

Thermal Physics Notes

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

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Contents

1	Lecture 1 (Week 13)	5
1.1	Definitions	5
1.1.1	Thermodynamic limit	5
1.1.2	Thermodynamic system	6
1.1.3	Thermal equilibrium	6
1.1.4	Extensive and intensive variables	6
1.2	Functions and equations of state	7
2	Lecture 2 (Week 13)	9
2.1	The First Law	9
2.1.1	Work done compressing a gas	9
2.1.2	Work done in other systems	10
2.2	Constraints	10
2.3	Heat capacities	10
2.4	Non-ideal gases	12
2.4.1	Virial Expansion	12
2.4.2	Van de Waals equation	12
3	Lecture 3 (Week 13)	13
3.1	The Second Law	13
3.2	The Carnot Cycle	13
3.2.1	The Carnot relation	14
3.2.2	The Carnot theorem	16
3.3	Thermodynamic absolute temperature	17
4	Lecture 4 (Week 14)	18
4.1	Clausius' Theorem	18
4.2	Entropy	20
4.3	Irreversibility—entropy cannot decrease	21
4.4	The thermodynamic arrow of time	22
4.5	Joule expansion	22
5	Lecture 5 (Week 14)	24
5.1	Thermodynamic Potentials	24
5.2	Internal energy	24
5.3	Helmholtz Free energy	24

Contents

5.4	Gibbs Free energy	25
5.5	Enthalpy	25
5.6	Maths of partial derivatives	25
5.6.1	Pseudo-proofs	26
5.6.2	Maxwell relations	26
6	Lecture 6 (Week 14)	28
6.1	Cooling gases and Joule-Thomson expansion	28
6.1.1	Conservation of enthalpy	28
6.1.2	The Joule-Thomson coefficient	30
6.1.3	Helium liquefier (not examined)	31
7	Lecture 7 (Week 15)	33
7.1	Chemical potential	33
7.1.1	Physical meaning of chemical potential	34
7.1.2	Heat flow	35
7.1.3	Particle flow	35
7.2	Gibbs-Duhem equation	35
7.3	Clausius-Clapeyron equation	35
7.4	Phase diagrams	37
8	Lecture 8 (Week 15)	39
8.1	The Third Law	39
8.1.1	Consequences of the third law	39
9	Lecture 9 (Week 15)	42
9.1	Introduction	42
9.2	Counting states	42
9.3	Stirling's formula	42
9.4	Statistical Ensembles	43
9.4.1	Types of Ensemble	43
9.5	Principle of equal equilibrium probability	44
9.6	Ergodic hypothesis	44
10	Lecture 10 (Week 15)	45
10.1	Energy and states	45
10.2	Statistical Temperature	45
10.3	Boltzmann entropy	47
11	Lecture 11 (Week 16)	48
11.1	Boltzmann distribution	48
11.2	Boltzmann-Gibbs Entropy	50
12	Lecture 12 (Week 16)	51
12.1	The average of a distribution function	51

Contents

12.2	Internal energy in terms of Z	51
12.3	Entropy in terms of Z	51
12.4	Helmholtz Free energy in terms of Z	52
12.5	Combining partition functions	52
12.6	Classical Equipartition theorem	52
12.6.1	Gaussian Integrals (not examinable)	53
12.6.2	Does the equipartition theorem work in a quantum system?	53
13	Lecture 13 (Week 16)	54
13.1	Kinetic theory of an ideal gas	54
13.1.1	Assumptions of our model	54
13.2	Speed distribution	55
13.3	Pressure distribution	56

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.

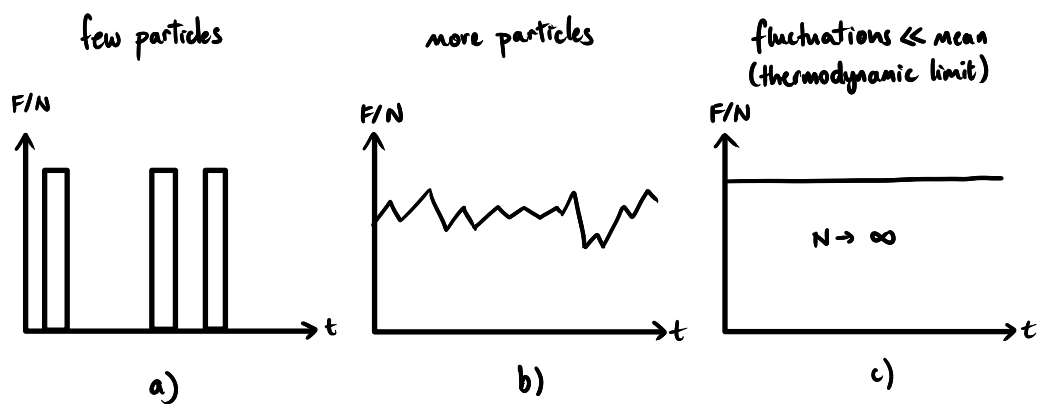


Figure 1.1: Force per particle versus time as we reach the thermodynamic limit.

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.

