

Thermal Physics Notes

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

Last update: January 29, 2022

Contents

1	Lecture 1 (Week 13)	3
1.1	Definitions	3
1.1.1	Thermodynamic limit	3
1.1.2	Thermodynamic system	4
1.1.3	Thermal equilibrium	4
1.1.4	Extensive and intensive variables	4
1.2	Functions and equations of state	5
2	Lecture 2 (Week 13)	7
2.1	The First Law	7
2.1.1	Work done compressing a gas	7
2.1.2	Work done in other systems	8
2.2	Constraints	8
2.3	Heat capacities	8
2.4	Non-ideal gases	10
2.4.1	Virial Expansion	10
2.4.2	Van de Waals equation	10
3	Lecture 3 (Week 13)	11
3.1	The Second Law	11
3.2	The Carnot Cycle	11
3.2.1	The Carnot relation	12
3.2.2	The Carnot theorem	14
3.3	Thermodynamic absolute temperature	15

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 very 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.

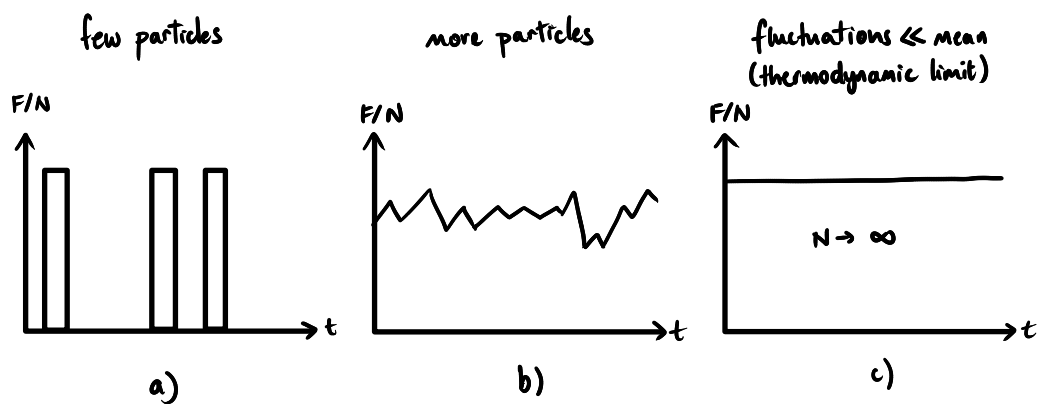


Figure 1.1: Force per particle versus time as we reach the thermodynamic limit.

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.

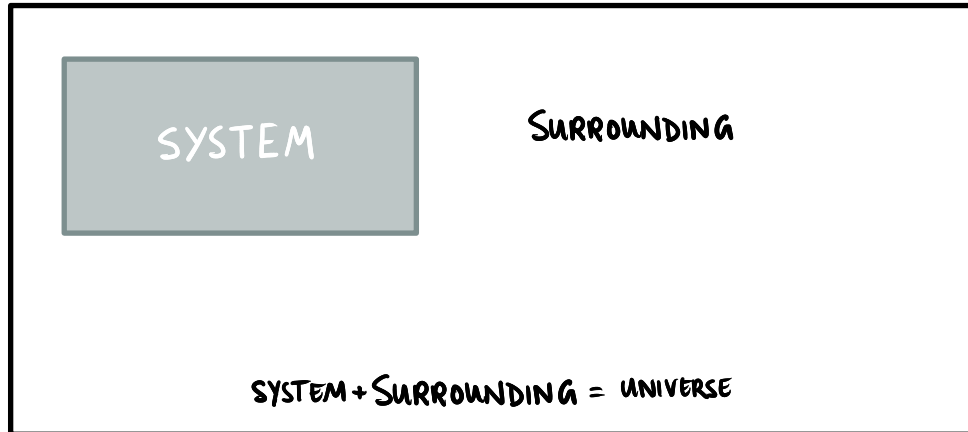


Figure 1.2: A thermodynamic system

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 very 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 out 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.

