

# On the states of thermodynamic equilibrium

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**Abstract.** A review of the existing literature shows a variety of definitions of equilibrium states. Although this definition determines the systems and the processes which are feasible to be treated within the framework of classical thermodynamics, we have found that these definitions are not equivalent; however, it is possible to reduce them to two, and our aim here is to show that only one of these is logically acceptable.

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## 1. Introduction

The axiomatic form of Classical Thermodynamics requires four postulates in order to be a complete theory [1]. The first two postulates establish the existence of certain thermodynamics states, called equilibrium states, which are completely determined by extensive parameters (internal energy, volume, etc.), and the entropy is postulated as an extensive parameter of the system. The third one is related with the equilibrium states in which the entropy is an extreme. The last one characterizes the zero entropy system [1].

Within this framework, knowledge of the fundamental function of the system the internal energy, or the entropy is sufficient in order to describe it completely. This function depends only on the extensive parameters, but it may be written in terms of associated intensive parameters using Legendre transformations. In the former case, we obtain the thermodynamics potentials whereas the Massieu functions are obtained in the case of entropy. On this basis, it is possible to describe some particular processes called reversible transformations, whose successive states are equilibrium states. So, the assumed definitions of this kind of states determine the processes which are to be treated by the theory. This definition has a great importance in the subsequent application of the third postulate. An extension of Classical Thermodynamics is the local equilibrium thermodynamics, whose principal characteristics is to consider that the system is completely described by the same parameters and the time; the parameters dependent of the spatial variables (hypothesis of local equilibrium), *i.e.*, the local equilibrium hypothesis establishes that some processes develop forming states where the classical postulates are valid at any time and for each point of the system.

We discuss in this work the definitions of equilibrium states which have been found in the literature. We solve a system of one component in the presence of an

external field of forces, assuming one definition as valid and making explicit use of the hypothesis of local equilibrium. Finally we develop some illustrative examples.

## 2. Definition of equilibrium states

A review of the texts of Classical Thermodynamics commonly used at the undergraduate level, shows a variety of equilibrium definitions which may be reduced as follows:

Two authors [2,3] admit the difficulty to establish the definition of equilibrium states. Other authors [4,5,6] do not define them. We have found that it is possible to resume the different definitions to only two:

1. Equilibrium states are spatially homogeneous stationary states [7].
2. Equilibrium states are zero flux stationary states [8,9,10,11].

It is clear that the second definition includes the first one, for which the stationary cases with spatial dependence are not equilibrium states. In opposition to it, the second one considers in equilibrium those states in which mass or energy fluxes do not exist but they are not necessarily homogeneous states. Systems in the presence of external fields may be treated, according to this definition, with methods of the classical theory. But when one examines some of these cases the additional hypothesis on local equilibrium appears as an extra input to the second definition. This is not logically acceptable.

We should remark that the states where local equilibrium hypothesis can be valid include the stationary states, time independent states, inhomogeneous systems and so on. One example of the last case are systems immersed in an external field of forces. It is remarkable that this system can be looked as a homogeneous system on the equipotential surfaces.

## 3. Ideal gas system in the presence of an external field of forces

Let us consider an ideal gas at constant temperature and volume acted by an external force field. The standard procedure to find the density distribution is based on the fact that at constant temperature and volume, the system is in equilibrium, according to the second definition, and therefore the Helmholtz free energy must be a minimum [12]. From the classical point of view, the solution is only obtained if one supposes an additional condition related to local equilibrium. Let us assume the system divided in homogeneous layers, each one in equilibrium (*i.e.*, a spatially homogeneous stationary state). These layers are selected according to the particular symmetry of the system being treated. The pressure in the *i*th-layer is given by

$$P_i = P_{i-1} + \frac{F_{i-1}}{A_{i-1}}, \quad (1)$$

where  $A_{i-1}$  is the area of the boundary between the  $i$ th-layer and  $(i-1)$ th-layer and  $F_{i-1}$  is the "molal force" which is as yet unspecified. Using the equation of state for the ideal gas we obtain a recurrent expression for the gas density

$$\rho_i = \rho_{i-1} + \frac{MF_{i-1}}{RTA_{i-1}}. \quad (2)$$

Here  $M$  is the molal mass of the gas,  $T$  is the absolute temperature and  $R$  the universal constant of gases. Eq. (2) may be used in order to find the density distribution by making the number of layers infinite.

