the velocity distribution is time-independent.

We can argue that in space there are no preferred directions, so we can use isotropy. Moreover, we may also argue that the velocity vector's components must be independent:

$$f(\boldsymbol{v}) = g(v_x^2)g(v_y^2)g(v_z^2) = h(v^2) \iff \ln\Big(g(v_x^2)g(v_y^2)g(v_z^2)\Big) = \ln h(v^2) \tag{7.3.1}$$

If we let $\phi(v_x^2) = \ln g(v_x^2)$ and $\varphi(v^2) = \ln h(v^2)$:

$$\phi(v_x^2) + \phi(v_y^2) + \phi(v_z)^2 = \varphi(v_x^2 + v_y^2 + v_z^2) \tag{7.3.2}$$

If we take the derivative with respect to v_x^2:

$$\partial v_x^2 \phi(v_x^2) = \partial v_x^2 \varphi(v_x^2 + v_y^2 + v_z^2) \tag{7.3.3}$$

Similarly:

$$\partial v_y^2 \phi(v_x^2) = \partial v_y^2 \varphi(v_x^2 + v_y^2 + v_z^2) = \partial v_x^2 \varphi(v_x^2 + v_y^2 + v_z^2) \tag{7.3.4}$$

and

$$\partial v_z^2 \phi(v_x^2) = \partial v_z^2 \varphi(v_x^2 + v_y^2 + v_z^2) = \partial v_x^2 \varphi(v_x^2 + v_y^2 + v_z^2) \tag{7.3.5}$$

implying that:

$$\partial_{v_x^2}\phi(v_x^2) = \partial_{v_y^2}\phi(v_y^2) = \partial_{v_z^2}\phi(v_z^2) = \qquad (7.3.6)$$

The only possible family of functions ϕ satisfying (7.3.6) are functions linear in their argument (we use $-\alpha$ as a convention, it turns out that α is positive):

$$\phi(v_x^2) = -\alpha v_x^2 + \beta, \ \ \phi(v_y^2) = -\alpha v_y^2 + \beta, \ \ \phi(v_z^2) = -\alpha v_z^2 + \beta, \qquad (7.3.7)$$

so that:

$$\varphi(v^2) = -\alpha v^2 + 3\beta \qquad (7.3.8)$$

Thus:

$$f(\boldsymbol{v}) = e^{3\beta}e^{-\alpha v^2} = ce^{-\alpha v^2} \qquad (7.3.9)$$

We can now use the normalization condition:

$$1 = \int f(\boldsymbol{v})d^3\boldsymbol{v} \qquad (7.3.10)$$

$$= c \int e^{\alpha v_x^2}dv_x \int e^{\alpha v_y^2}dv_y \int e^{\alpha v_z^2}dv_z \qquad (7.3.11)$$

$$= c\left(\frac{\pi}{\alpha}\right)^{3/2} \qquad (7.3.12)$$

$$\iff c = \left(\frac{\alpha}{\pi}\right)^{3/2} \qquad (7.3.13)$$

Thus, the velocity distribution becomes:

$$f(\boldsymbol{v}) = \left(\frac{\alpha}{\pi}\right)^{3/2}e^{\alpha v^2} \qquad (7.3.14)$$

Let us analyze the dimensions of α. Clearly, $\frac{1}{\sqrt{\alpha}} = v_{th}$ where v_{th} is some velocity characteristic of our gas sample. Then:

$$\boxed{f(\boldsymbol{v}) = \frac{1}{(\sqrt{\pi}v_{th})^3}e^{-v^2/v_{th}^2}} \qquad (7.3.15)$$

and the related speed distribution is:

$$\boxed{g(v) = \frac{4\pi v^2}{(\sqrt{\pi}v_{th})^3}e^{-v^2/v_{th}^2}} \qquad (7.3.16)$$

Note that:

$$\langle v \rangle = \int_0^\infty v g(v) dv = \int_0^\infty \frac{4\pi v^3}{(\sqrt{\pi} v_{th})^3} e^{-v^2/v_{th}^2} dv \tag{7.3.17}$$

$$= \frac{4\pi v_{th}^4}{2(\sqrt{\pi} v_{th})^3} \tag{7.3.18}$$

$$= \frac{2}{\sqrt{\pi}} v_{th} \tag{7.3.19}$$

Moreover:

$$\frac{dg(v)}{dv} = \frac{4}{\sqrt{\pi} v_{th}} \frac{2 v e^{-v^2/v_{th}^2}(v_{th}^2 - v^2)}{v_{th}^2} = 0 \iff v = v_{th} \tag{7.3.20}$$

In other words, v_{th} is the most likely speed, since the speed distribution is peaked there.

Now note that:

$$P = \frac{1}{3} mn \int v^2 \frac{1}{(\sqrt{\pi} v_{th})^3} e^{-v^2/v_{th}^2} d^3\boldsymbol{v} = \frac{nmv_{th}^2}{2} \tag{7.3.21}$$

so we have that:

$$v_{th} = \sqrt{\frac{2P}{nm}} \tag{7.3.22}$$

For an ideal gas:

$$P = nk_B T \implies \boxed{\frac{mv_{th}^2}{2} = k_B T} \tag{7.3.23}$$

This is a monumental result. The temperature of an ideal gas is the kinetic energy of a particle moving with the most likely speed of the Maxwell speed distribution. Using this expression, the Maxwell distribution takes its final form:

$$\boxed{f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)} \tag{7.3.24}$$

Also, we may rewrite $\langle v \rangle$ as:

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \tag{7.3.25}$$

and similarly:

$$\langle v^2 \rangle = \frac{3k_B T}{m} \tag{7.3.26}$$

Then, we may retrieve the ideal gas law:

$$p = \frac{1}{3} Nm \langle v^2 \rangle = nk_B T \implies pV = Nk_B T \tag{7.3.27}$$

7.4 Effusion

We place an ideal gas in a container with a small hole in it. The diameter d of the hole is much smaller than the average path that particles travel between each collision, known as the particle mean free path λ_{mfp}. This ensures that the particles are removed randomly, without changing the overall velocity distribution.

The differential of the particle flux through the hole (which is the number of particles per unit area per unit time with velocities lying in $[\boldsymbol{v}, \boldsymbol{v} + d\boldsymbol{v}]$) is given by:

$$d\Phi(\boldsymbol{v}) = nv_z f(\boldsymbol{v})d^3\boldsymbol{v} = nv^3 f(\boldsymbol{v})dv \cos\theta \sin\theta d\theta d\phi \tag{7.4.1}$$

since $v_z = v\cos\theta$, and $d^3\boldsymbol{v} = v^2 \sin\theta dv d\theta d\phi$ for an isotropic distribution inside the container. For an isotropic sample, we may further assume that $f(\boldsymbol{v}) = f(v)$.

It follows that the distribution of the particles exiting the container is not isotropic, due to the extra $\cos\theta$ factor. This is physically interpreted by the fact that particles with a small θ, that is perpendicular to the wall with the hole, are more likely to be ejected. Similarly, the distribution is not Maxwellian due to the extra v factor, since faster particles are more likely to exit the container.

The flux of the particles with speed within $[v, v + dv]$ can be found by integrating[1]:

$$d\hat{\Phi}(v) = nv^3 f(v)dv \int_0^{\frac{\pi}{2}} d\theta \cos\theta \sin\theta \int_0^{2\pi} d\phi = \pi nv^3 f(v)dv = \frac{1}{4}nvg(v)dv \tag{7.4.2}$$

The total flux of effusing particles is then:

$$\Phi = \int_0^\infty dv \frac{1}{4}nvg(v) = \frac{1}{4}n\langle v\rangle \tag{7.4.3}$$

Since we assume a Maxwell speed distribution inside the container, we find that:

$$\boxed{\Phi = \frac{n}{4}\sqrt{\frac{8k_B T}{\pi m}} = \frac{P}{\sqrt{2\pi m k_B T}}} \tag{7.4.4}$$

This is the number of particles effusing per unit time, per unit area through the hole. The total effusion rate is given by $\Phi \cdot A$.

Example.
a) A gas effuses into a vacuum through a small hole of area A. and collimated by passing through a very small circular hole of radius a, in a screen a distance $d \gg a$ from the first hole. Calculate the rate at which particles emerge from the circular hole. b) Show that if a gas were allowed to leak into an evacuate sphere and the particles condensed where they first hit the surface they would form a uniform coating.

Solution   a) We know that the number of particles passing through the first hole

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[1]note that the upper limit for θ is $\frac{\pi}{2}$, since we only consider the particles moving towards the hole

per unit time is the particle flux times the surface of the first hole:

$$T' = \Psi \cdot a = \frac{1}{4} n A \langle v \rangle \tag{7.4.5}$$

The ratio of the particles which then pass through the second collimating hole is:

$$T = An \int_0^\infty v^3 \int_0^\pi \int_0^{\theta'} v f(v) \cdot v^2 \sin \theta \, dv \, d\theta \, d\phi \tag{7.4.6}$$

$$= 2\pi An \int_0^\infty v^3 f(v) \left[\frac{1}{2} \sin^2 \theta \right]_0^{\theta'} dv \tag{7.4.7}$$

$$= \frac{An}{4} \sin^2 \theta' \int_0^\infty v g(v) dv \tag{7.4.8}$$

$$= \frac{An \langle v \rangle}{4} \sin^2 \theta' \tag{7.4.9}$$

Since $d \gg a$, we may use small angle approximation to write $\sin \theta' \approx \frac{a}{d}$ so that:

$$T = \frac{An a^2 \langle v \rangle}{4 d^2} \tag{7.4.10}$$

b) The differential flux through the hole into the evcuated sphere is:

$$d\Phi = n v^3 f(v) \sin \theta \cos \theta \, dv \, d\theta \, d\phi \tag{7.4.11}$$

$$= \frac{1}{2} n v^3 f(v) \sin 2\theta \, dv \, d\theta \, d\phi \tag{7.4.12}$$

$$= \frac{1}{4} n v^3 f(v) \sin 2\theta' \, dv \, d\theta' \, d\phi \tag{7.4.13}$$

where $\theta' = 2\theta$. Taking the origin to be centered at the sphere's center, then we see that θ' becomes the angular measure and replaces θ. We see that this does indeed produce a uniform coating.

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Example. A gas is a mixture of hydrogen and deuterium in the proportion $7000 : 1$. As the gas effuses through a small hole from a vessel at constant temperature into a vacuum, the composition of the remaining mixture changes. By what factor will the pressure in the vessel have fallen when the remaining mixture consists of hydrogen and deuterium in the proportion $700 : 1$.

Solution The flux of particles effusing through the hole is:

$$\Phi_H = \frac{1}{4} n_H \langle v_H \rangle = n_H \sqrt{\frac{k_B T}{2\pi m_H}} = \frac{p_H}{\sqrt{2\pi m_H k_B T}} \tag{7.4.14}$$

$$\Phi_D = \frac{1}{4} n_D \langle v_D \rangle = n_D \sqrt{\frac{k_B T}{2\pi m_D}} = \frac{p_D}{\sqrt{2\pi m_D k_B T}} \tag{7.4.15}$$

Using the definition of particle flux as the number of particles moving through a surface of unit area per unit time, then taking a volume V and recalling $N = n \cdot V$ for a homogeneous system:

$$\frac{1}{A}\frac{dN_H}{dt} = -\frac{N_H}{V}\sqrt{\frac{k_B T}{2\pi m_H}} \tag{7.4.16}$$

$$\frac{1}{A}\frac{dN_D}{dt} = -\frac{N_D}{V}\sqrt{\frac{k_B T}{2\pi m_D}} \tag{7.4.17}$$

Therefore, defining the characteristic time constants $\tau_H = \frac{V}{A}\sqrt{\frac{2\pi m_H}{k_B T}}$ and $\tau_D = \tau_H = \frac{V}{A}\sqrt{\frac{2\pi m_D}{k_B T}}$ then:

$$N_H = N_{0H} e^{-t/\tau_H} \tag{7.4.18}$$

$$N_D = N_{0D} e^{-t/\tau_D} \tag{7.4.19}$$

It follows that if at time $t = 0$ we have $\frac{N_{0H}}{N_{0D}} = 7000$, and at t we have $\frac{N_H}{N_D} = 700$ then:

$$e^{t/\tau_H - t/\tau_D} = 10 \implies t = \ln 10 \frac{\tau_H \tau_D}{\tau_D - \tau_H} \tag{7.4.20}$$

Using the ideal gas law, $\frac{pV}{k_B T} = N$ we find that:

$$p_H = \frac{k_B T N_{0H}}{V} e^{-t/\tau_H} = p_{0H} e^{-t/\tau_H} \tag{7.4.21}$$

$$p_D = \frac{k_B T N_{0D}}{V} e^{-t/\tau_D} = p_{0D} e^{-t/\tau_H} \tag{7.4.22}$$

so that:

$$\frac{p}{p_0} = \frac{p_{0H} e^{-t/\tau_H} + p_{0D} \frac{k_B T N_{0D}}{V} e^{-t/\tau_D}}{p_{0H} + p_{0D}} \tag{7.4.23}$$

$$= \frac{p_{0H} 10^{-\frac{\tau_D}{\tau_D - \tau_H}} + p_{0D} 10^{-\frac{\tau_H}{\tau_D - \tau_H}}}{p_{0H} + p_{0D}} \tag{7.4.24}$$

$$= \frac{N_{0H}}{N_0} 10^{-\frac{\tau_D}{\tau_D - \tau_H}} + \frac{N_{0D}}{N_0} 10^{-\frac{\tau_H}{\tau_D - \tau_H}} \tag{7.4.25}$$

$$\approx 0.000412 \tag{7.4.26}$$

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7.5 Collisions

In the previous section, we mentioned the particle mean free path, but how would be calculate such a quantity?

Let us model the particles in the gas as rigid spheres of diameter d. For each particle, we can construct a virtual cylinder whose axis is aligned with $\boldsymbol{v}$, and whose cross section is $\sigma = \pi d^2$. Any particle whose center is within this cylinder must therefore collide with this particle, which is why σ is known as the collisional cross section.

After some time t each particle will have swept a volume $\sigma v t$, and since the average number of particles in this volume is $n_c = \sigma v t n$, we define the collision time $t = \tau_c$ such that $n_c = 1$, that is:

$$\sigma v \tau_c n = 1 \implies \tau_c = \frac{1}{\sigma n v} \tag{7.5.1}$$

But which velocity to use? It is common notation to use the thermal velocity, thus defining:

$$\boxed{\tau_c = \frac{1}{\sigma n} \sqrt{\frac{m}{2 k_B T}}} \tag{7.5.2}$$

It is then straightforward to calculate the mean free path, that is, the average distance travelled by a particle between collisions:

$$\boxed{\lambda_{mfp} = v_{th} \tau_C = \frac{1}{\sigma n}} \tag{7.5.3}$$

This is also the length of the collision cylinder such that at least one particle is included in it.

Heat transport phenomena

8

8.1 Particle distribution function

Let us define the **particle distribution function in the phase space** as the average number of particles with velocities in the velocity space volume $d^3\boldsymbol{v}$ and in the spatial volume $d^3\boldsymbol{r}$, denoted as:

$$F(t,\boldsymbol{r},\boldsymbol{v})d^3\boldsymbol{r}d^3\boldsymbol{v} \tag{8.1.1}$$

Normalization thus requires that for a system of N particles in total:

$$\iint d^3\boldsymbol{r}d^3\boldsymbol{v}F(t,\boldsymbol{r},\boldsymbol{v}) = N \tag{8.1.2}$$

In a homogeneous system we obviously require that $F(\boldsymbol{r},\boldsymbol{v}) = F(\boldsymbol{v}) = nf(\boldsymbol{v})$ where $n = n(\boldsymbol{r})$ is the density of particles, which has to be constant.

Indeed, if we integrate F over the velocity space:

$$\int d^3\boldsymbol{v}F(t,\boldsymbol{r},\boldsymbol{v}) \equiv n(t,\boldsymbol{r}) = n \tag{8.1.3}$$

The **first moment** of F is defined as the mean momentum density:

$$\int d^3\boldsymbol{v}m\boldsymbol{v}F(t,\boldsymbol{r},\boldsymbol{v}) = mn(t,\boldsymbol{r})\boldsymbol{u}(t,\boldsymbol{r} \tag{8.1.4}$$

where $\boldsymbol{u}(t,\boldsymbol{r})$ is the mean velocity of the gas. Indeed F is the number of particles per unit volume with speed in the neighborhood of $\boldsymbol{v}$, so multiplying it by the momentum carried by such a particle, $m\boldsymbol{v}$, and integrating gives the average momentum density.

In a similar fashion, the **second moment** is defined as the mean energy density:

$$\int d^3\boldsymbol{v}\frac{mv^2}{2}F(t,\boldsymbol{r},\boldsymbol{v}) = \int d^3\boldsymbol{w}\frac{m|\boldsymbol{u}+\boldsymbol{w}|^2}{2}F(t,\boldsymbol{r},\boldsymbol{v}) \tag{8.1.5}$$

$$= \frac{mu^2}{2}\int d^3\boldsymbol{w}F + m\boldsymbol{u}\cdot\overbrace{\int d^3\boldsymbol{w}\boldsymbol{w}F}^{0} + \int d^3\boldsymbol{w}\frac{mw^2}{2}F \tag{8.1.6}$$

$$= \frac{mnu^2}{2} + \left\langle\frac{mw^2}{2}\right\rangle n \tag{8.1.7}$$

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where $\boldsymbol{u}$ is defined as in the first moment, and $\boldsymbol{w} = \boldsymbol{v} - \boldsymbol{u}$ is the peculiar velocity of each particle in the gas frame. Indeed:

$$\int d^3\boldsymbol{w}\boldsymbol{w}F = \int d^3\boldsymbol{v}(\boldsymbol{v} - \boldsymbol{u})F = \boldsymbol{u}n(t, \boldsymbol{r}) - n(t, \boldsymbol{r})\boldsymbol{u} = 0 \tag{8.1.8}$$

Now the term $\frac{mnu^2}{2}$ may be interpreted as the kinetic energy density due to the gas' mean motion $\boldsymbol{u}$. Instead, the second term $\left\langle \frac{mw^2}{2} \right\rangle n$ is the internal energy density due to the gas' internal degrees of freedom. We may then define:

$$K = \int d^3\boldsymbol{r}\, \frac{mnu^2}{2} \tag{8.1.9}$$

as the total kinetic energy of the gas, and:

$$U = \int d^3\boldsymbol{r} \left\langle \frac{mw^2}{2} \right\rangle n \tag{8.1.10}$$

as the total internal energy.

All this is nice and dandy, but we are assuming that we are given an expression for $F(t, \boldsymbol{r}, \boldsymbol{v})$.

8.2 Maxwellian equilibrium

In most classical scenarios the dependence of F on position and time is associated with macroscopic perturbations, such as an oven or an open window. Therefore, the scales of these inhomogeneities are much larger than τ_c and τ_{mfp}.

