Classical Thermodynamics

basics

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CONTENTS

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Classical thermodynamics deal with energy, its forms and the ways it can be transferred.

Classical thermodynamics provides a macroscopic, average, description of complex systems composed by a "huge" number of elementary components, in equilibrium: equilibrium means statistical equilibrium, resulting in stationary macroscopic observable physical quatities - thermodynamic variables - even though non-stationary microscopic dynamics of the system. The development of thermodynamics is closely related with the development of chemistry and the re-born of an atomic theory of the matter. Classical thermodynamics is the results of studies on matter and energy performed from the early experiments of the XVII centuries on gas to the mathematical formulation of the late XIX century by Gibbs. A consistent theory of thermodynamics starts from conservation of mass and balance of total energy - whose changes result from input of work or heat -, provides a description of natural tendencies in nature, through Clausius' statement of the second principle - degradation of mechanical energy and heat direction from hot to cold bodiess - in terms of a thermodynamic state variable, called entropy, and provides a definition of a thermodynamic scale of temperature - defined in terms of energy and entropy.

BRIEF HISTORY OF THERMODYNAMICS

See introduction to thermodynamics in the material about physics for high-schools, relying on your browser translation (Italian only, so far)

- introduction to thermodynamics
- brief history of experiments in thermodynamics

TWO

PRINCIPLES OF THERMODYNAMICS

In this chapter, the principles of classical thermodynamics, along with the relevant concepts and mathematical formalism, are introduced. The principles of thermodynamics are presented for **closed systems**, and subsequently extended to open systems.

- The *principle of conservation of mass - Lavoisier's principle*, valid in classical mechanics and summarized by the formula *"nothing is created, nothing is destroyed, but everything is transformed"*, states that in a closed system, the mass is constant,

$$dM = 0 \, .$$

- The *first law of thermodynamics* provides the general form of the *total* energy balance of a closed system, recognizing the work done by external forces δL^{ext} and the heat δQ^{ext} exchanged between the system and the external environment as the causes of the variation of the total energy of the system.

$$dE^{tot} = \delta L^{ext} + \delta Q^{ext} \, .$$

- The work of **Gibbs** provides *the necessary concepts and a rigorous mathematical formalization* of classical thermodynamics. The concepts of internal energy, state variables, and Gibbs' phase rule are introduced; additionally, some phase diagrams for representing the state of a system and thermodynamic transformations are presented, which will be used in subsequent chapters.

- The *second law of thermodynamics* describes natural tendencies: the dissipation of macroscopic mechanical energy and the transfer of heat from a hot body to a cold body, in a principle expressible in terms of **entropy**,

$$dS \geq \frac{\delta Q}{T} \, .$$

- Finally, the balance of physical quantities for *open systems* is derived by modifying the balance equations for closed systems, introducing terms for the **flux of physical quantities due to the transport of matter** across the system's boundary.

2.1 Lavoisier's Principle

In the context of classical mechanics, the principle of mass conservation—also known as Lavoisier's principle—states that the mass M of a closed system is constant,

$$dM = 0 \, ,$$

that is, *"nothing is created, nothing is destroyed, everything is transformed."*

- This principle was discovered by early chemists through the measurement of the mass of products and reactants in chemical reaction experiments.

- This principle ceases to hold in the framework of Einstein's theory of relativity, which recognizes the equivalence of mass and energy: mass and energy are two representations of a single physical quantity and are part of a balance equation. In the special case of a body at rest, this reduces to the famous expression $E = mc^2$.

2.2 First Law of Thermodynamics

The first law of thermodynamics is the total energy balance for closed systems. The variation in total energy dE^{tot} of a closed system is due to the work δL^{ext} performed on the system by external macroscopic actions and the heat δQ^{ext} transferred to the system from the outside,

$$dE^{tot} = \delta L^{ext} + \delta Q^{ext} \ .$$

Classical thermodynamics provides an average macroscopic description of the microscopic dynamics of a large number of elementary components (**todo** *atomic theory*). The total energy of the system can thus be interpreted as the sum of a macroscopic kinetic contribution and a microscopic content, both kinetic and potential; heat can be interpreted as the work performed on the system by microscopic actions.

2.3 Gibbs: Internal Energy, Phase Rule, and Multivariable Functions

Following Gibbs' work, this section introduces concepts such as *state variables* and *internal energy*, as well as the *Gibbs phase rule*. Later, the *first law of thermodynamics is reformulated* using the formalism introduced by Gibbs, which allows identifying the state of a system with a limited number of independent state variables and expressing the other (dependent) state variables as functions of multiple variables.

2.3.1 State Variables

Definition 1 (State Variable)

A state variable of a system is a physical property of the system that depends exclusively on the current state of the system.

Example 1 (State Variables and Non-State Variables)

State variables include temperature, pressure, internal energy, entropy, etc. Non-state variables include work or heat exchanged by the system. **todo**

2.3.2 Internal Energy

Definition 2 (Internal Energy)

The internal energy of a system is defined as the difference between the total energy and the macroscopic kinetic energy of the system,

$$E = E^{tot} - K .$$

It is possible to derive a balance for the internal energy of a closed system by subtracting the balance of kinetic energy described by the kinetic energy theorem from the balance of total energy provided by the first law of thermodynamics,

$$dE^{tot} = \delta L^{ext} + \delta Q^{ext}$$
$$dK = \delta L^{ext} + \delta L^{int} ,$$

The energy balance for the internal energy of a closed system then becomes

$$dE = \delta Q^{ext} - \delta L^{int} .$$

2.3.3 Gibbs Phase Rule

Definition 3 (Phase)

A phase is defined as a portion of a chemical-physical system characterized by uniform chemical-physical (macroscopic) properties.

