The source of irreversibility in macroscopic dynamics

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1 Introduction

Distortion of macroscopic systems initiates spontaneous and irreversible dynamic processes tending to restore the previous state of equilibrium or to establish a new one. There is no doubt that in this context the word irreversibility points to the fact that the initial perturbation is not regenerated spontaneously. Unless promoted by some external action, it belongs to the past. Concerning the definition of an equilibrium state, the scientific literature is less specific, although everyone has a personal feeling about what this word should mean. The most common definition, but not the only one, relates equilibrium conditions to the extremum of certain thermodynamic potentials [1]. It will be shown that this definition is insufficient.

Historically, the debate on irreversibility started with Joule’s experiment, when he allowed an ideal gas to expand spontaneously from a small vessel into a larger one. The process was carried on inside a calorimeter. Expansion proceeds apparently without exchange of heat with the outside world. If by isolation it is meant that the system exchanges nor heat nor matter with the outside world, following the tradition in conventional thermodynamics, it must be concluded that spontaneous and irreversible expansion of the gas is the expression of a fundamental property of isolated systems. In the literature, the words closed and open system are sometimes used to indicate whether they are isolated or not. The latter expressions are however ambiguous and they will not be used here.

In passing, let it be stressed that the meaning the dictionary gives to the word isolation is stronger than that suggested above. It points to objects that are left alone and excludes therefore all possible interactions whatever with other systems. By contrast, the weak thermodynamic meaning allows elastic collisions with the boundaries (energy conservation).

The word irreversibility too has different connotations. At first, taking the colloquial meaning suggested above (no spontaneous recurrence of previous conditions), the word does not specify whether or not the memory of earlier
perturbations remains in the system under some hidden form.

Secondly, in the context of mechanics, the word expresses the response of the dynamics to the fictitious mathematical operation consisting in the sign reversal of the variable time. With this definition, systems for which the equations of the motion are not invariant with respect to changing \( t \) into \(-t\) are irreversible.

Closely connected to the latter and referred to mainly in numerical simulation of relaxing systems, irreversibility concerns also the effect of artificially reversing the sign of the time increment \( dt \), starting at some given instant in the course of the dynamic process. If this mathematical manipulation does not reproduce the initial conditions as an echo, the dynamics is called irreversible. The variety of definitions of this important keyword leads to frequent confusions.

In trying to rationalize irreversible dynamics of isolated systems, Ludwig Boltzmann suggested that the directionality with respect to time would be caused by inter-particle collisions or interactions. Considering that for his contemporaries isolation was understood almost \textit{stricto sensu} (only elastic reflections at the boundaries allowed), thereby validating Hamiltonian mechanics, and that the mathematical definition of irreversibility (time-symmetry) was withhold, Boltzmann’s suggestion unlocked a storm of dispute. Contrasting with the initial turmoil, a majority of authors seems now to be confident in Boltzmann’s kinetic theory \[2,3,4\], although intellectual discomfort remains apparent \[5,6\]. The question is still active in the scientific literature.

The microscopic deterministic laws that govern collisions are strictly symmetrical with respect to sign reversal of the variable \( t \). For justifying the apparently unexpected violation of the time-symmetry of global dynamics of many-particles systems, it is assumed by many that this is the consequence of the extremely large number individual interactions and also of their complexity. Progress booked in recent years both in mathematics and in statistics is alleged to support the suggestion. Chaotic motion is also are frequently referred to in view of strengthening the demonstration. However, arguments imported from neighbouring domains of sciences without double check concerning conformity of the definitions and compatibility of the initial assumptions lead to ambiguous conclusions.

Symmetry ranks undeniably among the most robust general features of nature, resisting all mathematical manipulations, limit operations or transitions from discontinuous to continuous models. This fact is confirmed in all
branches of sciences, like spectroscopy, crystallography, geometry etc. Considering the extreme strength of symmetry properties, mathematical manipulations consisting merely in limit operations performed on scaling factors in order to explain breaking of the time-symmetry in the global dynamics of isolated systems in the many-particle limit cannot be justified.