If we then break up the gas into small elements of size δl in time intervals δt such that:

$$l \gg \delta l \gg \lambda_{mfp}, \; t \gg \delta t \gg \tau_c \tag{8.2.1}$$

Each one of these small gas elements thus behaves as a homogeneous gas, and may be modelled with the local Maxwellian distribution:

$$F_M(t, \boldsymbol{r}, \boldsymbol{v}) = n(t, \boldsymbol{r}) \left(\frac{m}{2\pi k_B T(t, \boldsymbol{r})} \right) \exp \left[-\frac{m|\boldsymbol{w}(t, \boldsymbol{r})|^2}{2k_B T(t, \boldsymbol{r})} \right] \tag{8.2.2}$$

where $\boldsymbol{w}(t, \boldsymbol{r}) - \boldsymbol{v} - \boldsymbol{u}(t, \boldsymbol{r})$ is the constituent particle's particular velocity in the gas element's center of mass frame.

As before, if we define $v_{th} = \sqrt{\frac{2k_B T}{m}}$, then the maxwellian distribution reduces to:

$$F_M(t, \boldsymbol{r}, \boldsymbol{v}) = \frac{n(t, \boldsymbol{r})}{(\sqrt{\pi}v_{th}(t, \boldsymbol{r}))^3} e^{-w^2/v_{th}^2} \tag{8.2.3}$$

Local pressure is then

$$P(t, \boldsymbol{r}) = n(t, \boldsymbol{r})k_B T(t, \boldsymbol{r}) = \frac{2}{3}\varepsilon(t, \boldsymbol{r} \tag{8.2.4}$$

so that:

$$k_B T(t, \boldsymbol{r}) = \frac{2}{3} \frac{\epsilon(t, \boldsymbol{r})}{n(t, \boldsymbol{r})} = \frac{2}{3} \left\langle \frac{mw^2}{2} \right\rangle \tag{8.2.5}$$

8.3 Conservation laws

Gases can transport momentum, energy of particles through their motion. The properties of momentum, energy and particle transport are called transport properties of gases, and are closely related to conservation laws.

One quantity that must always be conserved is the total number of particles:

$$\int d^3\boldsymbol{r}\, n = N \tag{8.3.1}$$

We must also have conservation of total momentum, which we can set to 0 by moving to an appropriate reference frame:

$$\int d^3\boldsymbol{r}\, mn\boldsymbol{u} = 0 \tag{8.3.2}$$

Finally, the total energy must also be conserved:

$$\int d^3\boldsymbol{r}\, \frac{mnu^2}{2} + \int d^3\boldsymbol{r} \left\langle \frac{mw^2}{2} \right\rangle n = K + U \tag{8.3.3}$$

Now how do we evolve the variables $n, \boldsymbol{u}, T$ in such a way as to satisfy these conservation laws?

Let us initially consider a gas with $\boldsymbol{u} = 0$ and constant density. All the energy is clearly in the internal energy:

$$\epsilon = nc_1 T(t, \boldsymbol{r}) \tag{8.3.4}$$

where c_1 is the heat capacity per particle. Furthermore we also assume that the system is one dimensional with z-dependence.

If we have a hot region and a cold region, then there will be a flux of heat $J(z)$, defined as the internal energy flowing per unit time through unit area perpendicular to z-axis.

So for a small volume $A \times \left[z - \frac{dz}{2}, z + \frac{dz}{2} \right]$ then:

$$\frac{\partial}{\partial t}(nc_1 T \cdot A dz) = AJ_z \left(z - \frac{dz}{2} \right) - AJ_z \left(z + \frac{dz}{2} \right) \tag{8.3.5}$$

which yields:

$$nc_1 \frac{\partial T}{\partial t} = -\frac{J_z(z + dz/2) - J_z(z - dz/2)}{dz} = -\frac{\partial J_z}{\partial z} \tag{8.3.6}$$

In three dimensions this turns into:

$$\frac{\partial}{\partial t} \int_V d^3\boldsymbol{r}\, nc_1 T = -\int_{\partial V} d\boldsymbol{A} \cdot \boldsymbol{J} = -\int_V d^3\boldsymbol{r}\, \nabla \cdot \boldsymbol{J} \tag{8.3.7}$$

for all volumes V, so that:

$$\boxed{nc_1\frac{\partial T}{\partial t} + \nabla \cdot \boldsymbol{J} = 0} \tag{8.3.8}$$

The total flux of heat out of a system is equal to the rate of change of its internal energy, and thus is proportional to the rate of change of its temperature. This is just a restatement of conservation of energy, heat leaving the system must be equal to the energy being lost.

Similarly, the rate of change of a volume V of a gas is:

$$\frac{\partial}{\partial t} \int_V d^3\boldsymbol{r}mn\boldsymbol{u} \tag{8.3.9}$$

We now define the momentum flux as Π as a tensor with components Π_{ij} as the momentum component j leaving through a surface of unit area perpendicular to i per unit time.

Analogously to energy conservation, momentum conservation then requires:

$$\frac{\partial}{\partial t} \int_V d^3\boldsymbol{r}mn\boldsymbol{u} = -\int_{\partial V} d\boldsymbol{A} \cdot \boldsymbol{\Pi} \tag{8.3.10}$$

We may not apply Gauss' law directly since we have a tensor, instead we may take the j-th component of momentum:

$$\frac{\partial}{\partial t} \int_V d^3\boldsymbol{r}mnu_j = -\int_{\partial V} d\boldsymbol{A} \cdot \boldsymbol{\Pi}_j = -\int_V d^3\boldsymbol{r}\nabla \cdot \boldsymbol{\Pi}_j \tag{8.3.11}$$

Consequently:

$$mn\frac{\partial u_j}{\partial t} + \nabla \cdot \boldsymbol{\Pi}_j = 0 \tag{8.3.12}$$

But how do we find the momentum flux? Momentum fluxes are usually due to velocity gradients, and in gases one significant contribution is due to viscosity.

Viscosity is a fluid's resistance to deformation through shear stress. That is, if we place a fluid between two straight, parallel plates, and move the top plate, then viscosity will cause layers of gas closer to the top plate to move with greater speed compared to layers farther from the top plate.

Suppose the plates lie in the xy plane and the top one is moved in the x direction, causing shear stress $\tau_{xz} = \frac{F}{A}$. Here A is the area of the plate and F the force applied. Suppose the plate moves at speed u, then this will produce a velocity gradient $\frac{d\langle u_x \rangle}{dz}$ in the gas, because each layer in the gas will try to drag the neighbouring layers with it. Viscosity η is then defined as:

$$\tau_{xz} = \frac{F}{A} = \eta\frac{d\langle u_x \rangle}{dz} \tag{8.3.13}$$

Momentum conservation yields:

$$mn\frac{\partial u_x}{\partial t} + \eta\frac{\partial^2 \langle u_x \rangle}{\partial z^2} \tag{8.3.14}$$

Part III

Statistical Physics

The microcanonical ensemble

<div align="right">**9**</div>

9.1 What is statistical physics?

The aim of statistical physics is to derive the laws of physics at the macro-scale, using the governing laws of molecular dynamics. It provides a link between the behaviour of the micro-scale and the resulting effects in bulk properties at the macro-scale we are familiar with.

For example, what makes the specific heat of materials different from each other?

To do so we will need to find an intermediary connection between classical mechanics and thermodynamics, entropy and the phase space.

9.2 The classical Phase Space

Recall that in classical mechanics the coordinates $(\mathbf{q}(t), \mathbf{p}(t))$ are enough to fully specify the state of a system of N particles. These coordinates belong to an alternate space, called the **phase space**. For a three-dimensional "real space" with N particles, it follows that the phase space will be $6N$-dimensional.

Any point in the phase space is associated to a micro-state of the whole system's behaviour, that is, an instant in the motion of the system. The way this micro-state behaves through time is given by Hamilton's equations:

$$\boxed{\dot{q}_i = \frac{\partial H}{\partial p_i}, \ \dot{p}_i = -\frac{\partial H}{\partial q_i}} \tag{9.2.1a}$$

The solutions to the above equations are curves $(\mathbf{q}(t), \mathbf{p}(t))$ in the phase space. These curves are known as phase-space trajectories.

For an observable $A(\mathbf{q}(t), \mathbf{p}(t), t)$ its time-evolution is given by:

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right) \tag{9.2.2}$$

It is now convenient to introduce the Poisson bracket $\{A, H\} = \sum\limits_{i=1}^{3N} \left(\frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right)$ to simplify
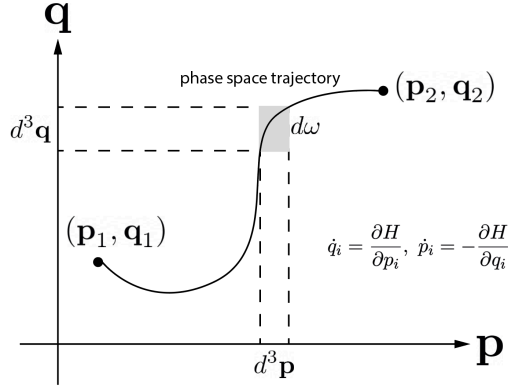
Figure 9.1. The phase space

the sum (9.2.2) to write:

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\} \tag{9.2.3}$$

Just like normal three dimensional space may be divided into infinitesimal volume elements, one may also partition the phase space into infinitesimal phase space volume elements $d\omega$ defined by:

$$d\omega = d^{3N}\mathbf{q}\,d^{3N}\mathbf{p} \tag{9.2.4}$$

Now if we consider two energy surfaces in the phase-space, with energies E and $E + \Delta e$, then the corresponding phase volume will be given by:

$$\Delta\omega = \omega(E + \Delta E) - \omega(E) = \left.\frac{\partial \omega}{\partial E}\right|_{V,N} \Delta E \tag{9.2.5}$$

However, we also have that if the area of the energy surface $H(\mathbf{q}, \mathbf{p}) = E$ is defined as $\sigma(E)$, the density of states at energy E, then:

$$\sigma(E) = \int_{H=E} d\sigma \tag{9.2.6}$$

so that:

$$d\omega = \sigma(E)dE \implies \boxed{\sigma(E) = \left.\frac{\partial \omega}{\partial E}\right|_{V,N}} \tag{9.2.7}$$

We could also see this using the fundamental theorem of calculus:

$$\omega(E, V, N) = \int_{E' < E} \sigma(E', V, N)dE' \iff \sigma(E, V, N) = \left.\frac{\partial \omega}{\partial E}\right|_{V,N} \tag{9.2.8}$$

from which it follows that:

$$\int_{E < H < E + \Delta E} d\omega = \sigma(E)\Delta E \tag{9.2.9}$$

Now for a closed, isolated system we have that the variables E (energy), N (number of particles) and V (volume) are enough to specify its macroscopic properties. They specify a **macrostate**.
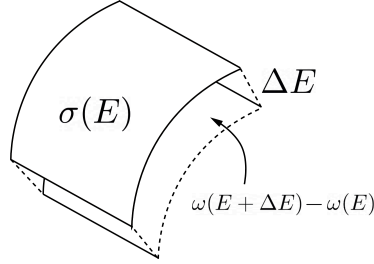

Figure 9.2. Phase space volume between energy surfaces $H(q_i, p_j) = E$ and $H(q_i, p_j) = E + \Delta E$.

However, this macrostate is highly degenerate. There are several ways one could arrange a system to give the corresponding values of E, V, N, which we denote by $\Omega(E, V, N)$, Each one of these states is called a **microstate**. We expect that $\Omega(E, V, N)$ will be proportional to $\sigma(E, V, N)$

$$\Omega(E, V, N) = \frac{\sigma(E, V, N)}{\sigma_0} = \frac{1}{\sigma_0} \frac{\partial \omega}{\partial E}\Big|_{V,N} \tag{9.2.10}$$

It turns out these microstates all have equal probabilities. Indeed, consider a isolated system which we subdivide into two subsystems with macroscopic variables E_i, V_i, N_i. Because the original system is closed, we require that:

$$dE = 0 \implies dE_1 = -dE_2 \tag{9.2.11}$$
$$dV = 0 \implies dV_1 = -dV_2 \tag{9.2.12}$$
$$dN = 0 \implies dN_1 = -dN_2 \tag{9.2.13}$$
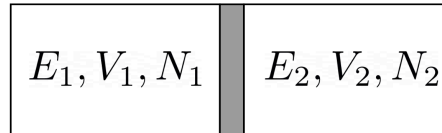
Figure 9.3. Composite system state counting

We must also have from elementary combinatorics that:

$$\Omega(E, V, N) = \Omega_1(E_1, V_1, N_1)\Omega_1(E_2, V_2, N_2) \tag{9.2.14}$$
$$\implies d\Omega = \Omega_1 d\Omega_2 + \Omega_2 d\Omega_1 \tag{9.2.15}$$
$$\implies d\ln\Omega = d\ln\Omega_2 + d\ln\Omega_1 \tag{9.2.16}$$

Now equilibrium occurs whenever we have a maximum number of possible microstates, so when $d\Omega = 0$. Therefore $d\ln\Omega = 0$. In classical thermodynamics, one may recall that equilibrium results in maximal entropy so $dS = dS_1 + dS_2 = 0$. Comparison with (9.2.16)

suggests the relation:

$$S(E, V, N) = k_B \ln \Omega(E, V, N)$$

(9.2.17)

where k_B is Boltzmann's constant. This is a remarkable important law because it allows us to find all other thermodynamic variables which we define as:

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N}, \ \frac{p}{T} = \frac{\partial S}{\partial V}\bigg|E, N$$

(9.2.18)

9.3 Probability density and expectation values

For isolated systems we have assumed that all microstates on the same energy surface have equal probability of being occupied. This is no longer true for open systems, where we must introduce a probability density $\rho(\mathbf{q}, \mathbf{p})$ which corresponds to the probability density of the system to occupy the phase state $(\mathbf{q}, \mathbf{p})$. Normalization is required as always:

$$\int \rho(\mathbf{q}, \mathbf{p}) \, d^{3N}\mathbf{q} \, d^{3N}\mathbf{p} = 1$$

(9.3.1)

Suppose we have some observable A of the system, then its expectation value is given by:

$$\langle f \rangle = \int \rho(\mathbf{q}, \mathbf{p}) f(\mathbf{q}, \mathbf{p}) \, d^{3N}\mathbf{q} \, d^{3N}\mathbf{p}$$

(9.3.2)

For an isolated system for example, we have that:

$$\rho(\mathbf{q}, \mathbf{p}) = \frac{1}{\sigma(E)} \delta(E - H(\mathbf{q}, \mathbf{p}))$$

(9.3.3)

This however is a very complicated expression due to the Dirac delta function. We can simplify it by allowing for a small energy deviation ΔE, for which:

$$\rho(\mathbf{q}, \mathbf{p}) = \begin{cases} \rho_0, & E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E \\ 0, & \text{otherwise} \end{cases}$$

(9.3.4)

Then normalization requires:

$$\int_{E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta} \rho_0 \, d^{3N}\mathbf{q} \, d^{3N}\mathbf{p} = 1$$

(9.3.5)

$$\iff \rho_0 \sigma(E, V, N) \Delta E = 1$$

(9.3.6)

$$\iff \rho_0 \Omega(E, V, N) h^{3N} \Delta E = 1$$

(9.3.7)

$$\iff \rho = \frac{1}{\Omega(E, V, N) h^{3N} \Delta E}$$

(9.3.8)

since the energy shell volume in the phase space is $\sigma(E, V, N)\Delta E = h^{3N}\Omega(E, V, N)\Delta E$ We may take $\frac{1}{h^{3N}}$ out of the integral by by defining:

$$\frac{1}{h^{3N}} \int \rho(\mathbf{q}, \mathbf{p}) \, d^{3N}\mathbf{q} \, d^{3N}\mathbf{p} = 1$$

(9.3.9)

An ensemble is then a very very large collection of identical copies of a system with distribution function $\rho(\mathbf{q}, \mathbf{p})$. There are special types of ensembles which we will study:

(i) micro-canonical ensemble

(ii) canonical ensemble

(iii) grand canonical ensemble

In the case of the micro-canonical ensemble it is defined by:

$$\rho_{mc}(\mathbf{q}, \mathbf{p}) = \begin{cases} \frac{1}{\Omega \Delta E}, & E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E \\ 0, & \text{otherwise} \end{cases} \tag{9.3.10}$$

9.4 Louiville's theorem

Hamilton's equations demand that:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} \tag{9.4.1}$$

Now consider the set of systems in the volume element ω at time t. As they evolve through time each of the phase space points will get mapped to another volume element ω' at time t'. However the initial and final number of phase space points must remain constant. We thus require that if we have a change in phase space volumes then a net amount of phase space points flowing out of ω:

$$\frac{\partial}{\partial t} \int d\omega \rho + \int \rho(\mathbf{v} \cdot \mathbf{n}) \cdot d\sigma \tag{9.4.2}$$

Here $\mathbf{v}$ is the "velocity" in the phase space of the trajectories, given by $(\dot{\mathbf{q}}, \dot{\mathbf{p}})$. Using the divergence theorem we find:

$$\int_\omega \left(\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{v}) \right) d\omega = 0 \tag{9.4.3}$$

where divergence is taken with respect to the phase space coordinates $\{q_1, q_2, ..., q_3 N, p_1, p_2, ..., p_{3N}\}$. Since (9.4.3) holds for any arbitrary volume ω we find the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{v}) = 0 \tag{9.4.4}$$

Let us expand the divergence:

$$\nabla(\rho\mathbf{v}) = \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i}(\rho\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\dot{p}_i) \right] \tag{9.4.5}$$

$$= \sum_{i=1}^{3N} \left[\frac{\partial\rho}{\partial q_i}\dot{q}_i + \rho\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\rho}{\partial p_i}\dot{p}_i + \rho\frac{\partial\dot{p}_i}{\partial p_i} \right] \tag{9.4.6}$$

$$= \sum_{i=1}^{3N} \left[\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} + \rho\overbrace{\left(\frac{\partial^2 H}{\partial q_i\partial p_i} + \frac{\partial^2 H}{\partial p_i\partial q_i}\right)}^{0} \right] \tag{9.4.7}$$

$$= \{\rho, H\} \tag{9.4.8}$$

Consequently:

$$\boxed{\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{\rho, H\} = \frac{\partial\rho}{\partial t} + \nabla(\rho\mathbf{v}) = 0} \tag{9.4.9}$$

so the time derivative of the phase-space density is null for a trajectory. Alternatively, a phase space density is constant along the trajectory of a system. This is known as **Louiville's theorem**.

