Thermal Physics Notes

Compiled by Nhat Pham
based on lectures from PHYS20027
and Blundells' *Concepts in Thermal Physics*

Last update: February 28, 2022

Contents

Contents

1 Lecture 1 (Week 13)

1.1 Definitions

1.1.1 Thermodynamic limit

Thermodynamics apply to system that is *in equilibrium* and also within the thermodynamic limit

Definition 1.1.1. The thermodynamic limit is when we study a large number of particles or a small number of particles for a long time. When we take this limit, we can describe the system without knowing all individual, *microscopic* properties of all the particles. Instead, we can completely describe the system using *macroscopic* properties.

Macroscopic properties can be variables such as pressure, time, volume, etc.
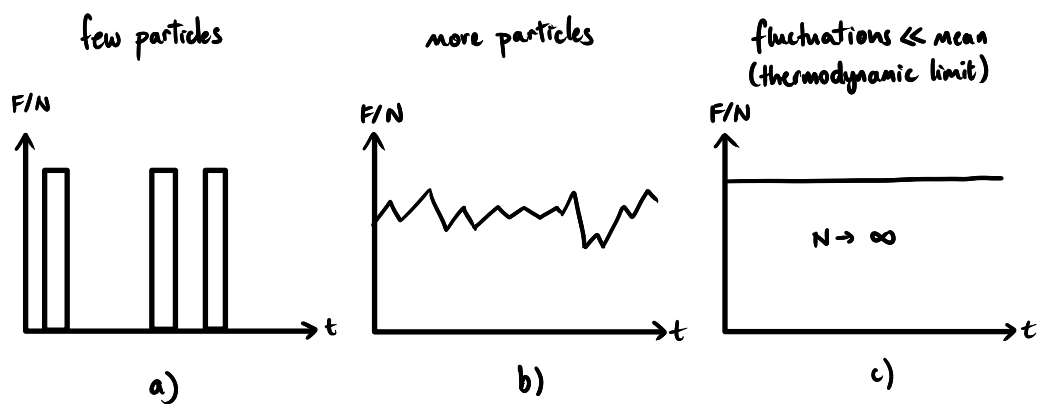
Figure 1.1: Force per particle versus time as we reach the thermodynamic limit.

1.1.2 Thermodynamic system

Definition 1.1.2. A thermodynamic system is a body which has well defined interactions with its surrounds and can be considered separately from them.

Example of a thermodynamic system: gas in an enclosure, where interactions with surrounding might be through heat or transfer through walls.
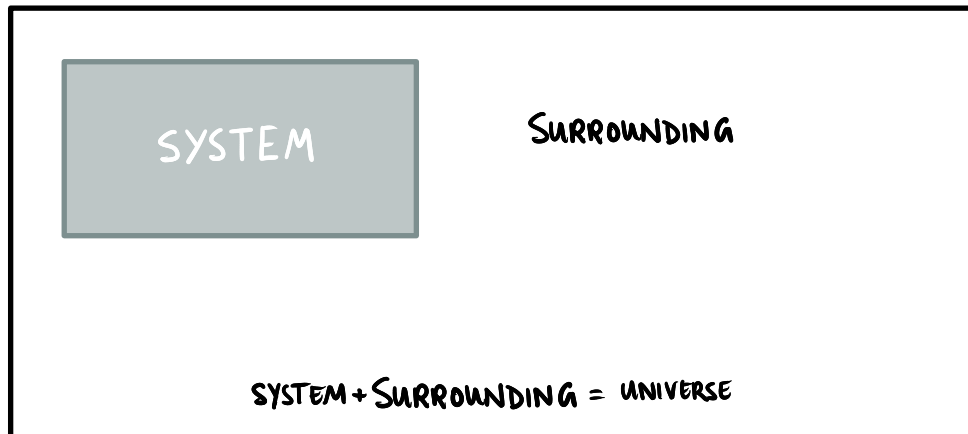
Figure 1.2: A thermodynamic system

1.1.3 Thermal equilibrium

Definition 1.1.3. A system is in thermal equilibrium when its macroscopic observables have ceased to change with time. Two systems are in thermal equilibrium if no heat flows between them when they are connected by a path permeable to heat.

There are also metastable states, where variables my change slowly with time, so the system is *not* in thermal equilibrium.

1.1.4 Extensive and intensive variables

- **Extensive** variables scales with the size of the system. Examples are the number of particles, volume, entropy, magnetic moment. They are mostly upper case.

- **Intensive** variables are independent of the size of the system. Examples are number density, temperature, magnetisation, pressure, entropy density. They are mostly lower case.

1.2 Functions and equations of state

Definition 1.2.1. A state function assumes a unique value for each equilibrium state of the system. The value does not depend on how they system got to the state—it is path independent.

Mathematically, functions of state have the following properties.

- Depend on (x, y) but not the path taken to (x, y).

- Have exact differentials, the number of variables does not matter. See 1.2.1.

Derivation 1.2.1. Recall the Taylor expansion of a function $f(x)$:

$$f(x + \delta x) = f(x) + f'\delta x + \frac{1}{2!}f''(\delta x)^2 + \dots \tag{1.1}$$

In the limit $\delta x \to \mathrm{d}x$ we can ignore higher order terms because they are sufficiently small. We are left with the first derivative, and rewrite it so that:

$$f(x + \mathrm{d}x) - f(x) = \frac{\mathrm{d}f}{\mathrm{d}x}\,\mathrm{d}x = \mathrm{d}f \tag{1.2}$$

We can use this result and expand it to 2 dimensions. We then arrive at the *exact differential* of $f(x, y)$:

$$\mathrm{d}f = f(x + \mathrm{d}x, y + \mathrm{d}y) - f(x, y) = \frac{\partial f}{\partial x}\,\mathrm{d}x + \frac{\partial f}{\partial y}\,\mathrm{d}y \tag{1.3}$$

The condition for a function to have an exact differential is that its mixed partial derivatives are equal. In other words:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{1.4}$$

On the other hand, functions that are path-dependent are *non-state functions*. In thermodynamics, heat and work are non-state functions. Their derivatives are inexact. The notation for this is:

$$đW, đQ$$

In the thermodynamic limit and thermodynamic equilibrium, the variables are dependent on each other and are constrained by an equation of state. For example $f(x, y, z) = 0$. The ideal gas equation is an equation of state.

$$pV - nRT = 0 \tag{1.5}$$

This allows us to relate thermodynamic variables to each other. For example:

$$\frac{\partial^2 m}{\partial T^2} = \frac{1}{T}\frac{\partial C}{\partial B}$$

We can find out the value of one side by knowing the other one.

2 Lecture 2 (Week 13)

A TL;DR overview of the laws of thermodynamics:

- **Zeroth Law:** If two systems are separately in equilibrium with a third system, then they are in equilibrium with each other.

- **First Law:** Energy is conserved. Heat and work are both forms of energy.

- **Second Law:** Heat cannot be converted to work with 100% efficiency. Entropy of the universe cannot decrease (this gives a definite direction of time).

- **Third Law:** You cannot cool anything to absolute zero (0 Kelvins)

These are statements of empirical facts, not deeper theory that sits below these laws.

2.1 The First Law

Heat is the energy in transfer between one system and another or one system and the surroundings.

- đQ is the heat supplied **to** the system.

Work is the change in energy of a system affected by changing its parameters.

- đW is the work done **on** the system.

Internal energy is the sum of all the components of energy in a system.

Definition 2.1.1. The conservation of energy of both heat (Q) and work (H):

$$\Delta U = \Delta Q + \Delta W \tag{2.1}$$

In differential form:

$$dU = đW + đQ \tag{2.2}$$

2.1.1 Work done compressing a gas

Suppose a piston can be moved into a chamber with a gas. If it moves fast, we generate sound waves, if there is friction, then energy will be dissipated as heat. These losses will not end up

in the gas so the change is **irreversible**.

To have **reversible** changes, we must have a frictionless piston and we must move it slowly.

Definition 2.1.2. The reversible work done to compress a gas is expressed by

$$đW = -pA \times \frac{dV}{A} = -p\,dV \tag{2.3}$$

The sign is negative because if we are doing work **on** the gas, then dV is negative because the volume is decreasing. For irreversible changes,

$$đW \geq -p\,dV \tag{2.4}$$

2.1.2 Work done in other systems

- Stretching a string: $đW = \vec{F} \cdot d\vec{l}$

- Expanding a surface: $đW = \gamma\,dA$

- Magnetic material: $đW = \vec{B} \cdot d\vec{m}$ or $\vec{m} \cdot d\vec{B}$

2.2 Constraints

- **Adiabatic** Thermally isolated system—there is no heat flow in or out. $đQ = 0$ or $dS = 0$

- **Isothermal:** Temperature is fixed by an external reservoir. $dT = 0$

- **Isobaric:** Pressure is fixed. $dp = 0$

- **Isochoric:** Volume is fixed. $dV = 0$

Paths are correspondingly called *adiabat, isotherm, isobar,* and *isochar.*

2.3 Heat capacities

A way to quantify the response of the system to external changes. Two heat capacities we study are

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

The equation of state for a general gas (not necessarily ideal) is $f(p, T, V) = 0$. We only have 2 independent variables that we can write our internal energy as a function of any two of those. For example, $U(p, V)$ or $U(V, T)$.

Let's qualitatively arrive at the expressions of C_V and C_p.

For C_V, suppose a box with fixed walls. Heat supplied into the system will increase the temperature of the gas inside.

For C_p, suppose a box with a piston. The gas is allowed to expand and move the piston to keep the pressure constant. If we put heat into the system, the gas expands, doing work on the system. Thus, not all of the heat supplied increased the temperature of the system. We expect then that $C_p \geq C_V$.

Derivation 2.3.1. Assume $U = U(V, T)$ and $f(p, V, T) = 0$. The exact differential of U is

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{2.5}$$

From the equation of the first law, 2.1, substitute đW with 2.3, set $dV = 0$ for constant volume, and divide by dT,

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V \tag{2.6}$$

Then for C_p, equate 2.5 with 2.1 then divide by dT and set d$p = 0$:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) + C_V \tag{2.7}$$

For a general gas, we can normally stop here.

With the general expression, we can evaluate this for different gasses. The most simple is monotonic ideal gas.

Example 2.3.1. For an ideal gas that is monotonic, $U = \frac{3}{2}nRT$ and thus is only a function of temperature. We can cancel any partial derivatives of U where T is kept constant.

$$C_V = \frac{3}{2}nR \tag{2.8}$$

$$C_p = \left(\frac{\partial V}{\partial T}\right)_p p + \frac{3}{2}nR \tag{2.9}$$

Using the ideal gas relation 1.5, we have:

$$C_p = \frac{3}{2}nR + nR = \frac{5}{2}nR \tag{2.10}$$

We can also consider **Virial Expansion** and the **Van de Waals** equation, which models real

gas.

2.4 Non-ideal gases

2.4.1 Virial Expansion

This is a general form for an equation of state of gas or fluid. For an ideal gas, $A = 1$ and all other coefficients are zero. Gases become ideal when $\rho \to 0$.

$$\frac{p}{RT\rho} = A + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{2.11}$$

2.4.2 Van de Waals equation

This is a special case of the virial expansion, for $\rho \ll 1$, the we can ignore second order terms and above.

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT \tag{2.12}$$

3 Lecture 3 (Week 13)

3.1 The Second Law

Definition 3.1.1. There are several equivalent statements of the second law:

- **Lord Kelvin 1851:** Work can be converted to heat with 100% efficiency but not the reverse.

- **Clausius 1854:** Heat flows from hot to cold, and not spontaneously the other way around.

Both of these statements are **equivalent**—to understand this we need to look at thermodynamic cycles, specifically the *Carnot cycle*. This concept is used in engines. Since internal combustion engines are difficult to understand, we look at the *external* combustion engines. One type is the *Stirling* engine.

Qualitatively, the source of heat is at the bottom (which can come from a hot plate). The difference between the hot plate and the cold plate runs the engine (cool video embedded in the lecture). Here's a link to diagrams & animations: Low Differential Stirling.

3.2 The Carnot Cycle

There are four stages in the cycle. This is a *closed cycle*. Thus, the work done can be described by integrating both sides of 2.3 to get

$$W = \int p \, \mathrm{d}V \tag{3.1}$$

On the other hand, the total change $\Delta U = 0$ after one complete cycle.

Here are the steps in the Carnot cycle:

1. **A to B:** Isothermal expansion at T_H. Volume increases as pressure decreases due to supplied heat Q_H.

2. **B to C:** Adiabatic expansion (gas cools to T_L) as pressure keeps decreasing and volume keeps increasing.

3. **C to D:** Isothermal compression at T_L. Heat leaves the system and the volume decreases while pressure increases.

