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MASTER EQUATIONS VERSUS THERMODYNAMICS

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ABSTRACT.

The common parenthood of Master Equations and of irreversible statistical thermodynamics is Liouville's equation. With thermodynamics, dissipativity is introduced in Liouville's equation as a source describing interaction of the system with its surroundings. This leads directly to Onsager's phenomenological equations and to the discussion of possible coupling of irreversible flows. The validity of this approach is not restricted to the neighbourhood of equilibrium. With Master Equations dissipativity is implicate in the relevant matrix elements. Their complexity requires however often approximations which may impair the results.

The physical properties of systems at equilibrium may be described indifferently using thermodynamics or statistical mechanics. Thermodynamics stresses the system's macroscopic behaviour while statistical mechanics documents in a first step its motion at the microscopic level. The relationship between the two approaches is well known and absolutely satisfactory.

Non-equilibrium systems are characterized by irreversible changes (flows) of their properties in the course of time. Their macroscopic description requires kinetic equations relating the flows to some driving forces. Since Onsager [1], these are coined as the "phenomenological" equations. They express the driving forces for irreversible flows as functions of local thermodynamic properties. They are immediately related to the experiment. Their validity has been confirmed many times. Their principal merit is a description of possible coupling of thermodynamic flows [2].

The statistical counterpart of irreversible thermodynamics for describing non-equilibrium systems is Liouville's equation. This is related to the canonical equations of hamiltonian mechanics for many-body systems [3]. Its most popular transcription is the Master Equation. The latter equation and its several approximations (e.g. Fokker-Planck equation) have been used by many authors to describe systems far from thermal equilibrium, for which it is often alleged that irreversible thermodynamics is unsuitable [4]. This paper is to comment on the relationship between the statistical approaches and experimentally verifiable phenomenological descriptions of non-equilibrium systems.

The discussion of Liouville's equation is often restricted to conservative systems, that is when all the forces are derivable from a potential. This indeed validates hamiltonian mechanics. However it is clear that systems are not conservative when friction or similar forces which are not derivable from a potential are present [5]. This precludes in fact considering Brownian motion (force proportional to the velocity) unless a number of additional assumptions are introduced (Langevin solution).

Defining the conditions for dissipativity of the equations of the motion is a fundamental problem in non-equilibrium statistical mechanics. Dissipativity is the property of many-particles systems to forget their initial conditions in the course of time. The thermodynamic expression of this property is the trend of the entropy to grow until it reaches a maximum value compatible with the external constraints imposed to the system. The system is then said to be "ergodic". Dissipativity has been discussed by several authors in the past [3] and it is still a matter for discussion [6]. It is sometimes considered to be caused by some non-integrable distortion of the hamiltonian (e.g. Henon-Heiles systems, hard disks in a stadion etc... in classical dynamics).

At this point it is convenient to introduce an additional restriction to the definition of conservativity. A set of forces should be claimed to be conservative only if their sum is identically ~~to~~ zero at every moment. This unusual restriction excludes interaction with earth's gravitation field and more generally with all odd power contributions to the hamiltonian, because they refer to forces having their sources external to the system (see the Henon-Heiles system). Hence they are "stricto sensu" non-conservative.

The restricted definition excludes also the forces prevailing in systems of particles translating in a container and colliding with the walls. Here the time averaged sum of the forces vanishes but their instantaneous sum is not zero because the collisions are uncorrelated. Every collision with the boundary results in transfer of impulse between the container and the system and this influences the system's trajectory in the phase space.

Considering aforementioned restrictions, strictly conservative systems are integrable and hence non-dissipative. No matter how complicated a conservative hamiltonian may be, its eigenvalues are constants of the motion. Classically this results in quasi-periodic trajectories. Transitions between eigenstates or

jumps between different quasi-periodic trajectories require external intervention. Unless such events are allowed to occur, the system keeps forever the information about its initial conditions.

