# NON-EQUILIBRIUM PROCESS

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**Summary**

An account is provided of the two existing approaches to the study of non-equilibrium processes. The macroscopic approach is illustrated with the principles of linear irreversible thermodynamics as applied to a multicomponent mixture of chemically inert fluids. Kinetic theory for a dilute gas and the fluctuation-dissipation relations are used to highlight the microscopic approach. Modern developments, merits and limitations of both approaches are briefly mentioned.

## 1. Introduction

Classical thermodynamics, which should perhaps be referred to more properly as thermostatics, deals with the study of macroscopic physical systems whose attributes (say temperature, pressure, magnetization, etc.) do not depend on time. That is, the subject of classical thermodynamics is the study of the equilibrium states of macroscopic systems. Although at first sight different, the air coming out of the hole in a punctured tire, the fact that when a pendulum is put to oscillate freely in air its oscillations become progressively damped until the pendulum eventually stops, and the fact that a living organism first is born, then grows and becomes older and older until it finally dies, share a common characteristic: in contrast with what happens say with melting and freezing or evaporation and condensation (which may be recognized as pairs of inverse or reversible processes well accounted for by classical thermodynamics), the aforementioned phenomena involve a time-dependent process, seem to occur spontaneously and in a single direction. A wealth of other phenomena occurring in nature also catches our attention because of this reason, namely the occurrence of irreversible (non-equilibrium) processes.

The study of such phenomena is probably as ancient as man himself. However solid understanding and theoretical developments were only achieved by the mid eighteenth

century and efforts to get a deeper insight into these phenomena continue up to the present day. These developments are the results of direct observation and experimentation as well as of the attempts to understand, interpret and predict them on the basis of the corpuscular nature of matter and radiation. A desirable goal within this latter approach is the derivation of general laws starting with the more basic ones that describe the behavior of the particles that form the system under observation. The phenomenological approach to the study of these irreversible phenomena lies within what is called nonequilibrium thermodynamics or thermodynamics of irreversible processes (TIP). On the other hand, the approach that takes as point of departure the fundamental laws that underlie the interactions between the particles of the system may be classified (due to subtle differences) as either the kinetic theory of matter, mainly applicable to fluids, or as statistical mechanics, but nowadays it is generally known as the statistical physics of irreversible processes.

In what follows, we will try to provide a rather brief but hopefully self-contained account of the macroscopic and microscopic approaches for the description of non-equilibrium processes. This will include a mention of the merits and limitations of the available developments as well as some perspective for future ones.

## 2. Non-equilibrium Thermodynamics

## 2.1. Classical (linear) Irreversible Thermodynamics

When dealing with the thermodynamic description and study of the non-equilibrium states and processes that occur in a given system, a fundamental question concerns the choice and number of macroscopic variables. A natural idea is to use in a judicious way the same thermodynamic variables that one considers in equilibrium. Hence, two basic hypotheses underlie the formulation of the classical theory of irreversible processes. One the one hand, for each position **r**, conceived as representative of a volume element small enough macroscopically to be considered a point at time *t* one assumes that it is possible to define univocally the thermodynamic parameters. And the other hypothesis, referred to as the local equilibrium hypothesis, states that the same functional relationship that these thermodynamic parameters maintain in equilibrium also holds for non-equilibrium situations. This implies in particular the local (in time and space) validity of the Gibbs relation which will now involve the time and space variation of the thermodynamic parameters. Equivalently, it also implies that the change in entropy per unit volume and unit time is equal to the entropy flux per unit area and unit time plus the entropy production per unit time. In accordance with the second law of thermodynamics, this (local) entropy production is assumed to be non-negative. In turn, since the space and time variation of the thermodynamic parameters appears in balance equations expressing the conservation of the relevant physical quantities, such parameters are referred to generically as conserved variables.

The forces required to drive a system out of (thermodynamic) equilibrium are in general related to the space and/or time variation of the thermodynamic variables. In an attempt to return to equilibrium, the response of the system to such forces is in terms of fluxes of the appropriate kind that arise to counteract their effect. Using the appropriate balance equations for the conserved variables of the system, one finds that the entropy

production is a sum of products of fluxes and thermodynamic forces. As a first approximation, one can reasonably assume that the forces (either gradients or time derivatives) and the fluxes are linearly related. The ensuing coupling (phenomenological) coefficients are the so-called transport coefficients. A theorem due to Curie also allows that forces and fluxes of the same tensorial nature be coupled. Within certain limits (loosely speaking *close* to equilibrium), these two facts have been amply confirmed by experiment. A final assumption, rooted on the regression of fluctuations hypothesis and on the principle of microscopic reversibility but also confirmed by experiment, is that the phenomenological coefficients associated to cross couplings of thermodynamic forces in different fluxes of the same tensorial nature are equal. This is known as the Onsager reciprocity relations. These assumptions, together with the requirement of a non-negative entropy production, impose restrictions on the sign of the transport coefficients.

