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NON-EQUILIBRIUM THERMODYNAMICS

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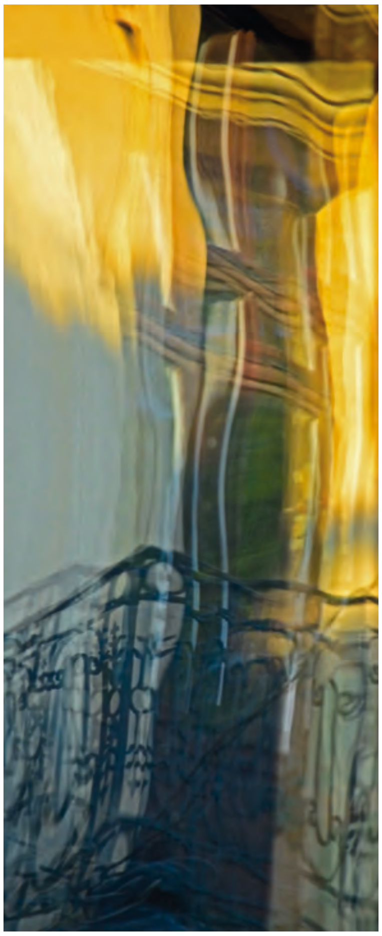
# Understanding non-equilibrium: a challenge for the future





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**Summary.** Far from equilibrium behavior is ubiquitous. Indeed most of the processes that characterize energy flow occur far from equilibrium. These range from very large systems, such as weather patterns or ocean currents that remain far from equilibrium owing to an influx of energy, to biological structures. Away-from-equilibrium processes occur on time scales ranging from nanoseconds to millennia. A difficulty of non-equilibrium physics is that usual thermodynamic functions of state like entropy or free energy do not generalize easily. The study of rare fluctuations of thermodynamic variables like densities or currents in stationary states has led to the identification of thermodynamic functions relevant in far from equilibrium situations. For a wide class of systems, called diffusive systems, it has been possible to develop a comprehensive unified theory, known as *Macroscopic Fluctuation Theory*, with considerable predictive power. Much remains to be done. Besides the purely scientific motivation, the challenge is to deal effectively with basic issues facing humanity like energy problems, climate control, understanding living matter. [**Contrib Sci** 11(2): 127-130 (2015)]

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## Introduction

Understanding non-equilibrium is considered a basic challenge in an authoritative report issued in 2007 by the Department of Energy of the United States with the significant title *Directing Matter and Energy: Five Challenges for Science and the Imagination* [1]. Non-equilibrium is the fifth challenge!

Far from equilibrium behavior is ubiquitous. Indeed (we freely quote from this report), most of the processes that characterize energy flow occur far from equilibrium. These range from very large systems, such as weather patterns or ocean currents that remain far from equilibrium owing to an influx of energy (in this case very large amounts of heat), to biological structures from humans to horseflies whose very existence requires the maintenance of non-equilibrium conditions through the consumption of energy. Non-equi-

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librium includes processes that store energy by pushing ions against a gradient and complex networks that carry out, for example, metabolic processes. Away-from-equilibrium processes occur on time scales ranging from nanoseconds to millennia.

The relevance of the subject emphasized in this report was brought to the attention of the physics community in 2008 in an article appeared in Physics Today, [2], a well-known journal of the American Institute of Physics.

Despite the pervasiveness of non-equilibrium systems and processes, most of the current understanding of physical and biological systems is based on equilibrium concepts even when they are not strictly applicable. The concepts of equilibrium and non-equilibrium belong to mechanics and thermodynamics. Here we are mainly interested in the thermodynamic point of view. Even when we deal with microscopic systems as in biological matter or nanostructures in advanced technology, the number of atoms or molecules involved is so large that thermodynamics and a statistical point of view provide the appropriate approach.

Classical thermodynamics deals with states of a system, possibly in contact with an environment, where no flow of energy is present. These states either do not change in time (equilibrium) or change very slowly so that they can be described by a sequence of equilibrium states. This is the notion of quasi static or reversible transformation. However, as emphasized in a well-known textbook on thermodynamics [3], to define in a precise way this notion we need to go beyond equilibrium:

> *"A quasi-static process is thus defined in terms of a dense succession of equilibrium states. It is to be stressed that a quasi-static process therefore is an idealized concept, quite distinct from a real physical process, for a real process always involves nonequilibrium intermediate states having no representation in the thermodynamic configuration space. Furthermore, a quasistatic process, in contrast to a real process, does not involve considerations of rates, velocities or time. The quasi-static process simply is an ordered succession of equilibrium states, whereas a real process is a temporal succession of equilibrium and non-equilibrium states."*

In spite of the inadequacy in clarifying its own foundations, classical thermodynamics has been very successful. Its principles were formulated in the 19th century at the time of the industrial revolution and provided the basis for conceiving and producing the necessary engines and machines. The first principle, recognizing that heat is a form of energy, states that

> 1. in a transformation of a system the variation of its energy is equal to the sum of the mechanical work and the heat exchanged.

Several formulations have been given for the second principle and we choose the one which is convenient for the ensuing discussion even though more abstract.

> 2. There is a quantity called *entropy* which in a transformation of an isolated system (universe) can either remain constant or increase. An equilibrium state is therefore a state of maximum entropy.

There is also a third principle which is of a more special character but will not be relevant in the following.

