

THERMODYNAMICS

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Summary

The present chapter is intended to give a short and critical overview of Continuum Thermodynamics, which macroscopically describes real systems. Roughly speaking such a description should be done by gaining gross information through the basic properties of the constituents forming such systems: this should be achieved through statistical thermodynamics and mechanics, where interactions between a large number of atoms or molecules should be taken into account. Nevertheless, direct phenomenological approaches have been very successful through the last centuries in engineering and physics; a milestone case has been the understanding of how to increase the efficiency of steam engines.

Important and yet illustrative examples where Continuum Thermodynamics plays a key role are non-reacting mixtures. This represents an illustrative case in its own rights, which would not be covered in this volume otherwise; the most interesting aspect is that coupling among mechanical, thermal and “chemical” effects arises and the implications of the laws of thermodynamics will be explained in this specific context.

Nevertheless, mixture theories turn out to have striking and unexpected applications, such as soft matter which, in this volume, are treated from a purely mechanical point of view. In our opinion, such applications may provide a useful direction for future researches, and furthermore these may suggest new perspectives about the formulation of suitable mathematical models for biological structures, such as membranes, liposomes and real cells.

1. Introduction

Thermodynamics is a field that analyzes real systems, such as fluids, solids, soft matters, undergoing changes in temperature, pressure (external forces and stresses), volume (motions and associated changes in stretching and spin), mass, concentration of the different species forming the system etc.

Because of the broadness of this subject, the present chapter neither has the aim to be fully comprehensive of all the aspects of thermodynamics nor does it have the purpose to blindly expose the most classical issues of it. For this reason, on the one hand the basics of the subjects will be heuristically described although, on the other hand, the most well known basics physics and engineering thermodynamics will be taken for granted.

The choice here is then:

- to critically give an overview of Continuum Thermodynamics and its links with some statistical aspects of it and then to see what are implications in a subject which

- is becoming more and more interesting in Sciences and Engineering; and
- to see how the concepts of thermodynamics may apply to a particular topic which has many interesting implications in Sciences and Engineering and it would not be covered in this volume otherwise.

Statistical thermodynamics and mechanics may be considered more detailed contexts from which macroscopic thermodynamics should derive. Many classical contributions from the first subject mentioned above are keystones in Science, such as Boltzmann's theory of gases [12], and subsequent fundamental developments in the theory, which may be found in [85], [77], [94], [87] and references cited therein.

Continuum thermodynamics describes systems at the macroscopic level. Roughly speaking, this is done by means of statistical mechanics, although phenomenological approaches have been very successful in many subfields of engineering and physics.

The origin of phenomenological thermodynamics goes back to Carnot (see e.g. [15]), who established a cornerstone in engineering with his celebrated theoretical machine. Indeed, thermodynamics was born as the subject allowing for the understanding how to increase the efficiency of steam engines.

Many are the physical items needed to have a first understanding of thermodynamics at the continuum level. For instance, it is everyday experience the evidence that heat moves from hot to cold zones of a given environment. Heating of systems is one of the keys of thermodynamics. Mechanical power may then be extracted by engines using the capability to convert thermal energy into mechanical.

Laws of classical thermodynamics confirm that heat or work (in better phrasing heating and power, i.e. working), are the two possible forms of exchanges of energy.

Such laws are stated thanks to a "toolbox". Here one finds the main screwdriver: the *entropy* of the system under exam. This is a measure of the quantity of heating flowing in/out-side the system, i.e. energy moving in or out, at a given temperature and henceforth entropy shows the possibility of conversion of that heating into mechanical power.

In the toolbox mentioned above there must be the measure of energy of the given system and the observed state, before any other transformation. This measure is the *absolute temperature*, which shall be discussed in the sequel.

Besides temperature then, heat is among the first concepts encountered in thermodynamics; *heating* of a system represents the thermal energy which is being transferred inside or outside the system across its boundary during a process, which sometimes is called transformation. Ultimately, thermodynamics has to do with the transfer of energy in all possible forms and with how does energy evolve. In continuum thermodynamics macroscopic systems are examined and, hence, interactions between a large number of atoms or molecules are investigated.

What is a system, what are the surroundings of such a system? What do we mean by state of a system? What is the meaning of transformation of the system from one state to

another?