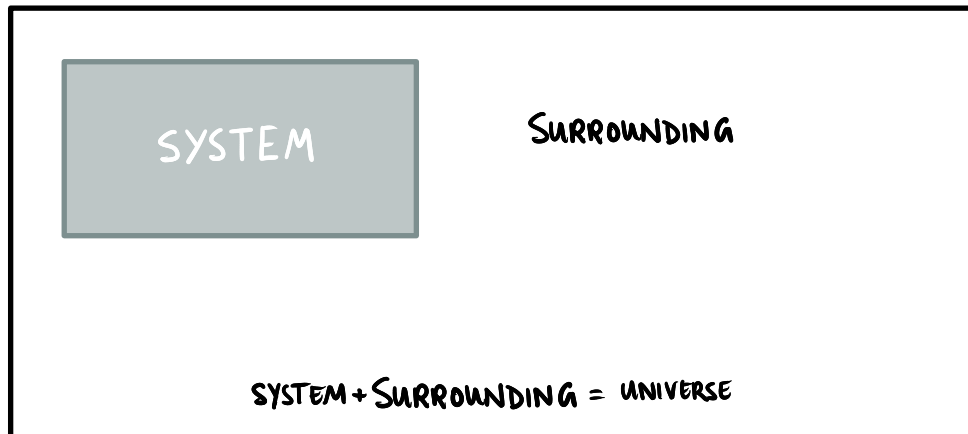


Figure 1.2: A thermodynamic system

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 may change slowly with time, so the system is *not* in thermal equilibrium.

1.1.4 Extensive and intensive variables

- **Extensive** variables scale 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 the 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 $f(x)$:

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

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

$$f(x + dx) - f(x) = \frac{df}{dx} dx = df \quad (1.2)$$

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

$$df = f(x + dx, y + dy) - f(x, y) = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad (1.3)$$

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

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (1.4)$$

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:

$$dW, dQ$$

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.

$$pV - nRT = 0 \quad (1.5)$$

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.

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

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

- δW 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 (W):

$$\Delta U = \Delta Q + \Delta W \quad (2.1)$$

In differential form:

$$dU = dW + dQ \quad (2.2)$$

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

$$\mathrm{d}W = -pA \times \frac{\mathrm{d}V}{A} = -p \mathrm{d}V \quad (2.3)$$

The sign is negative because if we are doing work **on** the gas, then $\mathrm{d}V$ is negative because the volume is decreasing. For irreversible changes,

$$\mathrm{d}W \geq -p \mathrm{d}V \quad (2.4)$$

2.1.2 Work done in other systems

- Stretching a string: $\mathrm{d}W = \vec{F} \cdot \mathrm{d}\vec{l}$
- Expanding a surface: $\mathrm{d}W = \gamma \mathrm{d}A$
- Magnetic material: $\mathrm{d}W = \vec{B} \cdot \mathrm{d}\vec{m}$ or $\vec{m} \cdot \mathrm{d}\vec{B}$

2.2 Constraints

- **Adiabatic** Thermally isolated system—there is no heat flow in or out. $\mathrm{d}Q = 0$ or $\mathrm{d}S = 0$
- **Isothermal:** Temperature is fixed by an external reservoir. $\mathrm{d}T = 0$
- **Isobaric:** Pressure is fixed. $\mathrm{d}p = 0$
- **Isochoric:** Volume is fixed. $\mathrm{d}V = 0$

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

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

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

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

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

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

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.

$$C_V = \frac{3}{2}nR \quad (2.8)$$

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

Using the ideal gas relation 1.5, we have:

$$C_p = \frac{3}{2}nR + nR = \frac{5}{2}nR \quad (2.10)$$

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 $\rho \rightarrow 0$.

$$\frac{p}{RT\rho} = A + B\rho + C\rho^2 + D\rho^3 + \dots \quad (2.11)$$

2.4.2 Van de Waals equation

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

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

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

$$W = \int p \, dV \quad (3.1)$$

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.

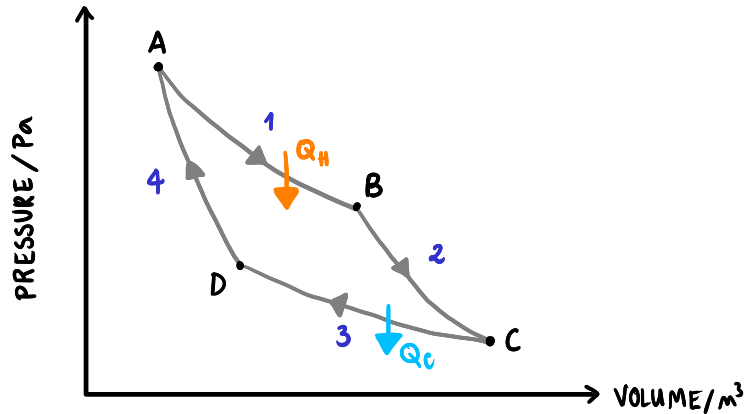


Figure 3.1: Carnot cycle P-V plot

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 $dT = 0$, 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.

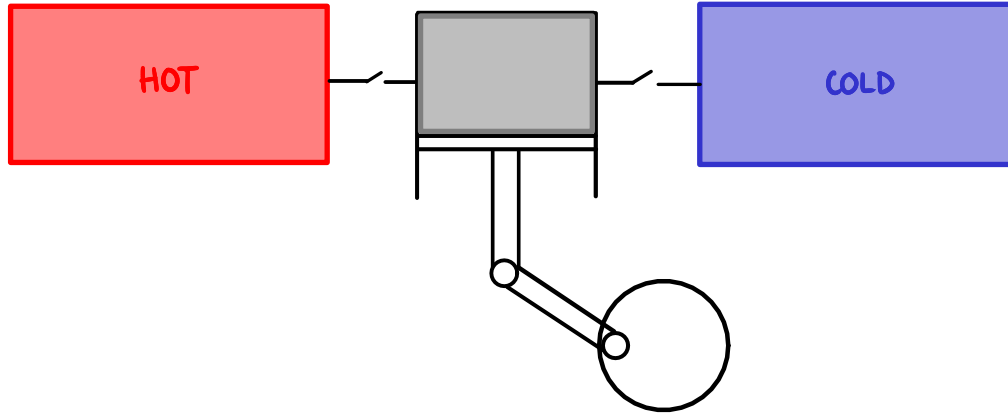


Figure 3.2: An example of what how the Carnot cycle might be implemented

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:

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \quad (3.2)$$

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

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

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.