4. **D to A:** Adiabatic compression (gas heats to T_H). Pressure increase as a result as temperature increases.
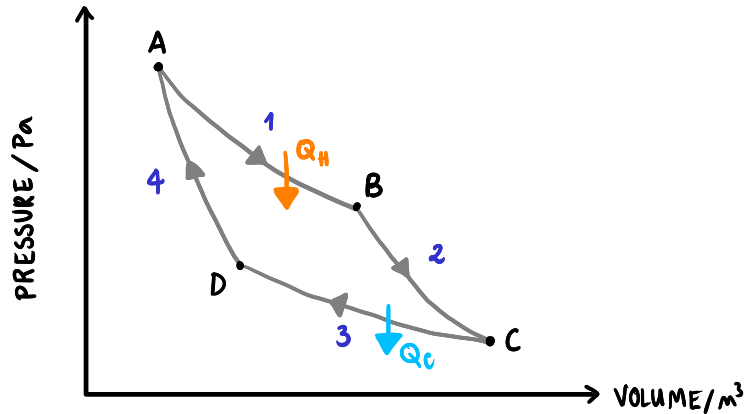
Figure 3.1: Carnot cycle P-V plot

Physically, there must be a hot reservoir and a cold reservoir connected to our system, which is an enclosed piston connected to a flywheel. These two are connected to a switch each (3.2).

Here's the physical interpretation:

1. The cold switch is open, and heat is supplied to the system. The gas must expand along the isotherm, pushes the piston and drives the flywheel.

2. In stage 2, both switches are open, the system is thermally isolated. The flywheel continues to spin while the gas continues to expand.

3. In stage 3, the cold switch is now closed. Heat leaves the system and the gas gets compressed.

4. In stage 4, both switches are open, the system is thermally isolated. The piston is back to its original position after the flywheel compresses the gas.

3.2.1 The Carnot relation

We can also analyse the Carnot cycle mathematically.

Let's consider an isothermal expansion. An isothermal expansion (see 2.2) demands d$T = 0$, but $U = U(T)$ thus $\Delta U = 0$. Therefore, $\Delta Q = -\Delta W$ from 2.1. From 3.1, we evaluate the integral using 1.5.
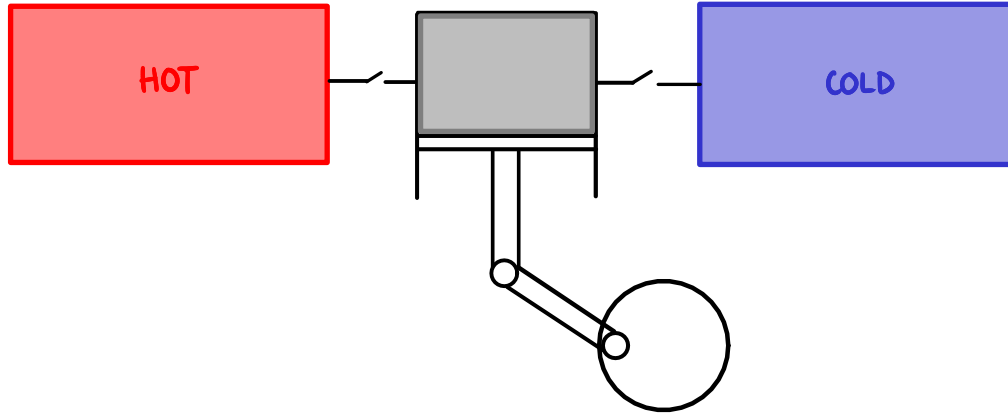
Figure 3.2: An example of what how the Carnot cycle might be implemented

Now let's consider an adiabatic expansion. Recall from first year that we can write $PV^\gamma = \text{const}$ and thus $TV^{\gamma-1} = \text{const}$. Since it is equal to a constant, the product TV at each stages are equal. Remember that $\gamma = \frac{C_p}{C_V}$.

Definition 3.2.1. We have the following mathematical relations for each stages of the Carnot cycle, with $\gamma = \frac{C_p}{C_V}$.

1. $Q_H = nRT_H \ln \frac{V_B}{V_A}$

2. $T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1}$

3. $-Q_L = nrT_L \ln \frac{V_D}{V_C}$

4. $T_L V_D^{\gamma-1} = T_H V_A^{\gamma-1}$

Use stages 2 and 4 from 3.2.1 to eliminate $\frac{T_H}{T_L}$. We arrive at:

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \tag{3.2}$$

Finally, using stages 1 and 3 and 3.2 which we just found, we arrive at the *Carnot relation*:

$$\frac{Q_H}{Q_L} = \frac{T_H \ln\left(\frac{V_B}{V_A}\right)}{T_L \ln\left(\frac{V_C}{V_A}\right)} = \frac{T_H}{T_L} \tag{3.3}$$

Finally, we can derive the efficiency of the cycle, which is the ratio between work done and heat available. The work done is the difference between heat flowing in and heat flowing out.

The heat available is what is supplied.

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \tag{3.4}$$

It could also be useful to consult simplified diagrams of Carnot engines and a reversed Carnot engine (a refrigerator).
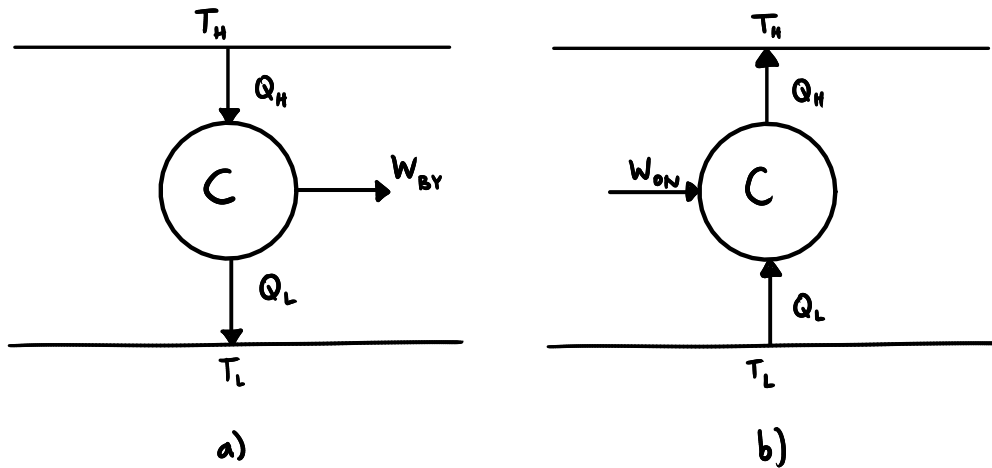
Figure 3.3: (a) shows the Carnot engine where the engine performs work and (b) shows the reversed Carnot engine where we perform work on the engine.

3.2.2 The Carnot theorem

The consequences of the Carnot engine are:

Theorem 3.2.1 *No engine operating between two reservoirs can be more efficient than the Carnot engine.*

Proof by contradiction will lead to this theorem. In essence:

Proof. Suppose there is an engine **X** such that its efficiency exceeds that of the Carnot engine, so that $\eta_x > \eta_c$. Connect engine **X** to the Carnot engine in reverse, and expand out the inequality to get

$$\frac{W}{Q_H^x} - \frac{W}{Q_H^C} > 0$$

From the first law, we find

$$W \equiv Q_H^C - Q_L^C = Q_H^x - Q_L^x$$

We rearrange this into

$$Q_H^C - Q_H^x = Q_L^C - Q_L^x$$

The LHS is > 0 as part of our assumption, this means the RHS is also > 0. However, the LHS is heat *dumped* from the hot reservoir, while the RHS is heat *removed* into the cold reservoir. If cold reservoir is losing heat and hot reservoir is gaining heat. Then energy is being transferred from cold to hot. This is a direct contradiction with the Second Law (Clausius' statement). Thus, we must abandon our initial assumption—there cannot be such an engine **X**. □

This leads to the second theorem.

Theorem 3.2.2 *All reversible engines have exactly the Carnot efficiency.*

It doesn't matter if we use an ideal gas or a non-ideal gas, if an engine is reversible, then the theorem holds.

Proof by contradiction will show this holds.

Proof. Suppose we now have an engine R which is less efficient than the Carnot engine. Connect the Carnot engine in forward direction to engine R in reverse. Like the previous proof, we have

$$Q_H^C - Q_H^R = Q_L^C - Q_L^R$$

Due to our assumption, both sides are negative. Once again, we have heat which is extracted from the hot reservoir and dumping it into the cold reservoir. This violates the second law, so we must abandon our assumption. □

The Carnot efficiency is exactly 1 if and only if $T_L = 0$.

$$\eta_c = 1 - \frac{T_L}{T_H} < 1 \tag{3.5}$$

3.3 Thermodynamic absolute temperature

Kelvin used the Carnot relation in 3.5 to define absolute temperature. This sets the **zero** of the temperature scale.

Prior to 2019, the size of Kelvin was set by the triple point of water. This all changed to the new S.I. system which is based on universal constants.

We use an ideal gas and ideal gas laws as a primary thermometer.

4 Lecture 4 (Week 14)

4.1 Clausius' Theorem

Results from a general analysis of the Carnot cycle. For each part of the cycle by index i, calculate

$$\sum_i \frac{\Delta Q_i}{T_i} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \tag{4.1}$$

For a Carnot cycle, the first term is equal to the second term, thus the whole sum is 0. If we look at the small addition of Q then $\Delta Q \to đQ$ then the sum becomes an integral. We have.

$$\oint \frac{đQ_{rev}}{T} = 0 \tag{4.2}$$

Definition 4.1.1. For a general cycle (either reversible or irreversible), Clausius' theorem states

$$\oint \frac{đQ}{T} \le 0 \tag{4.3}$$

We can prove this theorem through a set up of a generalised cycle (multiple parts that are either reversible or irreversible), as shown in Figure 4.1.

Consider the following *general* cycle:

Derivation 4.1.1. Because this is a closed cycle, it follow the first law, where $\Delta U = 0$, or $W_s = \sum_i \delta Q_i$ where W_s is the total work done by the system.

Assuming each reservoir is connected to the master reservoir at the temperature T_0 via an individual Carnot engine, we can form a schematic as shown in Figure 4.2.

For each of the engine, there is a bit of work done, and the rest is heat that goes into our system. This shows that

$$\delta Q_i^0 = \delta W_i + \delta Q_i \tag{4.4}$$
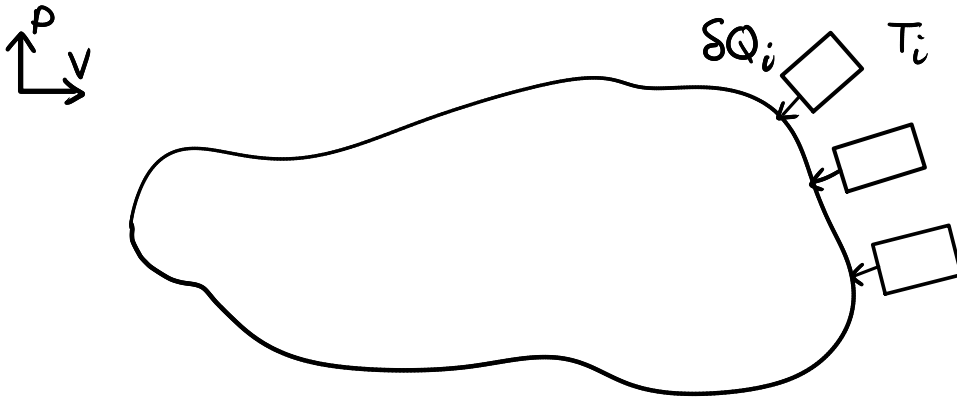
Figure 4.1: An engine with multiple sources of heat δQ_i.

If we sum over all the heat engines, we get

$$Q_0 = \sum_i \delta Q_i^0 = \sum_i \delta W_i + \sum_i \delta Q_i \tag{4.5}$$

We can group the first sum in W_C for the work done by the Carnot engines, and the second sum as W_S for the work done by the system, as established at the start.

$$Q_0 = W_C + W_S \tag{4.6}$$

Thus, the total heat that flows out from the master reservoir is the sum of the work done by the Carnot engine and the work done by the system.

Effectively, this is the perfect conversion of heat into work. From the second law, we insist that

$$W_C + W_S \leq 0 \tag{4.7}$$

otherwise there would be a violation. This inequality comes from the fact that the work that is coming out of the Carnot engine must actually be negative, so that we are doing work *on* these engines to convert heat from the master reservoir to work done by the system. If this quantity is negative, we expect that $W_S \leq W_C$ where both sides are positive, if this shows the magnitude of both terms, then it makes sense that the work we are doing on the system must either result in the same amount of work done by the system (perfect efficiency), or less than that. If $W_S > W_C$, this shows that the work we are doing on the system is resulting in more work than what we are putting in, which is forbidden.

Therefore, $Q_0 = \sum_i \delta Q_i^0 \leq 0$. Using the Carnot relation, which is that the ratio of the heat is equal to the ratio of the temperature, we get

$$T_0 \sum_i \frac{\delta Q_i}{T_C} = \sum_i \frac{\delta Q_i}{T_C} \leq 0 \tag{4.8}$$

If we take the limit as each δQ_i gets incredibly small or $i \to \infty$, the temperature of the reservoir becomes the temperature of the system. We arrive at

$$\oint \frac{dQ}{T} \leq 0 \tag{4.9}$$
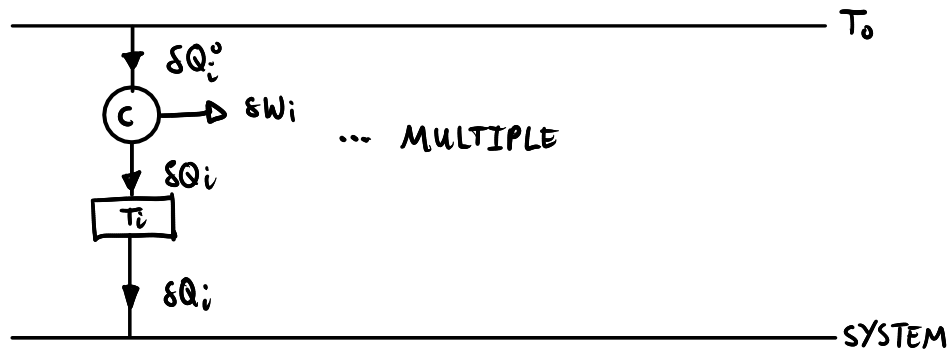
Figure 4.2: A master reservoir connected to the system via multiple Carnot engines.