If Q is the quantum degeneracy of a motion, that is the number of eigenstates which are compatible with the constraints imposed to the system, the entropy is by definition:

$$S = k_B \ln Q \quad (1)$$

If our knowledge about the system is complete, we have $Q = 1$ and the entropy vanishes. With strictly conservative systems the entropy remains zero at all times: in fact with such systems the concept "entropy" is essentially academic.

Strictly conservative systems are however hardly conceivable, excepting perhaps the universe as a whole. For radiating atoms, spontaneous emission (dipole emission in classical dynamics) backed by absorption of black body radiation issued from the surroundings couples the system to its neighbourhood. For non-radiating systems there is gravitational interaction with the surroundings. Considering the constraints imposed by the boundaries enclosing the system, exchange of extensive properties (energy, momentum, impulse, polarization etc...) occurs whenever the system "feels" its boundaries. This happens even with highly diluted "collisionless" atomic beams, the properties of which are determined by their initial strong interaction with the beam forming device.

Dissipative interactions generate incoherent transitions between the eigenstates, thereby increasing the uncertainty about the system. When the incoherent jumps caused by the non-conservative contributions to the equations of the motion have made all the eigenstates respecting the external constraints to be equally probable, the system has become ergodic and its entropy is maximized. Subsequent conservative interactions cannot destroy the ergodicity of the system's probability distribution.

Liouville's equation is a continuity equation of the proba-

bility density (n) in the phase space. If one isolates in the hamiltonian the conservative (H) and the non-conservative contributions, the canonical equations indicate that the former ones lead to a flow ($[H, n]$) in the phase space. The latter contributions behave as a source (J) modifying this flow.

$$\dot{n} = [H, n] + J \quad (2)$$

The introduction of a source as the expression of the interaction between the system and its surroundings in Liouville's equation is unusual. It clarifies however the special role of the non-conservative contributions to the general motion. If the system is in equilibrium with its surroundings the source vanishes.

Description of irreversible processes requires a correct expression for the source and ~~of~~ its effect on the system's macroscopic properties. The source has clearly a double role. By generating incoherent jumps between the system's accessible degenerate states the source ensures ergodicity of the motion. It allows also extensive properties (energy, impulse, etc...) to be exchanged or to flow between the system and its surroundings, thereby relaxing possible initial constraints.

There are in principle two routes for solving Liouville's equation. One of them starts by treating individual jumps in the phase space by means of kinetic equations and predicts in a second step the rate of changes of the system's macroscopic properties by integrating the individual jumps over the phase space. This is the "Master Equation" approach. By contrast, irreversible thermodynamics addresses directly the macroscopic properties and their changes or flows. The probability density in the phase space is therefore expressed as a function of the system's extensive properties. It will appear that this is equivalent to expanding $\ln(n)$ as a linear superposition of a complete set of orthogonal functions defined in the phase space, a procedure which mimics expansion of wave functions in a Hilbert space. In a second step the forces are defined which drive the irreversible flows. In doing so the symmetry properties of the system's hamiltonian are considered. We shall start with the second approach.

In quantum mechanics every state is completely determined by its set of eigenvalues (X_k) in response to a complete set of mutually commuting observables (operators) [7]. The number of independent observables equals the number of irreducible representations of the group of symmetry operations (acting of the coordinates) which keep the hamiltonian unchanged. The relevant set of eigenvalues may therefore be considered as the components of a vector. Vectors referring to orthogonal states are mutually orthogonal. The set of irreducible symmetry elements of the hamiltonian (R_i) interchanges degenerate orthogonal states. Their action on the eigenvalues themselves is:

$$R_i (X_k) = \omega_{ik} X_k \quad (3)$$

where ω_{ik} is the relevant member of the symmetry group's character table ($\omega_{ik} = \pm 1$). (e.g. sign reversal of the cartesian coordinates reverses the sign of the impulse while the internal energy remains unchanged).