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todo

- Discussion of properties

- Examples: a mixture of miscible gases constitutes a single phase, in which the individual components cannot be macroscopically distinguished; immiscible liquids remain macroscopically separated and thus constitute multiple phases, in which distinct chemical compositions can be macroscopically identified;…

Proposition 1 (Gibbs Phase Rule)

The thermodynamic (equilibrium) state of a system is identified by a number F of independent **intensive** state variables, determined by the **Gibbs phase rule**,

$$F = C - P + 1 + W ,$$

i.e., the number of independent intensive variables (or degrees of freedom), F, of a system is a function of the number of independent components C, the number of phases P, and the number W of ways the system can manifest internal work, such as:

- internal mechanical stresses

- contribution of surface tension

- bond energy of the molecules of the components

- contribution of the electromagnetic field

Discussion of the Gibbs Phase Rule

The equilibrium state of a system is defined by the values of the state variables, which for a non-electrically charged gas system are: temperature T, pressure p, and concentrations $C_{c,\phi}$ of the individual components $c = 1 : C$ in the individual phases $\phi = 1 : P$ within the system.

The state of the system is thus determined by the values of the $1 + W$ intensive thermodynamic variables, here $W + 1 = 2$ (T, p), and the $C\,P$ molar or mass fractions $n_{c,\phi}$, for a total of $N\,P + W + 1$ variables. In general, these variables are constrained by some conditions:

- $C\,(P - 1)$ phase equilibrium conditions for each component, described by the equality of chemical potentials

$$\mu_{c,\phi_1}(T, p) = \mu_{c,\phi_2}(T, p) = \cdots = \mu_{c,\phi_P}(T, p)$$

- P unitarity conditions of the fractions

$$\sum_c n_{c,\phi} = 1$$

Thus, with $C\,P + W + 1$ variables and $P + C\,(P - 1) = C\,P - C + P$ equations, we find that the problem can be determined by

$$C\,P + W + 1 - C\,P + C - P = C - P + W + 1 = F \,,$$

independent variables.

todo

- Provide examples that clarify the definition of phase (e.g., pure solids or liquids represent phases on their own), and of independent component (e.g., chemical reactions, with no excess components, create constraints that reduce the number of independent substances, thanks to stoichiometric relationships between substances)

- Discuss the role of phase fractions of a single component and the fact that they are not state variables; example phase transition from liquid to vapor: equilibrium is determined by the value of P (or T), and the vapor fraction is a result of other extensive variables of the system.

Example 2 (Closed system containing a single-component (or non-reactive), single-phase, electrically neutral (or not subjected to electromagnetic field))

In a system consisting of a compressible gas, single-component and single-phase (gas phase), electrically neutral, **todo** *other?*, the only form of internal work is related to compression, $\delta L^{int,rev} = P dV$, and thus $W = 1$. Therefore, the system requires

$$F = C - P + 1 + W = 1 - 1 + 1 + 1 = 2 \,,$$

state variables to define the system state.

Example 3 (Open system containing a single-component (or non-reactive), single-phase, electrically neutral (or not subjected to electromagnetic field))

In an open system, the variation in energy of the system also depends on the variation in the amount of gas contained in it. Thus, in general, there are $W = 2$ ways to change the system's energy: by compression work or by a flow of matter into the system. Therefore, $F = 3$ state variables are needed to define the system's state.

Example 4 (Reactive gas mixture in a closed system)

In a reactive gas mixture consisting of two compounds A, B in equilibrium according to the equilibrium reaction

$$n_a A + n_b B \leftrightarrow n A_a B_b$$
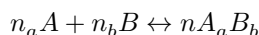
the energy of the system depends on the mechanical compression work of the gas mixture and the quantities of the 3 compounds present in the gas. However, the variation of these compounds is not independent but determined by the equilibrium reaction. Specifically,

$$dn_B = dn_A \frac{n_b}{n_a}$$
$$dn_{A_a B_b} = -dn_A \frac{n}{n_a}$$

The reaction is thus determined by a single parameter. The variation in energy of the system is thus determined by $W = 2$ processes: from the compression work done on the system, and from the state of the reaction. To define the state of the system, $F = 3$ independent state variables are needed, such as **todo** T, P, n_A? Are the chemical potentials μ_A, μ_B, $\mu_{A_a B_b}$ required? Are they uniquely determined?

Example 5 (Single-component system during a phase transition)

First-order phase transition. During a first-order phase transition, two phases, $P = 2$, are simultaneously present in the system. According to the Gibbs phase rule, the state of the system is determined by

$$F = C - P + 1 + W = 1 - 2 + 1 + 1 = 1 \,,$$

state variable.

Critical point. The critical point in the phase diagram of a single-component system defines the condition where three phases, $P = 3$, are simultaneously present in the system. According to the Gibbs phase rule, the state of the system is determined by $F = 0$ state variables: the state of the system at the critical point is uniquely defined, with no degrees of freedom.

Example 6 (Solid)

In the absence of other physical phenomena, the only form of work in a solid is related to deformation work, $\delta L^{int,rev} = \sigma_{ij}\, d\varepsilon_{ij} dV$. The strain tensor is second-order and symmetric, and therefore has 6 independent components in 3-dimensional space, so $W = 6$

Example 7 (Solid mixtures)

- Phases in solid mixtures **todo**

Example 8 (Influence of the electromagnetic field)

- Electric field and magnetization **todo**

2.3.4 First Law in terms of state variables

Internal energy is an extensive variable of a thermodynamic system. In general, it can be written as a function of extensive variables that represent the ways the system manifests its internal energy (**todo** *due to work done on it, heat transferred to the system, and its chemical composition, thus the energy contained in bonds*).

$$E(S, X_k)$$

where X_k are the state variables whose variations are associated with reversible internal work, and S is the state variable whose variation is associated with heat exchange with the external environment and internal dissipative actions. **todo** *referring to the chapter on functions and multivariable calculus*

Assuming the function E is continuous and differentiable, at least piecewise, the exact differential of internal energy can be written as a function of the increments of the independent variables:

$$dE = \left.\frac{\partial E}{\partial S}\right|_{\mathbf{X}} dS + \left.\frac{\partial E}{\partial X_k}\right|_S dX_k = T\,dS + \sum_k F_k\,dX_k$$

where F_k are the generalized forces associated with changes in the generalized coordinates X_k, and T and S correspond to temperature and entropy as discussed further below. **todo**.