We have proved that any valid system, reversible or irreversible, must obey this inequality.

4.2 Entropy

Definition 4.2.1. For a reversible closed cycle, the LHS expression in 4.3 is exactly equal to 0, which indicates that it is a state function. We write this state function as entropy S

$$dS = \frac{đQ_{\text{rev}}}{T}$$
$$T\,dS = đQ_{\text{rev}} \tag{4.10}$$

Like any state function, the difference of entry at two points is just the integral evaluated at those two points.

This is the thermodynamic definition of entropy. Later, we will look at the statistical interpretation in terms of disorder.

We can directly measure S as a function of temperature if we keep V the same. Taking the partial derivative of T on each side, we arrive at

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{4.11}$$

Definition 4.2.2. Entropy is expressed as a function of temperature as

$$S(T) = \int_0^T \frac{C(T)}{T}\,\mathrm{d}T \tag{4.12}$$

In other words, entropy is the area under a (C/T)-T curve.

Substitute the differential of entropy into the first law, expressed by equation 2.1, we can also write the first law for as

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{4.13}$$

This applies for irreversible changes as well as reversible processes. How can we justify this?

For reversible changes, đ$W = -p\,\mathrm{d}V$ and đ$Q = T\,\mathrm{d}S$, while for irreversible changes đ$W \geq -p\,\mathrm{d}V$ and đ$Q \leq T\,\mathrm{d}S$. If we add the irreversible terms together it all balances out and we still get dU. Another way of looking at it is that 4.13 is composed of only state function,s thus it must be valid for all changes, independent of path.

4.3 Irreversibility—entropy cannot decrease

We can prove that entropy cannot decrease. Consider a cyclic process which has irreversible and reversible parts, as shown in Figure 4.3.

Derivation 4.3.1. From Clausius' theorem in Equation 4.3,

$$\int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{\mathrm{rev}}}{T} \leq 0$$
$$\int_A^B \frac{đQ_{\mathrm{rev}}}{T} \geq \int_A^B \frac{đQ}{T} \tag{4.14}$$
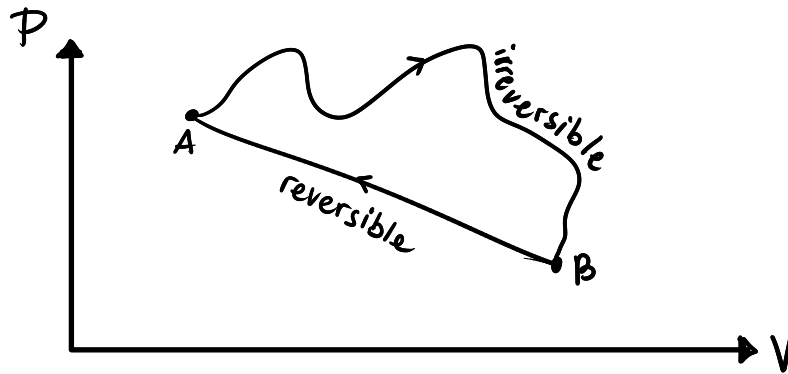
Figure 4.3: A cyclic process that has irreversible process from A to B and reversible process from B to A.

If we let A tend to B so the points become infinitesimally close together, we have the differential form instead, substitute in dS, we get that for an *isolated system*, where đ$Q = 0$

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T} \equiv \mathrm{d}S \geq 0 \tag{4.15}$$

This means for an isolated system, entropy **cannot** decrease.

4.4 The thermodynamic arrow of time

Hence, the entropy of the universe must increase with time, since the universe is an isolated system. Increasing entropy is synonymous with increasing "time". We can consider this to be the thermodynamic arrow of time.

Later, we will consider the statistical interpretation of entropy.

4.5 Joule expansion

Suppose we have two chambers that are thermally isolated. They are connected by a tube with a valve. Initially, all the gas is in the left chamber. When we suddenly open the valve, the change is *irreversible*, so the pressure and volume are not well-defined during the expansion. This is called a *free expansion* so the gas **does not do work on the surroundings.**

We now ask: What is the change in entropy when the system reaches its final state (it is in internal equilibrium)?

We don't know specifically the path, it is not well-defined. What we know, however, is the start and end points. Since entropy is a state function, we fortunately only need the start and end points. Effectively, we can use a well-defined path which would give us the same answer since we are dealing with path-independent functions.

We choose a reversible isothermal path. The path are different but if pressure and volume are the same at the start and end points, it will be equivalent to the irreversible path.

Since the path is isothermal, $U = U(T) = 0$ so from the first law and the ideal gas relations, we have

$$\mathrm{d}S = nR\frac{\mathrm{d}V}{V} \tag{4.16}$$

We can further integrate this to give us a simple result.

Definition 4.5.1. In the **isothermal** case, the change in entropy is given as

$$\Delta S = nR\ln\frac{V_1}{V_0} \tag{4.17}$$

We only calculated this for a system—the change in the entropy of the universe is not necessarily the same for the reversible and irreversible expansion.

5 Lecture 5 (Week 14)

5.1 Thermodynamic Potentials

We can combine state functions to make another state function. There are infinitely many possible combinations but only a few are useful. Here are several examples:

$$
\begin{array}{ll}
U & \text{Internal energy} \\
F = U - TS & \text{Helmholtz free energy} \\
G = U - TS + pV & \text{Gibbs free energy} \\
H = U + pV & \text{Enthalpy}
\end{array}
$$

These definitions are only correct where the work term $đW = -p\,dV$. Also, we assume that it is a closed system with a fixed number of particles (gas cannot leave the system). We will now look at each of the following examples in turn.

5.2 Internal energy

Looking at 4.13, we see that $U = U(S, V)$. We call S and V as the natural variables of U. Recall from Definition 1.2.1, we can find this for U since it is a state function.

Comparing the exact differential and the equation expressing the first law, we find that

$$
T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial U}{\partial V}\right)_S \tag{5.1}
$$

5.3 Helmholtz Free energy

Using the first law, we can expand the equation for the Helmholtz free energy. We find that

$$
F = F(V, T) \text{ and } dF = -p\,dV - S\,dT \tag{5.2}
$$

where its natural variables are V and T.

Its exact differential leads to the results that

$$
p = -\left(\frac{\partial F}{\partial V}\right)_T \text{ and } S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{5.3}
$$

This is particular useful because V and T are often common experiment conditions. The system will evolve to minimise F at constant V and T. This means as the system evolves, it will do work on the environment in order to minimise F, so that F is the maximum work you can get out of a system (hence "free" energy).

5.4 Gibbs Free energy

Doing similar steps as before, we find that

$$G = G(p, T) \text{ and } dG = -S\,dT + V\,dp \tag{5.4}$$

Its exact differentials show that

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \text{ and } V = \left(\frac{\partial G}{\partial p}\right)_T \tag{5.5}$$

Same with F, the system will evolve to minimise G. So G is the maximum work you can get out of the system with constant p, and T

5.5 Enthalpy

Doing similar steps as before, we find that

$$H = H(S, p) \text{ and } dH = T\,dS + V\,dp \tag{5.6}$$

Its exact differentials show that

$$T = \left(\frac{\partial H}{\partial S}\right)_p \text{ and } V = \left(\frac{\partial H}{\partial p}\right)_S \tag{5.7}$$

Note that constant S is the same as constant Q, the cycle is adiabatic. Enthalpy as a quantity is useful because if you have an adiabatic change at constant pressure, ΔH is the heat absorbed by the system at constant p (e.g., a chemical reaction). At constant pressure, $dH = dQ$.

5.6 Maths of partial derivatives

Proofs aren't necessarily, but these following identities are extremely useful.

Definition 5.6.1. Below are some partial derivative identities:

1. Chain rule (all terms must have the same constraints)

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial y}\right)_y \left(\frac{\partial y}{\partial x}\right)_y \tag{5.8}$$

2. Reciprocal theorem

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y} \tag{5.9}$$

3. Reciprocity theorem or triple product rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{5.10}$$

4. Convert an exact differential into a partial derivative into a partial one

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \implies \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{5.11}$$

5. Maxwell relations (exchange derivatives w.r.t. natural variables). See 5.6.2.

5.6.1 Pseudo-proofs

These proofs are not presented explicitly. They are meant to help understand the identities in 5.6.

To prove the **reciprocal** and **reciprocity** theorems, take a function $f(x, y, z) = 0$, with $x = x(y, z)$, $y = y(x, z)$, and $z = (x, y)$. If we write x and z in differential forms, and substitute $\mathrm{d}x$ into the expression for $\mathrm{d}z$, we notice that we can equate the coefficients of $\mathrm{d}z$, which shows the **reciprocal** theorem holds.

Then if we look at the coefficients of $\mathrm{d}y$, we can rearrange and use **reciprocal** theorem to show the **reciprocity** theorem.

5.6.2 Maxwell relations

To demonstrate the Maxwell relations, let's use the Helmholtz relation, see Section 5.3 for the differential forms.

If we take the derivatives again with respect to other natural variables,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V \partial T}\right)_{V,T} \text{ and } \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial^2 F}{\partial T \partial V}\right)_{V,T} \tag{5.12}$$

we can see that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.13}$$

This is a Maxwell relation. We don't have to memorise all the Maxwell equations, but we can easily derive them when needed.

6 Lecture 6 (Week 14)

6.1 Cooling gases and Joule-Thomson expansion

There are several ways to cool gases. One way is to expand gas *adiabatically* and make it do work on the environment. This is different from a Joule expansion, where the gas expands freely. A Joule expansion does not do work on the environment. We can either do this using a piston and a flywheel (Figure 6.1) or by using a turbine (turbo expander) (Figure 6.2).
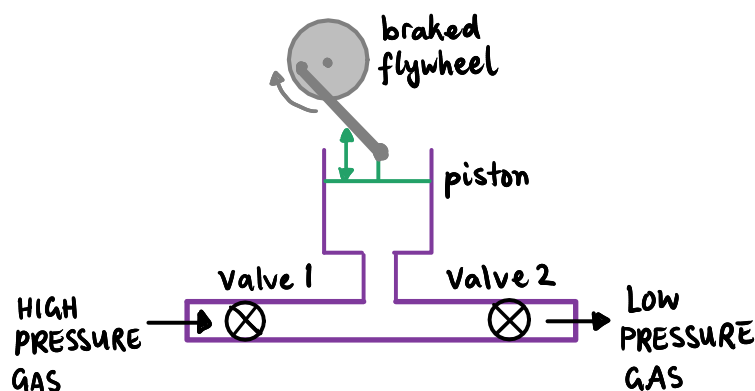
Figure 6.1: We open the high pressure valve, gas comes in the chamber and moves the piston up (doing work on the piston), the flywheel spins with friction to remove energy and once the piston reaches the highest position, it moves down. The low pressure valve is opened and low pressure gas is forced out by the lowering piston.

Adiabatic expansion is quite inefficient at low temperature. A better alternative is the *Joule-Thomson* or *Joule-Kelvin* expansion (JT or JK process). See Figure 6.3.

We assume the JT process is adiabatic—high pressure gas comes through and expands to the other side without any heat exchange.

6.1.1 Conservation of enthalpy

We might want to find the work done as gas moves through the plug in the centre.
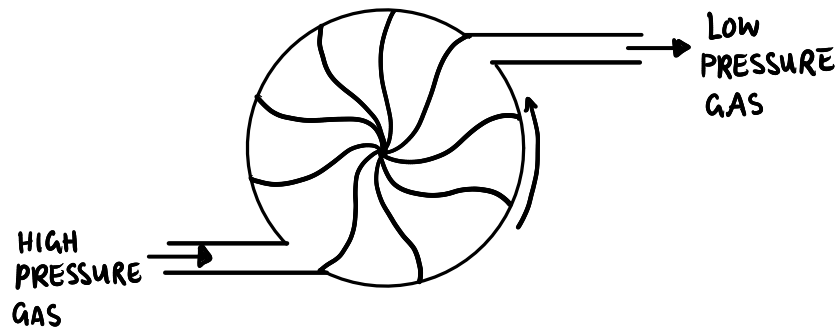
Figure 6.2: High pressure gas comes in, drives the turbine by doing work on it, heat is dissipated through friction, and then low pressure gas comes out.
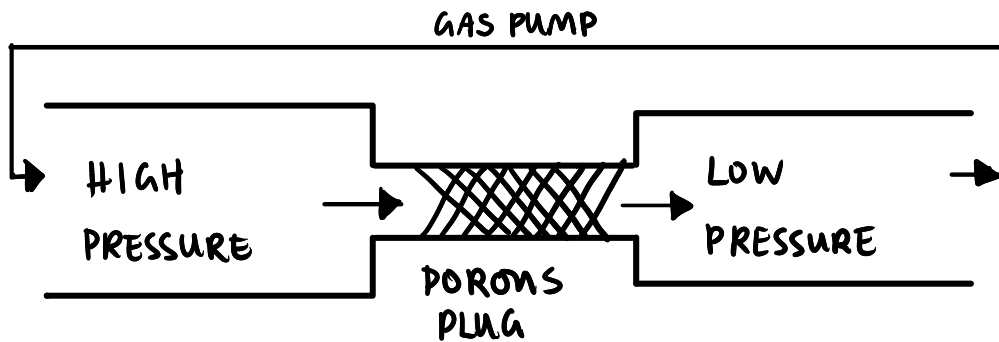
Figure 6.3: High pressure gas comes in and goes the rough a porous plug which removes a lot of energy through friction, low pressure gas comes out of the other end and is pumped back into the engine. The pressure difference is maintained with a compressor. This principle of cooling is used in many devices like refrigerators, or helium liquefiers.