The classical counterpart of quantum operators are functions defined in the phase space that give the corresponding expectation values [$\bar{g}_k(p, q)$] on weighted integration in the phase space (r):

$$X_k = \int n(p, q) \bar{g}_k(p, q) dr \quad (4)$$

From first principles [8] the classical entropy is given by:

$$S = k_B \int [n(p, q) - n(p, q) \ln n(p, q)] dr \quad (5)$$

The discussion which follows is classical (continuous phase space) but it is easily extended to a quantized phase space.

In non-equilibrium systems parts of the system or different degrees of freedom between which irreversible flows set in may be separately in equilibrium. Each subsystem (i) is characterized by its own distribution function [$n_i(r)$] which maximizes its partial or local entropy, while considering the local extensive properties (indexed "k") as constraints. Using the method of lagrangian multipliers, the local distribution function turns out to be (classical Maxwell-Boltzmann statistics):

$$n_i(r) = \exp[\lambda_{iN} + \sum_{k \neq N} \lambda_{ik} \phi_k(r)] \quad (6)$$

If the partition function is defined as follows:

$$Z_i(\lambda_{ik}) = \int \exp[\sum_{k \neq N} \lambda_{ik} \phi_k(r)] dr \quad (7)$$

it is easy to verify that the extensive properties (X_{ik}) are linked to the conjugate intensive variables (λ_{ik}) by the following equations:

$$X_{ik} = N(\partial \ln Z_i / \partial \lambda_{ik}) \quad (8)$$

Using equation (5), the local entropy becomes:

$$S_i = k_B [\ln(Z_i^N / N!) - \sum_{k \neq N} \lambda_{ik} X_{ik}] \quad (9)$$

Its partial derivatives versus the average value of the extensive properties yields the conjugate intensive variables:

$$\partial S_i / \partial X_{ik} = -k_B \lambda_{ik} \quad (10)$$

Hence the time derivative of the entropy reads:

$$\dot{S} = -k_B [\lambda_{iN} \dot{N}_i + \sum_{k \neq N} \lambda_{ik} \dot{X}_{ik}] \quad (11)$$

We consider now the set of symmetry operations which keep the hamiltonian unchanged. The entropy is by definition invariant under any such operations. Considering equations (9, 10 and 11) it appears that the extensive properties and their conjugate intensive variables are contravariant (their products are invariant).

Interactions between subsystems in a non-equilibrium system or between the system and its surroundings (thermostat) leads to exchange of extensive properties. The first law of thermodynamics (conservation law) says that efflux from any subsystem equals influx to its surroundings. We consider exchange between a system and a thermostat.

Exchange causes the thermostat's entropy to change according to an equation analogous to eq. (11). The total entropy change (sum of that of the system and that of the thermostat) appears to be:

$$\dot{S} = k_B [A_N J_N + \sum_{k \neq N} A_k J_k] \quad (12)$$

where A_k is the "affinity" conjugate to flow J_k . This equation is well known in irreversible thermodynamics [9]. The total entropy change is positive and it vanishes at equilibrium. Equilibrium is characterized by vanishing affinities.

Discussion of irreversible processes in terms of entropy creation is not very useful unless it is supplemented by suitable kinetic equations relating the flows to the affinities. Onsager

has suggested to use linear phenomenological equations. Here linearity is only a convenient approximation but it seems to be verified under wide ranges of experimental conditions. Coupling of flows generates off-diagonal coefficients [1]:

$$J_k = \sum_e L_{ke} A_e \quad (13)$$

Onsager has demonstrated in his famous paper that the matrix of the phenomenological coefficients is symmetric ($L_{ke} = L_{ek}$).

Introducing eq. (13) in eq. (12) yields:

$$\dot{S} = k_B \sum_k \sum_e L_{ke} A_k A_e \quad (14)$$

We apply now any abovementioned symmetry operation to equation (14). If the set of extensive properties which has been chosen to describe the system responds to equation (3) (linearly independent observables), invariance of the entropy creation implies that the matrix of the phenomenological coefficients be diagonal. If not, we have necessarily coupled flows.

The conclusion is that for the kinetic equations relating flows to generalized thermodynamic forces to be diagonal it is compulsory that the generalized forces be affinities (differentials or gradients of intensive variables) and the flows must be related to linearly independent observables. This is a generalization of Curie's well known symmetry rule [9].