These are key questions involving keywords of thermodynamics, often parts of the common language in engineering and sciences. The answers to such questions will be sketched in the next section.

Continuum thermodynamics then predicts how systems adjust to changes in their surroundings. This is what happens in phase transitions (solid-solid, liquid-vapor etc.), in mixtures (which could be of biological or inorganic species or both), in transport phenomena, machines, etc.

Very useful and yet systematic formulations of Continuum Thermodynamics have been performed in the last sixty years. It is worth noting the following contributions by Truesdell and coworkers (see e.g. [101], [102]) and [95] among many others.

It is very interesting the link pointed out in Ball and James [3] between Carnot and Truesdell. The latter noticed that Carnot in [15] never supposed that engines had to run slowly or near equilibrium.

Citing [3]: “He [Truesdell] based his work on Carnot’s own assumption: the work produced by a body undergoing a Carnot cycle is a function of its operating temperatures T_+ and T_- and of the heat absorbed at the higher temperature, and he showed how this hypothesis is independent of the Caloric Theory of Heat to which Carnot chose to join it. He then built up all of classical thermodynamics on the basis of a constitutive equation for the heat absorbed, the thermal equation of state, and Carnot’s axiom. His treatment of the efficiency of cyclic processes was immediately generalized by Fosdick and Serrin [43], who showed that, in the general setting of continuum thermodynamics, these efficiency estimates are more or less equivalent to the Clausius-Duhem inequality. This body of theory provides one of the most physically intuitive approaches to the second law of thermodynamics.”

The present volume, and so this chapter, wish to keep this intuitive perspective to the subject. On the one hand, this book is not devoted to the expert reader in Continuum Thermodynamics, on the other hand though the fundamental concepts and issues of basics physics and engineering are here taken for granted.

Obviously the main focus of this contribution is to go a bit farther than a mere section in which classical thermodynamic is revisited. One way to do so is to single out an interesting field, not covered otherwise in this volume, in which the basic concept of both Continuum Thermodynamics and some very basic Statistical Mechanics may go together.

This field which seems to be really a right environment where thermodynamics has a natural application and development is the *thermodynamics of non-reacting mixtures*. For this reason, and because this subtopic is not covered in other chapters of this book, we take this a key example where applications of most of the concept of Continuum Thermodynamics will be illustrated.

Furthermore, the theory of non-reacting mixtures seems to set a very promising ground for modern subjects in science where thermodynamics plays a central role. A sketch of this will be given in Sect. 5, where coupling with mechanical effects will be discussed.

The brief discussion above sets the stage for the development of the chapter. First of all, it is our opinion that it is necessary to have a very heuristic and concise perspective of thermodynamics before going into the announced application.

Henceforth, thermodynamics of non-reacting mixtures shall clarify most of the purely thermodynamic concepts.

Continuum thermodynamics of non-reacting mixtures shall finally be analyzed accounting for mechanical effects. Indeed, configurations of such mixtures do influence their behavior: it will be seen how thermodynamics is the key tool to analyze such systems.

The implications of the laws of thermodynamics, especially of the second law, will be explained in this specific context; in a different chapter of this volume, the same thing is done for solids. In particular, constitutive relations turn out to be restricted if the so called Coleman and Noll's procedure (see [18]) is applied to all possible processes suitable for the given system. This will be extensively covered for mixtures towards the end of this chapter.

This suggests that applications to soft matter not only may be a very good direction for future researches but also they may indicate some new perspective about formulating more suitable mathematical models for biological structures, such as membranes and liposomes.

1.1. Notation

Scalars will be denoted with small Greek letters, vectors with boldface small caps, second order tensor with boldface caps as well as Greek letters and fourth order tensors will be denoted by math bold caps.

2. Basic Notions of Thermodynamics

Theories of three-dimensional deformation of solids and flows for fluids may rely upon appropriate thermodynamic frameworks. As we already pointed out, some physical items are understood to be primary in a description of a thermodynamical system. A commentary of the basic ones may be given in the sequel.

2.1. A Few Definitions

A first set of primary physical quantities for such regions may be introduced.

- *Temperature.* The existence of an *absolute* temperature $\vartheta > 0$ is a commonly accepted concept. This comes from a naive and yet very intuitive statistical point of view.