Imagine, for the sake of representation, there are piston on both sides of the engine. The left piston maintains pressure p_1 as it forces gas through the plug, while the right piston moves to the right at p_1 as gas moves through plug. Force is $F = pA$, therefore:

The work done on gas to move distance L_1 in the left chamber $\quad W = p_1AL_1 = p_1V_1$
The work done on gas to move distance L_2 in the right chamber $\quad W = P_2AL_2 = p_2V_2$

Definition 6.1.1. The net work done on the gas in a Joule-Thomson expansion is

$$\Delta W = p_1V_1 - p_2V_2 \tag{6.1}$$

As the gas moves through the plug, there is a change in internal energy, $\Delta U = U_2 - U_1$. From the first law, for an adiabatic process (no heat transfer), $\Delta U = \Delta W$. We know ΔW from 6.1, so

$$p_1V_1 + U_1 = p_2V_2 + U_2 \tag{6.2}$$

This is the definition of *enthalpy* which we mentioned in Section 5.5, which means $H_1 = H_2$. In other words, enthalpy is conserved in a JT expansion.

6.1.2 The Joule-Thomson coefficient

We can quantify how much cooling takes place by defining a coefficient, called the Joule-Thomson coefficient as

$$\mu_{\text{JT}} = \left(\frac{\partial T}{\partial p}\right)_H \tag{6.3}$$

Since the constant H is difficult to use so we can derive an expression at constant pressure instead. We can use what we know from previous lectures and 5.6 to get to this.

Derivation 6.1.1. From the reciprocity theorem, we can write

$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1 \tag{6.4}$$

Substitute this into our definition for the JT coefficient so far to get

$$\mu_{\text{JT}} = -\frac{1}{\left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p} \tag{6.5}$$

We then borrow our results from Section 5.5 the differential form of enthalpy, divide by dT at constant p to get

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p \tag{6.6}$$

We also divide by dp at constant T

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V \tag{6.7}$$

Substitute back into what we got from reciprocity to get

$$\mu_{JT} = -\frac{1}{C_p}\left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right] \tag{6.8}$$

We use a Maxwell relation to make this nicer

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{6.9}$$

We can then use this for our final expression:

Definition 6.1.2. The JT coefficient at constant pressure is

$$\mu_{JT} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] \tag{6.10}$$

To get cooling we need $\mu_{JT} > 0$. For an ideal gas, $\mu_{JT} = 0$, so there's never any cooling. But for a real gas, this varies with temperature. We call the temperature below which you will get cooling via the JT process the **inversion temperature**.

Definition 6.1.3. The inversion temperature T_i for a JT process is

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T_i} \tag{6.11}$$

Below this temperature, we can cool gas using the JT process, beyond this temperature, we can use any adiabatic expansion to get to T_i.

There are JT coefficient curves at various temperatures for different gases.

6.1.3 Helium liquefier (not examined)

From a gas storage, the gas travels through a compressor. Next, it goes through a heat exchanger, then through the Turbine 1, then through another heat exchanger and finally

through Turbine 2. It is then pushed back around the circuit once again, in order to cool down other incoming gases (thus it functions as the heat reservoir in the heat exchangers). It goes through this step until the final low-pressure gas that leaves Turbine 2 cools from 300K to 10K.

At the same time, the compressor also has another stream coming into the liquefier, but only going through the heat exchanger and not through the turbines (the first stream is used to maintain heat exchange for this stream), after it leaves this, it has the same temperature as the other stream, but maintains a high-pressure.

After that this high-pressure gas enters the JT process to become liquefied.

7 Lecture 7 (Week 15)

7.1 Chemical potential

Consider 2 systems which can exchange heat and particles. When we add particles, we change the energy so we need to modify the first law. In a similar way to 5, we notice the natural variables when we write the expression in differential form.

$$dU = T \, dS - p \, dV + \mu \, dN \tag{7.1}$$

If we find the exact differential of U, we notice the new natural variable N, gives us a coefficient, μ. This is the chemical potential, it is given by

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \tag{7.2}$$

We add this extra potential to all the other equations we have looked at for potentials and energies. Thus, we end up with the following equations.

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} + \left(\frac{\partial F}{\partial N} \right)_{T,V} + \left(\frac{\partial G}{\partial N} \right)_{T,p} + \left(\frac{\partial H}{\partial N} \right)_{S,p} \tag{7.3}$$

However, these equations are not all the same. While V, S are extensive and scale with the size of the system, p, T are intensive and do not scale.

Thus, only G scales with the size of the system, since its intensive variables are kept constant.

Definition 7.1.1. For a homogeneous system, G is proportional to N, and we have the relation

$$\mu = \frac{G}{N} \tag{7.4}$$

Therefore, an alternative definition of the chemical potential is the *Gibbs* free energy per particle for an homogeneous system.

7.1.1 Physical meaning of chemical potential

Consider a box with a sliding partition which is porous and thermally conductive. The two sides can exchange heat and particles. Both partitions are isolated from the environment. See Figure 7.1.
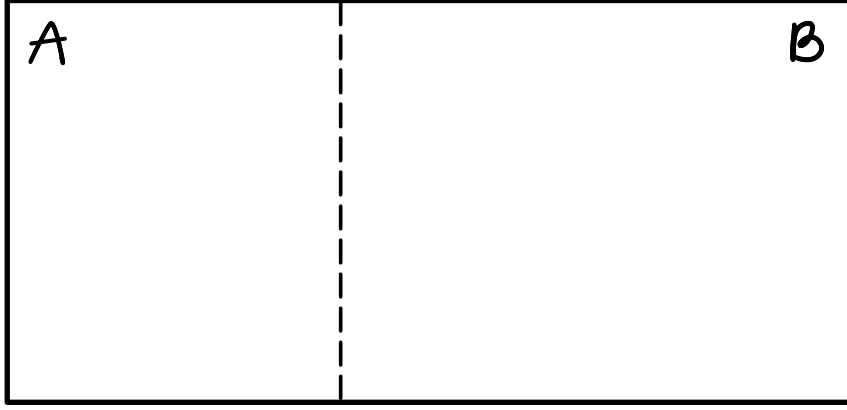
Figure 7.1: A movable partition separating A and B

We can establish a few relations:

$$
\begin{aligned}
\mathrm{d}V_A &= -\,\mathrm{d}V_B \\
\mathrm{d}N_A &= -\,\mathrm{d}N_B \\
\mathrm{d}U_A &= -\,\mathrm{d}U_B
\end{aligned}
\tag{7.5}
$$

Since $U = U(S, V, N)$, $S = S(U, V, N)$, the exact differential of S would be

$$
\left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{V,N} \mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{U,v} \mathrm{d}N
\tag{7.6}
$$

Rearrange the first law with the chemical potential for dS. We recognise that the total entropy the entropy of A plus the entropy of B. We can combine the relations derived above and get

$$
\mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\mathrm{d}U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\mathrm{d}V_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right)\mathrm{d}N_A
\tag{7.7}
$$

At equilibrium, the change in entropy $\mathrm{d}S$ is 0. This means we know at this state, $T_A = T_B$, $P_A = P_B$ and $\mu_A = \mu_B$. This is a simple case. We will now look at special cases.

7.1.2 Heat flow

Now, the partitions are fixed, and the holes are closed. We get rid of the dV and dN terms. In other words, we only have heat flow. Since the system evolves, and it is not in equilibrium $dS > 0$. Thus, if $T_B > T_A$ then $dU_A > 0$. All that means if partition B is hotter than partition A, then heat flows from B to A.

7.1.3 Particle flow

If we fix the partition again, but let the holes open, then temperature will remain the same for both partition. So we are left with only the dN term. Apply the same logic as the first case of heat flow, then we conclude that if chemical potential in B is higher than in A than the particles flow from B to A.

7.2 Gibbs-Duhem equation

Using Equation 7.2 we can write

$$dG = \mu\,dN + N\,d\mu \tag{7.8}$$

If we combine this with 5.4, we get the *Gibbs-Duhem* equation.

$$N\,d\mu = V\,dp - S\,dT \tag{7.9}$$

Definition 7.2.1. The Gibbs-Duhem equation in terms of intensive variables is

$$d\mu = \hat{v}\,dp - \hat{s}\,dT \tag{7.10}$$

where $\hat{v} = V/N$ and $\hat{s} = S/N$, which are specific volumes and specific entropy.

7.3 Clausis-Clapeyron equation

This equation is used to analyse the following situation. Consider a system where two phases of matter coexist. There is a first order discontinuous transition between the two phases with a latent heat. A common example would be a gas/liquid transition in H_2O. See Figure 7.2.

Now, consider a single point on the line at fixed (p, T). The total Gibbs energy is the sum of that in each phase.

$$dG = dG_1 + dG_2 \tag{7.11}$$
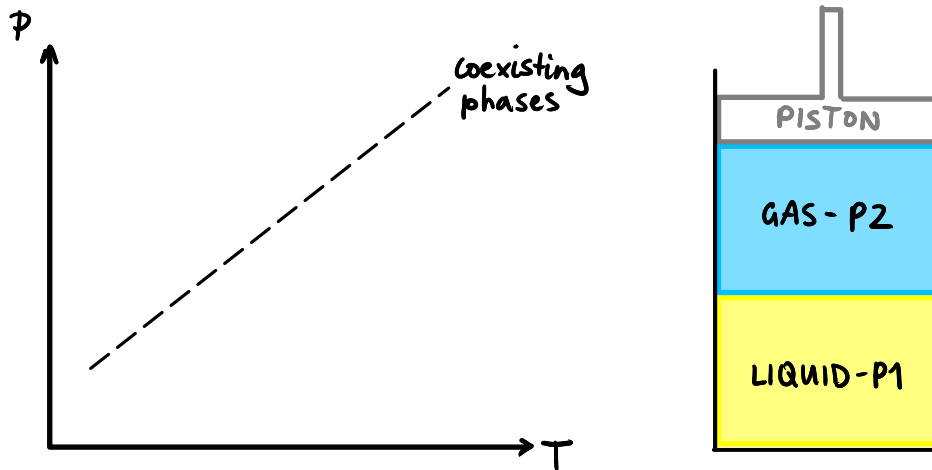
Figure 7.2: A system with pressure and temperature on the phase coexisting line. At any other (p, T) that does not lie on this line, there cannot be coexistence of the two phases.

In equilibrium, $dG = 0$ so using the expression for chemical potential in 7.2, we can establish that

$$dG = \mu_1 \, dN_1 + \mu_2 \, dN_2 = 0 \tag{7.12}$$

Because we have a closed system, $dN_1 = -dN_2$, thus, this proves that along the phase co-existence line $\mu_1 = \mu_2$. Now we can use the Gibbs-Duhem equation (5.4), we have

$$\hat{v}_1 \, dp - \hat{s}_1 \, dT = \hat{v}_2 \, dp - \hat{s}_1 \, dT$$
$$\frac{dp}{dT} = \frac{\hat{s}_1 - \hat{s}_2}{\hat{v}_1 - \hat{v}_2} \tag{7.13}$$

So the slope $\frac{dp}{dT}$ is related to the difference in specific entropy and specific volumes of the two phases.

We can also write the equation in terms of latent heat (the heat absorbed going from phase 1 to 2). Latent heat is expressed as

$$\hat{l} = \frac{L}{N} = \frac{\Delta Q}{N} = \frac{T}{N}\Delta S = \frac{T}{N}(S_2 - S_1) = T(\hat{s}_2 - \hat{s}_1) \tag{7.14}$$

Thus, our slope is now

$$\tag{7.15}$$

Definition 7.3.1. Therefore, we can write the Clausis-Clapeyron equations in two different ways:

$$\frac{dp}{dT} = \begin{cases} (\hat{s}_1 - \hat{s}_2)/(\hat{v}_1 - \hat{v}_2) \\ \hat{l}/T(\hat{v}_2 - \hat{v}_1) \end{cases} \tag{7.16}$$

The signs of L has to correspond to the change in volume.

7.4 Phase diagrams

For most materials, the density of the solid phase is higher than the liquid phase. However, for H_2O, the opposite is true due to hydrogen bonding in ice.

Relevantly, 2 phases exist along the $p-T$ line but 3 phases exist at the triple point, which is a single point of intersection between the different lines of coexisting phases.

