

## A path from equilibrium to nonequilibrium thermodynamics

*Personne n'ignore que la chaleur peut être la cause du mouvement, qu'elle possède même une grande puissance motrice: les machines à vapeur, aujourd'hui si répandues, en sont une preuve parlant à tous les yeux.*

On the basis of properties of rarefied gases (e.g. Boyle-Mariotte's law) Carnot develops, [1], his theorem on the **ideal efficiency** of machines operating by extracting or damping heat in two reservoirs and converting it into work.

The theorem shows that the most efficient machines **must operate running in a reversible cycle** in which vapor of water, air, alcohol or other liquid or solid materials, evolves through a **sequence  $\mathcal{P}$  of equilibrium states**.

Reversible transformations were essential in Carnot's analysis, and he *carefully insists* to clarify the subtle argument that permits to avoid regarding their definition, requiring for instance a difference in temperature which "can be considered as vanishing", an **oxymoron**:

*"À la vérité, les choses ne peuvent pas se passer rigoureusement comme nous l'avons supposé ...," [1, p.13-14].*

A few years later Krönig, [2], established **proportionality of absolute temperature** to average kinetic energy and Clausius, [3], wrote the first of the works leading to *entropy*, 1850, whose existence constitutes the *second law* of thermodynamics and is implied by Carnot's theorem.

If through a “path”  $\mathcal{P}$  a system *reversibly* evolves from state A to state B via successive equilibria then the the entropy variation is  $S_B - S_A = \int_{\mathcal{P}} \frac{dQ}{T}$

$dQ$  being the amount of heat received while in contact with a heat reservoir at absolute temperature  $T$ , whatever the reversible path  $\mathcal{P}$  is. This allows to set the value of the entropy of a generic equilibrium state, determining it up to an additive constant.

Entropy is important also in **irreversible processes**  $\mathcal{I}$ : by Clausius, in such a process  $S_B - S_A \geq \int_{\mathcal{I}} \frac{dQ}{T}$ .

**But** matter is constituted by atoms subject to mechanical laws: therefore the question arises **which is the mechanical interpretation of entropy ?**, hence of thermodynamics.

In 1866 Boltzmann, [4], proposed to link it to the purely mechanical Maupertuis's *Action Principle*, imagining atoms moving on a single periodic orbit **spanning all phase space points** compatible with mechanical conservation laws.

The continuous use of the second law, hence of Carnot's theorem, led to harsh **debates** on **ergodic hypothesis**, on **entropy**, and on resolution of the antinomy **reversible microscopic dynamics – irreversible macroscopic evolutions**, which in some respects is still going on.

It cannot be denied that in a adiabatic expansion of a gas (even perfect) the gas will settle on a new equilibrium: the entropy variation is easily computed to be strictly  $> \oint \frac{dQ}{T} = 0$ . So the gas **evolves via a reversible dynamics** to a state from which **it cannot return**: an apparent paradox.

Boltzmann and Thomson clearly pointed out the need to consider the time scale for the return, under the impossible invariability of the conditions of the experiment for a time far longer than time elapsed since birth of Universe. And it can be said that the problem is no longer considered one.

Attention evolved to inquire about the possibility of extending thermodynamics to cover phenomena which seem natural generalizations of the equilibria. Namely:

Phenomena in which external forces drive systems which, being in contact with thermostats, evolve towards a stationary state which is not an equilibrium state (because work of external forces is dissipated into the thermostats).

The question is then: is it possible to associate with each stationary state of a system quantities like “energy”, “pressure”, “temperature”, “entropy” ... among which exist general relations, possibly simple and universal, as it is the case if attention is restricted to equilibrium states.

A major step has been “Onsager’s reciprocity”, OR, of transport coefficients. It led to extending thermodynamics to the new stationary phenomena: with the OR being the first new universal, system independent relations.



However OR concern quantities expressing initial **deviation from equilibrium** (*i.e.* derivatives with respect to forcings evaluated **at zero value**): one would like to see what happens under more general situations, *i.e.* **reach generality and universality** comparable to that of equilibrium thermodynamics.

The modern approach has been to rely on Statistical Mechanics: in a way **giving up the idea** of building a theory of non equilibrium phenomena **on purely macroscopic grounds**, even though srestricted to stationary states.

Statistical Mechanics of equilibrium therm. is based on the **theory of ensembles**. To each **equilibrium state** is associated a **probability distribution** (Synonym="ensemble") on phase space (of huge dimension) yielding the average **in time of the few interesting** observables (pressure, density, energy, temperature,...) **far from all!**; and **even entropy** admits an expression in terms of the equil. probability distribution.

Is it possible to build a similar theory of ensembles, *i.e.* of families of PDF's depending on the macroscopic parameters determining the (properties of) stationary states of a system? There are key difficulties:

- (1) the connection Thermodynamics-Statistical Mechanics is via the ergodic hypothesis (motion visits a dense set on phase space)
- (2) and in equil. there is only one,[5, 6] or few (as at phase transitions) “reasonable” PDF on phase space which is invariant, *i.e.* does not change in time so that it can describe the frequencies of visit to phase space cells  $\Delta$  in an equilibrium state.

Assumption (1) which can be accepted in equilibrium **certainly cannot in non equilibrium**: simply because the presence of **driving** and the **corresponding dissipation** imply that at stationarity **only a subset** of the *a priori* available (*i.e.* compatible with the constraints and conservation laws) phase space, at least under strong forcing (**where OR fails**).

