

Thermodynamics

Università degli studi di Roma "La Sapienza"
Physics and Astrophysics BSc

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NOTES ON THERMODYNAMICS

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VERSION

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Contents

1	Thermodynamic Systems	3
1.1	Temperature	3
1.1.1	Macroscopic and Microscopic Systems	3
1.1.2	Zeroth Law of Thermodynamics	4
1.1.3	Temperature Measurements	5
1.2	Thermodynamic Equilibrium	7
1.2.1	Clausius-Clapeyron Diagrams	7
1.3	Equations of State	7
1.4	Work	7
1.4.1	Hydrostatic Systems	7
1.4.2	Quasi-static Processes	7
2	Heat	9
2.1	Adiabatic Processes	9
2.1.1	Internal Energy Function	9
2.2	First Law of Thermodynamics	9
2.2.1	Concept of Heat	9
2.3	Calorimetry	9
2.3.1	Heat Capacity	9
2.3.2	Calories	9
2.4	Heat Flow	9
2.4.1	Heat Conduction	9
2.5	Ideal Gases	9
2.5.1	Equation of State of an Ideal Gas	9
2.5.2	Internal Energy of an Ideal Gas	9
2.5.3	Heat Capacity of an Ideal Gas	9
2.5.4	Quasi-static Adiabatic Processes	9
3	Thermal Engines and Entropy	11
3.1	Heat Conversion	12
3.2	Engines	12
3.2.1	Stirling Engine	12
3.2.2	Internal Combustion Engines	12
3.3	Second Law of Thermodynamics	12

3.3.1	Kelvin-Plank Statement	12
3.3.2	Clausius Statement	12
3.4	Reversible Processes	12
3.4.1	Carnot Cycles	12
3.4.2	Carnot Theorem	12
3.4.3	Absolute Temperature	12
3.5	Entropy	12
3.5.1	Integrability of Heat	12
3.5.2	Entropy Function	12
3.5.3	Irreversible Processes	12
3.5.4	Principle of Increase of Entropy	12
4	Phase Transitions	13
4.1	Thermodynamic Potentials	13
4.1.1	Maxwell Relations	13
4.2	TdS Equations	13
4.2.1	Application of TdS Equations	13
4.2.2	Internal Energy Equations	13
4.2.3	Heat Capacity Equations	13
4.3	Phase Transitions	13
4.3.1	First Order Transitions	13
4.3.2	Second Order Transitions	13

1 Thermodynamic Systems

§ 1.1 Temperature

§§ 1.1.1 Macroscopic and Microscopic Systems

The study of any branch of natural science *must* begin with the definition of system

Definition 1.1.1 (System). A *system* is a finite region of space containing matter inside a closed surface, known as the *wall*.

Everything outside of the system, even other systems, that are in interaction with the system are known as the *surroundings* of the system.

A system is said to be *closed* if there's no matter flux between itself and its surroundings.

The set of the system, surroundings and all the rest is known as *universe*, and it's usually indicated with Ω .

All systems can be studied with two points of view

1. A microscopic point of view (molecular or less)
2. A macroscopic point of view (human scale or more)

Taking as our example system the cylinder chamber of a car, we can define the following *macroscopic coordinates*, i.e. descriptors of the system in a macroscopic point of view

1. Mass of gas contained
2. Volume of the chamber
3. Pressure of the gas
4. Temperature of the gas

These coordinates are *macroscopic* also because

- Do not involve assumptions about the structure of matter, fields or radiation
- Are low in number
- Are fundamental

- Can be, generally, directly measured

If we instead consider a system from the microscopic point of view, we can define the system as

1. N particles with energy states E_i
2. Particle interactions with fields and through collisions

And more.

Microscopic systems that can be considered isolated or embedded in other systems are known as *ensemble systems*. In microscopic systems, the equilibrium state is defined as the state with the highest probability, i.e. the state which will have a higher occupation number or *population*.

In general, microscopic coordinates

1. Consider the structure of matter, fields and radiation
2. Are many in number
3. Are described by mathematical models and usually not directly measurable
4. Must be calculated using the previous models

In the study of thermodynamics, in the next chapter or two, we will use the macroscopic description. The major difference with the other branches of science lays in the fact that in thermodynamics, a macroscopic quantity is always present and defined, known as *temperature*.