Indeed, one may think about either a fluid occupying a container or a solid placed in a region of the space both viewed as discrete systems of "fundamental" particles (for example either molecules or atoms etc., depending on the scale at which the system is examined) and evaluate the average kinetic energy of such systems per degree of freedom of the fundamental particle. We note that such degrees of freedom may be translational and rotational; a model for a molecule or for a multi-atomic gas demand both types of coordinates whereas a model for a perfect monoatomic gas requires translational coordinates only.

The *temperature* of a region is then defined to be the ratio between its average kinetic energy for that region and the Boltzmann Constant $k = 1.3806505 \times 10^{-23}$ Joule/Kelvin, where Joules and Kelvins are unit measures for energy and temperature respectively. Kinetic energy cannot be exactly zero, because each particle in the system may experience thermal fluctuations. Indeed, particles always move, sometimes even very slowly, so that their velocities cannot be exactly zero. For this reason, the temperature defined as above can never achieve negative values; this yields the concept of absolute temperature.

Pointwise temperatures may also be defined. Ideally, one may think about subregions, for example spheres, centered at different points of a given configuration, and define the average kinetic energy of each subregion. As the size of the region (e.g. the radius of each sphere) tends to zero, the ratio between the limiting average kinetic energies and k measures the absolute temperature pointwise

- *Mass.* This is a fundamental concept, which brings the idea of how much matter is contained in a given object region of the space under observation. The mass density instead is the amount of matter per unit volume contained in the same region; inhomogeneous regions may then a spatially non-constant density. Furthermore, there are many situations, such as gas dynamics etc., in which the mass density may change in space and time.

In relativistic terms, there are different notions of mass. These will not be addressed here, since relativity goes beyond the aim of this volume.

- *System.* The concept of *thermodynamic system* has very heuristic origins. Roughly speaking, a thermodynamic system is defined as each perceptible quantity of matter that can be macroscopicly observed, usually constituted by a (homo- or heterogeneous) set of substances. This may be regarded as material bodies or volumes in continuum physics, i.e. regions of the physical space, fixed or undergoing motion, endowed with a continuous distribution of *mass*.

The words perceptible and macroscopic are somehow glued together: indeed macroscopic variables can be defined, and yet measured, for systems consisting of a great amount of elementary particles, such as molecules, and so they are macroscopically perceptible.

- (*Internal*) *Energy.* From the statistical point of view, this is the total of the (average)

kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals. It includes the energy in all the chemical bonds, and the energy of the free conduction electrons in metals. Henceforth, the internal energy accounts for the latent one associated with the phase of the system. A rough explanation of phases will be given in the sequel.

The internal energy at the macrolevel represents both recoverable and non-recoverable contribution to the energy. The internal energy is a state function.

- *(External) Working.* It represents the power expended by external agents on the system across its boundary. Such agents may be thermal, mechanical (forces), magnetic, electric and chemical. All those agents interact with the system through the surroundings, i.e. the exterior of the system, through the boundary of the system itself. Roughly speaking, the types of actions such as heat transfer (heating), mass flux, and mechanical working, are recognized at the system boundary as they touch and/or cross it; these actions represent energy gains or losses by a system during a *transformation*, often called (dynamical) *process*.
- *Closed systems.* In such systems there is energy transport but not mass transport. Any material volume, consisting as it does of a fixed collection of fluid particles, is necessarily a closed system. In thermodynamics, common examples of closed systems are canisters and pistons.
- *Open systems.* Here both energy and mass transport are present. On both open and closed systems there may be forces exerting power (mechanical, electromagnetic, etc.) across its boundary.
- *Isolated systems.* Here there is no energy or mass transport across the boundary. For instance, a control volume traversed by a fluid in a flow across a pipe may be considered as a thermodynamic system (see e.g. [49]). This, in general, would be a system with changing mass. Another example of thermodynamic system is a solid occupying a given configuration in the three dimensional space and undergoing external forces and heat radiated on part of its surface; this is a case of constant mass.
- *Heat flux (or Heating).* The statistical viewpoint may also be useful to introduce such a concept. Indeed, the heat flux is related with the *transfer* of the average kinetic energy of particles from one region to another. Furthermore, the rate of this flux represents the heat rate supplied to the system across its boundary.
- *State.* First of all we may distinguish *microstates* and *macrostates* of a system. In statistical mechanics, a microstate describes a specific detailed microscopic configuration of a system, that the system occupies in the course of its fluctuations. A macrostate is meant to give information about the configuration of the body at the continuum level, i.e. without distinction among the particles.
- *Entropy.* Again, the statistical perspective helps to understand such a deep concept.