Entropy is a somewhat mysterious concept and when reading the original papers of its inventor, Robert Clausius, the first reaction is "How did he think of it?". Actually entropy was introduced by Clausius as a quantitative characterization of the equivalence of two transformations, i.e., transformations which can be substituted one to the other as they produce exactly the same effects. Its deep meaning was discovered by Boltzmann by taking a statistical point of view. He realized that the entropy is related in a simple way to the probability of a macroscopic state. A macroscopic state is characterized by few parameters like energy, density, temperature, pressure, etc. and many different microscopic atomic configurations are compatible with them. The probability of a macroscopic state is proportional to the number of the microscopic configurations compatible with these parameters. The more microscopic states correspond to the macroscopic parameters, the higher is the probability. Entropy is in fact the logarithm of such a probability times a universal constant. Intuitively, either a system stays in equilibrium, which in Boltzmann's view has maximal probability, or evolves spontaneously towards a more probable state. This is the reason why entropy increases. One may think of entropy as a measure of the microscopic complexity.

There is also a similar definition of entropy in information theory which measures the content of information of a message. A story says that such a terminology was suggested to Shannon, the inventor of the theory, by the famous mathematician John Von Neumann with the comment:

> *"You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statisti-*

*cal mechanics under that name, so it already has a name. In the second place, and more important, no one really knows what entropy really is, so in a debate you will always have the advantage."*

For systems out of equilibrium it does not exist yet a macroscopic description of a scope comparable with equilibrium thermodynamics. In non-equilibrium one has to cope with a variety of phenomena much greater than in equilibrium. From a conceptual point of view the non-equilibrium situations closest to equilibrium are the stationary non-equilibrium states which describe a steady flow through some system. Simple examples are the heat flow in an iron rod whose endpoints are thermostated at different temperatures or the stationary flow of electrical current in a given potential difference. For such states the fluctuations exhibit novel and rich features with respect to the equilibrium situation. For example, as experimentally observed, the space correlations of the density extend to macroscopic distances, which mean that the fluctuations of the density in different points of the system are not independent.

Stationary states appear as a natural generalization of equilibrium and the first important question is to what extent can we formulate a thermodynamics for these states based on general principles. The first difficulty encountered for such a program is that there is no obvious definition of basic thermodynamic concepts as free energy or entropy in states far from equilibrium. In the examples above energy flows through the bar or the wire and there is dissipation of heat in the environment, which is usually called production of entropy. In other words it is not easy to define entropy for the bar or the wire but it is natural to define entropy production in terms of the increase of the entropy of the environment which is supposed approximately in equilibrium.

We have considered so far two non-equilibrium situations. As we have remarked during a thermodynamic transformation, even if quasi-static, a system necessarily goes out of equilibrium. Another situation is provided by stationary states. Progress in the last twenty years has in fact concerned mainly these situations. Exact relations not restricted to quasistatic transformations have been established. A thermodynamics of stationary states has started to emerge.

The leitmotiv has been the study of fluctuations within a variety of approaches and physical models. Fluctuations of thermodynamic variables in equilibrium due to the atomic structure of matter is an old subject to which Einstein devoted a series of basic papers showing the strict connection between fluctuations and thermodynamic functions like free energy and entropy. In the last two decades important relationships have been established which are known under the heading *Fluctuation Theorems*. These refer mainly to microscopic systems characterized by a finite but arbitrarily large number of degrees of freedom, performing any transformation between equilibrium states. In particular these relationships permit to recover for example the variation of the free energy in a transformation by measuring the probability distribution of the fluctuations of the work done on a system over a certain interval of time. For a not too technical introduction see [4].

As an example of interesting application to biology of fluctuation theorems let us mention recent work on the statistical physics of phenomena like self-replication and adaptation [5]. In these papers it is argued that in many particle systems in contact with the environment there is a tendency towards self-organized states that form through increased dissipation and suppression of fluctuations. The authors suggest that these findings may lead to questioning a strictly Darwinian view of evolution.

The study of rare fluctuations of thermodynamic variables like densities or currents in stationary states has led to the identification of thermodynamic functions relevant in far from equilibrium situations. As one may expect such functions do not depend only on the state of the system but also on parameters describing the interaction with the environment. Besides a quantity which plays a role analogous to the free energy in equilibrium, other functions relevant for the thermodynamics of currents have been discovered. For a wide class of systems, called diffusive systems (the case of the bar or the electric wire above is included but also many biological processes), it has been possible to develop a comprehensive unified theory, known as *Macroscopic Fluctuation Theory*, with considerable predictive power [6]. For example, besides the already mentioned long range correlations, phase transitions possible in non-equilibrium but impossible in equilibrium are predicted or phase transitions in current fluctuations which may be relevant in view of minimizing the dissipation of energy.

It is important to realize that, due to the variety of non-equilibrium phenomena, the generalization of a thermodynamic notion may depend on the case in study.

An interesting example is provided by the so called active matter, typically biological matter like a "gas'' of bacteria in a fluid. A bacterium can be considered as a self-propelled particle. In this case the pressure in general does not satisfy an equation of state as it depends on the interaction of the bacteria with the confining walls [7].

Looking back on the progress of the last two decades we are definitely more confident in the possibility of understanding the many manifestations of non-equilibrium. Actually it is a very interesting time to work in this field both theoretically and experimentally as much has still to be done. Furthermore, besides the purely scientific motivation, the goal is to deal effectively with basic issues facing humanity like energy problems, climate control, understanding living matter.

**Competing interests.** None declared.

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**About the image on the first page of this article.** This photograph was made by Prof. Douglas Zook (Boston University) for his book *Earth Gazes Back* [www.douglaszookphotography.com]. See the article "Reflections: The enduring symbiosis between art and science," by D. Zook, on pages 249-251 of this issue [http://revistes.iec.cat/index.php/CtS/article/view/142178/141126]. This thematic issue on "Non-equilibrium physics" can be unloaded in ISSUU format and the individual articles can be found in the Institute for Catalan Studies journals' repository [www.cat-science.cat; http://revistes.iec.cat/contributions].