This paper is to show that the source of irreversibility is to be fetched in the unavoidable interaction with the outside world. To that end the discussion is structured as follows. In the first section, the traditional Joule experiment is analyzed. It stresses that the global process consists in the superposition of two fundamentally different independent mechanisms: one is conservative and the other one dissipative. Dynamic properties of the conservative part and of the dissipation part of many-particles mechanics are the subject of the two sections to follow. Finally, the entropy and its change in non-equilibrium processes are examined.

2 Joule experiment

In the literature, discussion concerning the directionality of the time’s arrow is often introduced intuitively on the basis of a simplified description of Joule’s experiment. We consider an isolated box consisting of two compartments, the parts being filled with gas at different pressures. The observed long time evolution towards homogeneous distribution following the rupture of the division is taken as picturing the irreversible behaviour of the global dynamics. In this context irreversibility means non-recurrence of the initial conditions.

Joule’s purpose was to investigate possible heat exchange with an external calorimeter as the result of spontaneous expansion. With an ideal gas, if no mechanical work is allowed to be performed, when the system has reached its final state, he observed no net heat exchange with the surroundings. His observation did however not preclude possible fluctuating exchange with zero balance. For the observer, the system behaves apparently as if it was isolated according to the usual thermodynamic meaning of the word.

Let us make the experiment more realistic by examining instead the effect of puncturing an air inflated bladder inside either an acoustic reverberation hall or an anechoic chamber. The conditions may be approximated simply by comparing the properties of a completely furnished room and that of the
same room stripped of its furniture, curtains and rags. In the two cases the excess air contained in the bladder disseminates spontaneously throughout the rooms but the subsequent process is very different indeed. In the reverberation hall an acoustic perturbation is created and, the better the walls’ reflecting quality, the longer it remains. By contrast, in the anechoic room, the perturbation vanishes promptly.

The first question the double experiment raises is that of the definition of the state of equilibrium. The final state reached in an ideal reverberation room allows some energy to be stored in a coherent collective motion (acoustic perturbation) where it remains as the memory of the initial conditions. With walls shaped in particularly favourable forms, the initial information may even be partially retrieved as echos. By contrast, in the anechoic room, memory of the past is soon forgotten. Clearly only the latter condition may be considered as an equilibrium state.

The air in the rooms is the same, and therefore also the frequency and the quality of the inter-particle collisions. The only difference between the two experiments is the nature of the walls. If we define relaxation as being the process whereby the distorted system reaches equilibrium, the role of the interaction with the neighbourhood (walls) is trivial. If equilibrium is to be reached, the system cannot be strictly isolated.

Let us examine the sequel of events leading to final relaxation. When the membrane is ruptured, a stream of gas is ejected from the vessel at the higher pressure, thereby forming a collective motion of the particles. Energy that is transferred into the jet is subtracted from the initial thermal supply (adiabatic expansion, constant entropy). As a result, the system’s temperature drops ¹.

The wall opposite the puncture reflects the jet and turns the collective motion progressively into an acoustic perturbation with the same energy. The spectrum and phases of this motion reflect the initial conditions and the shape of the reverberating walls (coherence). While dissemination of the particles throughout the system occurring during this part of the motion is irreversible according to the no recurrence definition (known in mathematics as mixing [7]), information about the past is not forgotten, no matter how intricate the motion of the particles may be.

Final relaxation of the coherent motion starts now. It consists in ther-

¹not the average kinetic energy but $(\partial S/\partial E)^{-1}$
malizing the energy stored in the acoustic perturbation, thereby balancing or neutralizing the initial temperature drop. When full equilibrium has been reached, the information about the initial conditions is completely lost.