Roughly speaking, entropy is a measure of the disorder of the particles in a given system (either for a fluid in a container or atoms of a solid, etc.). Indeed, entropy gives the number of the possible microscopic configurations of the system. It can be shown that entropy is a function of a quantity of heating flowing inside the system at a given temperature, owing for the possibility of conversion of that heating into mechanical working. Entropy is often viewed as a macroscopic measure of the disorder of the system.

Those state variables which depend upon the system size or on the amount of material contained in the system are called *extensive*, (e.g. the internal energy, the entropy, the mass); *intensive* variables do not depend on these properties of the system, (e.g. pressure, temperature, molar densities).

Pointwise quantities may be obtained, at a given time t and at a given location \mathbf{p} , by localization procedures (*Assuming that sufficient regularity of the sets describing both arbitrary parts of the system under investigation and the corresponding extensive quantity as a function of such sets hold.*). Henceforth, one may talk about local:

- (absolute) temperature $T(\mathbf{p}, t)$;
- heating or, better, the heat flux $\mathbf{q}(\mathbf{p}, t)$ across surfaces of three dimensional regions;
- mass density $\varrho(\mathbf{x}, t)$;

and so on. Much useful information regarding a submicroscopic description of a system and their counterpart at the macroscopic level may also be briefly discussed.

- *Molecule*. A molecule is the smallest particle in a chemical element or compound that has the chemical properties of that element or compound. Molecules are made up of atoms that are held together by chemical bonds. These bonds form as a result of the sharing or exchange of electrons among atoms.
- *Mole*. The mole is the amount of substance of a system which contains a number of elementary entities equal to the number of atoms in 0.012 kilogram of the isotope ^{12}C ; this number is known as the Avogadro's number and it is equal to $N_A = 6,022137 \cdot 10^{23}$ elementary entities.
- *Atomic and Molecular Weight*. Improperly referred to as a *weight*, it is the relative mass of an atom with respect of the *unit atomic mass*, equal to 1/12 of the mass of the isotope ^{12}C , that is $u = 1,66054 \cdot 10^{-27}$ kg; hence, atomic weight is an a-dimensional number. The molecular weight is obviously the sum of the atomic weights of all the atoms which constitute the molecule.
- *Concentration*. Generally speaking, concentration is the measure of how much a substance is mixed with other substances. There are many different ways to express quantitatively this kind of information; in particular we will deal with the following ones.
- *Mole Fraction*. The mole fraction of a chemical species in a mixture is the ratio

between the number of moles of the given species and the number of moles of all the chemical species appearing in the mixture.

- *Mass Fraction*. Obviously, it is the ratio between the mass of a given substance and the mass of the whole mixture. The mass fraction does not coincide with the mole fraction of the species.

2.2. More about Systems, States and Processes

The notion of thermodynamic *system* has been introduced above.

2.2.1. States

Heuristically this concept is associate to an entity, for example a fluid (for instance H_2O), capable of assuming different states i.e. liquid and vapor. In solids, such as ceramics (see e.g. GeO_2 etc) and smart materials (see e.g. Cu Al Ni, etc.) a given material point may be considered our system.

The state of the system may be characterized by two pieces of information: for example, the deformation gradient and the (Cauchy) stress suffice to determine the state itself. Alternatively, very often the value of the free energy achieved at that deformation gradient is given, instead of the stress.

In the common language of the scientists who extensively study such subjects (see e.g. [5], [38], [62], [84], etc.), states are really called as *phases*. A more precise one, yet still qualitative, will be given in Sect.1.

Strictly speaking, if either the energy or the stress is the only given information, in general one cannot determine the state of the system; this is due to the fact that the actual energy exhibits non-convexity.

In this case, different phases are identified by different values of the deformation gradient corresponding to the same value of free energy.