9.5 Ergodic hypothesis and Equal a priori probability

One may wonder why we should even worry about probability distributions in the phase space and taking ensemble averages. After all, when we perform experiments we are really taking a time average of one system, rather than the ensemble average of several systems. If we have some quantity $A(\mathbf{q}, \mathbf{p}, t)$ then its time average will be:

$$\tilde{A} = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(\mathbf{q}, \mathbf{p}, t)\ dt \tag{9.5.1}$$

How can we justify using the ensemble average instead:

$$\langle A \rangle = \int_{\text{ensemble}} A(\mathbf{q}, \mathbf{p}, t)\rho(\mathbf{q}, \mathbf{p})\ d\omega \tag{9.5.2}$$

The ergodic hypothesis postulates that these two averages should be equivalent in the thermodynamic limit. This hinges on the condition that the system visits the neighbourhood of all the available phase space points (gets arbitrarily close to them) after a sufficiently long time. If we average over time then under the ergodic hypothesis we are really just averaging over the ensemble.

Also, another fundamental assumption of statistical mechanics is the postulate of equal a priori probability. It states that for a system in equilibrium the micro-states corresponding to a macro-state have the same probability of being occupied.

The link between these two postulates is Louiville's theorem, which states that the a system takes trajectories along constant phase space density surfaces. Since systems in equilibrium have a constant phase space density for each macro-state, it follows that a system's trajectory will be in the neighborhood of all possible microstates.

9.6 The microcanonical ensemble

The microcanonical ensemble is a statistical ensemble used to model isolated systems, where there is no exchange of particles and energy. Therefore we will take E, V, N to be conserved quantities specifying an equilibrium macrostate. For such systems we previously stated without proof that for a given energy they are modelled by a constant phase-space density on the corresponding energy hypersurface, as described in (9.3.10)

Let us prove this result.

Consider an ensemble made up of $\mathcal{N}$ identical copies of an isolated system, each in a different microstate on the energy hypersurface $H(\mathbf{q}, \mathbf{p}) = E$.

Suppose we partition this surface into small elements $\Delta\sigma_i$ with n_i systems each:

$$\mathcal{N} = \sum_i n_i \tag{9.6.1}$$

How many ways are there to distribute the $\mathcal{N}$ systems into the energy surfaces? For $\mathcal{N}$ systems there are $\mathcal{N}!$ different ways to enumerate them. However, since within each surface $\Delta\sigma_i$ there are $n_i!$ internal exchanges which do not alter the overall distribution, the total number of ways to distribute the systems will be:

$$W\{n_i\} = \frac{\mathcal{N}!}{\prod_i n_i!} \tag{9.6.2}$$

In other words, order matters when distributing the n_i systems into the surfaces $\Delta\sigma_i$, but the ordering of each system within $\Delta\sigma_i$ is insignificant.

The most probable distribution will of course maximize $W\{n_i\}$, and hence $\ln W\{n_i\}$ (so entropy will be maximized, corresponding to equilibrium). Therefore we need:

$$\ln W_{tot} = \ln \mathcal{N}! - \sum_i \ln n_i! \tag{9.6.3}$$

$$\approx \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_i (n_i \ln n_i - n_i) \tag{9.6.4}$$

$$\Longleftrightarrow d\ln W_{tot} = -\sum_i \ln n_i \; dn_i = 0 \tag{9.6.5}$$

Since we are subject to the constraint (9.6.1) we need to use the method of Lagrange multipliers. We get that:

$$\lambda d\mathcal{N} = \lambda \sum_i dn_i = 0 \tag{9.6.6}$$

which we can sum to (9.6.5) to get:

$$\sum_i (\ln n_i - \lambda) dn_i = 0 \tag{9.6.7}$$

Equating the coefficients to zero one finds that:

$$\boxed{n_i = \text{cnst.}} \tag{9.6.8}$$

We easily identify this distribution as a homogeneous distribution:

$$\rho_{mc}(\mathbf{q}, \mathbf{p}) = \begin{cases} \frac{1}{\Omega \Delta E} & E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases} \qquad (9.6.9)$$

as desired. Hence the most likely distribution in a microcanonical ensemble is the ρ_{mc} distribution.

9.7 Relating the Boltzmann and Gibbs entropy

Recall that the Boltzmann entropy was identified to be:

$$S(E, V, N) = k_B \ln \Omega(E, V, N) \qquad (9.7.1)$$

In the microcanonical picture however (developed by Gibbs), it is seen as the ensemble average:

$$S(E, V, N) = \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} \rho(\mathbf{q}, \mathbf{p})(-k_B \ln \rho(\mathbf{q}, \mathbf{p})) \, d\omega \qquad (9.7.2)$$

which we recognize to be:

$$S(E, V, N) = \langle -k_B \ln \rho(\mathbf{q}, \mathbf{p}) \rangle \qquad (9.7.3)$$

Indeed, inserting (9.3.10) into (9.7.2) one finds that:

$$S(E, V, N) = \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} \frac{1}{\Omega \Delta E} k_B \ln(\Omega \Delta E) \, d\omega \qquad (9.7.4)$$

Since Ω is constant over the energy shell $E \leq H \leq E + \Delta E$ the integrand may be pulled out:

$$S(E, V, N) = \frac{1}{\Omega \Delta E} k_B \ln(\Omega \Delta E) \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} d\omega \qquad (9.7.5)$$

We now recognize:

$$\Omega \Delta E = \frac{1}{h^{3N}} \int_{E \leq H \leq E + \Delta E} d\omega \qquad (9.7.6)$$

so that in the microcanonical ensemble:

$$S(E, V, N) = k_B \ln(\Omega \Delta E) = \langle -k \ln \rho \rangle \qquad (9.7.7)$$

as desired. Alternatively, in the discrete case, we can insert $p_i = \frac{n_i}{\mathcal{N}}$ which is justified by the equal a priori probability postulate into (9.6.4) and find that

$$S = -k_B \left(\mathcal{N} \ln \mathcal{N} - \mathcal{N} \sum_i p_i \ln(\mathcal{N} p_i) \right) = \sum_i p_i \ln p_i \qquad (9.7.8)$$

as desired. We therefore infer that the Gibbs entropy is a generalization of the Boltzmann

entropy, which is only applicable for equilibrium systems in a single macrostate, where the equal a priori probability postulate is justified.

9.8 Entropy of an ideal gas (classical)

For an ideal gas which is interaction-free, the Hamiltonian takes the form:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{9.8.1}$$

The total phase space volume enclosed by the energy surface $E = H(\mathbf{q}, \mathbf{p})$ is

$$\omega(E, V, N) = \int_{H \leq E} d^{3N}\mathbf{q}d^{3N}\mathbf{p} = V^N \int_{H \leq E} d^{3N}\mathbf{p} \tag{9.8.2}$$

since there is no q dependence of the Hamiltonian surface we are integrating over. In the phase-space, we also see that E delineates a spherical surface of radius $p = \sqrt{2mE}$.
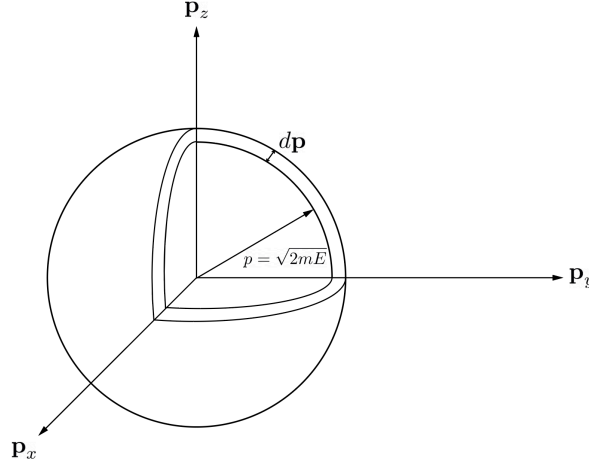
So the integral in (9.8.2) is simply the volume of an $3N$-dimensional sphere:

$$V_{\text{sphere}}^N = \frac{2\pi^{N/2}}{N\Gamma\left(\frac{N}{2}\right)} R^N \tag{9.8.3}$$

where R is the radius. We then find that:

$$\omega(E, V, N) = V^N \frac{2\pi^{3N/2}}{3N\Gamma\left(\frac{3N}{2}\right)} (2mE)^{3N/2} \tag{9.8.4}$$

Using (9.2.10) one may then find the number of microstates on the energy surface:

$$\Omega(E, V, N) = \frac{1}{\sigma_0} \frac{\partial}{\partial E} \Big(\omega(E, V, N) \Big) \tag{9.8.5}$$

$$= \frac{1}{\sigma_0} V^N \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2m)^{3N/2} E^{3N/2-1} \tag{9.8.6}$$

Consequently the volume occupied by the micro-canonical ensemble is:

$$\Omega(E,V,N)\Delta E = \frac{1}{\sigma_0} V^N \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{3N/2} \frac{\Delta E}{E} \tag{9.8.7}$$

One then gets an expression, albeit very complicated, for an ideal gas:

$$S(E,V,N) = k_B \ln\left[\frac{1}{\sigma_0} V^N \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{3N/2} \frac{\Delta E}{E} \right] \tag{9.8.8}$$

For very large systems where $N \gg 1$ then we may make the approximations $\ln\frac{\Delta E}{E} \approx 0$ (thus ignoring any terms not of order N). We also make use of Stirling's approximation:

$$\ln\Gamma(n) \approx n\ln n - n \tag{9.8.9}$$

to find that:

$$S(E,V,N) \approx Nk_B\left[\ln\left(\frac{V}{\sigma}(2\pi mV)^{3/2} \right) + \frac{3}{2} - \frac{3}{2}\ln\frac{3N}{2} \right] \tag{9.8.10}$$

where $\sigma = \sigma_0^{1/N}$. Further simplification gives:

$$S(E,V,N) \approx Nk_B\left[\frac{3}{2} + \ln\frac{V}{\sigma}\left(\frac{4\pi mE}{3N} \right)^{3/2} \right] \tag{9.8.11}$$

This gives the correct equations of state from classical thermodynamics:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3Nk_B}{2E} \implies E = \frac{3}{2}Nk_BT \tag{9.8.12}$$

$$\frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{Nk_B}{V} \implies pV = Nk_BT \tag{9.8.13}$$

which recast (9.8.11) into:

$$S(E,V,N) \approx Nk_B\left[\frac{3}{2} + \ln\left(\frac{V}{\sigma}(2\pi mk_BT)^{3/2} \right) \right] \tag{9.8.14}$$

However, it turns out that (9.8.11) is incorrect. Indeed, we know that entropy is an extensive quantity, yet the additional logarithmic term produces an extra $\ln\alpha$ term when the system is scaled up by α.

9.9 Gibb's paradox

Let's analyze where this inconsistency comes from. We consider a container containing gas A, and another container containing gas B. Now the total entropy of the two-container system is:

$$S^b = S_A^b(T,V_A,N_A) + S_B^b(T,V_B,N_B) \tag{9.9.1}$$

Now suppose we put the containers in contact so that the gases mix together and occupy

Figure 9.4. Caption

the total volume $V_A + V_B$. Once equilibrium has reached the entropy will be:

$$S^a = S_A^a(T, V_A + V_B, N_A) + S_B^a(T, V_A + V_B, N_B) \qquad (9.9.2)$$

The total entropy change is

$$\Delta S = N_A k_B \ln \frac{V_A + V_B}{V_A} + N_B k_B \ln \frac{V_A + V_B}{V_B} > 0 \qquad (9.9.3)$$

Throughout this derivation however, we have been assuming that gases A and B are distinguishable. If we use identical gases, then

$$S^b = S_A^b(T, V_A, N_A) + S_B^b(T, V_B, N_B) \qquad (9.9.4)$$
$$S^a = S(T, V_A + V_B, N_A + N_B) \qquad (9.9.5)$$

We have that:

$$S(T, V_A + V_B, N_A + N_B) = (N_A + N_B)k_B \left[\frac{3}{2} + \ln \frac{V_A + V_B}{\sigma} (2\pi m k_B T)^{3/2} \right] \qquad (9.9.6)$$

$$= N_A k_B \left[\frac{3}{2} + \ln \frac{V_A}{\sigma} (2\pi m k_B T)^{3/2} \right] + N_B k_B \left[\frac{3}{2} + \ln \frac{V_B}{\sigma} (3\pi m k_B T)^{3/2} \right]$$
$$(9.9.7)$$

$$= S^a = S_A^a(T, V_A + V_B, N_A) + S_B^a(T, V_A + V_B, N_B) \qquad (9.9.8)$$

so we again find that:

$$\Delta S = N_A k_B \ln \frac{V_A + V_B}{V_A} + N_B k_B \ln \frac{V_A + V_B}{V_B} > 0 \qquad (9.9.9)$$

This is quite a problem however, because the mixing of two identical gases is completely reversible, there is no change in the gases when they are put in contact. Therefore, we should have found $\Delta S = 0$.
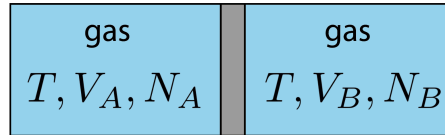

Figure 9.5. Caption

Note that this discrepancy is directly related to the non-extensivity of our (9.8.14), since

when we put the two dinstiguishable gas containers in contact we're essentially scaling the size of the system by two, whereas for identical gas containers we're doing absolutely nothing, yet our expressions for the entropy after mixing are the same for both situations.

To solve this problem, we must employ tools from quantum mechanics. Indeed we know that in quantum mechanics one cannot label particles. Hence different microstates with the same particle distribution but different particle labelling in the classical picture are considered equivalent in quantum mechanics. Since there are $N!$ ways to enumerate N particles it follows that:

$$\Omega(E, V, N) = \frac{1}{N!} \frac{\sigma(E, V, N)}{\sigma_0} \tag{9.9.10}$$

which provides the following correction to entropy:

$$S(E, V, N) = N k_B \left[\frac{3}{2} + \ln \frac{V}{\sigma} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] - k_B \ln N! \tag{9.9.11}$$

and using Stirling's formula:

$$\boxed{S(E, V, N) = N k_B \left[\frac{5}{2} + \ln \frac{V}{N\sigma} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]} \tag{9.9.12}$$

or alternatively:

$$\boxed{S(E, V, N) = N k_B \left[\frac{5}{2} + \ln \frac{V}{N\sigma} (2\pi m k_B T)^{3/2} \right]} \tag{9.9.13}$$

We see by inspection that this is indeed an extensive quantity, since the logarithm's argument is intensive overall.

Let's check that this correction does indeed solve Gibbs' paradox. We now get that

$$\Delta S = (N_A + N_B) k_B \left[\frac{5}{2} + \ln \frac{V_A + V_B}{N_A + N_B \sigma} (2\pi m k_B T)^{3/2} \right] \tag{9.9.14}$$

$$- N_A k_B \left[\frac{5}{2} + \ln \frac{V_A}{N_A \sigma} (2\pi m k_B T)^{3/2} \right] - N_B k_B \left[\frac{5}{2} + \ln \frac{V_B}{N_B \sigma} (2\pi m k_B T)^{3/2} \right] \tag{9.9.15}$$

Now we may impose:

$$\frac{V_A}{N_A} = \frac{V_B}{N_B} = \frac{V_A + V_B}{N_A + N_B} \tag{9.9.16}$$

since the density of gases will remain the same. Hence

$$\Delta S = 0 \tag{9.9.17}$$

as desired. It is important to remember that:

The Gibbs' correction factor must not be included for distinguishable microstates.

9.10   Entropy of an ideal gas (quantum)

There is one constant in this entire derivation that may be frustrating the reader, and that is the proportionality constant σ_0. We can determine its value by counting the number of states from a quantum mechanical point of view, and compare it with our semi-classical results.

Let us try to derive an expression for entropy for an ideal gas made up of distinguishable particles. We will model the container as an infinite quantum well of size L, within which the particles are non-interacting.

The individual particles are in the eigenstates:

$$\psi_{n_x,n_y,n_z} = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \tag{9.10.1}$$

with energy:

$$\epsilon_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{9.10.2}$$

Therefore, our quantum-mechanical phase space will consist of (n_x, n_y, n_z). Now the total
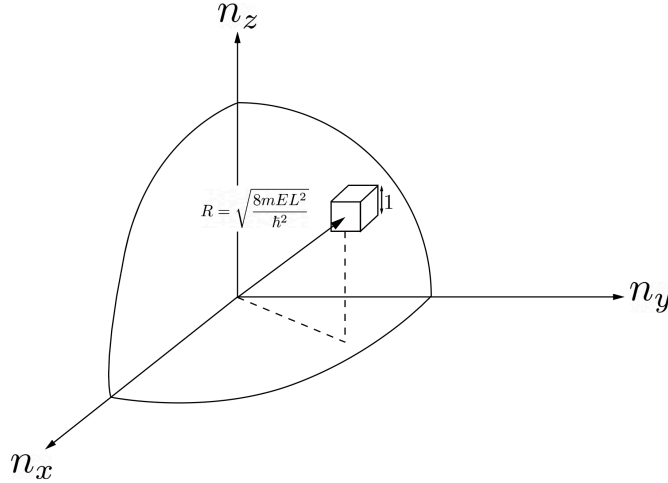
Figure 9.6. Quantum phase space (n_x, n_y, n_z) for an ideal gas

energy of an N-particle system will be given by:

$$E = \frac{h^2}{8mL^2} \sum_{i=1}^{3N} n_i^2 \tag{9.10.3}$$

We can use this to find $\Omega(E, V, N)$, where $V = L^3$, by determining the degeneracy of the energy eigenstate with energy E? Clearly, we must determine how many ways one can add up a number n in terms of a sum of $3N$ quadratic integer terms $\sum_{i=1}^{3N} n_i^2$.

Unfortunately, this is an impossibly difficult problem to solve. Indeed, if an exact expression does exist, it would be a very irregular function of energy. Luckily however, the

average behaviour of $\Omega(E, V, N)$ can be calculated, and we expect it to be increasing with energy. The larger the energy surface, the more likely it is for integer-coordinate points to lie on it.
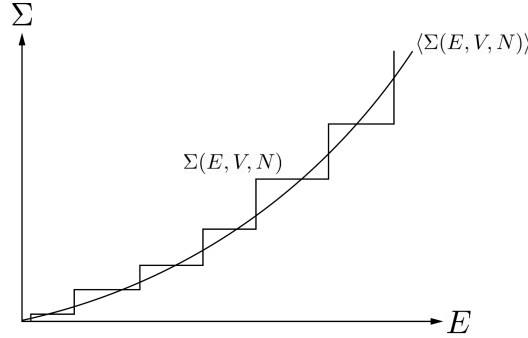
Figure 9.7. Behaviour of Σ and $\langle \Sigma \rangle$

Let us define the number of microstates within the energy sphere:

$$\Sigma(E, V, N) = \sum_{E' \leq E} \Omega(E', V, N) \tag{9.10.4}$$

This is again impossibly complicated to evaluate, but for large enough system, or systems with high enough temperature, then we can approximate it with its average $\langle \Sigma \rangle$. Then, we find that the density of states $g(E, V, N)$ at energy E is approximately:

$$g(E, V, N) = \frac{\partial}{\partial E}(\langle \Sigma(E, V, N) \rangle) \tag{9.10.5}$$

We remark the similarity between $g(E, V, N) \leftrightarrow \sigma(E, V, N)$ and $\langle \Sigma(E, V, N) \rangle \leftrightarrow \omega(E, V, N)$.