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \quad (3.4)$$

It could also be useful to consult simplified diagrams of Carnot engines and a reversed Carnot engine (a refrigerator).

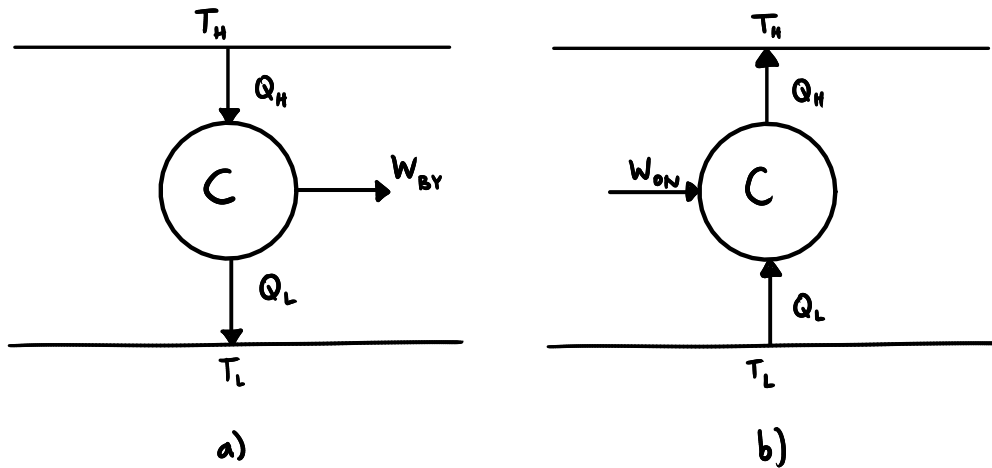


Figure 3.3: (a) shows the Carnot engine where the engine performs work and (b) shows the reversed Carnot engine where we perform work on the engine.

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**. \square

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. \square

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

$$\eta_c = 1 - \frac{T_L}{T_H} < 1 \quad (3.5)$$

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

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

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 $\Delta Q \rightarrow dQ$ then the sum becomes an integral. We have.

$$\oint \frac{dQ_{rev}}{T} = 0 \quad (4.2)$$

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

$$\oint \frac{dQ}{T} \leq 0 \quad (4.3)$$

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.

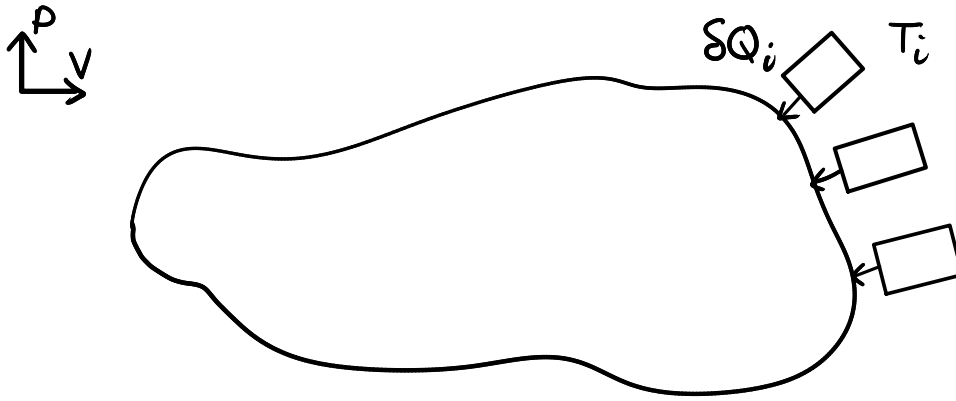
Consider the following *general* cycle:

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

$$\delta Q_i^0 = \delta W_i + \delta Q_i \quad (4.4)$$

Figure 4.1: An engine with multiple sources of heat δQ_i .

If we sum over all the heat engines, we get

$$Q_0 = \sum_i \delta Q_i^0 = \sum_i \delta W_i + \sum_i \delta Q_i \quad (4.5)$$

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.

$$Q_0 = W_C + W_S \quad (4.6)$$

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

$$W_C + W_S \leq 0 \quad (4.7)$$

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

$$T_0 \sum_i \frac{\delta Q_i}{T_C} = \sum_i \frac{\delta Q_i}{T_C} \leq 0 \quad (4.8)$$

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

$$\oint \frac{dQ}{T} \leq 0 \quad (4.9)$$

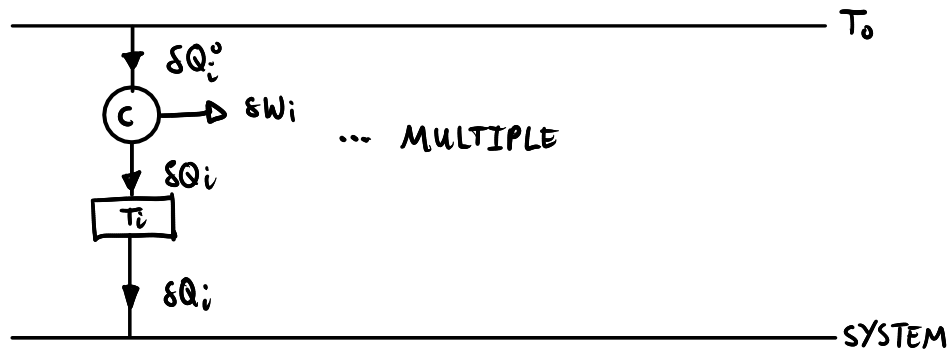


Figure 4.2: A master reservoir connected to the system via multiple Carnot engines.