Generally, in thermodynamics the quantities chosen are known as *thermodynamic coordinates*, which are macroscopic coordinates that determine the internal state of the system. Systems for which thermodynamic coordinates can be defined are known as *thermodynamic systems*

§§ 1.1.2 Zeroth Law of Thermodynamics

Consider a thermodynamic system A , for which we can define two independent coordinates, (X, Y) , the first being a generalized force and the other being a generalized displacement. We define:

Definition 1.1.2 (Equilibrium State). A state for which the coordinates (X, Y) are constant as long as the external conditions don't change, is known as an *equilibrium state*

Equilibrium states *depend on proximity of other systems and nature of the boundary*, if we put A in contact with another system B with coordinates (X', Y') we then can define two types of walls:

Definition 1.1.3 (Adiabatic Walls). If the walls between the system A and B are *adiabatic*, then the equilibrium states are *independent* and possible for each value of (X, Y) and (X', Y')

Definition 1.1.4 (Diathermal Walls). If the walls between the system A and B are *diathermal*, the equilibrium states of the two systems aren't independent anymore, and thus are defined only for a set of coordinates (X, Y, X', Y')

We subsequently define

Definition 1.1.5 (Thermal Equilibrium). Thermal equilibrium is defined as the state achieved by two or more systems, characterized by a restricted amount of values of system coordinates, after being put in contact through a diathermal wall.

From the definition of thermal equilibrium, an important law follows

Law 1 (0th Law of Thermodynamics). Suppose that two thermodynamic systems A and B are separated by an adiabatic wall and simultaneously in contact with a third system C through a diathermal wall. It follows that if:

- A is in thermal equilibrium with C
- B is in thermal equilibrium with C

Then, A must be in thermal equilibrium with B

Suppose that now that the system A and B are at equilibrium with each other at some coordinates (X_A, Y_A) and (X_B, Y_B) . If we remove the system A , the system B will undergo a change of state to coordinates (X_2, Y_2) which must be in thermal equilibrium with the state (X_B, Y_B) . It must follow then that there's a quantity, known as *temperature*, which remains constant during this transformation, thus:

Definition 1.1.6 (Temperature). We define the *temperature* as the property in common between states in thermal equilibrium. A change of state with constant temperature (i.e. in *thermal equilibrium*) is known as an *isothermal transformation* or an *isothermal process*.

Temperature *must* be a scalar quantity, and it's usually indicated with T . For each possible value of T there exists a defined family of isothermal processes.

§§ 1.1.3 Temperature Measurements

In order to define a *temperature scale*, we choose a thermodynamic system for which are known its properties, known as the *thermometer*, and define a set of empirical rules for assigning a value of T for each isotherm.

Suppose that the system is well described by the generalized force X and the generalized displacement Y . Then, for defining a temperature scale we will

- Choose a convenient path in the (X, Y) plane, like $Y = \text{const.}$. Then, since one of the two quantities is fixed, we must have that if the system undergoes an isothermal process, we must have that

$$\theta = \theta(X)$$

Where θ is our temperature scale

- We suppose, arbitrarily, that $\theta(X) \propto X$, thus

$$\theta_A(X) = aX$$

The scale that we defined previously has, in particular, that

$$\lim_{X \rightarrow 0} \theta_A(X) = 0$$

i.e. it's an *absolute* temperature scale. Examples of absolute scales are the *Kelvin* and *Rankine* temperature scales.

Experimentally, the standard gas for thermometric evaluations is molecular hydrogen H_2 .

For most thermodynamic scales, being $Y = \text{const}$ completely arbitrary, it's convenient to define $Y = Y_1 = \text{const}$ as the *triple point* of water, it being the point in which liquid water, ice and vapor exist in the same place and time. This point is measured to be at a temperature of

$$T_{TP} = 0.01^\circ\text{C} = 273.16\text{K}$$

From the absolute arbitrary temperature scale we have defined before, defined X_{TP} the coordinate at which we have the triple point, we have

$$\theta_A(X_{TP}) = aX_{TP} = 273.16\text{K} \implies a = \frac{273.16\text{K}}{X_{TP}}$$

Thus, in general, an absolute thermometric scale can be defined as follows

$$\theta_A(X) = 273.16 \frac{X}{X_{TP}} \text{K} \quad (1.1)$$

Thus, it's possible to define this scale in terms of pressures (generalized forces) or volumes (generalized displacements), using the triple point coordinates as reference point.