Note: As shown later, with this formalism, it is straightforward to express *the **second** and **third** laws of thermodynamics* as:

- $dS \geq \dfrac{\delta Q^{ext}}{T}$

- $T \geq 0$

The expression for the differential of internal energy can be compared with the energy balance written in terms of heat transferred to the system and internal work:

$$dE = \delta Q^{ext} - \delta L^{int} = \delta Q^{ext} + \delta^+ D - \delta L^{int,rev}$$

where the internal work δL^{int} is recognized as the sum of a reversible contribution and a dissipative contribution, which is never negative: $\delta L^{int} = \delta L^{int,rev} - \delta^+ D$.

Since dE is an exact differential and $\delta L^{int,rev}$ is a reversible contribution, it follows that the sum of the two non-reversible contributions, $\delta U := \delta Q^{ext} + \delta^+ D$, is a reversible contribution. Comparing the two expressions for the differential of internal energy, we can associate reversible internal work with the sum of works formed as the product of generalized forces F_k and changes in the state variables X_k, and the term δU with the product $T\,dS$:

$$\begin{cases} -\delta L^{int,rev} & = \sum_k F_k\,dX_k \\ \delta U & = T\,dS \end{cases}$$

Temperature, T, and entropy, S

In the absence of external work done on the system, and in the absence of dissipation $\delta^+ D = 0$, we get:

$$dE^{tot} = dE = \delta Q^{ext}$$

$$dS = \frac{\delta Q^{ext}}{T}$$

Consider a closed and isolated system made of two subsystems in equilibrium, which can exchange heat but not work.

The total energy of the system is constant, $E = E_1 + E_2$. If the two subsystems are not initially at the same temperature, we observe a heat flow from the hotter system to the colder one, which satisfies the inequality:

$$\frac{\delta Q_{12}}{T_1} + \frac{\delta Q_{21}}{T_2} \geq 0 \quad \rightarrow \quad dS_1 + dS_2 \geq 0$$

The quantity $S = S_1 + S_2$ is non-decreasing.

2.3.5 Second and Third Laws of Thermodynamics

The formalism introduced in this section allows for a rather natural formulation of the second law and a version of the third law of thermodynamics.

This formulation of the third law of thermodynamics states that the thermodynamic temperature is always positive:

$$T := \left.\frac{\partial E}{\partial S}\right|_{\mathbf{X}} > 0$$

todo *Add some words about the significance, in terms of molecular agitation and probability*

In cases where this form or consequence of the third law of thermodynamics holds, the second law of thermodynamics is a consequence of the non-negativity of dissipation and the heat transfer mechanism, as will be discussed in more detail in the discussion of *composite systems*.

In the general case of a **simple system**, using the definition $dS = \frac{\delta U}{T} = \frac{\delta Q^{ext} + \delta^+ D}{T}$, the non-negativity of dissipation, $\delta^+ D \geq 0$, implies:

$$dS \geq \frac{\delta Q^{ext}}{T}$$

This is an expression of the *Clausius statement of the second law of thermodynamics*.

todo oss *The third law of thermodynamics: 1. It seems not to be a fundamental principle; 2. For some systems with limited energy, the definition of temperature $T := \left(\frac{\partial E}{\partial S}\right)$ produces a negative temperature* **todo** *add a section on statistical mechanics?*

From L.E. Reichl, *A Modern Course in Statistical Physics*, with some inconsistencies **todo** *check!*

$$\delta W = -PdV + JdL + \sigma dA + V\left(\vec{e} \cdot d\vec{p} + \vec{h} \cdot d\vec{m}\right) + \phi dq$$

- where J, σ are tensions per unit length and area, dL, dA are changes in length or area,
- where $\vec{e}$, $\vec{h}$ are the electric and magnetic fields, $\vec{p}$, $\vec{m}$ are polarization and magnetization,
- ϕ is the electric potential, and q is electric charge (for open systems, otherwise $dq \equiv 0$ or net charge would be created!)

Example 9 (Closed Monocomponent Gas System)

The energy of the system, $E(S, V)$

$$dE = T\,dS - P\,dV$$

Example 10 (Open Monocomponent Gas System)

The energy of the system, $E(S, V, N)$

$$dE = T\,dS - P\,dV + \mu\,dN$$

Example 11 (Reactive Gas Mixture in a Closed System)

The energy of the system

$$dE = T\,dS - P\,dV + \mu_k\,dN_k =$$
$$= T\,dS - P\,dV + (\mu_k n_k)\,dN$$

where n_k are the stoichiometric coefficients (with sign) of the reaction, and N is a quantity that identifies the equilibrium of the reaction, such that the variation of each component can be written as $dN_k = n_k\,dN$.

Example 12 (Monocomponent Mixture During a Phase Transition)

todo how to treat the phase fractions?

Example 13 (Solid)

Solid system with initial volume V under uniform stress and strain, with small deformations

$$dE = T\,dS - V\,\sigma_{ij}\,d\varepsilon_{ij}$$

Example 14 (Solid Mixtures)

todo

Example 15 (Influence of the Magnetic Field)

$$dE = T\,dS - P\,dV + H\,dM$$

todo

2.4 Second Law of Thermodynamics - Clausius Statement

The Clausius statement of the second law of thermodynamics can be formulated quite naturally using the formalism introduced. There are two other famous statements of the second law of thermodynamics, the Planck and Kelvin statements, which will be presented in the context of heat engines.

2.4.1 Simple Systems

The elementary variation of entropy dS of a simple closed system at uniform temperature T is greater than or equal to the ratio of the elementary heat flux introduced into the system and the temperature of the system itself,

$$dS = \underbrace{\frac{\delta^+ D}{T}}_{\geq 0} + \frac{\delta Q^{ext}}{T} \geq \frac{\delta Q^{ext}}{T} \ .$$

This is the Clausius statement of the second law of thermodynamics for simple systems with uniform temperature.

2.4.2 Composite Discrete Systems

todo definition of a composite system. Heat conduction occurs between subsystems.