The term in the force in Eq. (2) may be written as

$$\frac{MF_i}{RTA_i} = f(i)\rho_i, \quad (3)$$

then the recurrent formula becomes

$$\rho_i = \rho_{i-1}(1 + f(i-1)). \quad (4)$$

Hence it follows that

$$\rho_n = \rho_1 \prod_{i=1}^{n-1} (1 + f(i)), \quad (5)$$

$\rho_1$  being the density at a given reference level. The convergence of Eq. (4) when  $n \rightarrow \infty$  is insured if

$$F_i \propto r^j \quad \text{and} \quad A_i \propto r^n, \quad (6)$$

with  $j < n$ , and  $r$  is the relevant spatial parameter. In this case, we have  $f(i) \rightarrow 0$  as  $n \rightarrow \infty$ , which is a necessary and sufficient condition [13] in order to find the limit of Eq. (5):

$$\rho = \rho_1 \exp \left[ \lim_{n \rightarrow \infty} \sum_{i=1}^n f(i) \right] \quad (7)$$

Conditions (3) and (6) are satisfied by force fields such as the uniform gravitational field and the centrifugal field.

We note that the condition of equilibrium of the layers and the process when



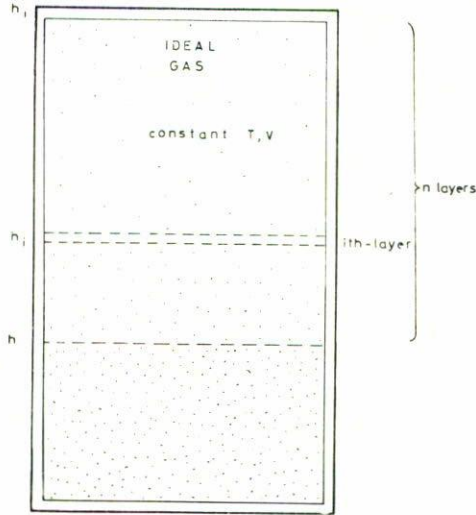


FIGURE 1. Model of an ideal gas in a gravitational field of forces.

$n \rightarrow \infty$  is equivalent to the hypothesis of local equilibrium for systems in a stationary state for which equipotential surfaces exist. We illustrate now the use of this procedure with two simple examples.

(a) *Uniform gravitational forces field*

Let us consider an ideal gas at constant temperature and volume acted by a uniform gravitational force field. The system is divided in thin homogeneous layers in equilibrium as shown at Fig. 1. The width of each layer is  $\Delta h$  and the pressure of each one is taken to be constant and equal to that in the highest part of it. The force on the top of the  $i$ th-layer is

$$F_{i-1} = \rho_{i-1} g \Delta h A_{i-1}, \tag{8}$$

where  $\rho_{i-1}$  is the density of the  $(i - 1)$ th-layer and

$$\Delta h = \frac{(h_1 - h)}{n}. \tag{9}$$

Note that in this case, the quotient  $F_i/A_i \propto 1/n$ , therefore the density of the  $n$ th-layer is

$$\rho_n = \rho_1 \prod_{i=1}^n \left( 1 + \frac{Mg\Delta h}{RT} \right),$$

or

$$\rho_n = \rho_1 \left( 1 + \frac{Mg\Delta h}{RT} \right)^{n-1} \quad (10)$$

It then follows that when  $n \rightarrow \infty$  Eq. (7) becomes:

$$\rho(h) = \rho_1 \exp \left[ \frac{-Mg(h - h_1)}{RT} \right]. \quad (11)$$

This expression is the well known exponential function for density of the air in the atmosphere, if  $T$  is constant [14].