3 Conservative trajectories

The scenario discussed above shows that the global motion of macroscopic systems is governed partly by Hamiltonian dynamics (jet forming and dissemination or mixing) and partly by dissipation interaction with the neighbourhood (final relaxation). We focus now on the Hamiltonian part, neglecting whatever would make strict isolation ineffective. If the Hamiltonian is not an explicit function of time, the dynamics it supports is by definition conservative and deterministic\(^2\).

A system is said to be conservative if the force field is such that work done around a closed orbit is zero \(8\). Physically it is clear that dynamics cannot be said to be conservative if friction or other dissipation forces are present.

In classical mechanics, determinism or causality is the property according to which, if two dynamical systems have the same laws of motion and are in the same dynamic state at some particular time \(t_0\), then they must be in the same dynamic state at all times \(9\). The corollary is that no more than one trajectory passes through each point in phase space, or else that different phase space trajectories never cross. Let it be stressed that this discussion uses the word trajectory as a reference to global many-particles motions but never to the individual paths of separate particles.

In the context just mentioned, dynamic state is the same as the word microstate used by some authors. It represents a point \(p_1...p_{3N}, q_1...q_{3N}\) in the many-particle phase space. A phase space trajectory is the succession of points (or phases) that pictures the system as time goes on. Hamilton’s canonical equations are its parametric equations. Considering that there is only one trajectory passing through a given phase point, there is a unique relationship between microstate and trajectory. Unless the investigation concerns singular properties of individual phase points along a given trajectory,

\(^2\)Conservative Hamiltonian mechanics is deterministic but friction and other irreversible macroscopic transport properties are too, without being conservative.
the definition of *microstate* may therefore equally be covered by the complete trajectory. The two words represent the same reality.

Action referred to as *mixing* is often quoted in the literature [7]. It describes the way our perception of the initial conditions changes as time goes on assuming a deterministic and conservative environment. This perception concerns the distribution of individual phase points along a single trajectory in phase space. In the above mentioned example of an expanding gas, dissemination of the particles throughout the volume is synonymous to mixing.

Let it be stressed that, parallelling ambiguity concerning the definition of true equilibrium, there is some confusion in the recent literature concerning the alleged relaxing property of mixing. The example of the expanding gas suggests that, contrasting with mixing, relaxation belongs to the second step of the global process.

Mixing does apparently not require inter-particle collisions or interactions [7]. The relevant dynamics may be exemplified by a system of many non-interacting particles, translating back and forth along a line between two boundaries (distance $2D$), where reflection of the individual motions is elastic (energy conservation).

We consider a many-particles system and assume that the velocity distribution is Gaussian (Boltzmannian). Hence

$$g(v) \approx \exp\left(-\beta \frac{mv^2}{2}\right).$$

(1)

The relevant parameter $\beta$ is not the reciprocal temperature $^3$.

We assume that the initial conditions determining the single global trajectory in phase space are represented by a giant density fluctuation at some given position along the line. It would be represented by a $\delta$-function. It is then easy to compute the density distribution at any later time. The sharp fluctuation disappears, leading at long times to a nearly flat particle distribution, as if the initial perturbation had relaxed. However, tiny irregularities persist indicating that the initial fluctuation has turned into noise.

If the number of particles is high, the initial fluctuation does not recur spontaneously after a reasonable delay (Poincaré recurrence). The process

^3In this model the system is forced to remain on a single global trajectory. As it will be shown later, its entropy is therefore zero and the concept temperature ($\partial S/\partial E$)$^{-1}$ is meaningless.
responds to the colloquial meaning of irreversibility. However, according to
the mathematical or mechanical definition of the word, the relevant dissemin-
ation is by no means irreversible. Indeed, if the sign of the velocities of
all the particles is artificially reversed at any instant, the global trajectory
defined by the initial fluctuation is made to run in the opposite direction
and the latter is reproduced as an echo. The information represented by
the initial conditions was still present in the system although, due to the
diversity of the individual velocities, the sharp starting impression has been
progressively hidden to the observer.

