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The source of irreversibility in macroscopic dynamics

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ABSTRACT. The dynamics of irreversible relaxation of non-equilibrium macroscopic systems is discussed. Arguments are developed showing that the general mechanism is supported by a succession of two independent processes. One concerns dissemination of the particles according straight conservative dynamics. It generates collective motions without leading to thermodynamic equilibrium. The second step involves dissipation to the outside world of the information stored in the collective motion. This implies interactions with the surroundings. The first step is isentropic. Entropy change implies the second step. Interaction with the surroundings justifies a global thermodynamic description of the non-equilibrium system. On this basis, the transport coefficients are readily predicted.

RÉSUMÉ. La dynamique irréversible de relaxation des systèmes macroscopiques hors équilibre est remise en chantier. On présente des arguments tendant à démontrer que le mécanisme global englobe une succession de deux processus indépendants. L'un est la dissémination des particules en parfait accord avec la mécanique Hamiltonienne conservatrice traditionnelle. Il engendre des mouvements collectifs mais ne conduit pas à l'équilibre thermodynamique. La seconde étape implique la dissipation vers le milieu avoisinant de l'information contenue dans le mouvement collectif et implique donc une interaction avec le voisinage. La première étape est isoentropique. Pour le changement d'entropie la seconde étape est indispensable. L'interaction avec l'environnement justifie un traitement thermodynamique global des états hors équilibre. Il est aisé de prédire les coefficients de transport à partir de ce formalisme.

1. Introduction.

Distortion of macroscopic systems initiates spontaneous and irreversible processes tending to restore the previous state of equilibrium or possibly to establish a new one. This fact is most often taken to be a genuine property of isolated Hamiltonian systems. Conflict between the time asymmetric behaviour of macroscopic relaxation and the strict reversible nature of microscopic dynamics of isolated systems has been the subject of discussions over nearly a century [1,2].

Results published in recent decennia in applied mathematics concerning the time dependent transformation of systems where the number of identical elements tends to infinity at constant density [3,4] have been a stimulus for trying to solve the irreversibility paradox. The arguments are related to the mathematical property of mixing. This expresses dissemination of the elements throughout the available space (phase space) towards homogeneous and statistically independent distributions. It associates irreversibility to an infinite Poincaré recurrence time for any possible initial fluctuation. Progress obtained in characterizing deterministic chaotic motion (Lyapounov exponents) has also oriented theoretical research towards relating the relevant numbers to the transport phenomena associated with irreversible relaxation dynamics of isolated macroscopic systems. In this context chaotic scattering of particles on hard disks (Lorentz gas) has been used as a model for describing irreversible diffusion in the context of reversible microscopic dynamics [5–8].

With Hamiltonian systems of ideal gases and a number of other systems (Lorentz gas, baker transformation [9] etc.), the mathematical property of mixing is brought in by performing limit operations, letting both the number of particles and the volume go to infinity [3,5,10] while performing simultaneously a scaling on the time parameter. This operation transforms discrete particles distributions into continuous functions where statistics are readily applied. The mathematical operation results however in levelling alternating fluctuations as soon as their wavelength is short enough (limit operation) (e.g. the baker transformation). In doing so the procedure by-passes or suppresses artificially an essential ingredient in the dynamics of physical systems. No matter how short a wavelength may be in whatever physical circumstances (e.g. ultrasonics, light, ...), it represents a coherent or correlated structure containing information and it cannot be assimilated to a continuum or a vacuum.

Furthermore, by inspecting the literature applied to Hamiltonian systems, when quoting the property of mixing, the authors refer to a truncated phase space. In the formal mathematical demonstrations, not all aspects of the dynamics are indeed treated with the same priority (configuration and momentum). The main question remains therefore whether Hamiltonian dynamics is mixing at all.

The research trend that relies on the mixing paradigm insists explicitly on the fact that irreversible processes would occur in systems that are isolated from the environment. The statistical properties of the time dependent random forces acting on the particles are assumed to be *completely* determined by the initial distribution and by the dynamics of the system [5]. By performing the mathematical manipulations referred to above (rescaling), phenomenological parameters (e.g. viscous drag controlling the motion of Brownian particles) are said to converge to genuine irreversible properties of the fluid. As a result, dissipative coupling with a reservoir is explicitly rejected by the relevant authors, being considered to be "artificial and unnecessary" [2,6].

Contrasting with the latter, others insist on the unavoidable interaction of macroscopic systems with their environment acting as a reservoir or heat bath [11,12,13]. Stress is lead on the environment where the fluctuating forces to be introduced into the equations of motion of the system of interest come from. Dissipation arises from a back-reaction of the environment to the evolution of the system [14]. As an example, concerning the viscous drag mentioned above, the relevant dissipative force is said to originate from the interaction of the Brownian particle with the surrounding fluid acting as a reservoir. The time average value of this force gives rise to Stokes' law, on which fluctuations are superimposed. Still others have approximated successfully the necessary additional non-Hamiltonian dissipative force by modelling the intervention of the surroundings as a third-body potential [13].