We also note that $\langle \Sigma(E, V, N) \rangle$ must be related to the volume enclosed by the energy surface of E. Indeed, suppose we divide this volume into individual unit cubes of unit volume.
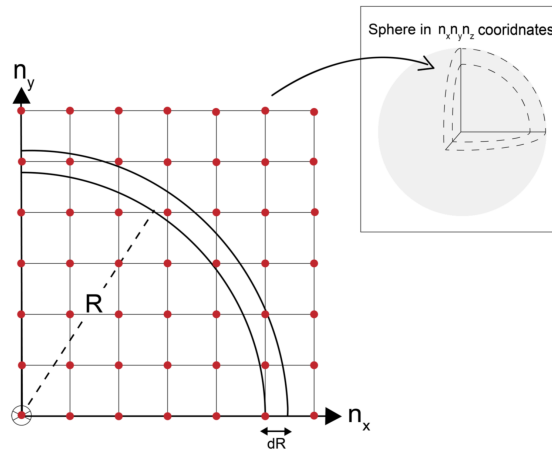
Figure 9.8. Partition of phase space into unit cubes

Then energy grid point will have an associated unit cube, and the mean number of grid points will then be the total enclosed volume divided by the volume of a unit cube, which by definition is 1.

It is also important to note that since $n_i > 0$ the enclosed volume will be an octant. Therefore, defining:

$$R = \sqrt{\frac{8mEL^2}{h^2}} \tag{9.10.6}$$

we get that $\Sigma(E, V, N)$ is the volume of a $3N$-hypersphere with this radius:

$$\langle \Sigma(E, V, N) \rangle = V_N(R) = \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} R^{3N} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} \tag{9.10.7}$$

Therefore the mean density of states at energy E is:

$$g(E, V, N) = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}-1} \tag{9.10.8}$$

Finally, multiplying this by ΔE and approximating $\frac{3N}{2}N - 1 \approx \frac{3N}{2}$ gives

$$\langle \Omega(E) \rangle = g(E)\Delta E = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} E^{\frac{3N}{2}} \Delta E \tag{9.10.9}$$

$$= \frac{\pi^{3N/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} R^{\frac{3N}{2}} \Delta R \tag{9.10.10}$$

Taking the logarithm, we will get an additional term $\ln \Delta R$ which we can set to zero when compared to the $\frac{3N}{2} \ln R$ term. Hence, we get that $\Delta R = 1$, as should be since the subdivision of the phase space was into unit blocks of volume 1. Hence:

$$\langle \Omega(E) \rangle = \frac{\pi^{3N/2}}{\Gamma(3N/2)} \frac{1}{2^{3N}} R^{\frac{3N}{2}} = \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \tag{9.10.11}$$

Comparison with the classical derivation shows that

$$\sigma = h^3 \iff \sigma_0 = h^{3N} \tag{9.10.12}$$

and hence

$$\boxed{S(E, V, N) = Nk_B \left[\frac{3}{2} + \ln \frac{V}{h^3}(2\pi mk_BT)^{3/2}\right]} \tag{9.10.13}$$

which is known as the **Sackur-Tetrode equation**.

9.11 General procedure using the microcanonical ensemble

This gives us a general procedure to derive classical thermodynamics using the microcanonical ensemble.

(i) Find the Hamiltonian $H(\mathbf{q}, \mathbf{p})$ of the system.

(ii) Find the phase space volume enclosed by the energy surface $E = H(\mathbf{q}, \mathbf{p})$.

(iii) Evaluate the number of microstates on the energy surface $\tilde{\Omega}$:

$$\Omega(E, V, N) = \frac{1}{h^{3N}} \frac{\partial \omega}{\partial E}\bigg|_{V,N} \tag{9.11.1}$$

(iv) Evaluate the number of microstates $\tilde{\Omega}$ in the ensemble $\Omega(E, V, N)\Delta E$, which is the number of states in the energy shell $E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E$:

$$\tilde{\Omega}(E, V, N) = \Omega \delta E \tag{9.11.2}$$

(v) Find the entropy:

$$S = k_B \ln \Omega \Delta E = k_B \ln \tilde{\Omega} \tag{9.11.3}$$

and ignoring any terms not order $o(N)$.

(vi) Derive classical thermodynamic quantities and equations of state:

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N} \tag{9.11.4}$$

$$\frac{p}{T} = \frac{\partial S}{\partial V}\bigg|_{E,N} \tag{9.11.5}$$

$$C_V = \frac{\partial E}{\partial T}\bigg|_{V} \tag{9.11.6}$$

9.12 Ultra-relativistic gas

Let us consider a gas made of N massless relativistic particles moving at the speed of light c, and thus satisfying the energy-momentum relation:

$$\epsilon = pc \tag{9.12.1}$$

The hamiltonian of this system then reads:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{N} \sqrt{p_{i,x}c^2 + p_{i,y}^2 + p_{i,z}^2} \, c \tag{9.12.2}$$

Now we find that since the particles are indistinguishable, we must insert the Gibb's correction factor:

$$\Sigma(E, V, N) = \frac{1}{h^{3N}} \omega(E, V, N) = \frac{1}{h^{3N}} N! \int_{H \leq E} d\omega \tag{9.12.3}$$

and since H does not explicitly depend on $\mathbf{q}$ we may integrate over spatial conjugate variables to find:

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!} \int_{H \leq E} d^{3N}\mathbf{p} \tag{9.12.4}$$

We need to find the volume of the energy surface in the momentum space. The square root really complicates things, so we shall instead average the relevant quantities:

$$\langle p^2 \rangle = 3 \langle p_x^2 \rangle = 3 \langle p_y^2 \rangle = 3 \langle p_z^2 \rangle \tag{9.12.5}$$

$$|\langle p^2 \rangle| = \sqrt{\frac{\langle p_x^2 \rangle}{3}} + \sqrt{\frac{\langle p_y^2 \rangle}{3}} + \sqrt{\frac{\langle p_z^2 \rangle}{3}} \tag{9.12.6}$$

$$= \frac{\sqrt{3}}{3}(|p_x| + |p_y| + |p_z|) \tag{9.12.7}$$

Then the volume enclosed by the energy surface $H = E$ is the locus of points in the phase space satisfying:

$$\sum_{i=1}^{3N} \frac{|p_i|c}{\sqrt{3}} \leq E \tag{9.12.8}$$

Hence, substituting $x_i = \frac{p_i c}{\sqrt{3}}$ and $dp_i = \frac{\sqrt{3}E}{c}$ then:

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!} \left(\frac{\sqrt{3}E}{c} \right)^{3N} \int_{\sum_i |x_i| \leq 1} d^{3N}\mathbf{x} \tag{9.12.9}$$

Clearly, if a set of points $(x_1, ..., x_{3N})$ satisfies the condition $\sum_i |x_i| \leq 1$ then so will $(-x_1, ..., -x_{3N})$. The volume over which we are integrating in (9.12.9) is therefore symmetric about the origin. We may therefore find the volume in one octant where $0 \leq x_i$ and then multiply the result by 2^{3N}. We therefore need to evaluate:

$$I_n = \int_{\sum_i x_i \leq 1} d^n x, \ x_i \in [0, 1] \tag{9.12.10}$$

for $n = 3N$. The geometric region we are integrating over is known as a n-simplex, some are shown below.
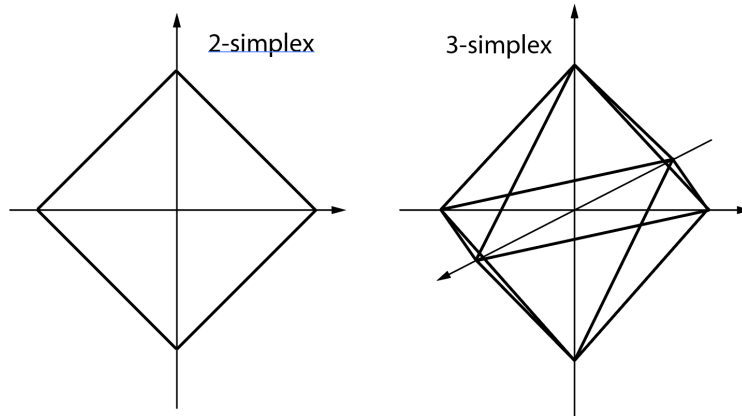
Figure 9.9. 2-simplex and 3-simplex

Consider the base of a n-simplex, which will itself by the corresponding $(n-1)$-simplex

in $n-1$ dimensions. Indeed setting $x_n = 0$ then we find $\sum_{i=1}^{n-1} x_i \leq 1$, defining the lower dimensional simplex. The "volume" of this hypersurface is

$$V_n = \frac{1}{n} A_n \cdot h = \frac{A_n}{n} \tag{9.12.11}$$

where h is the height (which in our case is taken to be 1 when setting $x_1 = x_2 = \ldots = x_{n-1} = 0$) and A_n is the volume of the base.
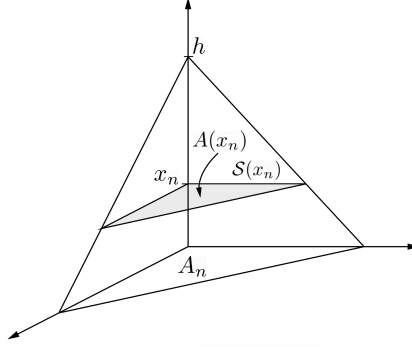
Figure 9.10. Evaluating volume of a simplex

To see why, let us consider sections of the simplex at constant x_n (height). Using similarity relations we must have that the sides $\mathcal{S}(x_n)$ are all scaled by $\frac{h-x_n}{h}$, so that:

$$A(x_n) = A_n \left(1 - \frac{x_n}{\hbar} \right)^{n-1} \tag{9.12.12}$$

Hence:

$$V_n = \int_0^h A_n \left(1 - \frac{x_n}{\hbar} \right)^{n-1} dx_n = \frac{h}{n} A_n \tag{9.12.13}$$

as desired.

However, note that V_n is really just I_n and $A_n = I_{n-1}$ so that:

$$I_n = \frac{I_{n-1}}{n} \implies I_n = \frac{1}{n!} \tag{9.12.14}$$

implying that:

$$\int_{\sum_i |x_i| \leq 1} d^{3N}\mathbf{x} = \frac{2^{3N}}{(3N)!} \tag{9.12.15}$$

The total number of states enclosed by the energy hypersurface is:

$$\Sigma(E, V, N) = \frac{V^N}{h^{3N} N!} \left(\frac{\sqrt{3}E}{c} \right)^{3N} \frac{2^{3N}}{(3N)!} \tag{9.12.16}$$

The density of states at energy E is:

$$g(E,V,N) = \frac{\partial \Sigma(E,V,N)}{\partial E} = \frac{V^N}{h^{3N}N!}\left(\frac{2\sqrt{3}}{c}\right)^{3N}\frac{E^{3N-1}}{(3N-1)!} \tag{9.12.17}$$

$$\approx \frac{V^N}{h^{3N}N!}\left(\frac{2\sqrt{3}}{c}\right)^{3N}\frac{E^{3N}}{(3N)!}\frac{1}{E} \tag{9.12.18}$$

Then the number of states occupied by the microcanonical ensemble is the volume of the shell $E < H < E + \Delta E$:

$$\Omega\Delta E = \frac{V^N}{N!}\left(\frac{2\sqrt{3}}{hc}\right)^{3N}\frac{E^{3N}}{(3N)!}\frac{\Delta E}{E} \tag{9.12.19}$$

and hence:

$$S(E,V,N) = k_b\ln(\Omega\Delta E) = k_B\ln\left[\frac{V^N}{N!}\left(\frac{2\sqrt{3}}{hc}\right)^{3N}\frac{E^{3N}}{(3N)!}\right] + k_B\ln\frac{\Delta E}{E} \tag{9.12.20}$$

$$= Nk_B\ln\left[V\left(\frac{2\sqrt{3}}{hc}\right)^3\right] - k_B\ln N! - k_B\ln(3N)! + k_B\ln\frac{\Delta E}{E} \tag{9.12.21}$$

Using Stirling's approximation:

$$S(E,V,N) = k_B\left(N\ln\left[V\left(\frac{2\sqrt{3}}{hc}\right)^3\right] - N\ln N - 3N\ln(3N) + 4N + \ln\frac{\Delta E}{E}^{\,0}\right) \tag{9.12.22}$$

We may ignore all terms not of order N (i.e. $\ln\frac{\Delta E}{E}$), giving upon some simplification

$$\boxed{S(E,V,N) = Nk_B\left(4 + \ln\left[\frac{V}{N}\left(\frac{2}{\sqrt{3}Nhc}\right)^3\right]\right)} \tag{9.12.23}$$

We may now derive the equations of state:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3Nk_B}{E} \iff E = 3Nk_BT \tag{9.12.24}$$

$$\frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{Nk_B}{V} \iff pV = Nk_BT \tag{9.12.25}$$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = 3Nk_B \tag{9.12.26}$$

and therefore find that:

$$p = \frac{1}{3}\frac{E}{V} \tag{9.12.27}$$

so the pressure is a third of the energy density. Suppose we want the probability distribution of $f(p_1)$. Then we need to integrate the microcanonical ensemble distribution ρ_{mc} over all

variables except p_1:

$$f(p_1) = \int \rho_{mc}(\mathbf{q}, \mathbf{p}) \, d^{3N}\mathbf{q} \, d^{3N-1}\mathbf{q} \tag{9.12.28}$$

$$= \int_{E<H<E+\Delta E} \frac{1}{\Omega \Delta E} \, d^{3N}\mathbf{q} \, d^{3N-1}\mathbf{q} \tag{9.12.29}$$

9.13 Harmonic oscillators

9.14 Two-state system

The canonical ensemble

10.1 Canonical phase-space density

We have encountered the microcanonical ensemble, which works perfectly for isolated systems, where the natural variables are E, V, N (energy, volume and particle number are conserved). Technically, one could also model an open system as isolated by including its surroundings, however this turns out to be impractical for most cases due to the complex mathematical calculations involved in finding $\omega(E)$. Instead we take an alternative approach, using something known as the partition function $\mathcal{Z}$ to link thermodynamics with statistical mechanics, rather than $\omega(E)$. The advantage is that while the latter requires evaluating hypervolumes, the partition function is delightfully simple to solve in contrast.

Consider a system S at a fixed temperature T and with energy E_S, connected to a heat bath R at the same temperature and with energy E_R. Now the heat bath plus the system form a isolated system so we must have that the total energy:

$$E = E_R + E_S \tag{10.1.1}$$

be a constant of motion. Furthermore, since the heat bath is much larger than the system in the macroscopic limit, we may assume that $\frac{E_S}{E} \ll 1$. Consequently, the microstates will now move on temperature surfaces rather than energy surfaces. All energy surfaces will be available, but the ones with large E_S will be less frequently occupied.

Let p_i be the probability of finding S in a microstate i with energy E_i, implying that the reservoir has energy $E - E_i$. The total number of microstates of the combined system is:

$$\Omega(E) = \sum_i \Omega_R(E - E_i) \tag{10.1.2}$$

where we sum over microstates. The entropy of the reservoir is given by the Taylor expansion:

$$S_R = k_B \ln \Omega_R(E - E_i) \approx k \ln \Omega_R(E) - \frac{\partial}{\partial E}(k \ln \Omega_R(E))E_i + o(E_i^2) \tag{10.1.3}$$

and since $E \approx E_R$:

$$\frac{\partial S_R}{\partial E} = k_B \frac{\partial}{\partial E}(\ln \Omega_R(E)) = \frac{1}{T} \tag{10.1.4}$$

we find that:

$$\Omega_R(E - E_i) \approx \Omega_R(E) \exp\left[- \frac{E_i}{k_B T}\right] \tag{10.1.5}$$

Hence the total number of microstates is:

$$\Omega(E) = \Omega_R(E) \sum_j \exp\left[- \frac{E_j}{k_B T}\right] \tag{10.1.6}$$

We now invoke the postulate of equal a priori probabilities, states of the combined system with the same energy must be equally likely. It follows that out of the $\Omega(E)$ states we have calculated, only $\Omega_R(E) \exp\left(- \frac{E_i}{k_B T}\right)$ correspond to a microstate i. Hence the probability of finding the system in microstate i is therefore normalized to:

$$p_i = \frac{\exp\left(- \frac{E_i}{k_B T}\right)}{\sum_i \exp\left(- \frac{E_i}{k_B T}\right)} \tag{10.1.7}$$

or in more common notation, where $\beta = \frac{1}{k_B T}$:

$$\boxed{p_i = \frac{\exp(-\beta E_i)}{\sum_j \exp(-\beta E_j)}} \tag{10.1.8}$$

It is important to note that we are summing over all states j, rather than energies E_j, since there are $\Omega_S(E_j)$ possible microstates for a given energy E_j. If we wanted to sum over energy then we would have that the number of microstates of the combined system where the system is in microstate i becomes:

$$\Omega(E) = \Omega_S(E_i)\Omega_R(E - E_i) \tag{10.1.9}$$

and thus:

$$p_i = \frac{\exp(-\beta E_i)}{\sum_{E_j} \Omega_S(E_j) \exp(-\beta E_j)} \tag{10.1.10}$$

Furthermore, if we want the probability of the energy E_i rather than the microstate i then:

$$p(E_i) = \frac{\Omega_S(E_i) \exp(-\beta E_i)}{\sum_{E_j} \Omega_S(E_j) \exp(-\beta E_j)} \tag{10.1.11}$$

For continuous microstates we instead have:

$$\boxed{\rho_c(\mathbf{q}, \mathbf{p}) = \frac{\exp(-\beta H(\mathbf{q}, \mathbf{p}))}{\frac{1}{h^{3N}} \int \exp(-\beta H(\mathbf{q}, \mathbf{p})) d^3\mathbf{q} d^3\mathbf{p}}} \tag{10.1.12}$$

known as the canonical phase space density.