Among the non-equilibrium states of a system, those that do not change with time, *i.e.*, the stationary states, are particularly important. In fact, provided the phenomenological coefficients *do not* depend on time either and obey Onsager reciprocity, it can be shown that in a stationary state the entropy production is a minimum. A more general result, not involving the above assumptions, indicates that for stationary states in which the change of the entropy production is due to the rate of change of the thermodynamic forces such a change will be negative. Further, if the sum of the products of the rate of change of the fluxes and the thermodynamic forces is also non-negative, the entropy production will decrease as time proceeds until the stationary state is reached.

In order to illustrate the above theoretical framework let us consider a multicomponent mixture of $N$ chemically inert fluids. Let us first of all recall that the balances of mass, momentum and energy for this system are given by

$$\frac{d\rho_i}{dt} + \nabla \cdot \mathbf{J}_i = -\rho_i \nabla \cdot \mathbf{u}, \tag{1}$$

$$\rho \frac{d\mathbf{u}}{dt} + \nabla \cdot \tau^{\mathrm{v}} = -\nabla p + \sum_{k=1}^{N} \rho_k \mathbf{F}_k^{\mathrm{ex}} \tag{2}$$

$$\rho \frac{de}{dt} = -\nabla \cdot \mathbf{J}_{\mathrm{q}} - p\nabla \cdot \mathbf{u} - \tau^{\mathrm{v}} := \nabla \mathbf{u} + \sum_{k=1}^{N} \mathbf{J}_k \cdot \mathbf{F}_k^{\mathrm{ex}}. \tag{3}$$

Here, $\rho_i$ is the mass density of species $i$, $\mathbf{J}_i$ is the mass flux of species $i$, $\mathbf{u}$ is the hydrodynamic velocity (associated with the momentum density), $\rho \equiv \sum_{i=1}^{N} \rho_i$ is the mass density, $\tau^{\mathrm{v}} \equiv \tau 1 + \tau'$ is the viscous stress tensor ($\tau$ being its trace, 1 the identity second rank tensor and $\tau'$ the traceless part) associated with the momentum flux, $p$ is the pressure, $\mathbf{F}_k^{\mathrm{ex}}$ is the external force acting on species $i$, $e$ is the internal energy density, $\mathbf{J}_{\mathrm{q}}$ the heat flux and $\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla$ stands for the material time derivative, with

$\nabla \equiv \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$ in Cartesian coordinates. Note that since $\sum_{i=1}^{N} \mathbf{J}_i = 0$, the usual continuity equation follows immediately from Eq. (1). Also note that the form of the balance equations has a simple structure. It states that the time rate of change of the conserved densities (indicated by the material time derivative) is due to the entrance or exit of the corresponding quantity at the particular position being considered (the term containing the divergence of the associated flux) and to the production or consumption (at the same location) of the quantity corresponding to each conserved density caused by internal processes. Thus for instance in the case of the balance equation for $\rho_i$ and in the absence of chemical reactions, mass of the $i^{\text{th}}$ component goes into or out of the position $\mathbf{r}$ (the mass flux is $\mathbf{J}_i$) but it is not produced in internal processes; on the other hand, for the internal energy density the associated flux is the heat flux but the internal energy density also changes in time because of viscous and external force dissipation.