Entropy in classical thermodynamics is an extensive physical quantity: the entropy of a system composed of N simple subsystems is the sum of the entropies of the subsystems,

$$S = \sum_{n=1:N} S_n \ .$$

The entropy balance of a single subsystem that exchanges heat with the other subsystems and the external environment is written as

$$\begin{aligned} dS_i &= \frac{\delta Q_i^{ext,i}}{T_i} + \frac{\delta^+ D_i}{T_i} = \\ &= \frac{\delta Q_i^{ext}}{T_i} + \frac{\sum_{k \neq i} \delta Q_{ik}}{T_i} + \frac{\delta^+ D_i}{T_i} \geq \\ &\geq \frac{\delta Q_i^{ext}}{T_i} + \frac{\sum_{k \neq i} \delta Q_{ik}}{T_i} \ . \end{aligned}$$

The entropy balance of the entire system is obtained by summing the entropy balances of the individual subsystems,

$$\begin{aligned} dS &= \sum_i dS_i \geq \\ &\geq \sum_i \left\{ \frac{\delta Q_i^{ext}}{T_i} + \frac{\sum_{k \neq i} \delta Q_{ik}}{T_i} \right\} = \\ &= \sum_i \frac{\delta Q_i^{ext}}{T_i} + \underbrace{\sum_{\{i,k\}} \delta Q_{ik} \left(\frac{1}{T_i} - \frac{1}{T_k} \right)}_{\geq 0} \geq \\ &\geq \sum_i \frac{\delta Q_i^{ext}}{T_i} \ . \end{aligned}$$

Using the relation that represents the natural tendency of heat transfer "from a system at a higher temperature to a system at a lower temperature,"

$$\delta Q_{ik} \left(\frac{1}{T_i} - \frac{1}{T_k} \right) \geq 0 \ .$$

todo *add reference to the natural tendency in heat transfer*

2.4.3 Increase of Entropy in the Universe

If we consider the universe as the closed and isolated system (but is this true? Who knows? Maybe it's reasonable for now, but many things that seem reasonable today might be nonsense in a few years) consisting of a system of interest sys and the external environment env.

The variation of entropy in the universe is the sum of the variation in the system and in the external environment. We denote by $\delta Q_{sys,env}$ the heat flux which, if positive, increases the energy of the system and decreases that of the external environment. Assuming that the two subsystems are internally homogeneous,

$$dS^{univ} = dS^{sys} + dS^{env} =$$
$$= \frac{\delta Q_{sys,env}}{T^{sys}} + \frac{\delta Q_{env,sys}}{T^{env}} =$$
$$= \frac{\delta Q_{sys,env}}{T^{sys}} - \frac{\delta Q_{sys,env}}{T^{env}} =$$
$$= \delta Q_{sys,env} \left(\frac{1}{T^{sys}} - \frac{1}{T^{env}} \right) \geq 0 \,,$$

we obtain the relation

$$dS^{univ} \geq 0 \,,$$

which predicts the "non-decrease" of the entropy of the universe.

2.4.4 Composite Continuous Systems

2.5 Open Systems

In general, the balance equation for a physical quantity in an open system is derived from the balance of the same physical quantity for a closed system, adding the contribution of the flux terms of the desired physical quantity through the system's boundary. Thus, if the balance of the physical quantity F for the closed system within volume V_t can be written as

$$\frac{d}{dt} F_{V_t} = R^e_{V_t} \,,$$

the balance of the same physical quantity for an open system identified by the (geometric) volume v_t can be written as

$$\frac{d}{dt} F_{v_t} = R^e_{v_t} - \Phi_{\partial v_t}(f) \,,$$

where f is defined as the specific quantity of F per unit mass. The flux term through the boundary ∂v_t can be written as the sum of the flux contributions through portions $s_{k,t}$ of the surface $\partial v_t = \cup_k s_{k,t}$,

$$\Phi_{\partial v_t}(f) = \sum_{s_{k,t}} \dot{m}_k f_k \,,$$

where $\dot{m}_k = \rho_k v i^{rel}_{n,k}$ is the mass flux through the surface $s_{k,t}$, and it is assumed that the quantity f_k is constant over the surface $s_{k,t}$, or that the average value over the surface has been considered.

Note: In case the quantity f is not uniform over the domain boundary and varies continuously, the flux term can be written as the summation of infinite terms through surfaces whose area tends to zero, via a surface integral, following the definition of a Riemann integral.

Note: A balance equation of a physical quantity for an open system also includes the balance equation of the same physical quantity for a closed system as a special case where the mass flux through the domain boundary is zero, $\dot{m}_k = 0$.

Here, we consider the balances (integrals, global of a system) of some fundamental physical quantities in classical mechanics: mass, momentum, angular momentum, and total energy.

2.5.1 Mass Balance

The mass balance, $F = M$, $f = 1$, for an open system is

$$\frac{d}{dt} M_{v_t} = -\sum_k \dot{m}_k$$

2.5.2 Momentum Balance

todo *reference to or from classical mechanics*

2.5.3 Angular Momentum Balance

todo *reference to or from classical mechanics*

2.5.4 Total Energy Balance

The total energy balance $F = E^{tot} = E + K$, $f = e^{tot} = e + \frac{|\vec{v}|^2}{2}$,

$$\frac{d}{dt} E_{v_t}^{tot} = P_{v_t}^{ext} + \dot{Q}_{v_t}^{ext} - \sum_k \dot{m}_k \, e_k^{tot} \;.$$

The power of external actions $P_{v_t}^{ext}$ can be written as the sum of contributions on the surfaces of the system's boundary through which there is mass flow, and impermeable surfaces that can be used to extract work from the system. If the effects of viscous stresses on the surfaces through which there is mass flow can be neglected, the power of the actions on the system can be written as

$$P^{ext} = P^{ext,mech} + P^{ext,\Phi} =$$
$$= P^{ext,mech} - \sum_k \dot{m}_k \frac{P_k}{\rho_k} \;,$$

and the total energy balance of the system becomes

$$\frac{d}{dt} E_{v_t}^{tot} = P_{v_t}^{ext,mech} + \dot{Q}^{ext} - \sum_k \dot{m}_k h_k^{tot} \;,$$

where the specific total enthalpy is defined as $h^{tot} = e^{tot} + \frac{P}{\rho} = e + \frac{P}{\rho} + \frac{|\vec{v}|^2}{2}$.