Two important remarks must be made about this distribution. Firstly, as expected, microstates with $E_i \geq k_B T$ are much less likely to be occupied. Furthermore, as $T \to 0$ the

system is forced to occupy the ground state. Indeed, we may rearrange (10.1.8) as:

$$p_{GS} = \frac{1}{1 + \sum_{j \neq GS} e^{-(E_j - E_{GS})/k_B T}} \tag{10.1.13}$$

and since $E_j - E_{GS} > 0$:

$$\lim_{T \to 0} p_{GS} = \lim_{T \to 0} \frac{1}{1 + \sum_{j \neq GS} e^{-(E_j - E_{GS})/k_B T}} = 1 \tag{10.1.14}$$

The denominator in (10.1.8) and (10.1.12) is known as the canonical partition function:

$$\boxed{\mathcal{Z} = \frac{1}{h^{3N}} \int \exp\left(-\beta H(\mathbf{q}, \mathbf{p})\right) d^3\mathbf{q} d^3\mathbf{p}} \tag{10.1.15}$$

Using the ensemble average definition of entropy:

$$S = -k_B \langle \ln \rho_c \rangle = h^{3N} \int \rho_c(-k_B \ln \rho_c) d^3\mathbf{q} d^3\mathbf{p} \tag{10.1.16}$$

$$= \hbar^{3N} k_B \int \rho_c(\beta H + \ln \mathcal{Z}) d^3\mathbf{q} d^3\mathbf{p} \tag{10.1.17}$$

$$= \frac{1}{T} \langle H \rangle + k_B \ln \mathcal{Z} \tag{10.1.18}$$

where $k_B \ln \mathcal{Z}$ is brought out of the integral since it is independent of the phase space variables. We now note that $\langle H \rangle$ may be identified as the internal energy U of the system, and that thus:

$$\boxed{\langle U \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} = k_B T^2 \frac{\partial}{\partial T}(\ln \mathcal{Z})} \tag{10.1.19}$$

and that consequently:

$$S = k_B \left(\ln \mathcal{Z} + T \frac{\partial}{\partial T}(\ln \mathcal{Z}) \right) \tag{10.1.20}$$

which may be elegantly put into the form:

$$\boxed{S = k_B \frac{\partial}{\partial T}(T \ln \mathcal{Z})} \tag{10.1.21}$$

It follows that both the average energy and the entropy may be expressed in terms of the partition function and temperature alone.

Introducing the Hemholtz free energy:

$$F = U - TS \implies dF = dU - d(TS) \tag{10.1.22}$$

then we may use the first law of thermodynamics to write $dU = TdS - pdV$ and hence:

$$dF = -SdT - pdV = \left.\frac{\partial F}{\partial T}\right|_V dT + \left.\frac{\partial F}{\partial V}\right|_T dV \tag{10.1.23}$$

We then recognize that:

$$S = -\frac{\partial F}{\partial T}\bigg|_V \tag{10.1.24}$$

$$p = -\frac{\partial F}{\partial V}\bigg|_T \tag{10.1.25}$$

which should be familiar from the first part of the lecture notes. This new definition of entropy allows us to write:

$$k_B\frac{\partial}{\partial T}(T\ln\mathcal{Z}) = -\frac{\partial F}{\partial T}\bigg|_V \implies \boxed{F = -k_BT\ln\mathcal{Z} = -\frac{1}{\beta}\ln\mathcal{Z}} \tag{10.1.26}$$

We could have also seen this *a priori* from:

$$F(T,V,N) = E - TS = k_BT^2\frac{\partial}{\partial T}(\ln\mathcal{Z}) - k_BT\frac{\partial}{\partial T}(T\ln\mathcal{Z}) = -k_BT\ln\mathcal{Z} \tag{10.1.27}$$

Note also that systems will tend to equilibrium by minimizing their Hemholtz free energy, and thus by maximizing the partition function as can be seen from (10.1.26). In other words, systems will tend to macrostates with the largest number of microstates associated with them, thus maximizing entropy as desired.

We see that the partition function in the canonical ensemble assumes the role of Ω in the microcanonical ensemble, where we could find $S(E,V,N)$ from Ω, and then all other macroscopic quantities using Maxwell's relations. Similarly in the canonical ensemble we firstly find the Hemholtz free energy from the partition function $\mathcal{Z}$, and then derive all other microscopic quantities using Maxwell's relations.

10.2 Important examples

10.2.1 The ideal gas

Let's consider the ideal gas with Hamiltonian:

$$H(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{3N}\frac{p_i^2}{2m} \tag{10.2.1}$$

The partition function is then (taking intoa ccount the Gibb's factor due to the particle's indistinguishability):

$$\mathcal{Z} = \frac{1}{N!h^{3N}}\int \exp(-\beta H(\mathbf{q},\mathbf{p}))d^3\mathbf{q}d^3\mathbf{p} \tag{10.2.2}$$

$$= \frac{1}{N!h^{3N}}\int \exp\left(-\beta\sum_{i=1}^{3N}\frac{p_i^2}{2m}\right)d^3\mathbf{q}d^3\mathbf{p} \tag{10.2.3}$$

$$= \frac{V^N}{N!h^{3N}}\prod_{i=1}^{3N}\int \exp\left(-\beta\frac{p_i^2}{2m}\right)dp_i \tag{10.2.4}$$

Substituting $x = \sqrt{\frac{\beta}{2m}} p_i$ then we find that:

$$\int e^{-x^2} dx = \sqrt{\pi} \implies \int \exp\left(-\beta \frac{p_i^2}{2m}\right) dp_i = \sqrt{\frac{2\pi m}{\beta}} \tag{10.2.5}$$

and thus:

$$\mathcal{Z} = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \tag{10.2.6}$$

We may now introduce the thermal wavelength:

$$\lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \implies \mathcal{Z} = \frac{V^N}{N!\lambda^{3N}} \tag{10.2.7}$$

We may thus construct the hemholtz free energy as:

$$F(T, V, N) = -k_B T \ln \frac{V^N}{N!\lambda^{3N}} = -k_B T\left[N \ln \frac{V}{\lambda^3} - \ln N!\right] \tag{10.2.8}$$

$$= -k_B T\left[N \ln \frac{V}{\lambda^3} - N \ln N + N\right] \tag{10.2.9}$$

$$= -N k_B T\left[1 + \ln \frac{V}{N\lambda^3}\right] \tag{10.2.10}$$

$$= -N k_B T\left\{1 + \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]\right\} \tag{10.2.11}$$

$$\tag{10.2.12}$$

Now that we have found the Hemholtz free energy, we can find all other thermodynamic quantities:

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{N k_B T}{V} \implies pV = N k_B T \tag{10.2.13}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = N k_B\left\{\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]\right\} \tag{10.2.14}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -k_B T \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] \tag{10.2.15}$$

Also:

$$U = F + TS = \frac{3}{2} N k_B T \tag{10.2.16}$$

10.2.2 The ultra-relativistic gas

The Hamiltonian for a non-interacting photon gas is given by:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{N} |\mathbf{p}_i| c \tag{10.2.17}$$

Since the particles are indistinguishable, we must include the Gibb's correction factor to the partition function:

$$Z(T, V, N) = \frac{1}{N! h^{3N}} \int \exp\{-\beta H(\mathbf{q}, \mathbf{p})\} d\mathbf{q} d\mathbf{p} \tag{10.2.18}$$

$$= \frac{V^N}{N! h^{3N}} \int \exp\left\{-\beta \sum_{i=1}^{N} |\mathbf{p}_i| c\right\} d\mathbf{q} d\mathbf{p} \tag{10.2.19}$$

$$= \frac{V^N}{N! h^{3N}} \prod_{i=1}^{N} \int \exp\{-\beta |\mathbf{p}_i| c\} d\mathbf{p}_i \tag{10.2.20}$$

It is now convenient to adopt spherical coordinates so that:

$$Z(T, V, N) = \frac{V^N}{N! h^{3N}} \prod_{i=1}^{N} \int \exp\{-\beta r_i c\} r_i^2 \sin\theta_i dr_i d\theta_i d\phi_i \tag{10.2.21}$$

$$= \frac{V^N}{N! h^{3N}} \prod_{i=1}^{N} \frac{8\pi}{(\beta c)^3} \tag{10.2.22}$$

$$= \frac{(8\pi V)^N}{N! (h\beta c)^{3N}} = \frac{(8\pi V)^N}{N! \lambda^{3N}} \tag{10.2.23}$$

where we define $\lambda = \frac{hc}{k_B T}$. Now that we have found the partition function it is straightforward to calculate the free energy:

$$F(T, V, N) = -k_B T \ln Z = -k_B T \ln \frac{(8\pi V)^N}{N! \lambda^{3N}} \tag{10.2.24}$$

$$= -k_B T \ln \left(\frac{(8\pi V)^N}{N! \lambda^{3N}}\right) \tag{10.2.25}$$

$$= -k_B T \left[N \ln \left(\frac{8\pi V}{\lambda^3}\right) - N \ln N + N \right] \tag{10.2.26}$$

$$= -N k_B T \left[\ln \left(\frac{8\pi V}{N \lambda^3}\right) + 1 \right] \tag{10.2.27}$$

$$= -N k_B T \left\{ \ln \left[\frac{8\pi V}{N} \left(\frac{k_B T}{hc}\right)^3\right] + 1 \right\} \tag{10.2.28}$$

The other thermodynamic quantities can be found very easily from $F(T, V, N)$ as follows:

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{N k_B T}{V} \implies pV = N k_B T \tag{10.2.29}$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = N k_B \left\{ 4 + \ln \left[\frac{8\pi V}{N} \left(\frac{k_B T}{hc}\right)^3\right] \right\} \tag{10.2.30}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = -k_B T \ln \left[\frac{8\pi V}{N} \left(\frac{k_B T}{hc}\right)^3\right] \tag{10.2.31}$$

giving us an expression for the internal energy:

$$U = F + TS = 3Nk_BT \tag{10.2.32}$$

10.2.3 The harmonic oscillator

Consider a collection of N indistinguishable harmonic oscillators in three dimensions. The Hamiltonian for this system reads:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2 \right) \tag{10.2.33}$$

The partition function reads:

$$\mathcal{Z}(T, V, N) = \frac{1}{N!h^{3N}} \int \exp\left\{ -\beta \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2 \right) \right\} d\mathbf{p}d\mathbf{q} \tag{10.2.34}$$

$$= \frac{1}{N!h^{3N}} \prod_{i=1}^{3N} \int \exp\left\{ -\beta \frac{p_i^2}{2m} \right\} dp_i \int \exp\left\{ -\frac{1}{2}\beta m\omega^2 q_i^2 \right\} dq_i \tag{10.2.35}$$

$$= \frac{1}{N!h^{3N}} \prod_{i=1}^{3N} \sqrt{\frac{2m\pi}{\beta}} \sqrt{\frac{2\pi}{\beta m\omega^2}} \tag{10.2.36}$$

$$= \frac{1}{N!} \left(\frac{2\pi}{h\beta\omega} \right)^{3N} = \frac{1}{N!} \left(\frac{1}{\hbar\beta\omega} \right)^{3N} \tag{10.2.37}$$

Consequently, the free energy is found to be:

$$F(T, V, N) = -k_BT \ln \mathcal{Z} = -k_BT \ln \left[\frac{1}{N!} \left(\frac{1}{\hbar\beta\omega} \right)^{3N} \right] \tag{10.2.38}$$

$$= -Nk_BT \left\{ \ln \left[\frac{1}{N(\hbar\beta\omega)^3} \right] + 1 \right\} \tag{10.2.39}$$

Therefore the pressure, entropy and chemical potential are found to be:

$$p = -\left. \frac{\partial F}{\partial V} \right|_{T,N} = 0 \tag{10.2.40}$$

$$S = -\left. \frac{\partial F}{\partial T} \right|_{V,N} = Nk_B \left\{ \ln \left[\frac{1}{N(\hbar\beta\omega)^3} \right] + 4 \right\} \tag{10.2.41}$$

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T,V} = -k_BT \ln \left[\frac{1}{N(\hbar\beta\omega)^3} \right] \tag{10.2.42}$$

and the internal potential thus takes the form of $U = F + TS = 3Nk_BT$.

10.3 The equipartition and virial theorems

Derivation in the canonical ensemble

Let $H(q_i, p_i)$ be the Hamiltonian of a system and let x_i denote all phase coordinates $\{q_i, p_i\}$. Therefore:

$$\langle x_i \frac{\partial H}{\partial x_k} \rangle = \frac{1}{h^{3N}} \int \rho(\mathbf{x}) x_i \frac{\partial H}{\partial x_k} d\mathbf{x} \tag{10.3.1}$$

$$= \frac{1}{h^{3N} \mathcal{Z}} \int x_i \exp(-\beta H(\mathbf{x})) \frac{\partial H}{\partial x_k} d\mathbf{x} \tag{10.3.2}$$

$$= -\frac{1}{\beta h^{3N} \mathcal{Z}} \int x_i \frac{\partial}{\partial x_k} (x_i \exp(-\beta H(\mathbf{x}))) d\mathbf{x} \tag{10.3.3}$$

We can now integrate by parts. First, we define $d\mathbf{x}'$ to be the infinitesimal volume element excluding dx_k. Moreover, we also assume that $x_i \exp\{-\beta H\}$ vanishes at the boundaries $\min x_k$ and $\max x_k$ (usually because $H \to \infty$).

$$\langle x_i \frac{\partial H}{\partial x_k} \rangle = -\frac{1}{\beta h^{3N} \mathcal{Z}} \left[\int \left[x_i \exp(-\beta H(\mathbf{x})) \right]_{\min x_k}^{\max x_k} d\mathbf{x}' - \int \delta_{ik} \exp(-\beta H(\mathbf{x})) d\mathbf{x} \right] \tag{10.3.4}$$

$$= \frac{1}{h^{3N} \beta} \delta_{ik} \int \frac{\exp(-\beta H(\mathbf{x}))}{\mathcal{Z}} d\mathbf{x} \tag{10.3.5}$$

$$= \delta_{ik} k_B T \tag{10.3.6}$$

It follows from that if we choose canonically conjugate variables, the expectation value of their product will be equal to $k_B T$. For example:

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \dot{p}_i \rangle = k_B T \tag{10.3.7}$$

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = k_B T \implies \langle \frac{p_i^2}{2m} \rangle = \frac{1}{2} k_B T \tag{10.3.8}$$

The latter can be used to find the mean kinetic energy of the ith particle in three dimensions:

$$\langle T_i \rangle = \frac{3}{2} k_B T \tag{10.3.9}$$

so for a collection of N particles the mean kinetic energy is:

$$\langle T \rangle = \frac{3}{2} N k_B T \tag{10.3.10}$$

Suppose the ith particle is acted on by a conservative force $\mathbf{F}_i = -\nabla V_i$. Then, we see that:

$$-\langle \mathbf{r}_i \cdot \mathbf{F}_i \rangle = \langle x_i \frac{\partial V_i}{\partial x_i} \rangle + \langle y_i \frac{\partial V_i}{\partial y_i} \rangle + \langle z_i \frac{\partial V_i}{\partial z_i} \rangle = 3k_B T \tag{10.3.11}$$

so for a central potential of the form $V_i \propto r_i^\alpha$ then $\mathbf{r}_i \cdot \mathbf{F}_i = -\alpha V_i$ giving:

$$\langle \alpha V_i \rangle = 3k_B T = 2 \langle T_i \rangle \implies \langle T \rangle_i = \frac{\alpha}{2} \langle V_i \rangle \tag{10.3.12}$$

which is known as the Virial theorem. Note that in this derivation we assumed that integration in x could be done. While in classical mechanics there is no ambiguity in this assumption, in quantum mechanics this implies that the temperature $k_B T$ must be larger than the quanta of energy in the system. In the special case where $\alpha = 2$ we get that $\langle T_i \rangle = \langle V_i \rangle$, the potential and kinetic energies contribute equally to the total energy.

More specifically, we have that for a hamiltonian with f degrees of freedom containing only quadratic terms:

$$H = \sum_{i=1}^{f} (a_i q_i^2 + b_i p_i^2) \tag{10.3.13}$$

then clearly:

$$H = \frac{1}{2} \sum_{i=1}^{f} \left(q_i \frac{\partial H}{\partial q_i} + p_i \frac{\partial H}{\partial p_i} \right) \tag{10.3.14}$$

$$\iff U = \langle H \rangle = \frac{1}{2} \sum_{i=1}^{f} \left(\langle q_i \frac{\partial H}{\partial q_i} \rangle + \langle p_i \frac{\partial H}{\partial p_i} \rangle \right) = f k_B T \tag{10.3.15}$$

In other words, since there are $2f$ quadratic terms, each quadratic term contributes $\frac{1}{2} k_B T$ to the internal energy. This result is known as the **equipartition theorem**. For $f = 3N$ then we get the familiar:

$$U = \langle H \rangle = 3N k_B T \tag{10.3.16}$$

which we have found several times already in the previous sections.

Derivation in the microcanonical ensemble

Let $H(q_i, p_i)$ be the Hamiltonian of a system and let x_i denote all phase coordinates $\{q_i, p_i\}$. In the microcanonical ensemble, we have that:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{h^{3N}} \int \rho(\mathbf{x}) x_i \frac{\partial H}{\partial x_j} d\omega \tag{10.3.17}$$

$$= \frac{1}{h^{3N}} \frac{1}{\Omega \Delta E} \int_{\Delta E} x_i \frac{\partial H}{\partial x_j} d\omega \tag{10.3.18}$$

$$= \frac{1}{h^{3N}} \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} x_i \frac{\partial H}{\partial x_j} d\omega \tag{10.3.19}$$

$$= \frac{1}{h^{3N}} \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} x_i \frac{\partial (H - E)}{\partial x_j} d\omega \tag{10.3.20}$$

where in the last line we used $\frac{\partial E}{\partial x_j} = 0$ where $x = q, p$. This allows us to integrate by parts:

$$\frac{1}{h^{3N}} \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} x_i \frac{\partial (H - E)}{\partial x_j} d\omega = \frac{1}{h^{3N}} \frac{1}{\Omega} \frac{\partial}{\partial E} \left[\int_{H < E} x_i [(H - E)]_{\min x_j}^{\max x_j} d\omega' \right. \tag{10.3.21}$$
$$\left. - \int_{H < E} (H - E) \frac{\partial x_i}{\partial x_j} d\omega \right]$$

where $d\omega'$ integrates over all variables except x_j. If x_j has an extremal value, then this means that it must lie on the energy surface $H = E$, and consequently the integrand vanishes.

The integral thus simplifies to:

$$-\frac{1}{h^{3N}}\frac{1}{\Omega}\frac{\partial}{\partial E}\int_{H<E}(H-E)\delta_{ij}d\omega = \frac{1}{h^{3N}}\frac{1}{\Omega}\delta_{ij}\int_{H<E}d\omega \tag{10.3.22}$$

$$= \frac{1}{h^{3N}}\frac{1}{\Omega}\delta_{ij}\omega \tag{10.3.23}$$

$$= \frac{\omega'}{\Omega}\delta_{ij} \tag{10.3.24}$$

where we defined $\omega' = \frac{1}{h^{3N}}\omega$. Using the definition of $\Omega = \frac{\partial \omega'}{\partial E}$ we retrieve the remarkable result:

$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = \frac{\omega'}{\frac{\partial \omega'}{\partial E}}\delta_{ij} = \frac{\omega'}{1}\frac{\partial}{\partial E}(\ln \omega')\delta_{ij} \tag{10.3.25}$$

$$= \frac{\omega'}{k_B}\frac{\partial S}{\partial E}\delta_{ij} = k_B T \delta_{ij} \tag{10.3.26}$$

as found previously.