To the latter symmetry rule there are no limitations regarding to how far the system is removed from equilibrium with its surroundings. Possible non-linearity of Onsager's phenomenological equations does not impair the general conclusion.

We turn now to the "Master Equation" approach. It is based on the kinetic treatment of individual jumps in the phase space [10]. Its predictions concerning coupling of thermodynamic flows should be identical to those presented above.

The "Master Equation" has been discussed by many authors [4]. It may be written:

$$\dot{n}(r) = \int W(r' \rightarrow r) n(r') dr' - \int W(r \rightarrow r') n(r) dr' \quad (15)$$

It is a transcription of Liouville's equation (2). Dissipativity is assumed implicitly in the transition probabilities.

Quoting Haken one could argue: "The crux to derive a

Master Equation is not so much writing down the expression which is rather obvious, but to determine the transition rates explicitly".

In fact, with truly conservative systems there is no mechanism to drive jumps between the system's eigenstates. It has been stressed above that transitions require external intervention. (One of such interventions may be spontaneous emission where the system couples with the light field).

Let us assume that the transitions required by equation (15) are stimulated by some unspecified mechanism. Our present goal is to predict experimentally observable macroscopic flows of extensive properties (relaxation = relief of constraints). This implies integration of the relevant contributions in the phase space.

Defining the transition probabilities from first principles is difficult and approximations are required.

With Brownian motion, relaxation involves exchange of "impulse" (friction) with the thermostat. Though transfer of impulse is hardly conceivable without simultaneous exchange of kinetic energy (heat), the latter is assumed to be so fast that the average kinetic energy remains locked to its heat bath value. This allows adiabatic elimination of the fast process. Relaxation is then controlled by its rate determining step: friction. In this particular case, the properties that are accessible to the experiment are clearly linearly independent (see comment after equation (3)). Flow of impulse and of kinetic energy are not coupled. The non-equilibrium (steady state = dynamical equilibrium) value of the system's temperature equals its true equilibrium value, that is the temperature of the thermostat (statical equilibrium). This is the ideal case to be solved by Master Equations.

In many cases however, irreversible flows are coupled (e.g. Soret effect, Hall effect, Knudsen effect etc.). This happens also in quantum optics (laser physics [11]) where interaction of light with radiators causes several extensive properties to flow between the system and its surroundings. Some of them may be linearly independent (energy or inversion and polarization)

for symmetry reasons but their intensities are not (the polarization squared and the inversion are not linearly independent).

The driving forces for the relevant flows, obtained by integration of the transitions in the phase space should reflect this interrelation of the relaxing properties. Approximations which would ignore their coupling should be rejected.

Some flows (e.g. inversion and impulse in gas lasers or in laser driven systems) are linearly independent when the electromagnetic field is off and grow oblique when the electromagnetic field is turned on. The resulting shift of dynamical equilibria versus the static values for the fastest relaxing properties, the flows of which may be eliminated adiabatically, are the cause of very interesting non-linear phenomena. (e.g. laser cooling [12,13], radiation induced osmosis [11] etc.). Their prediction using Master Equations requires care in considering the symmetry properties of the transition probabilities. Errors are easily generated on introducing the necessary additional assumptions or approximations.

It is not the purpose to censure Master Equations "in se". Only some of the assumptions are questioned that lead to results where irreversible flows are expressed as functions of the relaxing properties themselves (rate equations) and not of differences of intensive variables (affinities), as the equation for entropy production suggests they should.

It has been stressed above that statistical thermodynamics is based on fundamental properties of hamiltonian mechanics (symmetry). Excepting perhaps possible distortion of the linearity of phenomenological equations far from equilibrium, nothing restricts its principles to the immediate vicinity of equilibrium.

Thermodynamics is based on simple mathematical tools. Its results are immediately transferrable to the experiment. As a conclusion it is suggested that the present condemnation of irreversible (statistical) thermodynamics be reconsidered, also in quantum optics.

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