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

$$\begin{aligned} dS &= \frac{\delta Q_{\text{rev}}}{T} \\ T dS &= \delta Q_{\text{rev}} \end{aligned} \quad (4.10)$$

Like any state function, the difference of entropy 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

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

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

$$S(T) = \int_0^T \frac{C(T)}{T} dT \quad (4.12)$$

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

$$dU = T dS - p dV \quad (4.13)$$

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

For reversible changes, $dW = -p dV$ and $dQ = T dS$, while for irreversible changes $dW \geq -p dV$ and $dQ \leq T dS$. 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 functions, 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,

$$\begin{aligned} \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{\text{rev}}}{T} &\leq 0 \\ \int_A^B \frac{dQ_{\text{rev}}}{T} &\geq \int_A^B \frac{dQ}{T} \end{aligned} \quad (4.14)$$

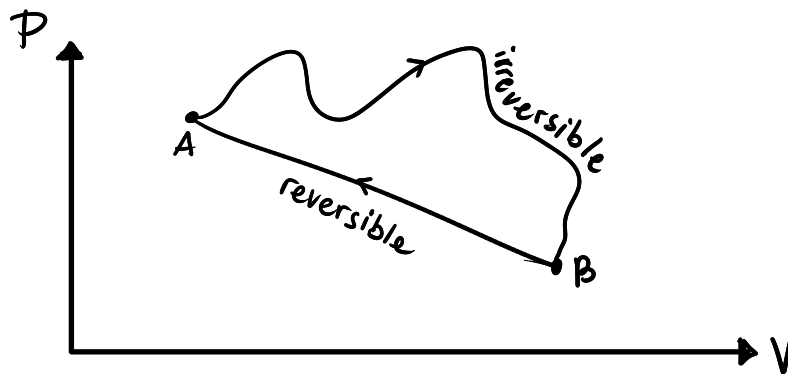


Figure 4.3: A cyclic process that has irreversible process from A to B and reversible process from B to A.

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 $dQ = 0$

$$dS \geq \frac{dQ}{T} \equiv dS \geq 0 \quad (4.15)$$

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

$$dS = nR \frac{dV}{V} \quad (4.16)$$

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

$$\Delta S = nR \ln \frac{V_1}{V_0} \quad (4.17)$$

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:

U	Internal energy
$F = U - TS$	Helmholtz free energy
$G = U - TS + pV$	Gibbs free energy
$H = U + pV$	Enthalpy

These definitions are only correct where the work term $\mathrm{d}W = -p \mathrm{d}V$. 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

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

5.3 Helmholtz Free energy

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

$$F = F(V, T) \text{ and } \mathrm{d}F = -p \mathrm{d}V - S \mathrm{d}T \quad (5.2)$$

where its natural variables are V and T .

Its exact differential leads to the results that

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

This is particularly 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

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

Its exact differentials show that

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

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

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

Its exact differentials show that

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

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)

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

2. Reciprocal theorem

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

3. Reciprocity theorem or triple product rule

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

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (5.11)$$

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 $z = z(x, y)$. If we write x and z in differential forms, and substitute dx into the expression for dz , we notice that we can equate the coefficients of dz , which shows the **reciprocal** theorem holds.

Then if we look at the coefficients of dy , 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,

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

we can see that

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

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).

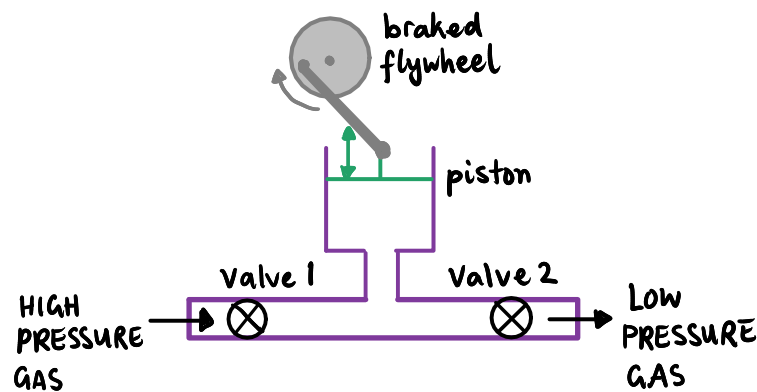


Figure 6.1: We open the high pressure valve, gas comes in the chamber and moves the piston up (doing work on the piston), the flywheel spins with friction to remove energy and once the piston reaches the highest position, it moves down. The low pressure valve is opened and low pressure gas is forced 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.

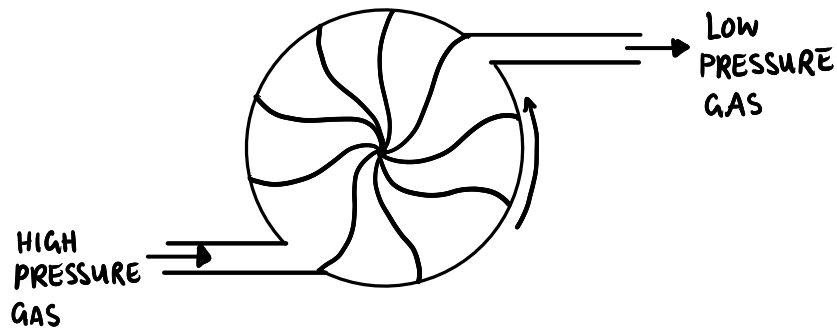


Figure 6.2: High pressure gas comes in, drives the turbine by doing work on it, heat is dissipated through friction, and then low pressure gas comes out.