Canonical examples of the canonical ensemble

The Grand Canonical Ensemble

12.1   Introduction

We have seen how to describe isolated systems which conserve both energy and particle number using the microcanonical ensemble, as well as closed systems which conserve only particle number, but allow variable energies, using the canonical ensemble. It is thus fitting to have a third ensemble which can handle open systems where neither energy nor particle number are constant. Such an ensemble is of particular use when describing systems where heat and particles can be exchanged through contact with a heat and particle bath.

The natural variables to be used are T, V and μ, the chemical potential.

The chemical potential is defined as the amount by which the internal energy will change when adding a particle to the system isentropically and isochorically (constant entropy and volume). We must therefore revisit our First Law of Thermodynamics and add a new term:

$$\boxed{dU = TdS - pdV + \mu dN} \tag{12.1.1}$$

giving us the following definition of μ:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{12.1.2}$$

Recalling the definitions of the other thermodynamic potentials:

$$F = U - TS \implies dF = -pdV - SdT + \mu dN \tag{12.1.3}$$

$$G = F + pV \implies dG = Vdp - SdT + \mu dN \tag{12.1.4}$$

and equivalently:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}, \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T} \tag{12.1.5}$$

The chemical potential can also be related to entropy and the second law of thermodynamics. Using U, V, N as natural variables then:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} + \left(\frac{\partial S}{\partial V}\right)_{U,N} + \left(\frac{\partial S}{\partial N}\right)_{V,U} \tag{12.1.6}$$

which when compared with

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN \tag{12.1.7}$$

yields:

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{V,U} = -\frac{\mu}{T}} \tag{12.1.8}$$

This can be used to investigate how and when a system reaches equilibrium. Indeed, suppose we have two systems decoupled to their surroundings which exchange heat and particles. It is clear that $dU_1 = -dU_2 = dU, dV_1 = -dV_2 = dV, dN_1 = -dN_1 = dN$ since the two systems combined form an isolated system. Then:

$$dS_{tot} = \frac{dU_1}{T_1} + \frac{p_1}{T_1}dV_1 - \frac{\mu_1}{T_1}dN_1 + \frac{dU_2}{T_2} + \frac{p_2}{T_2}dV_2 - \frac{\mu_2}{T_2}dN_2 \tag{12.1.9}$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)dV + \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)dN \tag{12.1.10}$$

For equilibrium to be established we need $dS_{tot} = 0$ and hence:

$$\boxed{T_1 = T_2, \quad p_1 = p_2, \quad \mu_1 = \mu_2} \tag{12.1.11}$$

Now suppose we have just one system which can exchange U, V, N with a reservoir. We then see that:

$$dS_{tot} = dS - \frac{dU}{T_R} - \frac{p_R}{T_R}dV + \frac{\mu_R}{T_R}dN \tag{12.1.12}$$

Define the availability as we have previously as $dA = -T_R dS_{tot}$, then:

$$dA = -T_R dS + dU + p_R dV - \mu_R dN \tag{12.1.13}$$

and inserting $dU = TdS - pdV + \mu dN$ we finally find:

$$\boxed{dA = (T - T_R)dS - (p - p_R)dV + (\mu - \mu_R)dN} \tag{12.1.14}$$

From our definition of the availability, equilibrium is established when availability is minimized (entropy maximized).

12.2 The Grand canonical phase space density

We consider an open system S with energy E_S and number of particles N_S at temperature T and chemical potential μ surrounded by a reservoir E_R and number of particles N_R at the same temperature and chemical potential. The system plus the reservoir form an isolated system which we refer to as the total system. Thus we define $E = E_S + E_R$ and $N = N_S + N_R$ to be the energy and number of particles of the total system, and assume that:

$$\frac{N_S}{N} \ll 1, \; \frac{E_S}{E} \ll 1 \tag{12.2.1}$$

The number of microstates of the system consistent with the macrostate E, N is:

$$\Omega(E, N) = \sum_{ij} \Omega_R(E - E_i, N - N_j) \tag{12.2.2}$$

where we sum over microstates with energy E_i with particle number N_j. Defining the Boltzmann entropy of the reservoir as $S_R = k_B \ln \Omega_R$ we find that:

$$S_R = k_B \ln \Omega_R(E - E_i, N - N_j) \tag{12.2.3}$$

$$\approx k_B \ln \Omega_R(E, N) - E_i \frac{\partial S}{\partial E} - N_j \frac{\partial S}{\partial N} \tag{12.2.4}$$

$$\approx k_B \ln \Omega_R(E, N) - -\frac{E_i}{T} + \frac{\mu N_j}{T} \tag{12.2.5}$$

where we used (12.1.8). Consequently we find that:

$$\Omega_R(E - E_i, N - N_j) = \Omega_R(E, N) \exp(-\beta(E_i - \mu N_j)) \tag{12.2.6}$$

giving the following probability distribution:

$$\boxed{p_{ij} = \frac{1}{\mathcal{Z}} \exp(-\beta(E_i - \mu N_j)), \ \ \mathcal{Z} = \sum_{ml} \exp(-\beta(E_m - \mu N_l))} \tag{12.2.7}$$

We define $\mathcal{Z}$ as the grand partition function.

An alternative way to derive (12.2.7) is by maximizing the Gibbs entropy.

We can extend (12.2.7) to the continuous case, letting $\alpha = \beta \mu$ it is given by:

$$\boxed{\rho(\mathbf{p}, \mathbf{q}, N) = \frac{1}{\mathcal{Z}} \exp(-\beta H + \alpha N), \ \ \mathcal{Z} = \sum_N \frac{1}{h^{3N}} \int \exp(-\beta H + \alpha N) d^{3N}\mathbf{p} \ d^{3N}\mathbf{q}} \tag{12.2.8}$$

Using the ensemble average definition of entropy we get that:

$$S = -k_B \langle \ln \rho \rangle = -\frac{k_B}{\mathcal{Z}} \int \exp(-\beta H + \alpha N)[-\ln \mathcal{Z} - \beta H + \alpha N] d\omega \tag{12.2.9}$$

$$= k_B[-\ln \mathcal{Z} - \beta U + \alpha \langle N \rangle] \tag{12.2.10}$$

We define $N = \langle N \rangle$ to write:

$$\boxed{\Phi_G = -\frac{1}{\beta} \ln \mathcal{Z} = -TS + U - \mu N = F - \mu N} \tag{12.2.11}$$

where we defined the grand canonical potential Φ_G. Alternatively, using the first law $U = TS + pV + \mu N$ then:

$$\Phi_G = -pV \tag{12.2.12}$$

which tells us that the Gibbs free energy takes the simple form:

$$G = U + pV - TS = \mu N \tag{12.2.13}$$

Finally, the thermodynamic variables can be expressed in terms of the grand potential:

$$d\Phi_G = \mu dN - dF = \mu dN - dU + TdS = \mu dN + pdV + SdT \tag{12.2.14}$$

$$\implies \mu = \left.\frac{\partial \Phi_G}{\partial N}\right|_{V,S}, \; p = \left.\frac{\partial \Phi_G}{\partial V}\right|_{S,N}, \; S = \left.\frac{\partial \Phi_G}{\partial T}\right|_{N,V} \tag{12.2.15}$$

Note also that:

$$\frac{\partial}{\partial \beta}(\ln \mathcal{Z}) = \frac{1}{\mathcal{Z}} \sum_N \int (-\beta H + \beta \mu N) \exp(-\beta H + \alpha N) d\omega \tag{12.2.16}$$

$$= -U + \mu N \tag{12.2.17}$$

Therefore the entropy can be found from the grand partition function by:

$$k_B T \ln \mathcal{Z} = TS - k_B T^2 \frac{\partial}{\partial T}(\ln \mathcal{Z}) \tag{12.2.18}$$

$$\implies \boxed{S = k_B \frac{\partial}{\partial T}(T \ln \mathcal{Z})} \tag{12.2.19}$$

Similarly we can see that the average particle number can be expressed as:

$$\boxed{N = k_B T \frac{\partial}{\partial \mu}(\ln \mathcal{Z})} \tag{12.2.20}$$

12.3 Relating the grand partition function and canonical partition functions

The canonical partition function Z_N for an N particle system can be related to the grand partition function of the same system with variable particle number via:

$$\boxed{\mathcal{Z} = \sum_N f^N Z_N, \; f = e^{\mu\beta}} \tag{12.3.1}$$

where f is known as the fugacity. We see that, much like the Boltzmann weight is used to average over microcanonical ensembles at different E to get the canonical ensemble, the fugacity is the weight used to average over the canonical ensembles at different N to get the grand canonical ensemble.

The fugacity may be used to express N in a different way. Indeed (we use $\langle N \rangle$ instead of N to avoid confusion):

$$\langle N \rangle = \sum_N N p_N = \sum_N N \sum_i \frac{\exp(-\beta e_I)}{\mathcal{Z}} f^N = \frac{1}{\mathcal{Z}} \sum_N N f^N Z_N \tag{12.3.2}$$

Note also that:

$$\frac{\partial \mathcal{Z}}{\partial f} = \sum_N N f^{N-1} Z_N \tag{12.3.3}$$

which allows us to write the particle number as a derivative with respect to fugacity rather

than chemical potential:

$$N = f\frac{\partial}{\partial f}(\ln \mathcal{Z}) \tag{12.3.4}$$

We would also like to find the fluctuation in $\langle N \rangle$ so we need to calculate $\langle N^2 \rangle$:

$$\langle N \rangle^2 = \frac{1}{\mathcal{Z}}\sum_N N^2 f^N Z_N \tag{12.3.5}$$

To do so we investigate the second order derivative of $\ln \mathcal{Z}$:

$$\frac{\partial^2 \mathcal{Z}}{\partial f^2} = \frac{\partial}{\partial f}\left(\frac{1}{\mathcal{Z}}\sum_N N f^{N-1} Z_N\right) \tag{12.3.6}$$

$$= -\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial f}\right)^2 + \frac{1}{\mathcal{Z}}\sum_N N(N-1) f^{N-2} Z_N \tag{12.3.7}$$

$$= -\left(\frac{\langle N \rangle}{f}\right)^2 + \frac{1}{\mathcal{Z}}\sum_N N^2 f^{N-2} Z_N - \frac{1}{\mathcal{Z}}\sum_N f^{N-2} Z_N \tag{12.3.8}$$

$$\implies f^2\frac{\partial^2 \mathcal{Z}}{\partial f^2} = \langle N^2 \rangle - \langle N \rangle^2 - \langle N \rangle \tag{12.3.9}$$

Substituting (12.3.4) into the above we find that:

$$(\Delta N)^2 = f^2\frac{\partial^2 \mathcal{Z}}{\partial f^2} - f\frac{\partial}{\partial f}(\ln \mathcal{Z}) = \left(f\frac{\partial}{\partial f}\right)^2(\ln \mathcal{Z}) \tag{12.3.10}$$

Part IV

Quantum statistical physics

Density operator methods

13.1 Making the jump to quantum

In classical statistical mechanics we assigned probabilities to microstates $(\mathbf{q}, \mathbf{p})$, which were points in the phase space. In quantum statistical mechanics our microstates will be quantum states $|\psi\rangle$ in the Hilbert space.

We also measure observables $A(\mathbf{q}, \mathbf{p})$ defined as functions in the phase space. In quantum mechanics observables are replaced by linear hermitian operators $\hat{A} \in \mathcal{L}(\mathcal{H})$ acting on the Hilbert space. The expectation value of some operator in a given state gives the expectation value, the average value measured in an experiment.

	CSM	QSM
Microstate	$(\mathbf{q}, \mathbf{p}) \in \mathcal{P}$	$|\psi\rangle \in \mathcal{H}$
Observable	$A(\mathbf{q}, \mathbf{p})$	$\langle A \rangle , \ \hat{A} \in \mathcal{L}(\mathcal{H})$
Canonical conjugation	$\{q_i, p_j\} = \delta_{ij}$	$[\hat{q}_i, \hat{p}_i] = i\hbar\delta_{ij}$
Time evolution	$\frac{dA}{dt} = \{A, H\} + \frac{\partial A}{\partial t}$	$\frac{d\langle A\rangle}{dt} = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}]\rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle$

Consider a quantum system prepared in an ensemble of states $\{|\psi_i\rangle\}$ each with probability p_i. That is, not only do we have uncertainties inherent to quantum mechanics, but we also have the uncertainty in the wavefunction of the system. The state of a system prepared like this is known as a mixed state. The ensemble averaged expectation value $\bar{\hat{f}}$ of some operator $\hat{f}$ is given by the weighted average of the expectation value for each state in the ensemble:

$$\langle \bar{f} \rangle = \sum_i p_i \langle \psi_i|\hat{f}|\psi_i\rangle \tag{13.1.1}$$

We can expand this in a given orthonormal basis as:

$$\langle \bar{f} \rangle = \sum_{imn} p_i \langle \psi_i|n\rangle \langle n|\hat{f}|m\rangle \langle m|\psi_i\rangle = \sum_{mn} \langle n|\hat{f}|m\rangle \sum_i \langle m|\psi_i\rangle \langle \psi_i|n\rangle \tag{13.1.2}$$

We define the density matrix related to the state of this system is given by:

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i| \tag{13.1.3}$$

which allows us to write:

$$\langle \bar{f} \rangle = \sum_{mn} \langle n|\hat{f}|m \rangle \langle m|\rho|n \rangle = \text{Tr}\left(\hat{\rho}\hat{f}\right) \tag{13.1.4}$$

So the expectation value of an observable f for a system in a mixed state defined by a density matrix ρ can be expressed as a trace:

$$\boxed{\langle \bar{f} \rangle = \text{Tr}\left(\hat{\rho}\hat{f}\right)} \tag{13.1.5}$$

(13.1.4) is reminiscent of the classical formula:

$$\langle f \rangle = \int f(\mathbf{p}, \mathbf{q})\rho(\mathbf{p}, \mathbf{q})d\omega \tag{13.1.6}$$

so we should identify the density matrix with the ensemble probability density. In other words $\rho(\mathbf{p}, \mathbf{q})$ got promoted to $\hat{\rho}$.

It is easy to see that:

(i) the density matrix has unit trace:

$$\text{Tr}\,\hat{\rho} = \sum_j \sum_i p_i \langle j|i \rangle \langle i|j \rangle = \sum_j p_j = 1 \tag{13.1.7}$$

corresponding to the normalization of classical probability densities.

(ii) the density matrix is hermitian:

$$\hat{\rho}^\dagger = \sum_i p_i(|i\rangle \langle i|)^\dagger = \rho \tag{13.1.8}$$

corresponding to the fact that classical probabilities are real numbers.

(iii) The density operator is positive definite:

$$\langle \psi|\hat{\rho}|\psi \rangle = \sum_i p_i |\langle \psi|\psi_i \rangle|^2 > 0, \ \forall \, |\psi\rangle \in \mathcal{H} \tag{13.1.9}$$

corresponding to the fact that the classical probability density must be positive.

Recall also that in classical physics the evolution of ρ was given by Louiville's theorem:

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \tag{13.1.10}$$

Note that in the Schrodinger picture we have a completely analogous result:

$$i\hbar\frac{d\hat{\rho}}{dt} = \hat{H}\sum_i p_i(|\psi_i\rangle \langle \psi_i| - |\psi_i\rangle \langle \psi_i|)\hat{H} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} \tag{13.1.11}$$

$$\implies \boxed{\frac{d\hat{\rho}}{dt} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}]} \tag{13.1.12}$$

which is known as the Von Neumman equation. It is important to notice the remarkable duality between Poisson brackets and commutators. Here we assumed that p_i does not change, this is reasonable as long as the system we consider is not interacting with its surroundings.

The equilibrium density operator must be time-independent so we need $[\hat{H}, \hat{\rho}] = 0$. Thus in statistical mechanics we require ρ to be a function of operators commuting with $\hat{H}$, thus corresponding to conserved quantities. A completely analogous statement applied to classical statistical mechanics.

The time evolution of the density operator is generally non-linear, unlike the Schrodinger evolution which only applies to pure states. It follows that:

$$i\hbar \frac{d\langle f \rangle}{dt} = i\hbar \frac{d}{dt}[\text{Tr}\left(\hat{\rho}\hat{f}\right)] = \text{Tr}\left([\hat{H}, \hat{\rho}]\hat{f} + i\hbar\hat{\rho}\frac{\partial \hat{f}}{\partial t}\right) = \text{Tr}\left([\hat{H}, \hat{\rho}]\hat{f}\right) + i\hbar\left\langle \frac{\partial \hat{f}}{\partial t} \right\rangle \quad (13.1.13)$$

so in equilibrium:

$$\left\langle \frac{\partial \hat{f}}{\partial t} \right\rangle = 0 \quad (13.1.14)$$

13.2 Quantum statistical ensembles

Microcanonical ensemble

We find that:

$$\rho_{mc} = \frac{1}{\Omega(E)}\delta_{H,E} \quad (13.2.1)$$

so the density matrix elements are:

$$\langle m|\rho_{mc}|n\rangle = \frac{1}{\Omega(E)} \begin{cases} 1, & \text{if } E_m = E \text{ and } m = n \\ 0, & \text{if } E_m \neq E \text{ or } m \neq n \end{cases} \quad (13.2.2)$$

The energy condition $E_m = E$ comes from the delta function $\delta_{H,E}$ while the diagonal condition $m = n$ comes from the orthonormality of energy eigenstates. It follows that the density matrix is diagonal whose only non-zero elements are those with energy E. Note that this density operator satisfies the equal-a-priori probability since eigenstates of equal energy have the same probability.