The thermohydrodynamic description is completed with the local Gibbs relation, which in this case, reads

$$T \frac{ds}{dt} = \frac{de}{dt} - \frac{p}{\rho^2} \frac{d\rho}{dt} - \sum_{i=1}^{N} \mu_i \frac{dc_i}{dt}, \qquad (4)$$

where $s$ is the entropy density and $\mu_i$ and $c_i \equiv \rho_i / \rho$ are the chemical potential and the concentration of species $i$, respectively. The time evolution of the entropy density as given in Eq. (4) is therefore intimately related to the balance equations (1) – (3). Furthermore, if rewritten in the form of a balance equation, it turns out that from the Gibbs relation one finds that the entropy flux $\mathbf{J}_s$ is given by

$$\mathbf{J}_s = \frac{1}{T} \left( \mathbf{J}_q - \sum_{k=1}^{N} \mu_k, \mathbf{J}_k \right), \qquad (5)$$

while the entropy production $\sigma$ is

$$\sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^{N} \mathbf{J}_k \cdot \left( T \nabla \frac{\mu_k}{T} - \mathbf{F}_k^{\text{ex}} \right) - \frac{1}{T} \tau \nabla \cdot \mathbf{u} - \frac{1}{T} \tau' : \nabla \mathbf{u}. \qquad (6)$$

Equations (1) – (6) do not constitute a closed set unless one can express the pressure $p$, the chemical potentials $\mu_i$ and the fluxes $\mathbf{J}_i$, $\tau$, $\tau'$ and $\mathbf{J}_q$ in terms of the independent variables $\rho_i$, $\mathbf{u}$ and $e$. Invoking the local equilibrium hypothesis, one can eliminate $p$, $\mu_i$ and $e$ in terms of the more convenient set of variables $\rho$, the $N-1$ concentrations $c_1, c_2, \ldots c_{N-1}$ and the temperature $T$ using the usual relations of equilibrium thermodynamics. In turn, the assumption on the linear laws together with the Curie theorem implies that

$$\tau = -\xi \nabla \cdot \mathbf{u}, \qquad (7)$$

$$\mathbf{J}_i = -\sum_{k=1}^{N-1} L_{ik}\left( T\nabla\frac{\mu_k}{T} - \mathbf{F}_k^{\mathrm{ex}} \right) - L_{iq}^{\mathrm{T}}\nabla T , \tag{8}$$

$$\mathbf{J}_q = -\lambda\nabla T - \sum_{k=1}^{N-1} L_{qk}\left( T\nabla\frac{\mu_k}{T} - \mathbf{F}_k^{\mathrm{ex}} \right) \tag{9}$$

and

$$\tau' = -2\nu\left[ \frac{1}{2}\left( \nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}} \right) - \frac{1}{3}\nabla\cdot\mathbf{u}1 \right], \tag{10}$$

where $\xi$ is the bulk viscosity, $L_{ik}$ are related to the diffusion coefficients, $L_{iq}^{\mathrm{T}}$ are related to generalized Soret coefficients, $\lambda$ is the thermal conductivity, $L_{qk}$ are related to generalized Dufour coefficients and $\nu$ is the shear viscosity. Note that the requirement that $\sigma$ be semi positive definite means that $\xi$, $\lambda$ and $\nu$ are positive, $L_{ik} = L_{ki}$ while the Onsager reciprocity implies that $L_{qi} = L_{iq}^{T}$ . Also note that, while other (more convenient) choices of forces and fluxes may be made depending on the physical problem under examination, the entropy production should remain invariant irrespective of the choice. Upon substitution of the linear laws, Eqs. (7) – (10) , into Eqs. (1) – (3) one gets the Navier-Stokes equations for the multicomponent mixture of inert fluids. Their explicit form is not very illuminating and therefore will be omitted. Suffice it to mention here that, from the mathematical point of view, such equations are parabolic partial differential equations so that the irreversible processes are described as diffusive phenomena. Application of these equations to actual problems depends on the specification of initial and boundary conditions on $\rho$ , $c_i$ , $\mathbf{u}$ and $T$ as well as on the availability of all the transport coefficients. These may come either from experiment or, in some cases, are the result of a microscopic approach.

While, as mentioned earlier, this theory has received vast experimental confirmation, the same experiments have provided a rather precise idea of the limits in which the assumptions cease to be valid. In one important class of experiments, a system is allowed to equilibrate in some sort of field, which is shut off, at $t=0$, and the relaxation back to the original equilibrium is followed. It takes a certain time, called the relaxation time, before the response of the system (the corresponding flux) becomes linearly related to the force. Within this period, the application of the classical theory is certainly inadequate. In turn, such knowledge (of which J. C. Maxwell was already aware) and other similar facts have given rise to different extensions and generalizations of the classical theory with varying degrees of success, in which the main (common) feature is the recognition that the purely diffusive description is no longer valid and that one should consider hyperbolic transport instead. However, none of these approaches, up to the present day, stands out as the universally accepted framework to deal with general non-equilibrium processes.

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**Biographical Sketches**

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