Example 16 (Turbine)

Example 17 (Compressor)

Example 18 (Combustion Chamber)

THERMODYNAMICS POTENTIALS

In this section, principles and the mathematical formalism of classical thermodynamics are reviewed.

3.1 First principle

For an extensive system

$$dE = T\, dS + \mathbf{F} \cdot d\mathbf{X}\,,$$

being E the internal energy, T temperature, S entropy, $\mathbf{F}$ generalized force, $\mathbf{X}$ generalized displacement.

Following Gibbs' formulation, internal energy E can be written as a function of a limited set of independent state variables,

$$E(S, \mathbf{X})\,.$$

Internal energy E, entropy S and the generalized displacement $\mathbf{X}$ are **extensive** physical quantities, and thus (**thus?**) the derivatives

$$T := \left.\frac{\partial S}{\partial E}\right|_{\mathbf{X}} \quad,\quad \mathbf{F} := \left.\frac{\partial E}{\partial \mathbf{X}}\right|_{S}$$

are **intensive** quantities. A discussion about the difference between the concept of *additivity* and *extensivity*[1]. Beside being extensive, internal energy in classical thermodynamics is an homogeneous function[2] of order 1 of its arguments, namely

$$E(a\, S, a\, \mathbf{X}) = a\, E(S, \mathbf{X})\,.$$

Euler's theorem for homogeneous functions holds.

Theorem 1 (Euler's theorem for homogeneous functions)

Let $f(x_i)$ and homogeneous function of order m, i.e.

$$f(a\, x_i) = a^m\, f(x_i)\,. \tag{3.1}$$

It follows that

$$f(x_k) = m\, x_i\, \frac{\partial f}{\partial x_i}(x_k)\,.$$

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[1] H.Touchette, When is a quantity additive, and when is it extensive?
[2] https://physics.stackexchange.com/q/677855

Proof immediately follows, evaluating the derivative of (3.1) w.r.t. a, and evaluating for $a = 1$, i.e.

$$x_i \frac{\partial f}{\partial x_i}(a\, x_k) = m\, a^{m-1}\, f(x_k)\,,$$

and for $a = 1$,

$$f(x_k) = x_i \frac{\partial f}{\partial x_i}(x_k)\,.$$

Thus, internal energy can be written as

$$E(S, \mathbf{X}) = T\, S + \mathbf{F} \cdot \mathbf{X}\,.$$

3.1.1 First principle for different systems

- Single-component fluid, $E(S, V, N)$

$$dE = T\, dS - P\, dV + \mu\, dN$$

- Multi-component fluid, $E(S, V, N_k)$

$$dE = T\, dS - P\, dV + \mu_k\, dN_k$$

  where the change of number of particles (or moles, it depends on the description - anyway a non-dimensional number) dN_k is governed by the stoichiometric ratios of the reactions occurring in the system.

- Single-component solid, $E(S, \mathbf{X})$

$$dE = T\, dS + \mathbf{F} \cdot d\mathbf{X}$$

3.1.2 First principle for specific quantities

First principle and thermodynamics can be writtenin terms of specific quantites, usually either for unit volume or for unit mass.

First principle per unit mass

All the extensive quantites are written as the product of the mass of the system M and its density, namely

$$E = Me \quad,\quad S = Ms \quad,\quad \mathbf{X} = M\mathbf{x}\,,$$

and, using the product rule for differential $dE = d(Me) = dM\, e + M\, de$, first principle can be written as

$$0 = dM\, \underbrace{(e - Ts - \mathbf{F} \cdot \mathbf{x})}_{=0} + M\,(de - Tds - \mathbf{F} \cdot d\mathbf{x})\,.$$

The first term is identically zero, since it's the expression of the internal energy divided by M. Being $M > 0$, the second term gives the first principle per unit mass

$$de = Tds + \mathbf{F} \cdot d\mathbf{x}\,.$$

Different systems

- Single-component fluid;

$$V = M\frac{1}{\rho} \quad , \quad N = M\frac{1}{m} \, ,$$

being ρ the mass density and m the mass of a particle (or mole, it depends on the description) of the medium; m is **constant**. First principle becomes

$$0 = dM \underbrace{\left(e - Ts + \frac{P}{\rho} - \frac{\mu}{m} \right)}_{=0} + M \left(de - Tds - \frac{P}{\rho^2} d\rho \right) \, ,$$

and thus

$$de = Tds + \frac{P}{\rho^2} d\rho \, .$$

- Multi-component fluid

$$V = M\frac{1}{\rho} \quad , \quad N_k = M_k \frac{1}{m_k} = M\frac{M_k}{M}\frac{1}{m_k} = M\frac{1}{m_k}\frac{\rho_k}{\rho} = M\frac{1}{m_k}w_k \, ,$$

being ρ the mass density and m the mass of a particle (or mole, it depends on the description) of the kth substance; m_k is **constant**. The first principle becomes

$$0 = dM \underbrace{\left(e - Ts + \frac{P}{\rho} - \frac{\mu_k}{m_k}w_k \right)}_{=0} + M \left[de - Tds - \frac{P}{\rho^2} d\rho - \frac{\mu_k}{m_k} dw_k \right] \, ,$$

and thus

$$de = Tds + \frac{P}{\rho^2} d\rho + \frac{\mu_k}{m_k} dw_k \, .$$

- Single-component solid

todo

First principle per unit volume

All the extensive quantites are written as the product of the mass of the system M and its density, namely

$$E = V\mathcal{E} \quad , \quad S = M\mathcal{S} \quad , \quad \mathbf{X} = M\boldsymbol{\chi} \, ,$$

and, using the product rule for differential $dE = d(V\mathcal{E}) = dV\,\mathcal{E} + V\,d\mathcal{E}$, first principle can be written as

$$0 = dV \underbrace{(\mathcal{E} - T\mathcal{S} - \mathbf{F} \cdot \boldsymbol{\chi})}_{=0} + V(d\mathcal{E} - Td\mathcal{S} - \mathbf{F} \cdot d\boldsymbol{\chi}) \, .$$