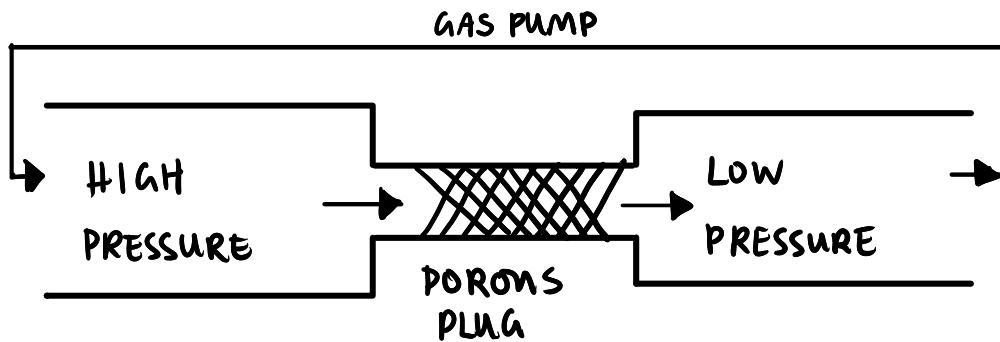


Figure 6.3: High pressure gas comes in and goes through a porous plug which removes a lot of energy through friction, low pressure gas comes out of the other end and is pumped back into the engine. The pressure difference is maintained with a compressor. This principle of cooling is used in many devices 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:

$$\begin{aligned} \text{The work done on gas to move distance } L_1 \text{ in the left chamber} & \quad W = p_1 AL_1 = p_1 V_1 \\ \text{The work done on gas to move distance } L_2 \text{ in the right chamber} & \quad W = P_2 AL_2 = p_2 V_2 \end{aligned}$$

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

$$\Delta W = p_1 V_1 - p_2 V_2 \quad (6.1)$$

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

$$p_1 V_1 + U_1 = p_2 V_2 + U_2 \quad (6.2)$$

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

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

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

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

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

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

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

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

We also divide by dp at constant T

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

Substitute back into what we got from reciprocity to get

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

We use a Maxwell relation to make this nicer

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

We can then use this for our final expression:

Definition 6.1.2. The JT coefficient at constant pressure is

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

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

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

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.

$$dU = T dS - p dV + \mu dN \quad (7.1)$$

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

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

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.

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

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

$$\mu = \frac{G}{N} \quad (7.4)$$

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.

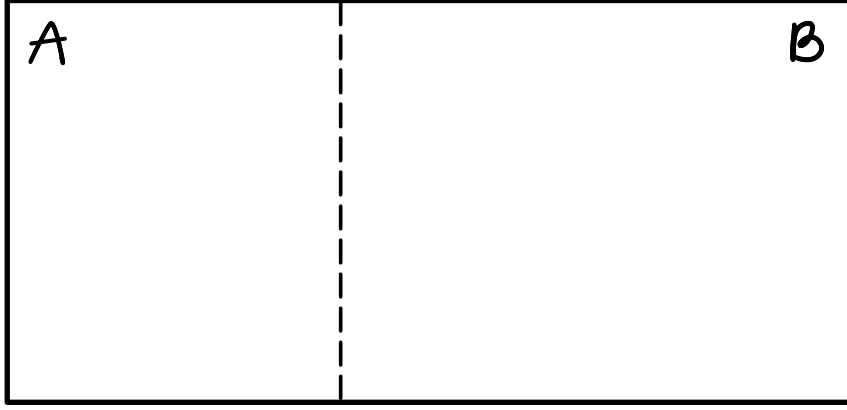


Figure 7.1: A movable partition separating A and B

We can establish a few relations:

$$\begin{aligned} dV_A &= -dV_B \\ dN_A &= -dN_B \\ dU_A &= -dU_B \end{aligned} \tag{7.5}$$

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

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \tag{7.6}$$

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

$$dS = dS_A + dS_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dN_A \tag{7.7}$$

At equilibrium, the change in entropy dS 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 is 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 then the particles flow from B to A.