§§§ 1.1.3.1 Temperature Scales

The most common temperature scales are two in the metric system of units and two in the imperial system. If we use the definition (1.1) for the Kelvin scale, we have

Definition 1.1.7 (Celsius Temperature Scale). Defined by Anders Celsius (SWE), used in the metric system of units

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

Definition 1.1.8 (Rankine Temperature Scale). Absolute temperature scale defined by William Rankine (UK), used in the imperial system of units

$$T(\text{R}) = \frac{9}{5}T(\text{K})$$

Definition 1.1.9 (Fahrenheit Temperature Scale). Temperature scale define by Daniel G. Fahrenheit (GER), used in the imperial system of units

$$T(^{\circ}\text{F}) = \frac{9}{5}T(\text{R}) - 459.67$$

With these definitions we can find conversions between these scales, and for commonly used scales like Fahrenheit and Celsius we get the following conversion formula

$$T(^{\circ}\text{F}) = \frac{9}{5}T(^{\circ}\text{C}) + 32 \quad (1.2)$$

Note that the Celsius temperature scale has the same dimensions of intervals of the Kelvin scale, thus, a temperature difference in Celsius degrees is the same in Kelvins. Thanks to future concepts, the Kelvin scale will be defined as the absolute scale of temperature, since it's tied to energetic properties of the system itself.

§ 1.2 Thermodynamic Equilibrium

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§§ 1.2.1 Clausius-Clapeyron Diagrams

§ 1.3 Equations of State

§ 1.4 Work

§§ 1.4.1 Hydrostatic Systems

§§ 1.4.2 Quasi-static Processes

2 Heat

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§ 2.1 Adiabatic Processes

§§ 2.1.1 Internal Energy Function

§ 2.2 First Law of Thermodynamics

§§ 2.2.1 Concept of Heat

§ 2.3 Calorimetry

§§ 2.3.1 Heat Capacity

§§ 2.3.2 Calories

§ 2.4 Heat Flow

§§ 2.4.1 Heat Conduction

§ 2.5 Ideal Gases

§§ 2.5.1 Equation of State of an Ideal Gas

§§ 2.5.2 Internal Energy of an Ideal Gas

§§ 2.5.3 Heat Capacity of an Ideal Gas

§§ 2.5.4 Quasi-static Adiabatic Processes

3 Thermal Engines and Entropy

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§ 3.1 Heat Conversion

§ 3.2 Engines

§§ 3.2.1 Stirling Engine

§§ 3.2.2 Internal Combustion Engines

§§§ 3.2.2.1 Otto Engine

§§§ 3.2.2.2 Diesel Engine

§ 3.3 Second Law of Thermodynamics

§§ 3.3.1 Kelvin-Planck Statement

§§§ 3.3.1.1 Refrigerators

§§ 3.3.2 Clausius Statement

§§§ 3.3.2.1 Equivalence of Kelvin-Planck and Clausius Statements

§ 3.4 Reversible Processes

§§ 3.4.1 Carnot Cycles

§§ 3.4.2 Carnot Theorem

§§ 3.4.3 Absolute Temperature

§ 3.5 Entropy

§§ 3.5.1 Integrability of Heat

§§ 3.5.2 Entropy Function

§§§ 3.5.2.1 TS Diagrams

§§ 3.5.3 Irreversible Processes

§§ 3.5.4 Principle of Increase of Entropy

4 Phase Transitions

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§ 4.1 Thermodynamic Potentials

§§ 4.1.1 Maxwell Relations

§ 4.2 TdS Equations

§§ 4.2.1 Application of TdS Equations

§§ 4.2.2 Internal Energy Equations

§§ 4.2.3 Heat Capacity Equations

§ 4.3 Phase Transitions

§§ 4.3.1 First Order Transitions

§§ 4.3.2 Second Order Transitions