The first term is identically zero, since it's the expression of the internal energy divided by V. Being $V > 0$, the second term gives the first principle per unit volume

$$d\mathcal{E} = Td\mathcal{S} + \mathbf{F} \cdot d\boldsymbol{\chi} \, .$$

Different systems

- Single-component fluid;

$$V = V \cdot 1 \quad , \quad N = V \frac{M}{V} \frac{1}{m} = V \frac{\rho}{m} \ ,$$

being ρ the mass density and m the mass of a particle (or mole, it depends on the description) of the medium; m is **constant**. First principle becomes

$$0 = dV \underbrace{\left(\mathcal{E} - T\mathcal{S} + P - \mu \frac{\rho}{m} \right)}_{=0} + V \left(d\mathcal{E} - Td\mathcal{S} + 0 - \frac{\mu}{m} d\rho \right) \ ,$$

and thus

$$d\mathcal{E} = Td\mathcal{S} + \frac{\mu}{m} d\rho \ .$$

This latter formulation is consistent with the principle per unit mass. Volume density can be written as the product of mass density and the mass density of the physical quantity of interest, namely $\mathcal{E} = \rho e$

$$0 = -d(\rho e) + Td(\rho s) + \frac{\mu}{m} d\rho =$$
$$= d\rho \left(-e + Ts + \frac{\mu}{m} \right) - \rho \left(de + Tds \right) =$$
$$= d\rho \underbrace{\left(-e - \frac{P}{\rho} + Ts + \frac{\mu}{m} \right)}_{\text{def. of } e} + \rho \underbrace{\left(-de + \frac{P}{\rho^2} d\rho + Tds \right)}_{1^{st} \text{ pr. per unit mass}} \ .$$

- Multi-component fluid

todo

- Single-component solid

todo

3.2 Potentials - specific quantities

Here mechanical $\mathbf{X}_m$ and non-mechanical $\mathbf{X}_n$ generalized forces and displacements are recognized to define enthaply and Gibbs' free energy later.

$$e(s, \mathbf{x}) = e \left(\frac{S}{M}, \frac{\mathbf{X}}{M} \right) = \frac{1}{M} E \left(\frac{S}{M}, \frac{\mathbf{X}}{M} \right) \qquad \textbf{todo check}$$

Internal energy, $e(s, \mathbf{x})$**.**

$$de = Tds + \mathbf{F} \cdot d\mathbf{x}$$

Helmholtz free energy, $f(T, \mathbf{x}) = e - Ts$**.**

$$df = de - Tds - sdT =$$
$$= -sdT + \mathbf{F} \cdot d\mathbf{x} \ .$$

Enthaply, $h(T, \mathbf{F}_m, \mathbf{x}_n) = e - \mathbf{F}_m \cdot \mathbf{x}_m$.

$$dh = de - d\mathbf{F}_m \cdot \mathbf{x}_m - \mathbf{F}_m \cdot d\mathbf{x}_m =$$
$$= Tds - \mathbf{x}_m \cdot d\mathbf{F}_m + \mathbf{F}_n \cdot d\mathbf{x}_n \ .$$

Gibbs' free energy, $g(T, \mathbf{F}_m, \mathbf{x}_n) = h - Ts = e - \mathbf{F}_m \cdot \mathbf{x}_m - Ts = f - \mathbf{F}_m \cdot \mathbf{x}_m = \mathbf{F}_n \cdot \mathbf{x}_n$.

$$dg = dh - Tds - sdT =$$
$$= -sdT - \mathbf{x}_m \cdot d\mathbf{F}_m + \mathbf{F}_n \cdot d\mathbf{x}_n =$$
$$= \mathbf{x}_n \cdot d\mathbf{F}_n + \mathbf{F}_n \cdot d\mathbf{x}_n \ .$$

Partial derivatives of potentials.

$$T = \left. \frac{\partial e}{\partial s} \right|_{\mathbf{x}} = \left. \frac{\partial h}{\partial s} \right|_{\mathbf{F}_m, \mathbf{x}_n}$$

$$s = - \left. \frac{\partial f}{\partial T} \right|_{\mathbf{x}} = - \left. \frac{\partial g}{\partial T} \right|_{\mathbf{F}_m, \mathbf{x}_n}$$

$$\mathbf{F}_m = \left. \frac{\partial e}{\partial \mathbf{x}_m} \right|_{s, \mathbf{x}_n} = \left. \frac{\partial f}{\partial \mathbf{x}_m} \right|_{T, \mathbf{x}_n}$$

$$\mathbf{F}_n = \left. \frac{\partial e}{\partial \mathbf{x}_n} \right|_{s, \mathbf{x}_m} = \left. \frac{\partial f}{\partial \mathbf{x}_n} \right|_{T, \mathbf{x}_m} = \left. \frac{\partial h}{\partial \mathbf{x}_n} \right|_{s, \mathbf{F}_m} = \left. \frac{\partial g}{\partial \mathbf{x}_n} \right|_{T, \mathbf{F}_m}$$

$$\mathbf{x}_m = - \left. \frac{\partial h}{\partial \mathbf{F}_m} \right|_{s, \mathbf{x}_n} = - \left. \frac{\partial g}{\partial \mathbf{F}_m} \right|_{T, \mathbf{x}_n}$$

Maxwell's relations.

todo Uncomment

THERMODYNAMIC COEFFICIENTS

In this section different related to first derivatives of thermodynamic state variables are introduced and discussed for different systems.

4.1 Thermodynamic coefficients of a single-component fluid

For a 1-component fluid with constant composition, the first principle reads

$$de = T ds - P dv = T ds + \frac{P}{\rho^2} d\rho \ .$$

Heat capacity.

$$c_x := T \frac{\partial s}{\partial T}\bigg|_x$$

For fluid systems, usually heat capacity at constant pressure or constant density are the most used.

Thermal expansion coefficients.

$$\alpha_x := \frac{1}{v} \frac{\partial v}{\partial T}\bigg|_x = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}\bigg|_x$$

For fluid systems, usually thermal expansion coefficent at constant pressure is the most used.