Canonical ensemble

We find that:

$$\hat{\rho} = \frac{1}{Z}e^{-\beta\hat{H}}, \ Z = \text{Tr}\left(e^{-\beta\hat{H}}\right) \quad (13.2.3)$$

or in the energy eigenbasis $\{|n\rangle\}$:

$$\hat{\rho} = \frac{1}{Z}e^{-\beta E_n}|n\rangle\langle n| \quad (13.2.4)$$

13.3   Particle in a box

Consider a free particle in a box of length L with periodic boundary conditions. Then the energy eigenstates in the position basis read:

$$\langle x|k\rangle = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{13.3.1}$$

with energy

$$E_k = \frac{\hbar^2 k^2}{2m}, \ k_{x,y,z} = \frac{2\pi}{L}n_{x,y,z} \tag{13.3.2}$$

We are interested in the matrix elements of the density matrix in the position representation. We look at the infinite L limit where the possible momenta now form a continuum. Then we must replace:

$$\frac{1}{V}\sum_{\mathbf{k}} = \int \frac{d^3\mathbf{k}}{(2\pi)^3} \tag{13.3.3}$$

where $V = L^3$. Therefore:

$$\langle \mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle = \int \frac{d^3\mathbf{k}}{(2\pi)^3}e^{-\beta E(k)}\langle \mathbf{r}|\mathbf{k}\rangle\langle \mathbf{k}|\mathbf{r}'\rangle \tag{13.3.4}$$

$$= \frac{1}{Z}V\int \frac{d^3\mathbf{k}}{(2\pi)^3}\exp\left[-\frac{\beta\hbar^2\mathbf{k}^2}{2m} + i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')\right] \tag{13.3.5}$$

$$= \frac{1}{Z}\frac{1}{(2\pi)^3}\left(\sqrt{\frac{2m\pi}{\beta\hbar^2}}\right)^3\exp\left(-\frac{m}{2\beta\hbar^2}(\mathbf{r}-\mathbf{r}')^2\right) \tag{13.3.6}$$

We define the thermal wavelength to be:

$$\boxed{\lambda = \frac{\hbar}{\sqrt{2\pi m k_B T}}} \tag{13.3.7}$$

which further simplifies (13.3.6) into:

$$\rho(\mathbf{r},\mathbf{r}') \equiv \langle \mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle = \frac{1}{Z\lambda^3}\exp\left(-\frac{\pi(\mathbf{r}-\mathbf{r}')^2}{\lambda^2}\right) \tag{13.3.8}$$

Calculating the partition function is also quite easy using the appropriate Gaussian integral:

$$Z = \int \frac{d^3\mathbf{k}}{(2\pi)^3}e^{-\beta\hbar^2\mathbf{k}^2/2m} = \frac{V}{\lambda^3} \tag{13.3.9}$$

giving:

$$\boxed{\rho(\mathbf{r},\mathbf{r}') = \frac{1}{V}\exp\left(-\frac{\pi(\mathbf{r}-\mathbf{r}')^2}{\lambda^2}\right)} \tag{13.3.10}$$

Clearly, for N distinguishable particles we would have:

$$\rho(\{\mathbf{r}_i\},\{\mathbf{r}'_i\}) = \frac{1}{V^N}\exp\left(-\sum_i \frac{\pi(\mathbf{r}_i-\mathbf{r}'_i)^2}{\lambda^2}\right) \tag{13.3.11}$$

13.4 Identical particles

The situation for identical particles gets much more complicated due to the (anti)symmetrization of the (fermionic) bosonic wavefunctions:

$$|k_1, k_2, ..., k_N\rangle_A = \frac{1}{\sqrt{N!}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) P_\sigma |k_1, k_2, ..., k_N\rangle \qquad (13.4.1)$$

$$|k_1, k_2, ..., k_N\rangle_S = \frac{1}{\sqrt{N! \prod_i (n_i!)}} \sum_{\sigma \in S_N} P_\sigma |k_1, k_2, ..., k_N\rangle \qquad (13.4.2)$$

where n_i are the number of particles in state $|k_i\rangle$. For simplicity let $|\psi\rangle_\eta$ denote the fermionic wavefunction if $\eta = -1$ and the bosonic wavefunction if $\eta = 1$, so that:

$$|k_1, k_2, ..., k_N\rangle_\eta = \frac{1}{\sqrt{N! \prod_i (n_i!)}} \sum_{\sigma \in S_N} \eta^{\text{sgn}(\sigma)} P_\sigma |k_1, k_2, ..., k_N\rangle \qquad (13.4.3)$$

since $n_k = 0, 1$ for fermions. We then find that:

$$\rho_\eta(\{\mathbf{r}_i\}, \{\mathbf{r}_i'\}) = \frac{1}{Z} \sum_{\{\mathbf{k}_i\}} \exp\left(-\sum_i \frac{\beta \hbar^2 k_i^2}{2m}\right) \langle \mathbf{r}_1', ..., \mathbf{r}_N' | \mathbf{k}_1, ..., \mathbf{k}_N \rangle_\eta \langle \mathbf{k}_1, ..., \mathbf{k}_N | \mathbf{r}_1', ..., \mathbf{r}_N \rangle_\eta \qquad (13.4.4)$$

Note that the sum over $\{\mathbf{k}_i\}$ is not unrestricted, since different sequences of $\mathbf{k}_i$ can still symmetrize to the same wave-function. It is easy to see that there are $\frac{N!}{\prod_i (n_i)!}$ wavefunctions that symmetrize to the same state. Hence:

$$\rho_\eta(\{\mathbf{r}_i\}, \{\mathbf{r}_i'\}) = \sum_{\{\mathbf{k}_i\}} \frac{\prod_i (n_i)!}{N! Z} \exp\left(-\sum_i \frac{\beta \hbar^2 k_i^2}{2m}\right) \langle \mathbf{r}_1', ..., \mathbf{r}_N' | \mathbf{k}_1, ..., \mathbf{k}_N \rangle_\eta \langle \mathbf{k}_1, ..., \mathbf{k}_N | \mathbf{r}_1, ..., \mathbf{r}_N \rangle_\eta \qquad (13.4.5)$$

where the sum is now unrestricted. We can now insert (13.4.4) into (13.4.5) to find that:

$$\rho_\eta(\{\mathbf{r}_i\}, \{\mathbf{r}_i'\}) = \sum_{\{\mathbf{k}_i\}} \sum_{\sigma, \sigma' \in S_N} \frac{1}{(N!)^2 Z} \exp\left(-\sum_i \frac{\beta \hbar^2 k_i^2}{2m}\right) \eta^{\text{sgn}(\sigma) + \text{sgn}(\sigma')} \qquad (13.4.6)$$

$$\langle \mathbf{r}_1', ..., \mathbf{r}_N' | P_{\sigma'} | \mathbf{k}_1, ..., \mathbf{k}_N \rangle \langle \mathbf{k}_1, ..., \mathbf{k}_N | P_\sigma | \mathbf{r}_1, ..., \mathbf{r}_N \rangle$$

This daunting sum becomes an even more daunting integral as $L \to \infty$. We do it piece by piece. Firstly:

$$\langle \mathbf{r}_1, ..., \mathbf{r}_N | P_\sigma | \mathbf{k}_1, ..., \mathbf{k}_N \rangle = \prod_i e^{i\mathbf{k}_{\sigma(i)} \cdot \mathbf{r}_i} \qquad (13.4.7)$$

so that:

$$= \sum_{\sigma, \sigma' \in S_N} \frac{1}{(N!)^2 Z} \eta^{\text{sgn}(\sigma) + \text{sgn}(\sigma')} \int \prod_i \frac{d^3 \mathbf{k}_i}{(2\pi)^3} \exp\left(-\frac{\beta \hbar^2 k_i^2}{2m}\right) e^{i\mathbf{r}_i' \cdot \mathbf{k}_{\sigma'(i)}} e^{-i\mathbf{r}_i \cdot \mathbf{k}_{\sigma(i)}} \qquad (13.4.8)$$

$$= \sum_{\sigma, \sigma' \in S_N} \frac{1}{(N!)^2 Z} \eta^{\text{sgn}(\sigma) + \text{sgn}(\sigma')} \int \prod_i \frac{d^3 \mathbf{k}_i}{(2\pi)^3} \exp\left(-\frac{\beta \hbar^2 k_i^2}{2m}\right) e^{i\mathbf{k}_i \cdot (\mathbf{r}_{\sigma^{-1}(i)} - \mathbf{r}_{\sigma'^{-1}(i)}')} \qquad (13.4.9)$$

where we rearrange the $e^{i\mathbf{r}'_i \cdot \mathbf{k}_{\sigma(i)}}$ terms so that the exponent contains $\mathbf{k}_i$. Now we again have:

$$= \sum_{\sigma,\sigma' \in S_N} \frac{1}{(N!)^2 Z} \eta^{\text{sgn}(\sigma)+\text{sgn}(\sigma')} \prod_i \frac{1}{\lambda^3} \exp\left[- \frac{\pi(\mathbf{r}_{\sigma^{-1}(i)} - \mathbf{r}'_{\sigma^{-1}(i)})^2}{\lambda^2} \right] \quad (13.4.10)$$

Finally, note that permuting all of $\sigma(i)$ will give back $\sigma(i)$ in some order. Thus we can write the sum over two permutations as the sum over just one permutation multiplied by $|S_N| = N!$ since the sum will be repeated every time for a different $\sigma' \in S_N$:

$$\boxed{\rho_\eta(\{\mathbf{r}_i\}, \{\mathbf{r}'_i\}) = \sum_{\sigma \in S_N} \frac{1}{(N!)Z \lambda^{3N}} \eta^{\text{sgn}(\sigma')} \exp\left[- \sum_i \frac{\pi(\mathbf{r}_{(i)} - \mathbf{r}'_{\sigma(i)})^2}{\lambda^2} \right]} \quad (13.4.11)$$

13.5 Boson and fermion gases in the GCE

Consider a non-interacting quantum gas with single particle dispersion relation $\epsilon_{\mathbf{k}} = \epsilon(\mathbf{k})$. We have seen how to calculate partition function in the free particle case using the momentum basis. We can also use the occupation basis $\{n_{\mathbf{k}}\}$ where:

$$Z = \sum_{\{n_{\mathbf{k}}\}} e^{-\beta \sum_k \epsilon(\mathbf{k}) n_{\mathbf{k}}} \quad (13.5.1)$$

However, since $\sum_k n_k = N$ this sum is restricted. We can relax this condition by moving to the grand canonical ensemble, this will allow us to sum over each n_k independently:

$$\mathcal{Z} = \sum_N e^{\beta \mu N} \sum_{\{n_{\mathbf{k}}\}_N} e^{-\beta \sum_k \epsilon(\mathbf{k}) n_{\mathbf{k}}} \quad (13.5.2)$$

$$= \sum_{\{n_{\mathbf{k}}\}} \exp\left[- \beta \sum_{\mathbf{k}} (\epsilon(\mathbf{k}) - \mu) n_{\mathbf{k}} \right] \quad (13.5.3)$$

$$= \prod_{\mathbf{k}} \sum_{\{n_{\mathbf{k}}\}} \exp\left[- \beta (\epsilon(\mathbf{k}) - \mu) n_{\mathbf{k}} \right] \quad (13.5.4)$$

where $\{n_{\mathbf{k}}\}_N$ is the set of occupation numbers such that $\sum_k n_k = N$. Now for fermions $n_{\mathbf{k}} = 0, 1$ so we find:

$$\mathcal{Z}_- = \prod_{\mathbf{k}} \left(1 + \exp\left[- \beta(\epsilon(\mathbf{k}) - \mu) \right] \right) \quad (13.5.5)$$

For bosons instead the occupation numbers are unrestricted $n_{\mathbf{k}} = 0, 1, 2, \ldots$ so we will obtain a geometric sum which converges provided that $\epsilon(\mathbf{k}) > \mu$. This must be true for all $\mathbf{k}$, so seeing as the ground state energy is $\epsilon_{GS} = 0$ we get that if $\boxed{\mu < 0}$ then:

$$\mathcal{Z}_+ = \prod_{\mathbf{k}} \frac{1}{1 - \exp\left[- \beta(\epsilon(\mathbf{k}) - \mu) \right]} \quad (13.5.6)$$

The interpretation of $\mu < 0$ is that since bosons experience an attractive potential, it costs no energy to add a particle to the boson ensemble. The grand canonical potential is given

by:

$$\Phi_G = \beta \eta \sum_{\mathbf{k}} \ln \left(1 - \eta e^{-\beta(\epsilon(\mathbf{k}) - \mu)} \right)$$

(13.5.7)

The average particle number is proportional to derivative of Φ_G with respect to μ:

$$\langle N \rangle_\eta = \frac{1}{\beta} \frac{\partial \Phi_G}{\partial \mu} = -\sum_{\mathbf{k}} \frac{e^{-\beta(\epsilon(\mathbf{k}) - \mu)}}{\eta e^{-\beta(\epsilon(\mathbf{k}) - \mu)} - 1} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon(\mathbf{k}) - \mu)} - \eta}$$

(13.5.8)

The precise importance of μ and the differences between $\eta = 1$ and $\eta = -1$ will be discussed in further detail in the next two chapters.

Bose-Einstein statistics

14.1 The density of states

Consider an ideal gas inside a box of volume $V = L^3$ on which we pose periodic boundary conditions. For a free gas the particles will be in eigenstates:

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{14.1.1}$$

where the wave-vector $\mathbf{k} = (k_x, k_y, k_z)$ satisfies the quantization condition:

$$k_{x,y,z} = \frac{2\pi}{L} n_{x,y,z}, \; n_{x,y,z} \in \mathbb{Z} \tag{14.1.2}$$

Each particle thus has energy:

$$E_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{4\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2\hbar^2}{2mL^2} n^2 \tag{14.1.3}$$

We calculated the partition function:

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta E_i} \tag{14.1.4}$$

in the previous section for indistinguishable particles. The sum can also be done by approximating it as an integral. Indeed, note that each term in the above sum is an exponential of (up to some proportion factor) $\lambda^2 n^2 / L^2$. For a sufficiently large box where $\lambda \gg L$ there will be a macroscopic number of states such that $E \lessapprox k_B T$ which contribute to the sum. The sum can therefore be transformed into an integral:

$$\sum_n \to \int d^3n = \frac{V}{(2\pi)^3} \int d^3\mathbf{k} = \frac{2V}{(2\pi)^2} \int_0^\infty k^2 dk \tag{14.1.5}$$

where $k = |\mathbf{k}|$. We can use the dispersion relation

$$dE = \frac{\hbar^2 k}{m} dk \implies k^2 dk = \frac{m}{\hbar^2}\sqrt{\frac{2mE}{\hbar^2}} dE \tag{14.1.6}$$

to write (14.1.5) as an integral over energy:

$$\frac{2V}{(2\pi)^2} \int_0^\infty k^2 dk = \int \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} dE \qquad (14.1.7)$$

We define $g(E)dE$ as the number of states with energy in an interval $[E, E + dE]$ divided by dE. Then, we see that:

$$g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} \qquad (14.1.8)$$

This quantity $g(E)$ is known as the density of states. It has a particularly simple form for free gases. For a gas of massless particles, we should instead use the dispersion relation:

$$E = \hbar ck \implies g(E) = \frac{V}{2\pi^2} \frac{E^2}{\hbar^3 c^3} \qquad (14.1.9)$$

14.2 Photon gas - a statistical perspective

One might naively think that the calculation in (14.1.9) applies to photons as well. This is not true however, since photons can be polarized in two different states (**E** parallel or **E** perpendicular) so each **k** state is two-fold degenerate. It follows that the density of states for photons is twice that for a normal massless relativistic particle:

$$g(E)dE = \frac{V}{\pi^2} \frac{E^2}{\hbar^3 c^3} dE \qquad (14.2.1)$$

Introducing the frequency $\omega = E/\hbar$ we find that:

$$\boxed{g(\omega)d\omega = \frac{V}{\pi^2} \frac{\omega^2}{\hbar c^3} d\omega} \qquad (14.2.2)$$

Note that $g(\omega)$ and $g(E)$ are not the same functions. One is the number of states per unit energy while the other is the number of states per unit frequency.

Suppose we have a gas of photons in thermal equilibrium inside a blackbody cavity of volume V at temperature T. Working in the canonical ensemble, the canonical partition for a gas of photons at frequency ω is:

$$Z_\omega = \sum_N e^{-\beta \hbar \omega N} = \frac{1}{1 - e^{-\beta \hbar \omega}} \qquad (14.2.3)$$

Instead of summing over all frequencies, we can use the density of states to perform an integral:

$$\log Z = \int_0^\infty \log(Z_\omega) g(\omega) d\omega = -\frac{V}{c^3 \pi^2} \int_0^\infty \omega^2 \log\left(1 - e^{-\beta \hbar \omega}\right) \qquad (14.2.4)$$

Therefore the Free energy of a photon gas reads

$$F = -\frac{1}{\beta} \log Z = \frac{V}{\beta c^3 \pi^2} \int_0^\infty \omega^2 \log\left(1 - e^{-\beta \hbar \omega}\right) d\omega \qquad (14.2.5)$$

while the internal energy is:

$$U = -\frac{\partial}{\partial\beta}\log Z = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\hbar\omega^3 e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \tag{14.2.6}$$

$$= \frac{V\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{14.2.7}$$

The energy density carried by a photon with frequency in the interval $[\omega, \omega + d\omega]$ is known as the spectral energy density and follows the distribution:

$$\boxed{u(\omega)d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega} \tag{14.2.8}$$

This result is known as Planck's law. The maxima of the energy distribution for a given frequency ω occurs when $\frac{dU}{d\omega} = 0$:

$$3\omega^2(e^{\beta\hbar\omega} - 1) - \omega^3\beta\hbar e^{\beta\hbar\omega} = 0 \implies \boxed{\omega_{max} \approx \frac{2.822}{\hbar\beta}} \tag{14.2.9}$$

which is known as Wien's displacement law.