The present paper strengthens and generalizes the arguments favouring the second general line of thoughts. Its main originality lies in the development of thermodynamic tools for describing interactions with the neighbourhood. In a first section, Gay-Lussac's experiment, often used as a reference to the problem of irreversibility, will be rediscussed. The next section concerns the definition of the concepts "microstate" and "macrostate". It stresses the implication of Hamiltonian dynamics on the phase space trajectories and specifies the mechanism driving jumps and transitions between trajectories. A general description of the mechanical properties of the environment acting as a reservoir for heat, possibly matter, and perhaps other parameters, implies a firm thermodynamic construction. This will be the core of section three. In the last section, the arguments developed earlier will be applied to the prediction of transport coefficients. For brevity, the discussion here will be limited to viscosity and thermal conduction of one-component gases [15].

2. Gay-Lussac's experiment.

In the literature, directionality of time's arrow is often introduced intuitively on the basis of a simplified representation of Gay-Lussac's experiment. A box is considered, consisting of two compartments, the parts being filled with gas at different pressures. Prior to the experiment the gas is assumed to be at equilibrium. The observed long time evolution following the rupture of the division, towards a new equilibrium distribution, is taken to be modelling the irreversible behaviour of the global dynamics (non-recurrence of the initial conditions).

Gay-Lussac's experiment has been repeated by Joule with great accuracy. His purpose was to measure 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 equilibrium state, no net exchange of heat with the surroundings is observed. Joule concluded that the system behaved as if it was isolated.

The dictionary definition of the word "isolation" points to hypothetical objects that are left completely alone, deprived from whatever interaction with the surroundings. This definition is clearly much too strong, as the system of interest are at least bound by walls. A slightly weaker definition applies then and is traditionally adopted. It allows elastic collisions with the boundaries. This implies absence of exchange of energy or heat with the surroundings. A third much weaker definition of the same word would allow possible fluctuating transient exchange of energy, momentum, or other parameters, with zero balance when averaged or integrated over the observation period. Joule's observation does by no means preclude the weakest unconventional definition.

Let us make the experiment more realistic by examining the effect of pricking an air inflated balloon inside either an acoustic reverberation hall or an anechoic chamber. In the two cases the excess air contained in the balloon 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. In the reverberation room, some energy is stored in a coherent or collective motion (acoustic perturbation) where it remains as the memory of the initial conditions. With walls correctly shaped, the initial information may even be partially retrieved as echoes. By contrast, in the anechoic room, memory of the past is soon forgotten.

Initial and final conditions are identical in the two cases and so is the air inside the rooms, and therefore the frequency and the quality of the inter-particle collisions (Hamiltonian dynamics) that are assumed elsewhere to be the source of relaxation. The only difference between the experiments is the nature of the walls. One is therefore forced to conclude that the relaxation dynamics of a spontaneously expanding gas depends on the acoustic quality of the walls, representing the system's environment.

Two separate and independent mechanisms control the reflectivity of the acoustic perturbations. One is the action of the walls perpendicular to the direction of propagation of the compression wave, the other is the shear effect caused by the gas sliding along the walls parallel to the direction of propagation. For the first component, ideal reflection locates acoustic nodes at the position of the walls, thereby inhibiting exchange of momentum to the surroundings: The impedances do not match. Changing the physical nature of the walls (softness) modifies the coupling to the outside world.

Shear strain of the gas moving collectively past the walls parallel to the direction of propagation is related to viscous effects. It causes the well known ultrasonic absorption which cannot be eliminated completely in real experiments (by no means restricted to the highest acoustic frequencies [15]). That is why an ideal reverberation room, where the acoustic perturbation would remain for ever, does not exist. At first, this restriction may seem to weaken the argument leading to external control of the relaxation dynamics. However, if the walls had not been there at all, the jet would have remained. Viscous effects being the result of transfer of collective shear momentum (correlated or coherent motion) to the outside world, and its replacement by an incoherent distribution of momentum, the role of the environment is trivial.

If the walls were ideally smooth, up to atomic dimensions, so that on impact every particle conserves identically its tangential component of momentum, reflections would be elastic, as implied by the traditional isolation assumption. There would be no viscous effect. The collective motion of the particles would not be slowed in the neighbourhood of an immobile wall. With elastic reflections, whatever the collective flow, boundary layers do not behave differently from the bulk.