Assumption (2) **relies on Liouville's theorem**: *i.e.* that the evolution transforms **BUT strongly deforms** a volume element in phase space **without changing its volume**.

However it has become very clear that the Liouville volume is not, by any means, the only way of measuring the volumes  $\Delta$  which is invariant under the mechanical evolution, *i.e.* suitable to be interpreted as frequency of visit to  $\Delta$ .

Therefore the often invoked argument that the microcanonical ensemble is privileged **fails**. And the problem remains **even for the equilibria**, hence for the **microscopic interpretation of thermodynamics**.

A solution, **essentially due to Ruelle**, [7, 8], answers the above two questions. And **relies on the properties of chaotic motions**.

A motion is **chaotic** if most pairs of close initial data **separate at an exponential rate**.

As in the theory of ordered motions we use the **paradigm of the harmonic oscillators** (like to model **pendulum, elastic chains and strings, integrable systems...**), **likewise** in the theory of chaotic motions the **paradigm is the *hyperbolic motion***, of which the simplest example are the Anosov systems, which entered the scene of Physics in the '960's. Like the harmonic oscillators case, their properties are **very elementary although not really well known yet** in the field.

In great generality the property of such systems is that **if the initial data  $x$  are chosen with a distribution  $\rho(x)dx$  which has a density  $\rho$  on phase space, no matter which  $\rho$  is, will evolve in time visiting, as  $t \rightarrow \infty$ , any number of prefixed volume elements  $\Delta$  with a frequency  $\mu(\Delta)$  independent of  $\rho$ .** This remains true even when evolution is very dissipative and motions approach an attractor not dense in phase space.

This gives the possibility of solving both problems (1) and (2) including the case of equilibria.

(a) Any laboratory measurement is based on a “**protocol for the set up**”: inevitably the protocol generates initial states that **have some randomness**, which depends on the protocol, **in spite of attempts at avoiding uncertainty**.

The basic assumption is that a given protocol generates data which depend on several unknown quantities: nevertheless all protocols designed to study a given system are supposed to have some randomness expressible as a PDF which has a density  $\rho_P(x)$ : the **density is not known** but **the assumption is that it exists**. Formally:

*a protocol for an experiment on a system produces initial data affected by a (usually very small) uncertainty whose PDF has a density on phase space.*



(b) if the evolution is chaotic, **which is generally the case in the systems of interest for thermodynamics**, then it is a **hyperbolic evolution**. Formally:

*In the vicinity of the attractor the evolution is hyperbolic.*

In particular this applies when **system is conservative**.

The property **(b), chaos, and (a), unknown but existent randomness of initial data**, solves the problem of the frequency  $\mu(\Delta)$  of visit to sets  $\Delta$ : **uniquely, as a theorem on chaotic evolution** (*i.e.* hyperbolic). And in the case of conservative systems it **identifies the Liouville volume** as the **privileged volume measurement**.

The Liouville volume is not privileged because it stands obviously out the wide variety of invariant volumes that exist (with “equal rights”) as soon as the system exhibits chaotic motions, rather because the data have intrinsically some randomness with a PDF (typically not invariant) but which has a density  $\rho(x)$  (typically  $\rho(x)$  is concentrated on a very small vicinity of what the protocol is designed for).

The (a),(b) assumption therefore (via the simple hyperbolic motions theory) assign a unique PDF **determining the statistical properties of the (few) observables of interest:** hence, whether in equilibrium or in stationary non equilibrium, the states of a system are **identified with a well determined collection of PDFs.**

This is well known to happen in equilibrium where elements of canonical, microcanonical, grand canonical ensembles can be put in correspondence so that corresponding PDFs assign the same distribution to the values of the (few) observables of interest.

Just as in equilibrium it is possible that for macroscopic systems the same stationary states can be described by different PDF's, which however assign the same distribution to the values of the (few) observables of interest: hence we see the possibility of occurrence of several “ensembles” and a corresponding theory of their equivalence.

The question is then whether the above general views can be subject to tests.

Starting in the '980s there have been many tests on the chaotic evolutions in systems with statistical mechanics relevance although not rarely the A have made clear, at least implicitly, that they were not following the ideas (a),(b). Still the results presented were actually confirming the view.

Among the results have been the

- (1) extension of the Green-Kubo formula, by Ruelle,
- (2) and its applications to Atmospheric phenomena, [9]
- (3) a very large number of simulations at small as well as large forcings
- (4) the development of distinct ensembles to represent the same phenomena. In particular it has become clear that the different equations of motion can describe the same macroscopic evolutions

(5) For reversible evolutions the fluctuations of the entropy production over a time  $\tau$  have been shown to obey a universal law (the “fluctuation theorem”) which can be regarded as a generalization of OR

(6) the existence of dissipation has been shown to be interpretable, in some cases, as a spontaneous symmetry breaking opening, possibly, the way to the extension of the fluctuation theorems to irreversible evolutions, [10]

Finally a key question is whether it is possible to define a state function which **extends to non stationary equilibria the notion of entropy**. There is debate on the question because the formula  $S = k \log W$  **does not have an obvious extension to nonequilibrium steady states**:  $W =$  Liouville volume of phase space invaded by evolution of generic initial datum.

But out of equilibrium the **frequency  $\mu(\Delta)$  of visit to a volume  $\Delta$**  is in general **not expressed by the Liouville volume nor by an integral over  $\Delta$  of a not constant density**.

The question is too much under debate and it is better to leave it as a problem here (or for discussion in a different talk), [11].

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