Let's now evaluate the integral in (14.2.6) by considering the slightly different integral (which shall be used later):

$$g_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}e^{-x}}{z^{-1} - e^{-x}} \tag{14.2.10}$$

$$= \frac{z}{\Gamma(n)}\int_0^\infty x^{n-1}e^{-x}\sum_{m=0}^\infty z^m e^{-mx}dx \tag{14.2.11}$$

$$= \frac{z}{\Gamma(n)}\sum_{m=0}^\infty z^m \int_0^\infty x^{n-1}e^{-(m+1)x}dx \tag{14.2.12}$$

$$= \frac{1}{\Gamma(n)}\sum_{m=1}^\infty z^m \int_0^\infty x^{n-1}e^{-mx}dx \tag{14.2.13}$$

$$= \frac{1}{\Gamma(n)}\sum_{m=1}^\infty \frac{z^m}{m^n}\int_0^\infty u^{n-1}e^{-u}du \tag{14.2.14}$$

Identifying the Gamma function $\Gamma(n) = \int_0^\infty u^{n-1}e^{-u}du$ we see that $g_n(z)$, known as Bose-Einstein functions, take the form:

$$\boxed{g_n(z) = \sum_{m=1}^\infty \frac{z^m}{m^n} \implies g_n(1) = \zeta(n)} \tag{14.2.15}$$

Consequently:

$$\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega = \frac{1}{\beta^3\hbar^3}\int_0^\infty \frac{x^3}{e^x - 1}dx = \frac{1}{\beta^4\hbar^4}\zeta(4)\Gamma(4) = \frac{1}{\beta^4\hbar^4}\frac{\pi^4}{15} \tag{14.2.16}$$

giving an energy density $u = \frac{U}{V}$ of:

$$u = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} T^4 \tag{14.2.17}$$

The energy per unit area per unit time (radiant emittance) j emitted by an object at temperature T is then given by:

$$j = \frac{uc}{4} = \sigma T^4, \ \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} \tag{14.2.18}$$

To see where $\frac{c}{4}$ comes from, note that the radiant emittance is the integral of $\frac{U}{At} = uc\cos\theta$ where θ is the angle of the emitted photon to the normal. Therefore:

$$j = \int_0^2 \pi \int_0^\pi uc\cos\theta d\theta d\phi = \frac{uc}{4} \tag{14.2.19}$$

as found earlier. Also, the integral in (14.2.5) can be calculated exactly to give an expression for the free energy:

$$F = \frac{V}{\beta c^3 \pi^2} \int_0^\infty \omega^2 \log\left(1 - e^{-\beta\hbar\omega}\right) = -\frac{V}{3\beta c^3 \pi^2} \int_0^\infty \frac{\beta\hbar\omega^3 e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \tag{14.2.20}$$

$$= -\frac{V\hbar}{3c^3\pi^2} \frac{1}{(\beta\hbar)^4} \int_0^\infty \frac{x^3}{e^x - 1} dx = -\frac{V\pi^2 k_B^4}{45\hbar^3 c^3} T^4 \tag{14.2.21}$$

or more succinctly:

$$F = -\frac{4\sigma V}{3c} T^4 \tag{14.2.22}$$

Therefore, the radiation pressure will satisfy the equation of state for a photon gas:

$$p = -\frac{\partial F}{\partial V}\bigg|_T = \frac{4\sigma}{3c} T^4 \implies \boxed{3pc = 4\sigma T^4} \tag{14.2.23}$$

14.3 Photon gas - a kinetic perspective

Some of the important results in the previous section could have been motivated using kinetic gas theory as well. We consider a gas of photons in thermal equilibrium within a blackbody cavity of volume V and temperature T. For a normal gas with N particles moving randomly, the number of particles per unit volume moving out within a solid angle $d\Omega$ with speed in the interval $[v, v + dv]$ would be given by:

$$\frac{d\Omega}{4\pi} n(v) dv = \frac{1}{4\pi} n(v)\sin\theta dv d\theta d\phi \tag{14.3.1}$$

For photons however $n(v) = \delta(v - c)$ so integrating over all possible speeds and over $\phi \in [0, 2\pi]$ we find that:

$$\frac{1}{2} n\sin\theta d\theta, \ n = \frac{N}{V} \tag{14.3.2}$$

particles move in the direction $[\theta, \theta + d\theta]$ per unit volume. For a photon in this cavity to hit a wall (oriented so that its normal is along z for simplicity) in a time Δt it must be within a distance $c \cos \theta dt$. Consequently the volume the gas particles must be inside of to collide with the wall is $Ac \cos \theta dt$. The number of gas particles within this volume is:

$$\frac{1}{2} n A c \cos \theta \sin \theta d\theta = \frac{1}{4} n A c \sin(2\theta) d\theta dt \tag{14.3.3}$$

the number of particles hitting the wall per unit area per unit time, or the incident particle flux per unit time is then:

$$\Phi = \int_0^{\frac{\pi}{2}} \frac{1}{4} n c \sin(2\theta) d\theta = \frac{1}{4} n c \tag{14.3.4}$$

where we integrated over $\theta \in [0, \pi/2]$ since particles with $\theta \in [\pi/2, \pi]$ are moving away from the wall.

Each particle has momentum $\frac{E}{c}$ so the momentum density is given by $\frac{u}{c}$. The momentum perpendicular to the wall carried by the gas particles incident on the wall per unit area per unit time is:

$$\int_0^{\frac{\pi}{2}} \frac{1}{4} \frac{u}{c} \cos \theta c \sin(2\theta) d\theta = \frac{1}{6} u \tag{14.3.5}$$

The pressure on the wall is twice this since the particles are also reflected back:

$$p = \frac{1}{3} u \tag{14.3.6}$$

as found earlier. Also, considering that each photon has energy $\hbar\omega$, the radiant emittance (energy per unit time per unit area incident) on the wall is:

$$j = \hbar\omega\Phi = \frac{1}{4} n \hbar\omega c \tag{14.3.7}$$

We may define $u = \langle n\hbar\omega \rangle$ as the energy density to write:

$$j = \frac{1}{4} uc \tag{14.3.8}$$

Finally, using the first law:

$$u = \left.\frac{\partial U}{\partial V}\right|_T = \left.T\frac{\partial S}{\partial V}\right|_T - p = \left.T\frac{\partial p}{\partial T}\right|_V - p = \left.\frac{1}{3}T\frac{\partial u}{\partial T}\right|_V - \frac{u}{3} \tag{14.3.9}$$

which gives after some simplification:

$$4u = \left.T\frac{\partial u}{\partial T}\right|_V \tag{14.3.10}$$

This PDE has a solution $u = AT^4$ for some constant A, yielding:

$$j = \frac{1}{4} A c T^4 \tag{14.3.11}$$

which is the Stefan-Boltzmann law. It is important to note that these calculations do not allow us to calculate the pressure and radiant emittance since we are missing u, the energy density. Only a quantum statistical calculation would have allowed us to calculate this quantity.

14.4 Blackbodies and Kirchoff's law

In this section we try to understand how to quantify the aptitude of a surface in absorbing and emitting electromagnetic radiation at particular frequencies and temperatures. With this in mind, we define the spectral absorptivity $\alpha(\omega)$ as the fraction of the incident radiation absorbed at frequency ω and the spectral emissive power $j^*(\omega)$ for a surface so that $j^*(\omega)d\omega$ gives the power emitted per unit area with frequency in $[\omega, \omega + d\omega]$. In thermal equilibrium the radiation emitted by a surface must be equal to the radiation absorbed. Using our previous definitions we find that:

$$\text{emitted radiation} = j^*(\omega)d\omega \tag{14.4.1}$$

$$\text{absorbed radiation} = \alpha(\omega)\frac{1}{4}cu(\omega)d\omega \tag{14.4.2}$$

so:

$$j^*(\omega)d\omega = \alpha(\omega)\frac{1}{4}cu(\omega)d\omega \implies \boxed{\frac{j^*(\omega)}{\alpha(\omega)} = \frac{1}{4}cu(\omega) = j(\omega) > 0} \tag{14.4.3}$$

This result is known as Kirchoff's law. If we fix ω then the RHS will be a constant, and thus $\alpha \propto j^*$, if a body is a good absorber then it will also be a good emitter. A perfect absorber of radiation, known as a blackbody, will have $\alpha(\omega) = 1$ for all frequences ω. Thus Kirchoff's law implies that the spectral emissive power $j^*(\omega)$ will be equal to its maximum possible value j, the radiant emittance (all of the absorbed radiation is emitted) which we calculated earlier. If we thus place a gas of photons inside a cavity whose walls are blackbodies, then through perfect absorption and emission of photons the radiation contained within such a black-body is known as black-body radiation. This radiation follows the Planck distribution in (14.2.8) no matter what the absorbed radiation looked like. All that determines the distribution the radiation emitted by a blackbody is the temperature at which it is in equilibrium. It follows that the process of blackbody radiation is not reversible in general.

14.5 Phonons

14.6 Bose-Einstein condensation

After having looked at two important examples of Bose-Einstein statistics, let's now give a complete statistical description of the ideal Bose gas. We assume the thermal fluctuations are larger than the energy gaps in the gas, so that we may write the average number of particles as (we omit the $\langle \rangle$ unless otherwise stated):

$$N = \int \frac{g(E)}{e^{\beta(E-\mu)} - 1}dE = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int \frac{E^{1/2}}{e^{\beta(E-\mu)} - 1}dE \tag{14.6.1}$$

Traditionally, we let $z = e^{\beta\mu}$ be the fugacity. Substituting $x = \beta E$ we find that:

$$N = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{1}{\beta^{3/2}}\int_0^\infty \frac{x^{3/2}}{z^{-1}e^x - 1}dE \tag{14.6.2}$$

$$= \frac{V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\Gamma(3/2)\sum_{m=1}^\infty \frac{z^m}{m^{3/2}} \tag{14.6.3}$$

$$\implies \boxed{n = \frac{1}{\lambda_{th}^3}\sum_{m=1}^\infty \frac{z^m}{m^{3/2}} \equiv \frac{g_{3/2}(z)}{\lambda_{th}^3}} \tag{14.6.4}$$

where $\Gamma(3/2) = \frac{\sqrt{\pi}}{2}$ and $n = \frac{N}{V}$ is the particle density. Suppose we slowly reduce the temperature in (14.6.4) keeping n constant. As $T \to 0$, $\lambda_{th} \to \infty$. Since $\mu < 0$ the fugacity $z = e^{\beta\mu}$ will also increase, but it cannot be larger than 1 since $z \in (0,1)$ for negative chemical potentials. The critical temperature T_c at which $z = 1$ can be found from (14.6.4):

$$\frac{\zeta(3/2)}{\lambda_{th}^3} = n \implies \boxed{T_c = \frac{2\pi\hbar^2}{mk_B}\left(\frac{n}{\zeta(3/2)}\right)^{2/3}} \tag{14.6.5}$$

What would happen if we decreased the temperature further? Looking at the plot of $g_{3/2}(z)$:
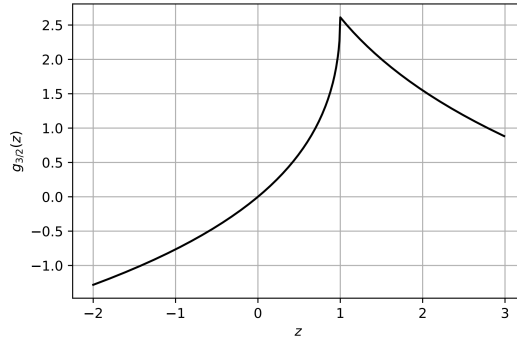
it seems like $g_{3/2}(z)$ and thus n should decrease. However this makes no sense, where do the particles go? At such low temperatures we have a violation of our initial assumption that a sum over microstates may be approximated by an integral. Indeed the integral in (13.4.5) does not receive a contribution by the ground state $E_{GS} = 0$. Using the Bose-Einstein distribution we see that the number of particles in the ground state is:

$$N_0 = \frac{1}{z^{-1} - 1} \implies \boxed{N = \frac{Vg_{3/2}(z)}{\lambda_{th}^3} + \frac{z}{1-z}} \tag{14.6.6}$$

This resolves our paradox, since as z approaches 1 we see that more and more particles occupy the ground state until N_0 becomes macroscopic when $z = 1$. If we add more particles they will just go to the ground state so the number of excited particles $N_e = \frac{Vg_{3/2}(z)}{\lambda_{th}^3}$ will

remain constant, making z level off at $z = 1$:

$$z = \begin{cases} 1, & \frac{V\zeta(3/2)}{\lambda_{th}^3} \leq N \\ g_{3/2}^{-1}(N\lambda_{th}^3/V), & \frac{V\zeta(3/2)}{\lambda_{th}^3} > N \end{cases} \tag{14.6.7}$$

Now as we decrease the temperature below the critical temperature, we have that the ratio of particles occupying the ground state will be:

$$\frac{N_0}{N} = \begin{cases} 1 - \left(\frac{T}{T_c}\right)^{3/2}, & T < T_c \\ 0, & T > T_c \end{cases} \tag{14.6.8}$$

This new state of matter where all (or almost all) particles occupy the ground state is known as a Bose-Einstein condensate. Let's also look at the pressure (since the ground
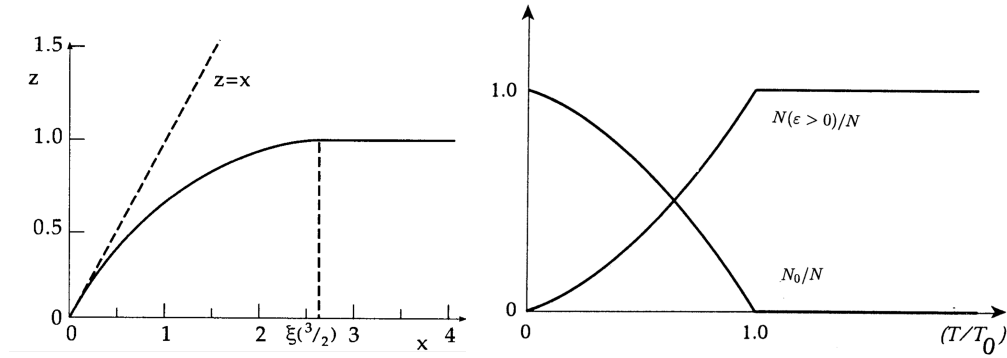
state has zero momentum it will not contribute to the total pressure in the thermodynamic limit):

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \log \mathcal{Z} \tag{14.6.9}$$

We calculate:

$$\log \mathcal{Z} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty E^{1/2} \log\left(1 - ze^{-\beta E}\right) dE \tag{14.6.10}$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3}\beta \int_0^\infty \frac{E^{3/2}}{z^{-1}e^{\beta E} - 1} dE \tag{14.6.11}$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3} \frac{1}{\beta^{3/2}} \int_0^\infty \frac{x^{3/2}}{z^{-1}e^x - 1} dx \tag{14.6.12}$$

$$= \frac{V}{\lambda_{th}^3} g_{5/2}(z) = \frac{V}{\lambda_{th}^3} \sum_{m=1}^\infty \frac{z^m}{m^{5/2}} \tag{14.6.13}$$

so that:

$$p = \frac{k_B T}{\lambda_{th}^3} g_{5/2}(z) \tag{14.6.14}$$

In the condensate regime $T < T_c$ we have that $z = 1$ and thus:

$$p = \frac{k_B T}{\lambda_{th}^3} \zeta(5/2) \tag{14.6.15}$$

Note that this value is independent of the number of particles. This makes sense, since in a BEC any particles that are added will be in the ground state, and such particles will not contribute to the total pressure.

Similarly, the internal energy reads (again the ground state gives a vanishing contribution to the internal energy in the thermodynamic limit):

$$U = -\frac{\partial}{\partial \beta} \log Z = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty E^{1/2} \frac{\partial}{\partial \beta} \log\left(1 - z e^{-\beta E}\right) dE \tag{14.6.16}$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E^{3/2}}{z^{-1} e^{\beta E} - 1} dE \tag{14.6.17}$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\beta^{5/2}} \Gamma(5/2) \int_0^\infty \frac{x^{3/2}}{z^{-1} e^x - 1} dx = \frac{3}{2} \frac{V k_B T}{\lambda_{th}^3} g_{5/2}(z) = \frac{3}{2} pV \tag{14.6.18}$$

The heat capacity is then given by:

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \frac{15}{4} \frac{k_B V}{\lambda_{th}^3} g_{5/2}(z) + \frac{3}{2} \frac{V k_B T}{\lambda_{th}^3} \frac{\partial g_{5/2}(z)}{\partial T} \tag{14.6.19}$$

For $T < T_c$ we have that $z = 1$ is roughly constant, and thus the second term will be very small, giving a heat capacity per unit volume:

$$\boxed{c_V = \frac{15}{4} \frac{k_B}{\lambda_{th}^3} \zeta(5/2), \ T < T_c} \tag{14.6.20}$$

Importantly, at the critical temperature:

$$C_V = \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} N k_B, \ T = T_c \tag{14.6.21}$$

For $T > T_c$ the second term in (14.6.19) becomes relevant. Since $\frac{V}{\lambda_{th}^3} = \frac{N}{g_{3/2}(z)}$ we have that:

$$U = \frac{3}{2} N k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)} \tag{14.6.22}$$

$$\implies C_V = \frac{3}{2} N k_B \frac{g_{5/2}(z)}{g_{3/2}(z)} + \frac{3}{2} N k_B T \frac{\partial}{\partial T}\left(\frac{g_{5/2}(z)}{g_{3/2}(z)}\right) \tag{14.6.23}$$

$$= \frac{3}{2} N k_B \frac{g_{5/2}(z)}{g_{3/2}(z)} + \frac{3}{2} N k_B T \frac{1}{z}\left(1 - \frac{g_{5/2}(z) g_{1/2}(z)}{g_{3/2}^2(z)}\right) \frac{\partial z}{\partial T} \tag{14.6.24}$$

We can write $\frac{\partial z}{\partial T}$ in a useful form by differentiating (14.6.4) which applies for $T > T_c$ only:

$$\frac{1}{z} g_{1/2}(z) \frac{\partial z}{\partial T} = -\frac{3}{2} \frac{N}{V} \frac{\lambda_{th}^3}{T} \implies \frac{\partial z}{\partial T} = -\frac{3z}{2T} \frac{g_{3/2}(z)}{g_{1/2}(z)} \tag{14.6.25}$$

This allows us to write:

$$\boxed{C_V = \frac{3Nk_B}{4} \left(5 \frac{g_{5/2}(z)}{g_{3/2}(z)} - 3 \frac{g_{3/2}(z)}{g_{1/2}(z)} \right),\ T > T_c} \tag{14.6.26}$$

Firstly, note that as $T \to \infty$ then $z \to 0$ and since $\lim_{x \to 0} \frac{g_m(x)}{g_n(x)} = 1$ for all positive integers m, n we have that $C_V \to \frac{3}{2} Nk_B$, which is the correct value for a classic ideal gas. A high temperature bose gas behaves as a high temperature classical gas. Secondly, note that as $T \to T_c$ from above, $z \to 1$ ans since $\zeta(1/2)$ diverges the second term vanishes, giving $C_V \to \frac{15Nk_B}{4} \frac{\zeta(5/2)}{\zeta(3/2)}$ which is the same value as in the condensate phase. We provide a plot for C_V beside (taken from Greiner).
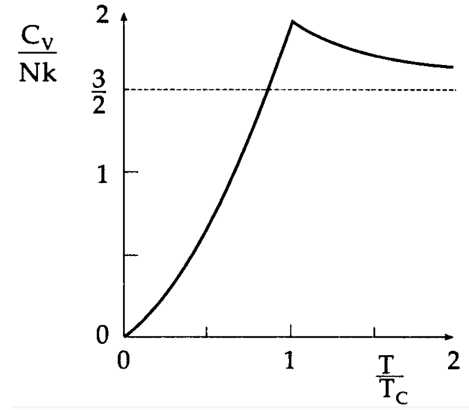
We see that in the Bose condensation regime $T < T_c$ the specific heat capacity grows as $T^{3/2}$. Instead for $T > T_c$ it decays into the classical ideal gas heat capacity. At $T = T_c$ we see a kink, and while a C_V is continuous its first derivative is not. Since the second derivative of the internal energy is discontinuous, we call this a second order phase transition.

It may appear like the only reason we obtained a discontinuity is that we ignored the $\frac{\partial z}{\partial T}$ term in the $T < T_c$ regime:

$$z = \left(1 + \frac{1}{N_0} \right)^{-1} = \left[1 + \frac{1}{N} \left(1 - \frac{T}{T_c} \right)^{-3/2} \right]^{-1} \implies \frac{\partial z}{\partial T} \propto N^{-1} \tag{14.6.27}$$

For finite N this is a nonzero contribution, and indeed the kink would be smooth at some scale. There would be a smooth transition between the two temperature regimes. However, note that as $N \to \infty$ this contribution vanishes, and we do effectively get a discontinuity.

Fermi-Dirac statistics

15

Interacting systems

16.1 Virial expansion

Phase transitions

17.1   Order parameters

Diffusion and Brownian motion

18.1   Langevin equation

Renormalisation group

Acknowledgments

This is the most common positions for acknowledgments. A macro is available to maintain the same layout and spelling of the heading.

Note added. This is also a good position for notes added after the paper has been written.

Bibliography

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