Example 7.4.1. How can we melt ice with pressure? How much pressure do I need to liquefy ice at −5 °C? Looking at the phase diagram of water, we can draw a line from −5 °C to the line of coexistence (that's the critical point at which ice starts to melt), and find what temperature this is. To do this, we first must know the slope $\frac{dp}{dT}$.
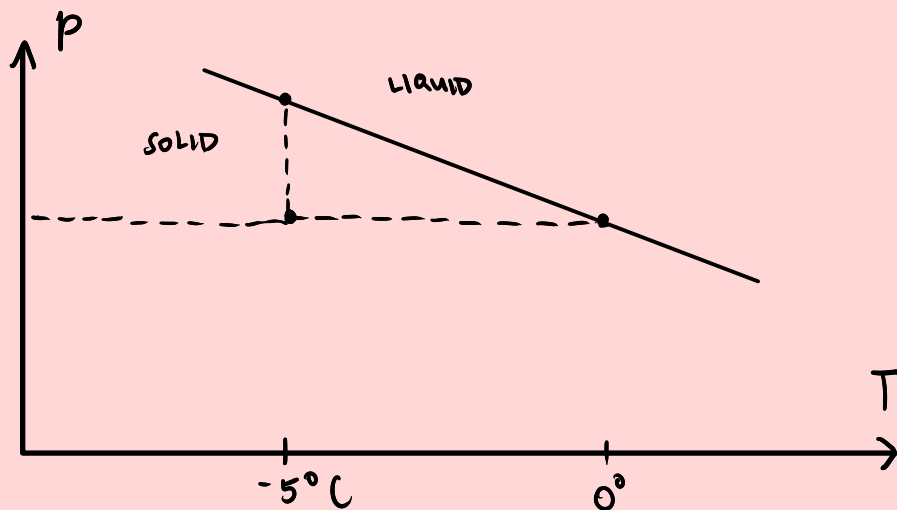
Figure 7.3: Phase diagram with a coexisting line between solid and liquid phases.

We know Clausis-Clapeyron equations from 7.16 and we also know about some quantities about water, $\hat{l} = 3.3 \times 10^5 \, \mathrm{J\,kg^{-1}}$. The specific volume $\hat{v}$, when using kilograms, is inversely proportional to the density, so that

$$\Delta \hat{v} = \frac{1}{\rho_{\text{water}}} - \frac{1}{\rho_{\text{ice}}} \tag{7.17}$$

We also know the corresponding densities at $0\,^{\circ}\text{C}$. This gives us a value for $\frac{\mathrm{d}p}{\mathrm{d}T}$. We need $\Delta p = \frac{\mathrm{d}p}{\mathrm{d}T}\Delta T$. The answer is about 68 MPa. This is equivalent to a person who weights 80 kg wearing ice-skating shoes of length 20 cm with width 60 μm.

8 Lecture 8 (Week 15)

8.1 The Third Law

Walter Nernst (1906): *At absolute zero all reactions take place with no change in entropy.* In other words:

$$\Delta G - \Delta H \to 0 \text{ as } T \to 0 \tag{8.1}$$

Definition 8.1.1. The third law is stated by Max Planck (1911) as:

Entropy of all systems in internal equilibrium tends to a constant at absolute zero, and so may be taken at zero.

Although note that not everything is in *internal* equilibrium, e.g., a glass. It is a disordered solid. It does not have a crystallise structure but rather a random arrangement. It would take a very long time to come into internal equilibrium (a meta-state).

Remember that we can calculate entropy by integrating the specific heat, as stated in Equation 4.12.

8.1.1 Consequences of the third law

1. Any system must have only one available state at $T = 0$, in other words, there must be no degenerate ground states. $S = 0$ at $T = 0$.

2. Heat capacity must go to zero at $T = 0$. $\ln \to -\infty$ as $T \to 0$.

$$C = \frac{dQ}{dT} = T\frac{dS}{dT} = \frac{dS}{d\ln T} \tag{8.2}$$

3. It is impossible to cool something to $T = 0$ in a finite number of steps.

From these consequences, we see that for an ideal gas where $C = \frac{3}{2}k_B N$. This is inconsistent with the third law. When we look later at Fermi gas, or a crystal lattice, these are all T-dependent. Thus, they are consistent with the third law.

Example 8.1.1. Let's apply the third law for a magnetic system. Where

$$\text{đ}W = B\,\text{d}m \tag{8.3}$$

Since B replaced p and m replaced V, we can use the relations in Section 5.4 to arrive at

$$S = \left(\frac{\partial G}{\partial T}\right)_B \text{ and } m = -\left(\frac{\partial G}{\partial B}\right)_T \tag{8.4}$$

Taking the second derivative to get the Maxwell equation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \tag{8.5}$$

We can use Curie's Law which states that the susceptibility, χ of a paramagnet is inversely proportional to T, where χ is

$$\chi = \frac{M}{\mu_0 B} = \frac{m}{\mu_0 v B} \tag{8.6}$$

Equate the two and we get that

$$\left(\frac{\partial S}{\partial B}\right)_T \equiv \frac{\partial m}{\partial T} \propto -\frac{1}{T^2} \tag{8.7}$$

But at $T = 0$, $S = 0$ thus Curie's Law must break down at absolute zero.

We can explore this by looking at magnetic cooling with a paramagnetic solid. For a paramagnet, the magnetic field causes spins to align with field, thus lowering entropy. The higher the field, the more aligned the spins are.

If we start a low B state, we magnetise it isothermally (increase B) by connecting it to a cold bath, this decreases the entropy. If we release the switch and turn off the field, then the system cools down adiabatically. We end up again at low B. We essentially just cooled down the paramagnet we started with, with B unchanged. But both curves get closer and closer together, so we need an infinite number of steps to reach 0. See the curves below
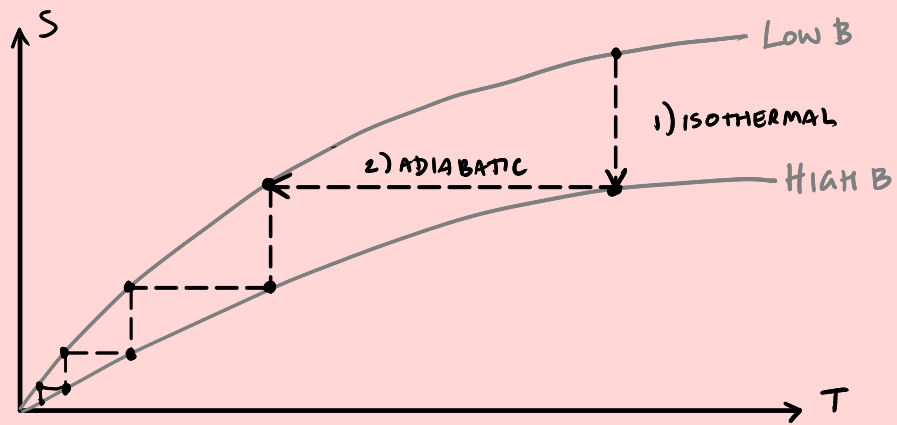
Figure 8.1: $S-T$ curves for low and high B.

9 Lecture 9 (Week 15)

9.1 Introduction

Now that we have covered Classical Thermal Physics, we will look at Statistical Mechanics

Statistical mechanics involve statistical averages of properties of the system, such as energy. We are expected to work out the set of possible configurational states of the system, calculate the probability distribution of these states, and calculate the macroscopic thermodynamic properties (p, S, U) from the probability distribution.

9.2 Counting states

A microstate is the number of permutations. It is similar to asking for the number of ways of putting n balls into r boxes (permutations). It concerns *individual* arrangement. Whether the balls are identical or different, or that $r \neq n$, will affect our formula for calculating the answers.

A macrostate is the number of balls and boxes. It is the overall picture of the system.

Example 9.2.1. Electrons have spin which can either be up or down. If we have $N = 4$ lattice sites, then this is our macrostate. Let's say we have 4 electrons, two are up and two are down, $N_u = 2$ and $N_d = 2$. There are 6 distinguishable microstates. We get this through the following formula.
$$\Omega = \frac{N!}{N_d! N_u!} \tag{9.1}$$
There are N electrons and N sites, that means there are $N!$ ways of rearranging them. However, since all the N_u are identical and all the N_d are identical, we divide by $N_u! N_d!$

Later, we find that $S = k_B \ln \Omega$. So if we know Ω, we can find S.

9.3 Stirling's formula

We often work with $\ln \Omega$ so approximations are useful, note that the second one is better than the first one.

Definition 9.3.1. Stirling's approximations for $\ln n!$ are

$$\ln n! \simeq n \ln n - n, \quad n \gg 1$$
$$\ln n! \simeq n \ln n - n + \frac{1}{2} \ln 2\pi n, \quad n \gg 1$$

(9.2)

9.4 Statistical Ensembles

Definition 9.4.1. An ensemble is a large number of virtual copies of a system which are all the same but configured in random ways.

An ensemble average is then the average state of all these virtual systems.

An statistical ensemble is then a probability distribution of all possibles states of the system

Averages are calculated by two following ways (we assume they give the *same* answer)

1. Take a **single** system and follow it over a long time, so that the system goes through all possible configurations.

2. Take a large number of identical (but randomly configured) systems and average over these at a single snapshot in time. This is called the ensemble average.

9.4.1 Types of Ensemble

Gibbs categorised three types of ensembles which refer to a system and how it interact with the surroundings. See Figure 9.1 for diagrams.

1. **Micro-canonical ensemble:** This is an isolated system with fixed U, V, N. We can apply this ensemble to a whole gas as an isolated system.

2. **Canonical (standard) ensemble:** System is in contact with a thermal reservoir. V, N, T fixed for the system. We can apply this ensemble if we consider each atom in the gas is a separate system, and the rest of the gas is the reservoir.

3. **Grand-canonical ensemble:** System can exchange heat and particles with the reservoir. V, T, μ are fixed for the system. We can apply this ensemble if a microstate of the configuration of the gas is a system. The rest of gas is reservoir.
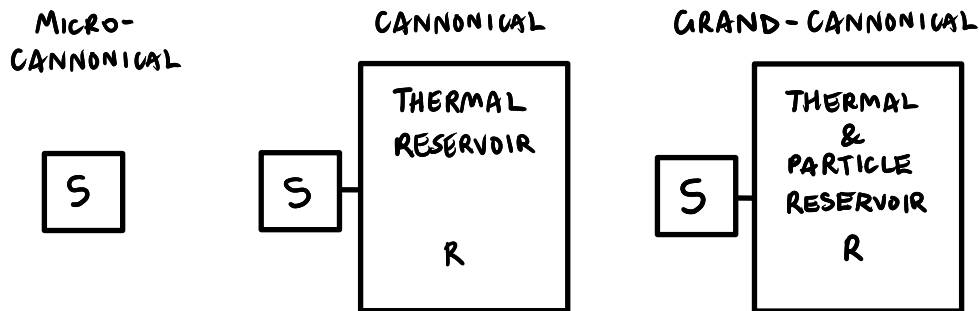
Figure 9.1: Different types of Ensembles

9.5 Principle of equal equilibrium probability

Definition 9.5.1. When a thermally isolated system comes into thermal equilibrium, then the state probabilities of any set of mutually accessible states become **equal**.

In a microcanonical ensemble, there is equal probability of any state begin occupied.

9.6 Ergodic hypothesis

Definition 9.6.1. Given enough time the systems will explore all possible microstates and will spend an equal amount of time in each of them.

Implication of this is that in equilibrium an isolated system will choose the macrostate with the most microstates. This is the Second Law (to maximise entropy).

10 Lecture 10 (Week 15)

10.1 Energy and states

The problem for x quanta and N boxes is the same as asking how many ways you can arrange x quanta and $N - 1$ partitions in a line.

The partitions separate the boxes, excluding the walls. Thus if there are N boxes, there must be $N - 1$ partitions.

The total number of ways to arrange this would be $(x + N - 1)!$. Partitions are identical and so are quanta, thus we have to divide by $(N - 1)!x!$.

Our final result is therefore

Definition 10.1.1. To arrange x quanta in $N - 1$ partitions or N boxes, there would be

$$\Omega = \frac{(x + N - 1)!}{x! \, (N - 1)!} \tag{10.1}$$

ways of doing this.

The number of states is a very rapidly (slightly slower than exponential) increasing function of the total energy x (if you plot a log plot versus x it would appear almost linear). See 10.1

10.2 Statistical Temperature

Consider 2 systems **A** and **B** in thermal contact with each other but isolated from the surroundings, i.e. a Microcanonical ensemble.

Find the conditions where the number of available states is maximum. This gives condition of thermal equilibrium.