Contrasting with the latter extremely idealized model, physical walls are not smooth up to atomic dimensions. An alternative ideal but equally unphysical model assumes convex surface atoms that would be strictly immobile both in tangential and normal directions (infinite masses). The returning path of the particles following collision with the wall depends then only on the relative position of the impact with respect to the relevant surface atom. This picture is the analogous of the Sinai billiards problem, the convex scatterers being replaced by defocussing walls [8]. On reflection, coherent parallel flows of particles are defocussed, but the correlation of individual motions of the particles in the beam is not lost. The process shows some analogy with reflection of a beam of laser light. This too does not change its coherence properties by reflection on a convex mirror or on any other strictly immobile defocussing object. The particular shape of the reflecting surface only activates additional collective modes but the global motion remains non-thermal.

Physical walls (finite mass of the surface atoms with thermally fluctuating motions) superimpose on the effect just mentioned an incoherent action tending to absorb and overrun the collective perturbation. In systems where transport of information through the bulk is relatively slow (thermodynamic regime, i.e. non-Knudsen regime), impedance match occurs in the boundary layers. The local properties depend on the coupling efficiency to the walls at one end and to the resistance to transport of collective momentum from the bulk to the walls at the other. Viscosity measures the latter resistance but the source of relaxation is clearly to be located in the exchange with the walls (environment), not in the mechanism controlling the rate of transfer through the bulk.

As soon as the membrane between the two parts of Gay-Lussac's box is ruptured, a stream of gas is ejected from the compartment at the highest pressure, thereby creating a collective motion of the particles. By performing work on itself, the system transfers energy adiabatically into the jet. This energy is subtracted from the initial thermal supply (adiabatic expansion). Loss of thermal energy is equivalent to cooling the system, or else, if the system is strongly thermostated, heat is transiently imported from the surroundings.

On reaching the wall opposite the puncture, the jet is reflected and the initial collective motion turns progressively into an acoustic perturbation with same energy. The spectrum and phases of this motion are the memory of the initial conditions and of the shape of the reverberating walls (coherence).

Relaxation of the coherent motion starts now. It consists in rethermalizing the energy initially accumulated in the jet and later stored in the acoustic perturbation. As a result, if the system is an ideal gas (hard spheres allowed), the initial temperature drop is neutralized or the heat that was initially absorbed is identically reinjected into the neighbourhood, as expected by Joule's result. When final equilibrium has been reached, the collective motion has relaxed and information about the initial conditions is completely lost.

Initial dissemination of the particles throughout the system is irreversible, according to the weak definition of this word. It says that the Poincaré recurrence time of the initial conditions is extremely (infinitely) long. However, information about the past is by no means forgotten, no matter how intricate the motion of individual particles may be. In dynamics, the more subtle connotation of the word "irreversibility" refers to processes that are asymmetric with respect to sign reversal of the variable *time*. This stronger definition of the word does not cover the initial dissemination step.

3. Microstate and macrostate.

The scenario discussed above shows that the global motion of macroscopic systems is governed partly by Hamiltonian dynamics (jet forming and dissemination) and partly by dissipation of the collective motion by incoherent interaction with the neighbourhood (final relaxation). The two steps of the global process are very different in their dynamics. Depending on the system of interest, they may be almost concomitant but we shall consider them here for simplicity as frankly separated in the time. The Hamiltonian part comes first, so that in the relevant subsection, whatever would make strict isolation ineffective is neglected.

A. Hamiltonian dynamics:

The Hamiltonian may be stationary or explicitly time dependent. Explicit time dependence denotes a correlated action from the outside world. It does therefore not intervene in strictly isolated systems.

A system is said to be conservative if the force field is such that work done around a closed orbit is zero. A stationary (time independent) Hamiltonian produces by definition conservative dynamics. Physically it is clear that dynamics cannot be said to be conservative if friction or other dissipation forces are included [16].

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 [17]. 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 the present discussion uses the word "trajectory" as a reference to global many-particles motions but never to the individual paths of separate particles.

In the contemporary literature, the words "determinism" and "conservation" are often taken for each other. This generates confusion between strictly Hamiltonian dynamics and hydrodynamics, where dissipative forces are included (e.g. viscosity). The difference between the two is most clearly highlighted in H. Schlichting's textbook on hydrodynamics where it is stressed *that the equations which relate the surface forces to the flow field must be obtained by perceptive interpretation of experimental results...* [22]. Conservative motion is deterministic, but the opposite may not be true.

The concepts "dynamic state" mentioned above and the word "microstate" used by many authors are synonymous. They represent a point $(p_1...p_{3N}, q_1...q_{3N})$ in the many-particle phase space.

A phase space trajectory is a line joining the succession of phase points representing the system as time goes on. Hamilton's canonical equations are its parametric equations. Considering that only one trajectory passes through a given phase point, there is a unique relationship between any "microstate" and the "trajectory" it belongs to.