The impression the observer has about the system’s conditions and its
change in the course of time may be expressed by the evolution of the position
of the centre of mass. Let \( X(t) \) be this position. If \( x(v, t) \) is the position of
any particle with velocity \( v \) at time \( t \), \( X(t) \) is defined as

\[
\frac{X(t)}{X(0)} = \frac{\int g(v) x(v, t) \, dv}{\int g(v) x(v, 0) \, dv}.
\] (2)

Starting from the initial giant fluctuation, supposing this is eccentric with
respect to the boundaries, as time goes on, the particles disseminate and the
centre of mass moves towards the system’s geometrical centre (\( X(t = \infty) = 0 \)). By computation, the general expression for the dynamical evolution of
\( X(t)/X(0) \) is easily shown to be

\[
X(t) = X(0) \exp[-\phi(t^2)].
\] (3)

There are no odd powers of \( t \) in the dynamics. If the initial fluctuation is
situated at \( x = \pm 0.8D \), the result is almost a pure Gaussian:

\[
X(t) - X(\infty) \approx X(0) \exp[-0.62 \left( \frac{t}{\tau} \right)^2],
\] (4)

\[
\tau = \sqrt{\frac{\beta m}{2}} D.
\]

For other initial conditions the decay is not very different. In all cases, the
very fast Gaussian-like decay is by no means comparable to the exponential
or multi-exponential dynamics of conventional relaxation.

The general conclusion is not modified if collisions or chaos generating ele-
ments (e.g. Sinai billiards) are included in the dynamics. Only computation
becomes harder. Possible rounding-off errors produced at every iteration step cause an artificial relaxation that has nothing in common with exact dynamics.

4 Dissipation and fluctuations

Conservative motion defines trajectories in the many-particle phase space. By forbidding transitions between different trajectories it preserves the memory of the initial conditions. For transitions between trajectories to occur, the conservative motion must be perturbed. This occurs every times the system interacts with its boundaries or with whatever represents its neighbourhood, like the ubiquitous thermal electromagnetic radiation and gravitation fields. Export and import of information being uncorrelated, the transitions cause loss of information and irreversible relaxation of the initial single microstate.

A macrostate is by definition the observational condition of a system where some or perhaps all the trajectories (microstates) belonging to a narrow band of energy hypersurfaces or energy shells in phase space are accessible.

With systems of translating particles, interaction with the outside world occurs every time a particle hits the walls. Every collisions of any particle with a wall interrupts the running canonic global trajectory and starts a new one with possibly modified initial conditions. The average lifetime of the trajectories depends on the impact frequency of particles with the walls.

More assumptions are needed to predict the effect of collisions with the walls. If the latter are perfectly rigid, so that they behave as virtual particles with infinite masses, only momentum is transferred. When the impact is over, the wall has gained momentum from the particle but no velocity, because its mass is infinite. In the same time the wall has given to the particle an equal amount of momentum in the opposite direction, allowing the new trajectory to start in conditions that are rigourously correlated with the previous one. The conservative character of the motion remains.

Real atoms and molecules in the walls have finite (effective) masses and they oscillate about their equilibrium positions. The result is that, contrasting with the picture drafted above, transfer of momentum at every impact is associated with some transfer of energy. Given the initial trajectory of the incident particle, the exact return path is unpredictable, because the motions
of the collision partners are uncorrelated. Some impacts with the wall atoms hit the incident particle harder and some less.

If the wall atoms oscillate about fixed positions, the average transfer of energy over a period of time that is long when compared to the collision periodicity with the walls is nil, while every single impact imports fluctuations about this average value.

The average lifetime of conservative trajectories in phase space is an important dynamic parameter. Its value equals the reciprocal of the average global periodicity of the collisions with the walls times an efficiency parameter. Referring to Joule’s experiment mentioned above, with hard reflecting walls the efficiency parameter is extremely small; with soft walls it approaches 1.