Total energy at any point is fixed because the system is thermally isolated.

$$U_A + U_B = U_0 \implies \frac{dU_A}{dU_B} = -1 \tag{10.2}$$

The number of microstates is given by $\Omega(U_A)$ or $\Omega(U_B)$. The total number of states as a function of U_A would be

$$\Omega_{AB} = \Omega\,(U_A)\,\Omega\,(U_B) = \Omega\,(U_A)\,\Omega\,(U_0 - U_A) \tag{10.3}$$

Since $\Omega\,(U_0)$ is a very fast increasing function, the negative of that would be a fast decreasing function.
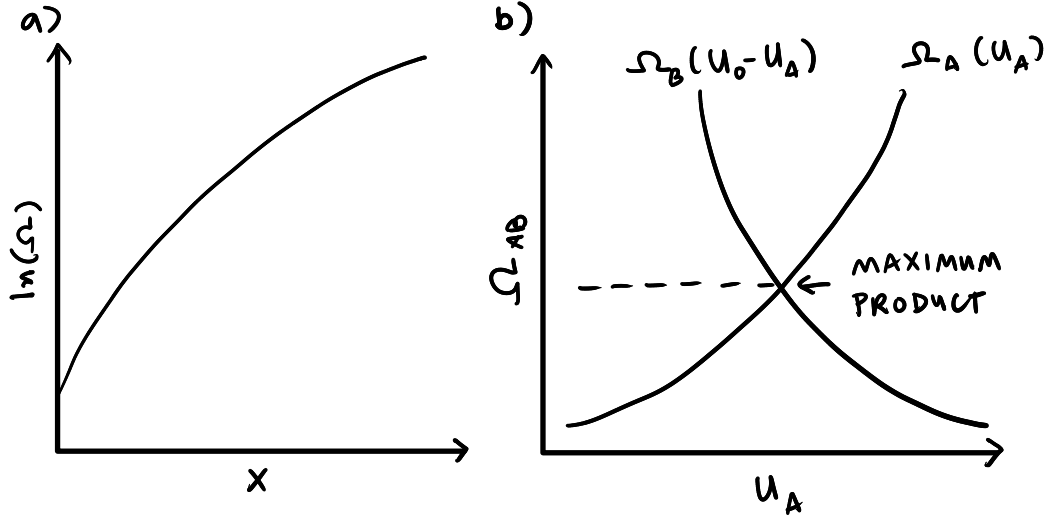
Figure 10.1: **(a)** shows the log plot of Ω and x, the total energy, **(b)** shows the number of states of two microcanonical systems as a function of the energy of one.

We can actually derive the mathematical relations for the maximum number of states, where the derivative of Ω_{AB} is zero. The steps are outlined briefly.

Derivation 10.2.1. We start of with our definition for the total states and find its derivative and rearrange a bit.

$$\Omega_{AB} = \Omega\,(U_A)\,\Omega\,(U_B)$$

$$\frac{d\Omega_{AB}}{dU_A} = \frac{d\Omega_A}{dU_A}\Omega_B + \frac{d\Omega_B}{dU_A}\Omega_A = 0$$

$$\frac{d\Omega_{AB}}{dU_A} = \frac{d\Omega_A}{dU_A}\Omega_B - \frac{d\Omega_B}{dU_B}\Omega_A = 0, \quad \text{since} \quad \frac{dU_A}{dU_B} = -1 \tag{10.4}$$

$$\frac{1}{\Omega_A}\frac{d\Omega_A}{dU_A} = \frac{1}{\Omega_B}\frac{d\Omega_B}{dU_B}$$

This is equivalent to

$$\frac{d\ln\Omega_A}{dU_A} = \frac{d\ln\Omega_B}{dU_B} \tag{10.5}$$

This is our condition for thermal equilibrium. Think of Figure 10.1 (b), if the two derivatives are the same then that's where the two curves meet.

Now, we can define the **statistical temperature** as

$$\frac{1}{k_b T_A} = \frac{d \ln \Omega_A}{dU_A} \tag{10.6}$$

This is a bit of a leap in definition, but it is dimensionally correct, and the Boltzmann constant k_B is included so that it agrees with the kelvin scale.

10.3 Boltzmann entropy

If we use the first law equation 4.13, we can write T as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \tag{10.7}$$

If we compare this to Equation 10.6, we get the Boltzmann's equation for entropy.

Definition 10.3.1. The Boltzmann's equation for entropy state that

$$S = k_b \ln \Omega \tag{10.8}$$

A system will evolve to maximise Ω. This is consistent with the second law—the system will evolve to maximise S.

11 Lecture 11 (Week 16)

11.1 Bolztmann distribution

We note that random exchange lead to an exponential distribution. From the definition of entropy, we can confirm it does lead to a logarithmic distribution.

Consider a small system **S**, with a single occupied state, in contact with a large reservoir **R** but otherwise thermally isolated. This is a *canonical ensemble*. See 9.4 for further definitions.

We can say a few things about this system.

- The total energy is E_0

- The energy in **S** is E_i

- The energy in **R** is $E_0 - E_i$

- Assume $E_i \ll E_0$

What is the probability that the system has a particular energy E_i?

We expect the probability to be proportional to the product of the number of states available to the small system (exactly one) and the number of states available to the reservoir (equals to $\Omega\left(E_0 - E_i\right)$). We can find this using Taylor expansion.

Derivation 11.1.1. Expand $\ln \Omega\left(E_0 - E_i\right)$

$$\ln \Omega\left(E_0 - E_i\right) = \ln \Omega\left(E_0\right) + \frac{d \ln \Omega\left(E_0\right)}{dE}\left(-E_i\right) + \frac{1}{2}\frac{d^2 \ln \Omega\left(E_0\right)}{dE^2}E_i^2 \tag{11.1}$$

From our definition of statistical temperature in Equation 10.6, we can rewrite this into

$$\ln \Omega\left(E_0 - E_i\right) = \ln \Omega\left(E_0\right) - \frac{E_i}{k_B T} - \frac{1}{2k_B T^2}\frac{dT}{dE}E_i^2 \tag{11.2}$$

We can neglect the second order term if the reservoir is sufficiently large. Then we can take the exponential of both sides.

$$\Omega\left(E_0 - E_i\right) = \Omega\left(E_0\right) \exp\left(-\frac{E_i}{k_B T}\right) \tag{11.3}$$

Thus, the probability of of a given state being occupied can be given as

$$P(E_i) \propto \exp\left(-\frac{E_i}{k_B T}\right) \tag{11.4}$$

we call this the Boltzmann distribution function.

We also have to normalise this probability distribution function such that the sum of all probabilities is 1. This gives us the normalisation constant $1/Z$. Where Z is called the *partition function* and is given as

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right) \tag{11.5}$$

Note that this is the sum of *all* states, not just all energy levels. Thus, if an energy level is degenerate (can have multiple states), we need to factor in the degeneracy factor g_i, so that the energy level is counted the correct number of times.

Definition 11.1.1. For a canonical system, the Boltzmann Distribution is given as

$$P(E_i) = \frac{1}{Z} \exp\left(-\frac{E_i}{k_B T}\right) \tag{11.6}$$

where Z is given as

$$Z = \sum_i g_i \exp\left(-\frac{E_i}{k_B T}\right) \tag{11.7}$$

Example 11.1.1. Consider a system with two energy levels that are non-degenerate. Then the partition function Z would be

$$Z = \sum_i e^{-\beta \epsilon_i} = e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} \tag{11.8}$$

Next, consider rotational energy levels of molecules. We have calculated the quantum energy levels $E_J = \hbar^2 J(J+I)/2I$, where J is the angular momentum quantum number and I is the constant moment of inertia. The levels are degenerate, for J there are $2J+1$ states. Then, the partition function is

$$Z = \sum_{J=0}^{\infty} (2J+I) \exp\left(-\frac{J\beta\hbar^2}{2I}(J+1)\right) \tag{11.9}$$

49

11.2 Boltzmann-Gibbs Entropy

For an isolated system (a microcanonical ensemble), we have

$$S = k_B \ln \Omega \tag{11.10}$$

The entropy can be viewed as a lack of information, i.e., the system can be in any of the Ω different microstates.

The probability that the system is in any particular state is inversely proportional to Ω.

For the canonical ensemble, however, the probability is not the same for all states of the system. Instead, it is given by the Boltzmann factor in Equation 11.6.

Definition 11.2.1. The general equation for Boltzmann-Gibbs entropy is

$$S = -k_B \sum_i P_i \ln P_i \tag{11.11}$$

This applies for a canonical system. For a microcanonical distribution, $S = k_B \ln \Omega$.

12 Lecture 12 (Week 16)

12.1 The average of a distribution function

Definition 12.1.1. For a discrete distribution, the average is given by

$$\langle X \rangle = \sum_i P_i X_i \tag{12.1}$$

For a continuous distribution, the average is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} P(x)\, x \,\mathrm{d}x \tag{12.2}$$

12.2 Internal energy in terms of Z

The internal energy can be calculated as

$$U = \sum_i P_i E_i = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \tag{12.3}$$

But we can express this in terms of the partition function as well.

Definition 12.2.1. The internal energy is given as

$$U = -\frac{1}{Z}\frac{\mathrm{d}Z}{\mathrm{d}\beta} = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} \tag{12.4}$$

12.3 Entropy in terms of Z

We start with the Boltzmann-Gibbs entropy expression, and with a bit of rearranging we can derive entropy in terms of the partition function as well.

Definition 12.3.1. The entropy is given as

$$S = \frac{U}{T} + k_B \ln Z \tag{12.5}$$

12.4 Helmholtz Free energy in terms of Z

Definition 12.4.1. The Helmholtz Free energy is given as

$$F = -k_B T \ln Z \tag{12.6}$$

12.5 Combining partition functions

A system may have two or more contributions to the energy (rotation, vibration, motion along x, y, z). Thus, we have to sum these contributions.

$$Z = \sum_i \sum_j e^{-\beta\left(E_i^x + E_j^y\right)} = Z_x Z_y \tag{12.7}$$

So, partition functions from independent contributions *multiply*.

But for the free energy, depends on the logarithm of Z, thus the contributions are *additive*.

$$F = F_x + F_y \tag{12.8}$$

12.6 Classical Equipartition theorem

Each 'degree of freedom' of a classical system adds $\frac{1}{2}k_b T$ to the total energy. Works in the classical limit as long as the degree of freedom adds an extra term to the energy which varies as the variable squared (like kinetic energy, elastic potential energy).

We can derive this by computing some Gaussian integrals.

With this, we find that the internal energy $U = \langle E \rangle$ for one degree of freedom is

$$\langle E \rangle = \frac{k_B T}{2} \tag{12.9}$$

12.6.1 Gaussian Integrals (not examinable)

Definition 12.6.1. Here are important identities for Gaussian integrals:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} \, \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}} \qquad \int_{0}^{\infty} x e^{-\alpha x^2} \, \mathrm{d}x = \frac{1}{2\alpha} \tag{12.10}$$

Notice the limits on odd powers of x. For further powers, take derivative w.r.t. α on both sides.

12.6.2 Does the equipartition theorem work in a quantum system?

We can answer this question by considering an example.

Example 12.6.1. Consider a mass m on a spring where the modes of oscillation are quantised by the boundary conditions. I.e., only certain oscillation frequencies are allowed.

Recall the *Hamiltonian.* Applying it to a spring system, we have

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{k}{2}\hat{x}^2 \tag{12.11}$$

We recall our harmonic oscillators have energy levels

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \qquad \text{with} \quad \omega_0 = \sqrt{\frac{k}{m}} \tag{12.12}$$

Our partition function would be

$$Z = \sum_{n=0}^{\infty} \exp\left[-\beta\left(n + \frac{1}{2}\right)\hbar\omega_0\right] = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}} \tag{12.13}$$

We can arrive at this result by treating the double sum as an infinite geometric series r^n where $r = \exp\left(-\beta\hbar\omega_0\right)$. Then if we find the internal energy by finding $\langle E \rangle$, we find that it is

$$U = -\frac{\partial \ln Z}{\partial B} = \hbar^2\omega_0\left[\frac{1}{2} + \frac{e^{-\beta\hbar\omega_0}}{1 - e^{-\beta\hbar\omega_0}}\right] \tag{12.14}$$

Remember, we get to this result by computing the derivative of Z w.r.t. β.

The result we get is clearly quite different from the classic result. But for high temperature limit, we can expand the exponential in terms of its Taylor series and find that it *does* agree with the equipartition theorem for 2 degrees of freedom.

13 Lecture 13 (Week 16)

13.1 Kinetic theory of an ideal gas

We apply the Boltzmann distribution to calculate the velocity distribution of a gas.

13.1.1 Assumptions of our model

- Only translational degrees of freedom—no rotations
- Each molecule/atom has a unique velocity state
- Allowed velocity states are uniformly distributed in velocity space

Consider a canonical ensemble. Each molecule is a (sub)system connected to the thermal bath which is physically all the other molecules in the gas.

The probability of a given x-component of the velocity v_x

$$P\left(v_x\right) \propto \exp\left(-\frac{\epsilon}{k_B T}\right) \propto \exp\left(-\frac{mv_x^2}{2k_B T}\right) \tag{13.1}$$

To work this out, we integrate the Boltzmann distribution with respect to all three translational components $v_{x,y,z}$ and set it to 1 since probability distribution functions are normalised.

Derivation 13.1.1.

$$P = A \iiint e^{-\beta\epsilon} \, dv_x \, dv_y \, dv_z = 1 \tag{13.2}$$

We have

$$\epsilon = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) \tag{13.3}$$

Which gives us

$$P = A \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\beta m v_x^2}{2}} e^{-\frac{\beta m v_y^2}{2}} e^{-\frac{\beta m v_z^2}{2}} \, dv_x \, dv_y \, dv_z = 1 \tag{13.4}$$

We use Gaussian integral identities to get

$$P\left(v_x, v_y, v_z\right) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{\beta m}{2}\left(v_x + v_y + v_z\right)\right) \tag{13.5}$$

13.2 Speed distribution

For some application of the kinetic theory, we don't need the velocity distribution, but only the speed distribution.