Compressibility coefficients.

$$\beta_x := -\frac{1}{v} \frac{\partial v}{\partial P}\bigg|_x = \frac{1}{\rho} \frac{\partial \rho}{\partial P}\bigg|_x$$

For fluid systems, usually compressibility coefficent at constant temperature or entropy are the most used.

4.2 Relations between thermodynamic coefficients

Relation between c_v and c_p.

$$c_P - c_v = T v \frac{\alpha_P^2}{\beta_T} \ . \tag{4.1}$$

Relation between β_s and β_T - 1

$$\beta_s = \frac{c_v}{c_P} \beta_T \ . \tag{4.2}$$

Relation between β_s and β_T - 2

$$\beta_s - \beta_T = -\frac{vT}{c_P}\alpha_P^2 \ .$$

(4.3)

Relation between β_s and β_T - 3

$$\frac{1}{\beta_s} - \frac{1}{\beta_T} = \frac{T}{vc_v}\left(\partial_T P|_v\right)^2 \ .$$

(4.4)

Proof of the relation between heat capacities c_v, c_P

Changing independent variables from (T, v) to (P, v) in the expression of entropy $s(T, v) = s(T, P(v, T))$,

$$
\begin{aligned}
\frac{c_v}{T} := \left.\frac{\partial s}{\partial T}\right|_v &= \left.\frac{\partial s}{\partial T}\right|_P + \left.\frac{\partial s}{\partial P}\right|_T \left.\frac{\partial P}{\partial T}\right|_v = && \text{(Maxwell } \partial_P s|_T = -\partial_T v|_P) \\
&= \left.\frac{\partial s}{\partial T}\right|_P - \left.\frac{\partial v}{\partial T}\right|_P \left.\frac{\partial P}{\partial T}\right|_v = && \text{(relation below } \partial_T P|_v = \dots) \\
&= \partial_T s|_P + \frac{\left(\partial_P v|_T\right)^2}{\partial_P v|_T} = && \text{(def of TD coeffs)} \\
&= \frac{c_P}{T} - \frac{v\alpha_P^2}{\beta_T}
\end{aligned}
$$

having exploited the relation

$$\left.\frac{\partial P}{\partial T}\right|_v = \frac{\partial(P, v)}{\partial(T, v)} = \frac{\partial(P, v)/\partial(T, P)}{\partial(T, v)/\partial(T, P)} = -\frac{\partial_P v|_T}{\partial_P v|_T} \ .$$

Proof of the relation between β_s and β_T - 1

$$v\beta_T = \partial_P v|_T$$

$$v\beta_s = \partial_P v|_s = \frac{\partial(v, s)}{\partial(P, s)}\frac{\partial(v, T)}{\partial(v, T)}\frac{\partial(P, T)}{\partial(P, T)} = \underbrace{\frac{\partial(P, T)}{\partial(P, s)}}_{=\frac{1}{\partial_T s|_P}}\underbrace{\frac{\partial(v, T)}{\partial(P, T)}}_{\partial_P v|_T}\underbrace{\frac{\partial(v, s)}{\partial(v, T)}}_{\partial_T s|_v} = \frac{c_v}{c_P}\left(v\beta_T\right)$$

Proof of the relation between β_s and β_T - 2

$$\beta_s = \frac{c_v}{c_P}\beta_T = \frac{\beta_T}{c_P}\left[c_P - Tv\frac{\alpha_P^2}{\beta_T}\right] = \beta_T - Tv\frac{\alpha_P^2}{c_P} \ .$$

Proof of the relation between β_s and β_T - 3

$$
\begin{aligned}
\frac{1}{\beta_s} &= \frac{c_P}{c_v}\frac{1}{\beta_T} = \frac{1}{c_v\beta_T}\left[c_v + Tv\frac{\alpha_P^2}{\beta_T}\right] = \\
&= \frac{1}{\beta_T}\frac{1}{c_v}\left[c_v + Tv\frac{\alpha_P^2}{\beta_T}\right] = \\
&= \frac{1}{\beta_T} + Tv\frac{\frac{1}{v^2}(\partial_T v|_P)^2}{-\frac{1}{v}\partial_P v|_T}\frac{1}{-\frac{1}{v}\partial_P v|_T} = \\
&= \frac{1}{\beta_T} + Tv\left(\frac{\partial_T v|_P}{\partial_P v|_T}\right)^2 = \frac{1}{\beta_T} + Tv\left(\frac{\partial(v, P)}{\partial(T, P)}\frac{\partial(P, T)}{\partial(v, T)}\right)^2 = \frac{1}{\beta_T} + Tv\left(\left.\frac{\partial P}{\partial T}\right|_v\right)^2
\end{aligned}
$$

4.3 Thermodynamic equilibrium

Here thermodynamic equilibrium is discussed for a single-component fluid, for which the first principle reads

$$de = Tds - Pdv = Tds + \frac{P}{\rho^2}d\rho \ .$$

First conditions on energy, $e(s,\rho)$, as a function of entropy and density then the equivalent conditions on entropy $s(e,\rho)$, as a function of energy and density are discussed.

4.3.1 Conditions on energy

Thermodynamic equilibrium implies conditions on the second order term in series expansion of the function $e(s,\rho)$ (**todo** *why? Spend few words. Use Landau as a reference if needed*)

$$e(s+ds, \rho+d\rho) = e(s,\rho) + \partial_s e|_\rho(s,\rho)d\rho + \partial_\rho e|_s(s,\rho)ds+$$

$$+ \frac{1}{2}\left[\partial_{ss}e|_\rho(s,\rho)ds^2 + 2\partial_{s\rho}e(s,\rho)dsd\rho + \partial_{\rho\rho}e(s,\rho)d\rho^2\right] \ .$$

The equilibrium energy must be a *minimum* (**todo** check the function that must be a *minimum*, since $\partial_s e|_\rho = T$,... and T not zero, and thus it can be a minimum!): the second order term must be positive for any increment of independent physical variables $d\rho$, ds, i.e.