With experiments where the resolution time is made exceptionally fine (e.g. very short laser pulse experiments), the parameters of individual running motions are accessible and well defined single trajectories may be observed. The particular phase or the location of the system’s representative point along a defined trajectory in phase space is then observable. Such systems are practically isolated during the time of observation. Measurements on systems where immediate phase information remains pertinent follow the traditional laws of conservative mechanics. Statistics and thermodynamics are meaningless to them.

If by contrast the experimental resolution time is long enough, as it is the case with most relaxing properties, the system is allowed to perform stochastic jumps between the accessible trajectories by exchange of momentum, energy etc. with its surroundings. Phase information along single trajectories or even the definition of particular trajectories in phase space become irrelevant. Measurements are then restricted to statistics. Description of the system and eventually of its dynamics implies the use of thermodynamic arguments.

5 The Entropy

The macrostate of thermodynamic systems is defined unambiguously if the complete set of parameters representing the constraints, either external or internal, implied by the system’s particular observational state is mentioned both qualitatively and quantitatively. Any function determined completely
by such parameters is a function of state.

In 1865 Clausius discovered a function of state that changes when heat (energy, excluding work) is exchanged reversibly with the environment. This function, Clausius’ entropy, is defined as a differential. Assuming a reversible process, the definition reads

\[ dS \geq \frac{dQ}{T}, \]  

(5)

where \( T \) is the system’s temperature. Equal sign refers to reversible processes. This fundamental experimental definition implies net transfer of heat and therefore interaction of the system with its environment.

Clausius’ requirement that the process would be reversible for the equal sign to be valid means that the system may not depart from equilibrium during the whole process. This specification is rather ambiguous, as it relates to a property (equilibrium) that is by itself insufficiently defined. Instead, let us suggest that the word reversibility used in this context implies that no coherent or collective motion is allowed to be generated by the process or that it has been made to relax.

The physical meaning of the state function entropy and especially the discovery that it increases when the system is the subject of spontaneous or irreversible processes in apparently isolated conditions (conservation of energy and matter) has intrigued many physicists and philosophers. Having established a relationship between the entropy and some kind of observational probability, some try to attribute to this concept an anthropomorphic character [10]. It would be the measure of our personal lack of information concerning the system’s conditions. This strange suggestion that personalizes a function of state indicates that profound confusion prevails concerning the definitions.

In statistical mechanics, which is the theoretical branch of thermodynamics, the definition of entropy goes back to Ludwig Boltzmann. It is summarized by his famous equation

\[ S = k_B \ln[W(A)]. \]  

(6)

For the inventor, \( W(A) \) meant \textit{wahrscheinlichkeit} which is probability. Digging for the realities hidden behind this word may lead to some controversies but, using the same initial letter, most authors wisely prefer now the English \textit{weight of the given observational state}. The latter is interpreted as the
volume accessible to the motion in phase space, given the set of constraints (represented here by the collective variable $A$) that describe the system’s particular macrostate (observational state). Let it be noted that an equilibrium macrostate is usually defined by its total energy $E$, particle number of any sort $N_r$, and physical volume $V$, which are the traditional microcanonical variables.

As such, the definition of $W(A)$ misses normalization. This leads to the introduction of an arbitrary constant in the entropy. Planck filled the blank [11] by suggesting that $W(A)$ is the total number of independent quantum states (quantum state = microstate) compatible with the given macrostate. The latter represents the third law of thermodynamics according to which, if only one state is accessible, the entropy is zero.

Rephrased with Planck’s conclusion, Boltzmann’s entropy clearly favours a quantum description of the motion. Unfortunately, quantum mechanics does not refer directly to phase points or trajectories in phase space as does classical mechanics. By contrast, the quantum-classic correspondence implies that every global quantum state is pictured in the classical phase space by a finite region with a $6N$ dimensional phase volume measuring $\hbar^{3N}$. The number of available classical trajectories respecting the state defining constraints equals the ratio of the accessible phase space volume to $\hbar^{3N}$.