Physically, the system may posses some crystal symmetry at that level of energy and stress. Nevertheless, under some suitable circumstances, the crystal symmetry may change at that stress to jump to a completely different value of deformation gradient. In one dimension, this value of stress is called the *Maxwell value*. In the sequel we shall see an analog phenomenon arising in non reacting mixture.

States are normally meant to be observable for a given system, yet *accessible* for the system itself. Accessibility may be achieved in some approximate way: this is the case for generic dissipative systems, where, for instance, closed cycles in the state space may not be possible in general. Approximately closed cycles may instead occur; the discrepancy with exactly closed cycles may be measured through the value of the working (e.g. the power expended by external agents on the system across its boundary) on that approximately closed path.

A precise mathematical theory of thermodynamics which includes this issue may be found in [22] and in a more suitable version for beginners in [82].

One example of a specific system may be a given solid undergoing suitable isothermal strain *processes* allowing for changes of *states* of the solid itself. As it is well known, this may be the case for a shape-memory alloy, for which the cells at a given material point undergo a phase transition from one symmetry to a different one; the piece of information characterizing each of these symmetries may be one of the entries of the list which is required to define what is the state of such material.

We here talk about *material* and not about *body*: indeed, the notion of state is normally meant to be local, i.e. the information is given either at a point (for a solid) or at some location (for a fluid), although a global notion of state for a solid body or for a fluid (including soft matter or structured fluids) in a given volume may be also be given.

For example, in linear elasticity, the local notion of state implies that one either gives information about the pair stress and strain at that point (or location) or by the pair strain and constitutive tensor of moduli or to any other equivalent pair. Extensive discussions and precise definitions may be given in [22].

2.2.2. Processes

Transformations driving a system from one state to another are called *processes*. They are descriptions of what happens to a system leaving one state and reaching another one. This is tantamount to saying that suitable processes for a system seem to be the ones connecting reachable states. Nevertheless, it is of great importance to keep in mind that approximately reachable states are crucial when it comes to describing theoretical “almost” closed cycles.

A mathematical representation of processes is possible: paths traced in the state space may be conceived. The issue of having both accessible and not-accessible states may then arise. One way to visualize processes may be to think about a time parameterization of a given path in the state space. Different time parameterizations of the same path (hence with the same values) may indicate that this can be traversed at different speeds. In this way to view processes, time parameterizations of a path correspond to these different ways of traversing it, leading to different time rescaling of the same process, from the slowest to the fastest.

As it is well known from elementary physics, particular processes may be singled out. The reader may be familiar with the thermodynamics of gases (especially ideal ones), in which polytropic transformations in the state space may be considered. Some of these are very intuitive, such as:

- *isobaric processes*, which occur at constant pressure;
- *isochoric processes*, which occur at constant volume;
- *isothermal processes*, occurring at constant temperature.

Other transformations may appear slightly less immediate, such as

- *adiabatic processes*, which do occur without exchange of heat;
- *isentropic processes*, which occur at a constant entropy. In the sequel one shall see that such transformations are nothing but reversible adiabatic processes;
- *iso-enthalpic processes*: which occur at a constant enthalpy which, roughly speaking it means that the overall total potential energy (including the thermal energy and the mechanical work) is preserved.

2.3. A Few Words about Extended Thermodynamics

This subject, which will be briefly sketched, is fairly technical, yet extremely useful, especially for the thermodynamics of gases.

Here we cite the work by I. Muller and T. Ruggeri [76]. As the authors explain, Extended Thermodynamics is a framework which allows for stating a full set of hyperbolic balance laws, rather than having some laws which are instead parabolic. This is the case of famous particularizations of the localized versions of the balance of linear momentum (the Navier-Stokes equation) and of the balance of energy (Fourier's Equation). The need of producing a framework owing hyperbolic equations only was strongly pushed by physicists.

Mathematically, the advantage of having such kind of equations allows for well-posedness of the initial value problem for the given thermodynamic system. In [76] is highlighted how this approach is characterized by having (i) balance field equations only, (ii) no past history of the states occupied by the system are involved, (iii) entropy is a concave of the state variables.

More details may be found in the given reference and in the references cited therein.

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SAMPLE CHAPTERS