Now, we assume that the number of allowed velocity states is uniform in velocity space. Our integral now becomes an integration over all velocity space. In 2D, we consider a small element, a ring of a circle. In 3D, we want to integrate over a sphere, thus, we consider a small surface element (then we want to extent the radius of this sphere, which is our velocity v, to infinity).

So, we have

$$f(v)\, dv \propto v^2 \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{13.6}$$

Derivation 13.2.1. To start, write out the integral as

$$f(v) = A \int_0^\infty v^2 \exp\left(-\beta \frac{mv^2}{2}\right) = 1 \tag{13.7}$$

Then once again, using Gaussian integral identities, we arrive at

$$f(v) = \frac{4}{\pi}\left(\frac{\beta m}{2}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{\beta m v^2}{2}\right) \tag{13.8}$$

Definition 13.2.1. The Maxwell-Boltzmann speed distribution curve is

$$f(v) = \frac{4}{\pi}\left(\frac{\beta m}{2}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{\beta m v^2}{2}\right) \tag{13.9}$$

See Figure 13.1 for the shape of this distribution. It is a slightly asymmetric curve. The lower T is, the less symmetrical it becomes. The higher T is, the lower the highest probability peak. As expected, the average speed increases at higher temperature.

Because this is a probability distribution, we can calculate the mean average. We are particularly interested in the root-mean-square speed. Here's how to derive it.

Derivation 13.2.2. Begin with the standard integral for the mean-square, and apply the Gaussian integral to immediately get the result.

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\, dv = \frac{3k_B T}{m} \tag{13.10}$$
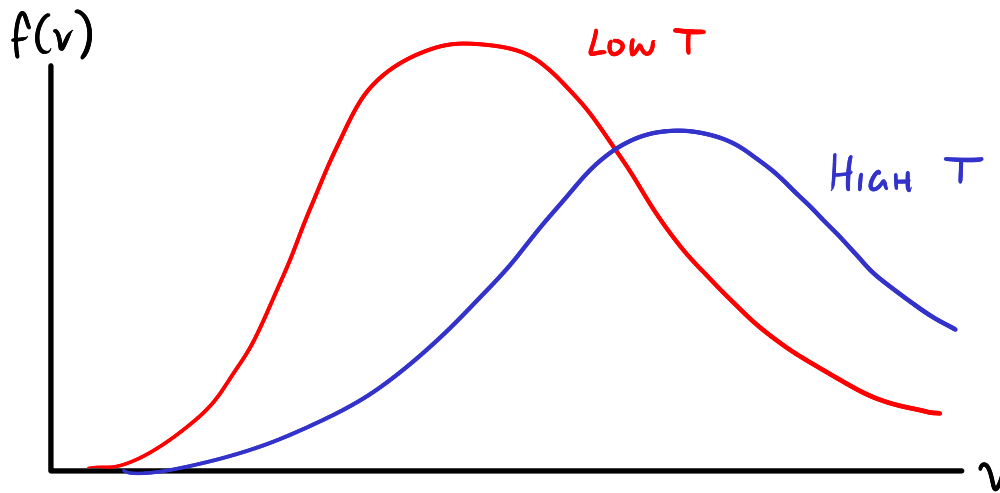
Figure 13.1: The Maxwell-Boltzmann speed distribution curve for high and low temperatures

We can then find the average kinetic energy, which is given as

$$\langle E \rangle = \frac{1}{2}m \left\langle v^2 \right\rangle = \frac{3}{2}k_B T \tag{13.11}$$

We expected this expression, since we have derived this in the equipartition theorem for three degrees of freedom. See Section 12.6.

13.3 Pressure distribution

We break this calculation down into several steps. First, we start with the definition of pressure as the force over the area.

Next, when a particle hits the wall of the container, the change in momentum is double the incoming momentum.

$$\Delta P_m = 2mv \cos \theta \tag{13.12}$$

If we have n atoms per unit volume moving at speed v at angle θ, then the number that hit a wall of area A in time dt is

$$N_\theta = nv \cos \theta A \, dt \tag{13.13}$$

We can rationalise this by thinking that if we take a snapshot of time dt, each atom is currently on the same angle towards the wall. But after that interval of time, they would have moved $v \, dt$ and hit the wall. So all the particles in that region hit the wall in that interval of time. This

forms a parallelepiped of volume $v \, dt \cos \theta A$, and we can get the total atoms by multiplying it by the atom per unit volume n. See Figure 13.2.
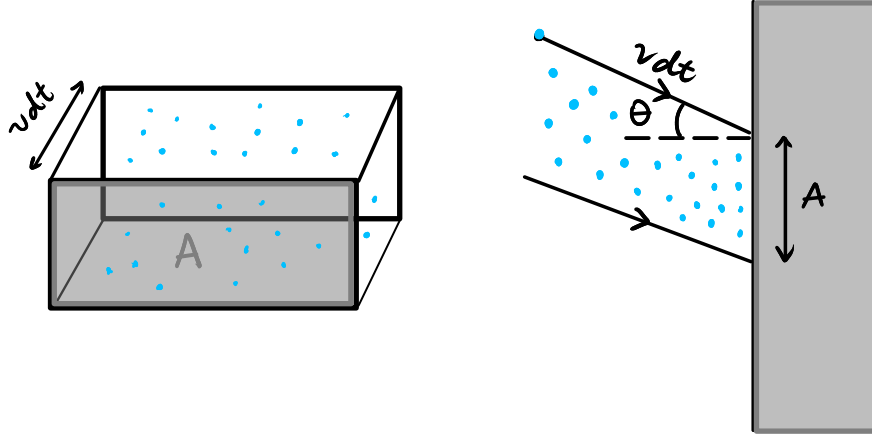

Figure 13.2: Consider a unit volume of particles that hit the wall in a short time interval dt. It forms a parallelepiped.

Consider a collection of particles with $|v| = 1$, the velocity vectors will be on a sphere with the unit radius. The velocity vectors are all random, but it will be within this sphere.

If we want to know how many are moving at the angle θ, then we need to consider a ring on the sphere between the angle θ. In essence, we want to consider a fraction of atoms travelling at an angle $\theta \to \theta + d\theta$. All the atoms which travel at that angle is in the ring, thus this would be the area of the ring divide by the area of the whole sphere

$$\frac{2\pi \sin \theta \, d\theta}{4\pi} = \frac{1}{2} \sin \theta \, d\theta \tag{13.14}$$

Putting it all together, we have the following derivation

Derivation 13.3.1. We integrate over the velocity function in that ring

$$P = \frac{\frac{dp}{dt}}{A} = \int_0^\infty \int_0^{\frac{\pi}{2}} 2 \frac{1}{2} f(v) \, mv \cos \theta nv \cos \theta A \, dt \sin \theta \frac{1}{A \, dt} \, d\theta \, dv \tag{13.15}$$

If we use the substitution $y = \cos \theta$, and use a Gaussian integral identity, we get the following

$$P = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2} \right)^{\frac{3}{2}} \frac{nm}{3} \frac{3\sqrt{\pi}}{8} \left(\frac{\beta m}{2} \right)^{-\frac{5}{2}} \tag{13.16}$$

Simplifying the answer gives us

$$P = nk_BT \tag{13.17}$$

Where $n = N/V$ and $N = N_a n$. We notice that we get the ideal gas law from this.

14 Lecture 14 (Week 17)

14.1 Statistical mechanics of ideal gas

The basic idea is to:

- Calculate the allowed energy modes of the system, E_i

- We calculate the partition function Z.

- Finally, we can calculate the thermodynamic properties from the partition function. These were derived in 12. We recall them as:

$$F = -k_B T \ln Z \tag{14.1}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \tag{14.2}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{14.3}$$

14.2 Calculate the energy modes

First, we treat the gas quantum mechanically. Consider a particle in a box of side L, with volume $= L^3$. We solve the Schrödinger equation for the system.

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{14.4}$$

The solutions of these are plane waves

$$\Psi = \Psi_0 \exp\left[i\left(\vec{k}\cdot\vec{r} - wt\right)\right] \tag{14.5}$$

If we apply the momentum operator to the solution, we can find that it is

$$\hat{p}\Psi = p\Psi \quad p = \hbar k \tag{14.6}$$

Finally, the energy is

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{14.7}$$

Now, we impose the *periodic* boundary conditions. Recall that the quantisation of k and E comes from the periodic boundary conditions.

$$\exp\left(ik_x\left(x+L\right)\right) = \exp\left(ik_x\right) \tag{14.8}$$

Thus, the allowed values are $k_x = n_x 2\pi/L$. Extending this to 3D, we get

$$\Psi\left(x,y,z\right) \propto \exp\left(ik_x x + k_y y + k_z z\right) \quad \text{where} \quad -\infty < n_{x,y,z} < \infty \tag{14.9}$$

14.3 Density of states

The allowed states are on a uniform grid in k-space ('frequency' space). In 2D, the number of states per unit area of k-space is $= \left(L/2\pi\right)^2$ and in 3D, the number of states is $= \left(L/2\pi\right)^3$.

This is called the *density of states $g\left(k\right)$*. If we write $k = \left|\vec{k}\right|$, then we have in 3D the number of states between k and $k + dk$ presented as a sphere (with k as the radius). Since we are considering a small element, we consider a shell with surface area $4\pi k^2$ (for k from 0 to ∞). Then, the general density of states is

$$g\left(k\right)\,dk = 4\pi k^2\,dk\,\frac{V}{\left(2\pi\right)^3} \tag{14.10}$$

14.4 Calculate the partition function of a single atom

We performed the intermediate step of finding $g\left(k\right)$ so that we can find Z. Since we have the density of states, we can sum the energy levels, this becomes a integral of states over all volume.

$$\sum_i \rightarrow \int_0^\infty g\left(k\right)\,dk \tag{14.11}$$

Derivation 14.4.1. Let's derive the expression for Z_1

$$Z_1 = \sum_{k_x,k_y,k_z} \exp\left(-\beta\hbar k^2/2m\right) = \int_0^\infty g\left(k\right)\exp\left(-\beta\hbar k^2/2m\right)\,dk \tag{14.12}$$

We get the following integral

$$\frac{4\pi V}{\left(2\pi\right)^3} \int_0^\infty k^2 e^{-\alpha k^2}\,dk \quad \text{with} \quad \alpha = \frac{\beta\hbar^2}{2m} \tag{14.13}$$

Using a standard Gaussian integral, we get

$$Z_1 = \frac{V}{\lambda^3} \quad \text{with} \quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}} \tag{14.14}$$

where λ is the thermal de Broglie wavelength.

The classic atom thermal energy $E = \frac{3}{2}k_B T = \frac{p^2}{2m}$, $p = \sqrt{3mk_B T}$ and thus $\lambda = h/\sqrt{3mk_B T}$. Between the two, there is only a factor of $\sqrt{2\pi/3}$ difference.

14.5 Thermal de Broglie wavelength

This is the characteristic size of system where quantum effects become important. For example, if we put an electron in a box, since the de Broglie wavelength depends on the mass and temperature. If we set the mass as the mass of an electron, then a box with a side of $\lambda_{\text{th}} = 1\,\text{m}$ would have $T = 5 \times 10^{-15}\,\text{K}$. This has not been achieved experimentally. If, instead we have a box of side $\lambda_{\text{th}} = 3 \times 10^{-4}\,\text{m}$ would have $T = 6 \times 10^4\,\text{K}$. This is about the distance between 2 atoms in a solid. Thus, electrons in a solid are always in the quantum regime.

15 Lecture 15 (Week 17)

15.1 Partition function of an ideal gas

The partition function for a single atom is Z_1, but a real gas has got N atoms. We then 2 cases.

Case 1: The atoms are distinguishable (each one different colour). Then, we would have a system (each being an atom), connected to a reservoir (the other atoms). Each atom is in a different configuration, then we would have to take into account all the permutations as one atom can take the configuration of the other. The probability of a particular macrostate of gas is $\propto \exp\left(-\beta E_{i1} + -\beta E_{i2} + -\beta E_{i3} + \ldots\right)$, and thus

$$Z_{N,D} = \left(\sum_{i1} e^{-\beta E_{i1}}\right)\left(\sum_{i2} e^{-\beta E_{i2}}\right) \times \left(\sum_{i3} e^{-\beta E_{i3}}\right)\ldots \tag{15.1}$$

But each sum is the same and equal to Z_1, thus

$$Z_{N,D} = Z_1^N \tag{15.2}$$

However, a real gas does not have distinguishable atoms. Recalling from Section 10, if all the atoms are indistinguishable, then we have over-counted our states by $N!$. However, this is only approximately true because we have neglected the possibility that two atoms have exactly the same energy levels. This would be like putting two particles in the same box in the example below.

Case 2: If the atoms are indistinguishable, then we have to divide by $N!$

$$N_{N,I} \simeq \frac{Z_1^N}{N!} \equiv Z_G \tag{15.3}$$

This is approximately true as long as we can neglect any atoms which, in this approximation, would have the same quantum numbers. This is OK as long as the number of possible states is *much larger* than the number of atoms. This corresponds the regime where the linear size of the system $\gg \lambda_{\text{th}}$.