For Boltzmann’s entropy to be a pertinent function of state, accessibility of several (many) quantum states or trajectories is required. In a strictly conservative environment, the dynamics being described by a single global trajectory, no matter how intricate (chaotic) this may be, the necessary transitions between different trajectories or quantum states are not allowed. Then, according to the definition, the entropy is zero and it does never change. This conclusion is consistent with Liouville’s theorem that claims conservation of the measure in phase space when the mechanics is conservative.

Relaxation implies relief of constraints. It opens the way to an enhanced choice of quantum states or trajectories. Accessibility of more trajectories increases Boltzmann’s entropy.

Accessibility implies swift transitions between many trajectories or quantum states during the observation period. This depends on fast uncorrelated action of the environment with exchange of mechanical properties (momentum, energy). As a corollary and as expected by the statistical nature of the thermodynamic functions it appears that the definition of the entropy implies averaging over the time. The time resolution linked to the definition
of the entropy is the average life time of the conservative trajectories.

In view of the high impact rate of macroscopic systems with their boundaries, the period of time over which averaging is required may be extremely short indeed. For complex relaxing systems, equilibration of the different constraints with the outside world may not be equally fast. The fastest relaxing process concerns usually thermalization of the translational energy. The relevant intensity (translational temperature) reaches its environment value. The residual dynamics is governed by the least efficiently exchangeable properties.

In describing equilibrium states (e.g. for a one-component gas), the extensive variables mentioned traditionally are $E, V$ and $N$. That are the basic microcanonical constraints. In order to specify unambiguously non-equilibrium macrostates, where additional constraints prevail, additional extensive properties must be included. This may be for example the momentum associated with a possible collective or coherent motion of the system, in which some of the total energy is stored (e.g. the jet or the acoustic motion in Joule’s experiment). Many other possible distortions with respect to equilibrium may be envisaged, like moments of the energy or density distribution, etc.

Let the list of the extensive properties of a macroscopic system defining a particular macrostate be written in general $X_r$. By differentiating the entropy with respect to the set of $X_r$, we get by definition the set of conjugate intensive variables or intensities $\xi_r$.

$$dS = \sum_r \frac{\partial S}{\partial X_r} dX_r = -k_B \sum_r \xi_r dX_r. \quad (7)$$

The temperature $(\partial S/\partial E)^{-1}$ and the chemical potential $-T(\partial S/\partial N)$ are not new. In non-equilibrium conditions, the equation generalizes the definition, covering now also the intensities conjugate to the additional non-equilibrium constraints representing the particular macrostate. The non-conventional procedure consisting in mentioning the latter intensities has been introduced elsewhere [12].

Equation (7) is Gibbs’ celebrated differential equation, generalized by including the non-equilibrium constraints explicitly. In a simplified model of the spontaneously expanding jet referred to above (velocity of the collective motion: $\vec{v}$), the new version of Gibbs’ equation reads

$$dS = \frac{dE}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN - k_B \vec{\sigma} \cdot d\vec{P}, \quad (8)$$
where $\vec{P} = Nm\vec{v}$ is the collective momentum and $\vec{\sigma}$ the conjugate intensity. It may be shown (see reference [12]) that $\vec{\sigma} = \vec{v}/k_BT$. In the last term, change of the collective or coherent energy is easily recognized. We have therefore equivalently

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN - \frac{1}{T}d(\text{coherent energy}).$$

Conservation of energy throughout the expansion process makes $dE = 0$. During the adiabatic dissemination or mixing period, the second term (work performed by the expansion) is very exactly balanced by the last contribution (energy stored in the coherent motion), making $dS = 0$. This result is in full agreement with Liouville’s theorem in isolated (conservative) conditions. Final relaxation involves transformation of the coherent motion into thermal energy. When this has been achieved, thanks to momentum rephasing of the individual particles on inelastic exchange at every impact with the boundaries, the last term vanishes and integration of the Gibbs equation yields the correct final equilibrium entropy after expansion.