7.2 Gibbs-Duhem equation

Using Equation 7.2 we can write

$$dG = \mu dN + N d\mu \quad (7.8)$$

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

$$N d\mu = V dp - S dT \quad (7.9)$$

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

$$d\mu = \hat{v} dp - \hat{s} dT \quad (7.10)$$

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

7.3 Clausius-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.

$$dG = dG_1 + dG_2 \quad (7.11)$$

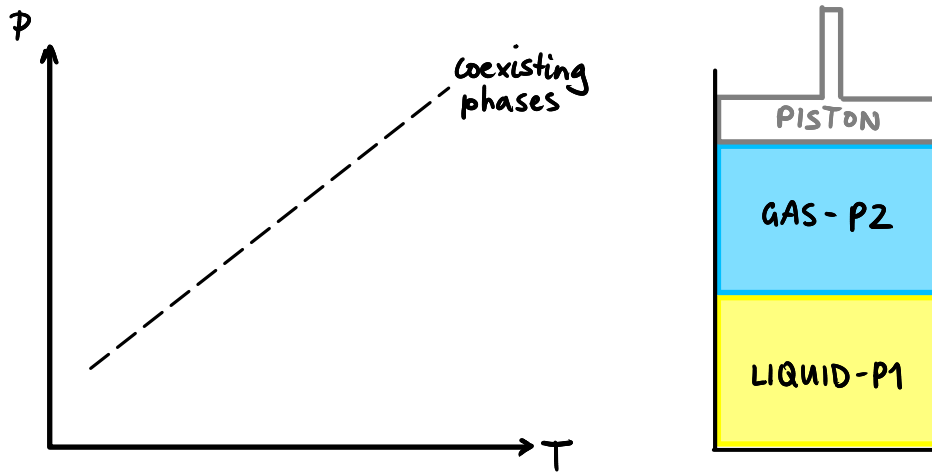


Figure 7.2: A system with pressure and temperature on the phase coexisting line. At any other (p, T) that does not lie on this line, there cannot be coexistence of the two phases.

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

$$dG = \mu_1 dN_1 + \mu_2 dN_2 = 0 \quad (7.12)$$

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

$$\begin{aligned} \hat{v}_1 dp - \hat{s}_1 dT &= \hat{v}_2 dp - \hat{s}_2 dT \\ \frac{dp}{dT} &= \frac{\hat{s}_1 - \hat{s}_2}{\hat{v}_1 - \hat{v}_2} \end{aligned} \quad (7.13)$$

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

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

Thus, our slope is now

$$(7.15)$$

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

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

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 $\frac{dp}{dT}$.

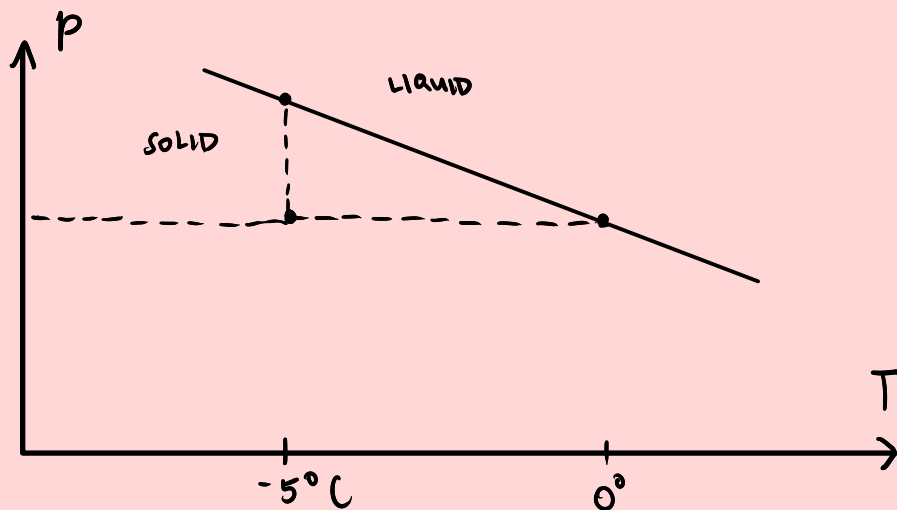


Figure 7.3: Phase diagram with a coexisting line between solid and liquid phases.

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

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

We also know the corresponding densities at 0 °C. This gives us a value for $\frac{dp}{dT}$. We need $\Delta p = \frac{dp}{dT} \Delta T$. 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:

$$\Delta G - \Delta H \rightarrow 0 \text{ as } T \rightarrow 0 \quad (8.1)$$

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 crystalline 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 $T = 0$. $\ln \rightarrow -\infty$ as $T \rightarrow 0$.

$$C = \frac{dQ}{dT} = T \frac{dS}{dT} = \frac{dS}{d \ln T} \quad (8.2)$$

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

$$dW = B dm \quad (8.3)$$

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

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

Taking the second derivative to get the Maxwell equation

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

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

$$\chi = \frac{M}{\mu_0 B} = \frac{m}{\mu_0 v B} \quad (8.6)$$

Equate the two and we get that

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

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

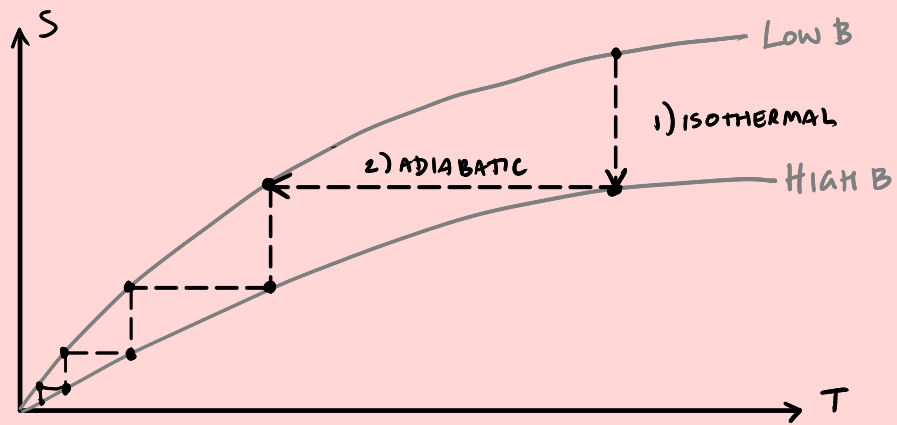


Figure 8.1: S - T curves for low and high B .