So the expression of Z works in the classical regime, since the size of the system satisfies the condition above.

$$Z_G = \frac{V}{\lambda_{\text{th}}^3}^N / N! = V\left(mk_BT/2\pi\hbar^2\right)^{3/2}{}^N / N! \tag{15.4}$$

15.2 Pressure of an ideal gas

If we recall the definitions for pressure and entropy in terms of Z and F, then we can derive this for a whole system of an ideal gas. While the expressions are similar to what we have derived before, we can get a particular equation for entropy for a monoatomic ideal gas

Definition 15.2.1. The Sackur-Tetrode equation for entropy of a monoatomic ideal gas is

$$S = N k_B \left[\left(\ln \frac{V}{\lambda^3 N} \right) + \frac{5}{2} \right] \tag{15.5}$$

15.3 Gibbs Paradox

We can use the equation for entropy we just quoted to discuss this paradox. Consider two boxes separated with a partition. Each box has N particles of either type A or B and both have volume V. Now, we remove the partition. What happens?

Case 1: If the atoms A and B are indistinguishable. Then before, the total entropy is

$$S = 2 \times N k_B \left[\left(\ln \frac{V}{\lambda^3 N} \right) + \frac{5}{2} \right]. \tag{15.6}$$

After we remove the partition, the volume is $2VS$, and the total number of particles is $2N$. Thus, we have the same entropy as before. The change in entropy is 0.

Case 2: The atoms A and B are distinguishable. Before, we have

$$S = 2 \times N k_B \left[\left(\ln \frac{V}{\lambda^3 N} \right) + \frac{5}{2} \right]. \tag{15.7}$$

After we remove the partition, there would be N atoms of each type in a volume of $2V$. Since this is an ideal gas, the atoms of different types don't interact. Each set of atom types move freely in a volume of $2V$. Thus, the entropy is

$$S = 2 \times N k_B \left[\left(\ln \frac{2V}{\lambda^3 N} \right) + \frac{5}{2} \right]. \tag{15.8}$$

Therefore, the total change in entropy is $\Delta S = 2 N k_B \ln 2$.

The paradox is that if the particles have some property X which we can't measure, but someone else could? So they appear to be identical but are in fact not. Would the entropy change when suddenly we are able to measure the difference?

The answer, from the two cases, is *yes*. Entropy depends on our knowledge of the system. There is a connection between entropy and connection. The way to interpret the extra entropy is to note that after mixing A and B, to restore the system to its original state, we would need to do work on the system equal to at least $T\Delta S$.

16 Lecture 16 (Week 17)

16.1 Grand canonical ensemble

The grand canonical ensemble is when we can exchange heat *and* particles with a reservoir.

There are two equivalent ways to describe a system. First, we consider each atom separately as a subsystem. Each atom has a set of energy levels. Otherwise, we can consider the whole gas as the system. Each energy level of the system is the sum of some particular combination of the energy levels of each atom. There are multiple particles in the system. In principle each level could be multiply occupied. This is the grand canonical ensemble.

When we dealt with ideal gas in the canonical ensemble, we had to deal with identical configurations and had to ignore the issues with degeneracy. This is not feasible in quantum regime, due to *Pauli's exclusion principle.*

16.2 Gibb's distribution

Similar to how we derived the Boltzmann's distribution, we have a system and a reservoir, except now it can exchange energy and particles. Both reservoir and system are isolated, which means there is a total energy and a total number of particles.

Our strategy: We assume the system has only one state to find the number of states available to the reservoir. Then, we Taylor expand the state number as a function of energy and number of particles. The probability is proportional to the number of states, which we then equate as an exponential.

Derivation 16.2.1.

$$\ln \Omega \left(U_0 - E_i, N_0 - N_i \right) = \ln \Omega \left(U_0, N_0 \right) - E_i \left(\frac{\partial \ln \Omega}{\partial U} \right)_{N,V} - N_i \left(\frac{\partial \ln \Omega}{\partial N} \right)_{U,V} \tag{16.1}$$

Now, we use the first law with the chemical potential in Equation 7.1. We then write its exact differential. We get

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N} \right)_{U,V} \tag{16.2}$$

Using $S = k_B \ln \Omega$, we now have

$$\ln \Omega = \ln \Omega \left(U_0, N_0 \right) - \frac{E_i}{k_B T} + \frac{N_i \mu}{k_B T} \tag{16.3}$$

Taking the exponential of both sides yields

$$P \left(N_i, E_i \right) \propto \exp \left(\beta \left(\mu N_i - E_i \right) \right) \tag{16.4}$$

where the normalisation constant is $1/Z_G$, where Z_G is the Grand Partition function

$$Z_G = \sum_i \exp \left[\beta \left(\mu N_i - E_i \right) \right] \tag{16.5}$$

We can now use the grand partition function to work out U, the average energy of the system. These quantities turn out to be

$$\langle N \rangle = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln Z_G}{\partial \mu} \right)_\beta \tag{16.6}$$

and

$$U = \sum_i E_i P_i = - \left(\frac{\partial \ln Z_G}{\partial \beta} \right)_\mu + \mu \langle N \rangle \tag{16.7}$$

17 Lecture 17 (Week 17)

17.1 Statistics of quantum particles

Two types of quantum particles are fermions and bosons.

17.1.1 Fermions

Fermions are any particles with half integer spin, $S = 1/2, 3/2$ etc. in units of $\hbar$. An example would be an electron. A composite fermion consist of multiple particles, and the entity as a whole has a half integer spin. For example, a carbon nucleus.

The total wavefunction for a fermion system must be antisymmetric with respect to particle exchange. Mathematically, this means

$$\Psi(a, b = -\Psi(b, a) \tag{17.1}$$

if the space and spin coordinates of two identical particles are interchanged, then the total wave function must changes spin.

This property implies that each fermion must have a unique quantum number (e.g., k_x, k_y, k_z, spin). We can only have one fermion in any single quantum state.

For example, $A(x, y) = -A(y, x)$. If $y = x$ then this is only true if $A = 0$. In general, $A(x, x) \neq -A(x, x)$. This property is called the *Pauli exclusion principle*.

17.1.2 Bosons

Bosons are particles with integer spin $S = 0, 1, 2$. An example would be a photon with spin $S = \pm 1$. This corresponds to left or right hand polarisation. Phonon are quantised lattice vibration in a solid ($S = 0$).

For a system of Bose particles the total wavefunction must be symmetric with respect to particle exchange.

$$\Psi(a, b) = \Psi(b, a) \tag{17.2}$$

So there are no restrictions on the number of bosons in a single quantum state. Both fermion and boson were terms coined by Paul Dirac.

17.2 Distribution functions of particles

Distribution function describes the mean occupancy of a particular state. For a fermion system, the state can either be occupied or not, but on average (ensemble average), there will be some mean occupancy somewhere between 0 and 1. Similarly for bosons, each state will have some mean occupancy.

17.2.1 Fermi-Dirac distribution function

Consider a very simple system which has just one state, with energy ϵ, connected to a heat and particle reservoir (a grand canonical ensemble). Here, we use Gibb's distribution derived in Section 16. There can either be 0 or 1 particle in the state.

$$Z_G = \sum_i e^{\beta(\mu N_i - E_i)} \tag{17.3}$$

The two possibilities are $N_0 = 0 \quad E_0 = 0$ and $N_1 = 1 \quad E_1 = \epsilon$. Thus

$$Z_G = 1 + e^{\beta(\mu - \epsilon)}. \tag{17.4}$$

We can find the mean occupancy from the grand partition function

$$\langle N \rangle = k_B T \left(\frac{\partial Z_G}{\partial \mu} \right)_\beta. \tag{17.5}$$

Definition 17.2.1. The Fermi-Dirac distribution function for fermions is

$$\langle N \rangle = \frac{1}{\exp\left(\beta[\epsilon - \mu]\right) + 1}. \tag{17.6}$$

17.2.2 Bose-Einstein distribution function

Consider the same system as the fermions, but now there is no restriction on the number of particles allowed in the state. Now, the possible states of the systems are

$$
\begin{aligned}
N_0 &= 0 & E_0 &= 0 \\
N_i &= 1 & E_1 &= \epsilon \\
&\vdots \\
N_i &= n & E_i &= n\epsilon
\end{aligned}
\tag{17.7}
$$

We find the mean occupancy using the same equation.

Definition 17.2.2. The Bose-Einstein distribution function for bosons is

$$\langle N \rangle = \frac{1}{\exp\left(\beta[\epsilon - \mu] - 1\right)} \tag{17.8}$$

These distribution functions tells the mean occupancy of some state with energy E in terms of the chemical potential.

17.2.3 General distribution function

In general, for systems with many different energy states, we need to generalise these results.

Definition 17.2.3. The mean occupancy for a general system with an energy level ϵ_i and particles is

$$\langle N_i \rangle = \frac{1}{\exp\left(\beta[\epsilon_i - \mu] \pm 1\right)} \tag{17.9}$$

where it is $+$ for fermions and $-$ for bosons.

For the Fermi-Dirac relation, $\langle N \rangle = f(\epsilon)$ varies between 0 and 1, and it is 0.5 at $\epsilon = \mu$. The width in energy of the step is $\sim k_B T$.

For the Bose-Einstein relation, $\langle N \rangle = b(\epsilon)$ varies between 0 and ∞. $> \mu$ because $b(\epsilon) \to \infty$ at $\epsilon = \mu$.

See Figure 17.1.

17.3 Classical limit

At low occupancy $\langle N \rangle \ll 1$, the Fermi-Dirac, Bose-Einstein and Boltzmann distribution functions (with a energy zero shifted to μ) all become equal. This is because in this limit there is very little chance of multiple occupancy so the quantum nature of the particles is irrelevant.

If we plot $\langle N \rangle$ against $\beta(\epsilon - \mu)$, we see all functions tend asymptotically towards each other (the Fermi-Dirac and Bose-Einstein becomes similar to the Boltzmann's distribution with 0 shifted to μ). See Figure 17.2.

Note that if we shift the energy in the Boltzmann distribution, we are basically multiplying the original distribution with a constant. It is equivalent to setting the total number of particles in the system.
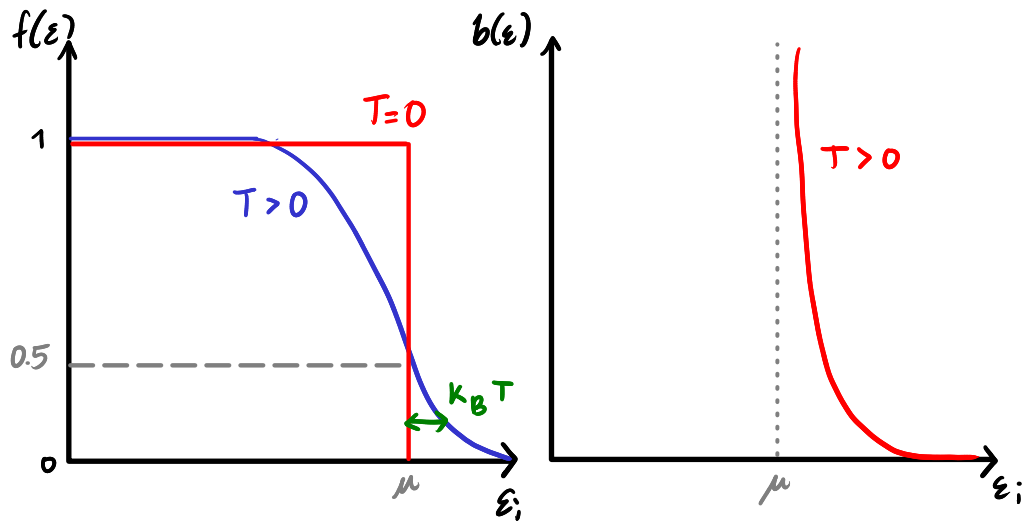
Figure 17.1: The graph on the left shows the Fermi-Dirac mean occupancy while the one the right shows the Bose-Einstein mean occupancy.
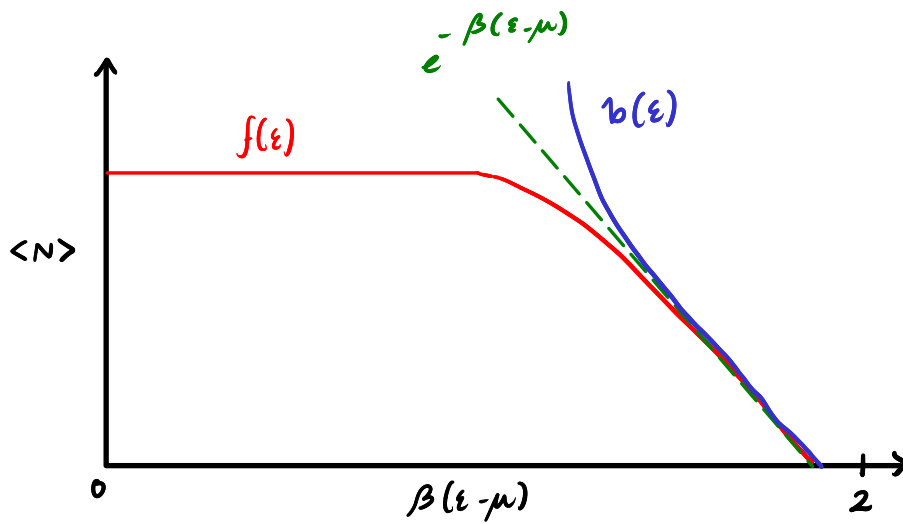

Figure 17.2: Plot to illustrate the classical limit of the Fermi-Dirac and Bose-Einstein mean mean occupancy