(b) *Centrifugal force field*

We consider now an ideal gas at constant temperature and volume in a container that rotates with a constant angular velocity  $\omega$ . The force at a distance  $r_i$  of center of gyration is given by:

$$F_i = m_i \omega^2 r_i; \quad (12)$$

here  $m_i$  is the mass of the  $i$ th-layer. The layers are taken to be cylindrical shells of thick  $\Delta r$  (Fig. 2). The expression for the quotient  $F_{i-1}/A_{i-1}$  is

$$\frac{\omega^2 r_i (r_i^2 - r_{i-1}^2) \pi h \rho_{i-1}}{2\pi r_i h} = \frac{\omega^2 r (2i - 1) \rho_{i-1}}{2n}, \quad (13)$$

where  $r_i = ir/n$  with  $r$  the radius of the centrifuge. From Eq. (5), it follows immediately that

$$\rho_{n+1} = \rho_1 \prod_{i=1}^n \left[ 1 + \frac{M\omega^2 (2i - 1) r^2}{2RTn} \right]. \quad (14)$$

When  $n \rightarrow \infty$  we obtain

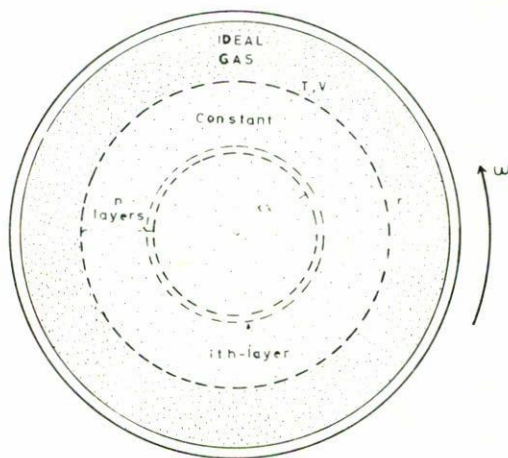


FIGURE 2. Model of an ideal gas in a centrifugal field of forces.

$$\rho(r) = \rho_1 \exp \left[ \lim_{n \rightarrow \infty} \sum_{i=1}^n \frac{(2i-1)\gamma}{n} \right], \quad (15)$$

with  $\gamma = Mr^2\omega^2/2RT$ . As it may be proved

$$\lim_{n \rightarrow \infty} \sum_{i=1}^n \frac{(2i-1)\gamma}{n} = \gamma. \quad (16)$$

Therefore Eq. (15) becomes

$$\rho(r) = \rho_1 \exp \left[ \frac{M\omega^2 r^2}{2RT} \right]. \quad (17)$$

This result is obtained also when one assumes the second definition of equilibrium state and minimizes the Helmholtz free energy [12].

## 4. Conclusions and remarks

The definition of a thermodynamic equilibrium state determines the set of processes to be studied by Classical Thermodynamics (CT). We have found in the literature two nonequivalent definitions of equilibrium: 1) those states in which the system is in spatial homogeneous and stationary condition and 2) those states in which fluxes in the system do not exist and this is also in a stationary condition.

The first definition is more restrictive than the second one, but it has no logical problems. The second one accepts as equilibrium states those stationary states of the system in presence of time-independent external force fields, but in order to allow use of CT, recourse has to be made of an additional assumption: the local equilibrium hypothesis. In the examples we have dealt with, we have shown some evidence of the necessity of including this hypothesis in the treatment of nonhomogeneous systems in the framework of CT.

We conclude from above that only spatially homogeneous and stationary states must be considered as equilibrium states of CT. The stated examples may be used to illustrate the concept of local equilibrium.

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**Resumen.** Una revisión de la literatura existente muestra una variedad de definiciones de estado de equilibrio. Aunque estas definiciones condicionan los sistemas y procesos que son susceptibles de ser tratados con el formalismo de la termodinámica clásica, se encontró que estas definiciones no son equivalentes; sin embargo, es posible reducirlas a dos, mostrándose que solamente una de ellas es lógicamente aceptable.