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.

$$\Omega = \frac{N!}{N_d!N_u!} \quad (9.1)$$

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

$$\begin{aligned}\ln n! &\simeq n \ln n - n, \quad n \gg 1 \\ \ln n! &\simeq n \ln n - n + \frac{1}{2} \ln 2\pi n, \quad n \gg 1\end{aligned}\tag{9.2}$$

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 possible 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.

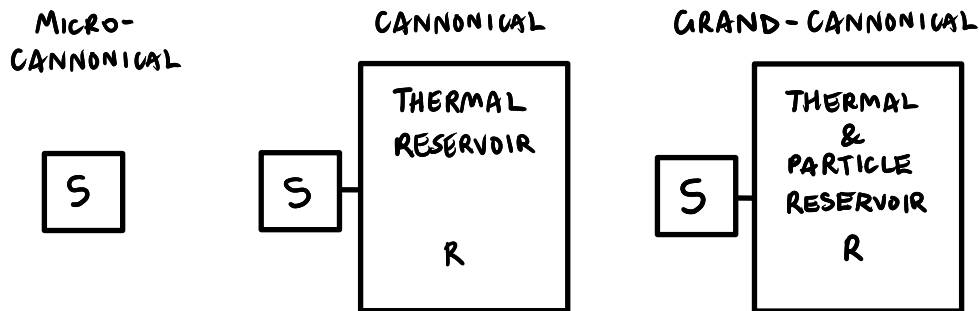


Figure 9.1: Different types of Ensembles

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 being 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

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

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.

$$U_A + U_B = U_0 \Rightarrow \frac{dU_A}{dU_B} = -1 \quad (10.2)$$

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

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

Since $\Omega(U_0)$ is a very fast increasing function, the negative of that would be a fast decreasing function.

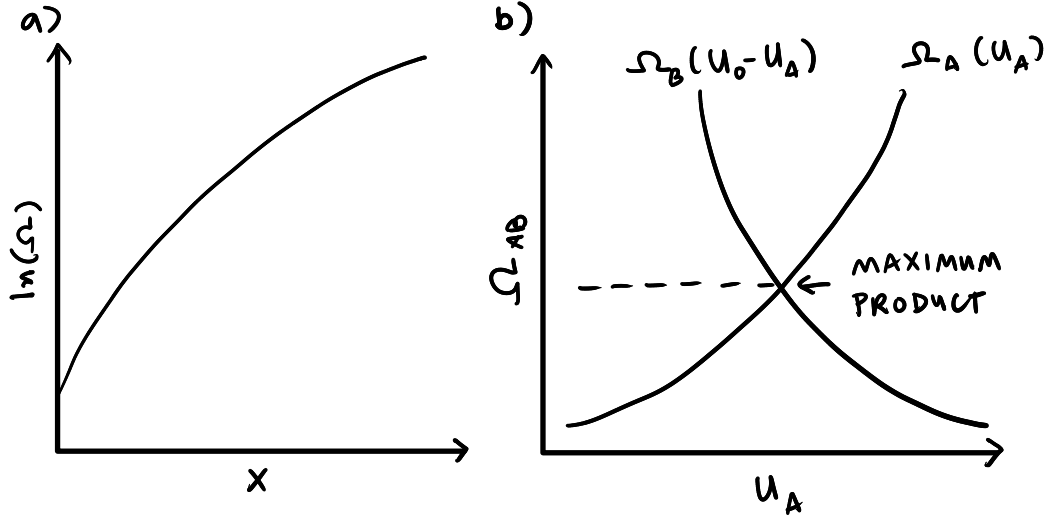


Figure 10.1: (a) shows the log plot of Ω and x , the total energy, (b) shows the number of states of two microcanonical systems as a function of the energy of one.

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.

$$\begin{aligned} \Omega_{AB} &= \Omega(U_A) \Omega(U_B) \\ \frac{d\Omega_{AB}}{dU_A} &= \frac{d\Omega_A}{dU_A} \Omega_B + \frac{d\Omega_B}{dU_A} \Omega_A = 0 \\ \frac{d\Omega_{AB}}{dU_A} &= \frac{d\Omega_A}{dU_A} \Omega_B - \frac{d\Omega_B}{dU_B} \Omega_A = 0, \text{ since } \frac{dU_A}{dU_B} = -1 \\ \frac{1}{\Omega_A} \frac{d\Omega_A}{dU_A} &= \frac{1}{\Omega_B} \frac{d\Omega_B}{dU_B} \end{aligned} \quad (10.4)$$

This is equivalent to

$$\frac{d \ln \Omega_A}{dU_A} = \frac{d \ln \Omega_B}{dU_B} \quad (10.5)$$

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

$$\frac{1}{k_B T_A} = \frac{d \ln \Omega_A}{dU_A} \quad (10.6)$$

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

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

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

$$S = k_B \ln \Omega \quad (10.8)$$

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 Boltzmann 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 $\Omega(E_0 - E_i)$). We can find this using Taylor expansion.

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

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

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

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

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

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

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

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

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

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

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

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

where Z is given as

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

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

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

Next, consider rotational energy levels of molecules. We have calculated the quantum energy levels $E_J = \hbar^2 J(J+1)/2I$, 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

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

11.2 Boltzmann-Gibbs Entropy

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

$$S = k_B \ln \Omega \quad (11.10)$$

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

$$S = -k_B \sum_i P_i \ln P_i \quad (11.11)$$

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

$$\langle X \rangle = \sum_i P_i X_i \quad (12.1)$$

For a continuous distribution, the average is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} P(x) x \, dx \quad (12.2)$$

12.2 Internal energy in terms of Z

The internal energy can be calculated as

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

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

Definition 12.2.1. The internal energy is given as

$$U = -\frac{1}{Z} \frac{dZ}{d\beta} = -\frac{d \ln Z}{d\beta} \quad (12.4)$$

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

$$S = \frac{U}{T} + k_B \ln Z \quad (12.5)$$

12.4 Helmholtz Free energy in terms of Z

Definition 12.4.1. The Helmholtz Free energy is given as

$$F = -k_B T \ln Z \quad (12.6)$$

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.