The present discussion concerning the two distinct mechanisms that are involved in non-equilibrium processes resolves endless debates on the relative merits of Boltzmann’s and Gibbs’ approaches to the total entropy change [11]. Their conclusions refer indeed to different steps of the process. Gibbs considers the adiabatic one and concludes correctly that $dS = 0$ on mixing. By contrast, Boltzmann’s entropy change relates to the relaxation step but he assumes incorrectly compatibility of this step with isolation of the relaxing system.

If the contribution relating to the non-equilibrium constraint is omitted in Gibbs’ differential expression, one is forced to replace the equality sign in the equations by the $\geq$ sign, in agreement with Clausius’ original inequality.

6 Conclusions

The main conclusion to be drawn from the discussion above is that dissipation of the non-equilibrium constraints of macroscopic systems involves interaction with the outside world. The word irreversibility is ambiguous. If it is understood in the sense of non-recurrent change in the course of time, conservative mixing belongs indeed to that class of phenomena. This sort of
irreversibility might however be qualified as apparent or weak. Its end-point is indeed not thermodynamic equilibrium. Memory of the initial conditions is still present under hidden form. By contrast, the opening of the system to a broad choice of new accessible conditions by exchange with the environment, thereby replacing and perhaps even neutralizing the former ones ensures the strict or strong irreversible character of dissipation.

An objection sometimes raised against the privileged role of the neighbourhood is that the proposal merely moves the difficulty step-wise further, while it is often assumed that the universe itself should be isolated. To this it must be answered that extrapolating the conclusions valid at our observational level to the whole universe is mixing up physics and metaphysics. The two are respectful domains of sciences but their tools and objectives are very different indeed. The first goal remains focusing on facts that are directly accessible to the experiment rather than elaborating a theory that is beyond our reach.

The properties of the environment are crucial, also in defining the state of equilibrium. If the system’s container is moving, equilibrium conditions imply that the system would be moving too. At equilibrium, collective properties of the system and of the surroundings are related. The intensities (differentials of the entropy with respect to the values of the exchangeable extensive properties) in the system and in its neighbourhood are equal. It is not correct to define the equilibrium state on the only basis of the extremum conditions of functions of state.

The objective of Boltzmann’s equation

\[
\frac{\partial f_1}{\partial t} = - \frac{p}{m} \frac{\partial f_1}{\partial q} + \mathcal{C}(f_1, f_1')
\]  

was to rationalize the relaxation processes observed in macroscopic systems assumed to be isolated from the outside world. It was obtained from intuitive arguments with the purpose to justify irreversible dynamics. It describes the conservative flow of a density of points in a single particle phase space, perturbed by an interaction term. The latter represents the modification to single-particle trajectories brought about by inter-particle collisions. The theory of Sinai billiards shows indeed that collisions do perturb individual paths, making them even strongly chaotic, but the global motion remains strictly symmetrical with respect to the sign reversal of \( t \). This contrasts
with Boltzmann’s perturbation term. Boltzmann’s procedure is therefore strongly conflicting with the first principles of mechanics.

Contrasting with mixing, dissipation to the surroundings is an exponential or possibly a multi-exponential process. Let us assume that the system’s particular non-equilibrium state is related to an extensive constraint represented by a given collective motion. This represents part of the total energy. By definition, this component of the energy is shared proportionally by the individual particles. At every individual impact of a particle with the boundaries, the part of the collective energy that is carried by the relevant particle (or a proportional part of it) is thermalized. The rate of change of the non-equilibrium constraint is therefore proportional to its actual value in the system, leading to the expected exponential decay. This simplified model is worked out completely elsewhere [12] and generalized to the transport coefficients (viscosity, heat conduction etc.) and other relaxation phenomena.

Transport coefficients belong clearly to the realm of dissipative dynamics. They are meaningless in isolated systems. It must therefore be stressed that the many types of phenomenological equations that describe non-equilibrium dynamics and where such coefficients are introduced, often on intuitive arguments (Navier-Stokes equations, Fokker-Planck equations etc.) all relate to non-isolated systems.

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