$$\frac{1}{2}\left[\partial_{ss}e|_\rho ds^2 + 2\partial_{s\rho}e dsd\rho + \partial_{\rho\rho}e|_s d\rho^2\right]$$

is a positive-definite quadratic form, i.e. the Hessian

$$\begin{bmatrix} \partial_{ss}e|_\rho & \partial_{s\rho}e \\ \partial_{s\rho}e & \partial_{\rho\rho}e|_s \end{bmatrix}$$

is definite positive, and thus teh following conditions must hold

$$\begin{cases} \partial_{ss}e|_\rho > 0 \\ \partial_{ss}e|_\rho \partial_{\rho\rho}e|_s - \left(\partial_{s\rho}e\right)^2 < 0 \end{cases}$$

4.3.2 Conditions on entropy

Using e, ρ as independent thermodynamic state variables, and the entropy $s(e,\rho)$ it can be proved that the condition on $e(s,\rho)$ for the thermodynamic equilibrium implies that $s(e,\rho)$ is a *maxiumum* (**todo** *check the meaning of maximum here*), and thus

$$\frac{1}{2}\left[\partial_{ee}s|_\rho de^2 + 2\partial_{e\rho}s ded\rho + \partial_{\rho\rho}s|_e d\rho^2\right]$$

is a positive-definite quadratic form, i.e. the Hessian

$$\begin{bmatrix} \partial_{ee}s|_\rho & \partial_{e\rho}s \\ \partial_{e\rho}s & \partial_{\rho\rho}s|_e \end{bmatrix}$$

is definite positive, and thus teh following conditions must hold

$$\begin{cases} \partial_{ee}s|_\rho < 0 \\ \partial_{ee}s|_\rho \partial_{\rho\rho}s|_e - \left(\partial_{e\rho}s\right)^2 < 0 \end{cases}$$

Relation between partial derivatives of $e(s, \rho)$ and $s(e, \rho)$

The relation

$$e = e_{s\rho}(s_{e\rho}(e, \rho), \rho) \,,$$

provides the link between the two representations, having written $e_{s,\rho}()$, $s_{e,\rho}()$ the functions with the arguent indicated as indices. This relation contains only e, ρ as independent variables. All the required relations are evaluated computing partial derivatives of this relation.

First-order derivatives. It can be proved that

$$\partial_e s|_\rho = \frac{1}{\partial_s e|_\rho}$$

$$\partial_\rho s|_e = -\frac{\partial_\rho e|_s}{\partial_s e|_\rho}$$

Second-order derivatives. It can be proved that

$$\partial_{ee} s|_\rho = -\frac{1}{\left(\partial_s e|_\rho\right)^3} \partial_{ss} e|_\rho$$

$$\partial_{e\rho} s = \frac{\partial_\rho e|_s}{\left(\partial_s e|_\rho\right)^3} \partial_{ss} e|_\rho - \frac{\partial_{s\rho} e}{(\partial_s e|_\rho)^2}$$

$$\partial_{\rho\rho} s|_e = -\frac{1}{\left(\partial_s e|_\rho\right)^3} \left[\left(-\frac{\partial_\rho e_s}{\partial_s e|_\rho}\right)^2 \partial_{ss} e|_\rho + 2 \left(-\frac{\partial_\rho e_s}{\partial_s e|_\rho}\right) \partial_{s\rho} e + \partial_{\rho\rho} e|_s \right]$$

Equivalence of conditions on $e(s, \rho)$ and on $s(e, \rho)$ for thermodynamic equilibrium

Exploiting first condition on partial derivatives of $e(s, \rho)$, the first condition on the partial derivatives of $s(e, \rho)$ is

$$\partial_{ee} s|_\rho = -\frac{1}{\left(\partial_s e|_\rho\right)^3} \partial_{ss} e|_\rho = -\frac{1}{T^3} \partial_{ss} e|_\rho < 0$$

since $T > 0$ and $\partial_{ss} e|_\rho > 0$.

Second condition for derivatives of $s(e, \rho)$ is

$$\partial_{\rho\rho} s|_e \partial_{ee} s|_\rho - \left(\partial_{\rho s} e\right)^2 = \dots$$

$$= \frac{1}{T^4} \left[\partial_{ss} e|_\rho \partial_{\rho\rho} e|_s - \left(\partial_{s\rho} e\right)^2 \right] < 0 \,.$$

STATI DELLA MATERIA E MODELLI

Stati della materia.

- gas

- liquidi

- solidi

- plasma

Alcune leggi costitutive.

- solidi elastici:

  - solidi lineari elastici isotropi

- fluidi:

  - in base all'equazione di stato:

    * gas perfetti

    * gas reali

    * …

  - in base all'espressione degli sforzi:

    * fluidi newtoniani

    * fluidi non-newtoniani

basics

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5.1 Gas ideali

Legge di Boyle-Mariotte. $PV = $ cost. a T costante (trasformazione isoterma).

Legge di Gay-Lussac I (o Charles). $V \propto T$ a P costante (trasformazione isobara).

Legge di Gay-Lussac II. $P \propto T$ a V costante (trasformazione isocora).

Legge dei gas ideali. $PV = nRT$

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TRASFORMAZIONI TERMODINAMICHE

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SEVEN

CICLI TERMODINAMICI E MACCHINE TERMICHE

Le macchine termiche sono sistemi che sfruttano scambi di calore per produrre lavoro (**macchine dirette**, come i motori a combustione) o lavoro per scambiare calore da sistemi freddi a sistemi più caldi (**macchine inverse**, come i frigoriferi).

Di solito, le macchine termiche sfruttano un fluido di lavoro. Le macchine a fluido possono essere un sistema aperto (es. motori aeronautici) o chiuso (circuiti delle centrali elettriche e di frigoriferi), o un sistema che è aperto solo in alcune fasi (es. nei motori alternativi, la camera di combustione è un sistema aperto solo durante le fasi di aspirazione e scarico, se si trascurano le perdite).

Macchine ideali. *Macchina ideale di Carnot; efficienza massima; enunciati di Planck e Kelvin del secondo principio della termodinamica.*

Macchine reali. *Cicli ideali: Otto, Diesel, Rankine, Joule-Brayton,…;*

basics

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EIGHT

MECCANISMI DI TRASMISSIONE DEL CALORE

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