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

So, partition functions from independent contributions *multiply*.

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

$$F = F_x + F_y \quad (12.8)$$

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

$$\langle E \rangle = \frac{k_B T}{2} \quad (12.9)$$

12.6.1 Gaussian Integrals (not examinable)

Definition 12.6.1. Here are important identities for Gaussian integrals:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad \int_0^{\infty} x e^{-\alpha x^2} dx = \frac{1}{2\alpha} \quad (12.10)$$

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

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

We recall our harmonic oscillators have energy levels

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

Our partition function would be

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

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

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

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

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

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.

$$P = A \iiint e^{-\beta\epsilon} dv_x dv_y dv_z = 1 \quad (13.2)$$

We have

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

Which gives us

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

We use Gaussian integral identities to get

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

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 extend the radius of this sphere, which is our velocity v , to infinity).

So, we have

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

Derivation 13.2.1. To start, write out the integral as

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

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

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

Definition 13.2.1. The Maxwell-Boltzmann speed distribution curve is

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

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.

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = \frac{3k_B T}{m} \quad (13.10)$$

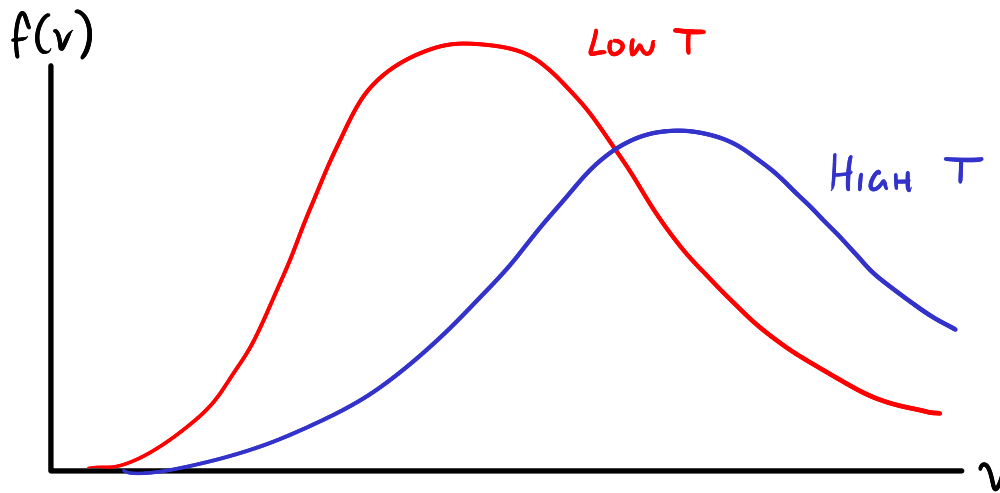


Figure 13.1: The Maxwell-Boltzmann speed distribution curve for high and low temperatures

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

$$\langle E \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \quad (13.11)$$

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.

$$\Delta P_m = 2mv \cos \theta \quad (13.12)$$

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

$$N_\theta = nv \cos \theta A dt \quad (13.13)$$

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.

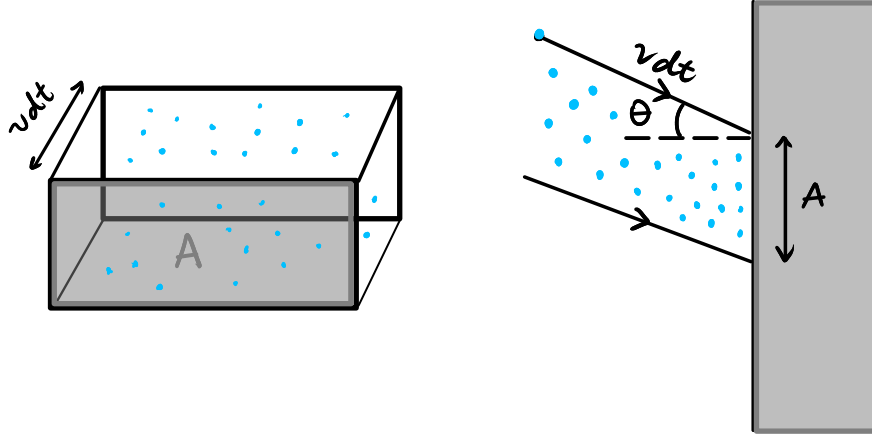


Figure 13.2: Consider a unit volume of particles that hit the wall in a short time interval dt . It forms a parallelepiped.

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 $\theta \rightarrow \theta + d\theta$. 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

$$\frac{2\pi \sin \theta d\theta}{4\pi} = \frac{1}{2} \sin \theta d\theta \quad (13.14)$$

Putting it all together, we have the following derivation

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

$$P = \frac{dp}{A} = \int_0^\infty \int_0^{\frac{\pi}{2}} 2 \frac{1}{2} f(v) m v \cos \theta n v \cos \theta A dt \sin \theta \frac{1}{A dt} d\theta dv \quad (13.15)$$

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

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

Simplifying the answer gives us

$$P = nk_B T \quad (13.17)$$

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