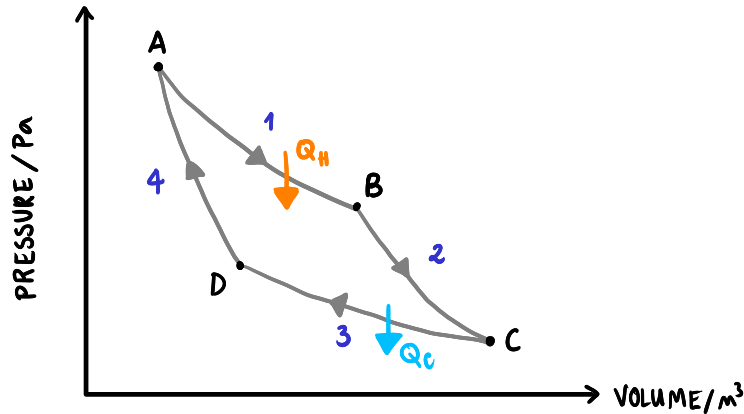


Figure 3.1: Carnot cycle P-V plot

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.

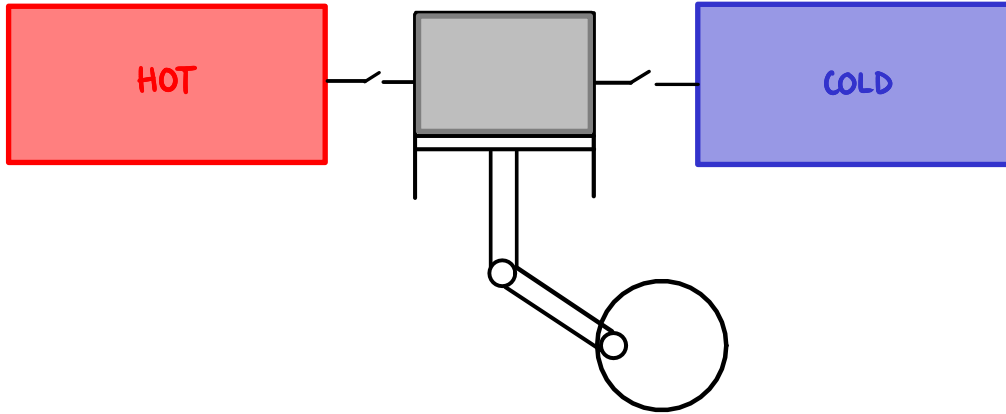


Figure 3.2: An example of what how the Carnot cycle might be implemented

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*:

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

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).

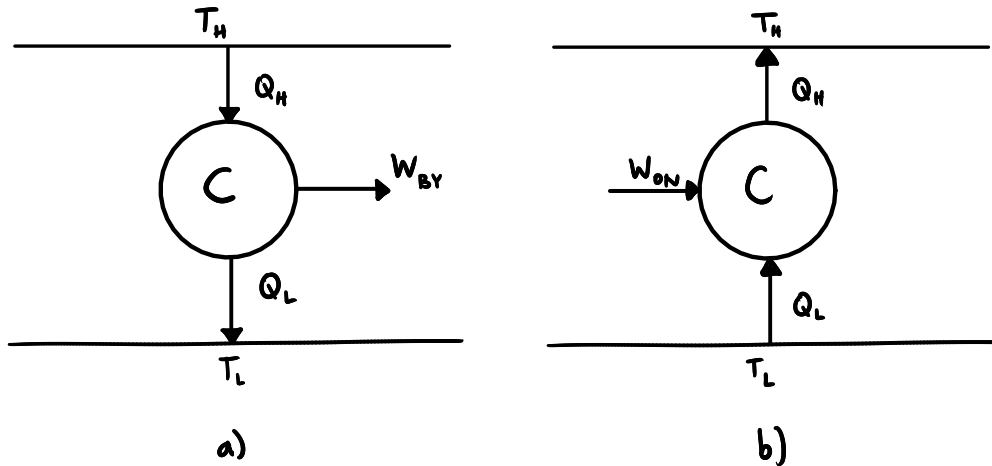


Figure 3.3: a) shows the Carnot engine where the engine performs work and b) shows the reversed Carnot engine where we perform work on the engine.

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.