Two different situations may be considered. Sometimes the investigation concerns particular properties of individual phase points and possibly changing properties of the system during the evolution of the phase points as the trajectory unfolds in function of time. In particular, with systems of particles, this may be the case when the experimental time resolution is made exceptionally fine compared to the internal characteristic time of periodic motions (e.g. very short laser pulse experiments). Contrasting with the latter situation, with time independent Hamiltonians, the exact position of the phase point along a given trajectory may possibly not be observable or may be irrelevant. The definition of "microstate" may then be extended to the complete trajectory, the two words representing the same reality. In quantum mechanics, “microstate” and “quantum state” are synonymous.

With systems of many translating particles, if their velocity distribution is broad, the physical perception of the initial conditions may change strongly as time goes on. This perception concerns dissemination and redistribution of individual particles in the configuration space. The relevant dynamics may be exemplified by a system of many non-interacting particles, translating back and forth along a line between two boundaries where reflection of the individual motions is elastic (energy conservation).

Let us assume for instance a Gaussian (Boltzmannian) velocity distribution.

$$g(v) \simeq \exp(-v^2). \tag{1}$$

If the initial conditions are represented by some δ-function density fluctuation at some given position along the line, it is easy to compute the density distribution at any later instant. The sharp fluctuation disappears, leading at long times to a flat particle distribution, as if the initial perturbation had relaxed.

If the number of particles is high ($N \to \infty$), the initial fluctuation does not recur spontaneously after a reasonable delay (Poincaré recurrence). The process responds to the weak colloquial meaning of irreversibility, not to the strong thermodynamic definition of the word. By reversing artificially the sign of the velocities of all the particles, the global trajectory is made to run in the opposite direction and the initial fluctuation 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 $x_i(v,t)$ is the position of the i-th particle with velocity v at time t, $X(t)$ is defined as

$$X(t) = \sum_i x_i(v,t). \tag{2}$$

Starting from the initial fluctuation, as time goes on the particles disseminate and the centre of mass moves towards the system’s geometrical centre. By computation, the general expression for the dynamical evolution of $X(t)$ is easily shown to be an even function of time.

While the particle distribution in configuration space homogenizes, the system's average velocity

$$V(t) = \sum_i v_i(t) \tag{3}$$

presents a strong permanent oscillating character due to the alternating sign reversals of the individual velocities $v_i(t)$ every times a given particle is reflected at one of the two boundaries. This oscillation does not relax as time goes on. It is clearly in momentum space that this conservative system stores the information about its initial conditions.

The oscillation, though extremely intricate, presents a periodic character. It may be made chaotic by having the motion performed in higher dimensional space and with defocussing walls. However the system does not grow ergodic. If the information concerning the initial conditions is to vanish, something more is needed than mere elastic reflection at every impact with the walls.

B. Dissipation and Fluctuations:

Conservative Hamiltonian motion, including inter-particle potentials, defines trajectories in the many-particle phase space. By forbidding transitions between such independent 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 any of the system's particles interacts with the boundaries or with whatever represents the neighbourhood, like the ubiquitous thermal electromagnetic radiation and the gravitation field. Export and import of information being uncorrelated, the transitions cause loss of information and irreversible relaxation of the initial microstate. Every collision with a wall interrupts the running canonic global trajectory. A new one starts, 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 infinite mass particles, only momentum is transferred. When the impact is over, the wall has gained momentum from the particle but no velocity. In the same time the wall renders to the particle an equal amount of momentum in the opposite direction, allowing the new trajectory to start in conditions that are rigorously correlated with the previous one. The conservative character of the motion remains.

Real atoms and molecules in the walls oscillate about their equilibrium positions. As a result, contrasting with the picture above, return paths are unpredictable because the motions of the collision partners are uncorrelated. They allow the system to perform stochastic jumps between different accessible trajectories or to modify the phase information of the running trajectory. Depending on whether during a particular impact the relevant wall atom moves towards the colliding particle or in the opposite direction, work is transferred to the system or to the environment. Energy fluctuates about its average value. The condition that average energy transfer is zero is the thermodynamic requirement that the system and its neighbourhood be at the same temperature.

It is impossible to specify exactly the microstate of a complex macroscopic system. We must content ourselves with descriptions that are considerably less than complete, the more that the short lifetime of the global (multi-particle) trajectories and the transitions between them reduces drastically the number of relevant constrained properties. In fact, our exact information about the properties of many-particle systems is restricted to a small number of observables.

A “macrostate” is by definition the observational condition of a system where many multi-particle trajectories in phase space (microstates) are accessible. Frequent uncorrelated transitions occur between them. The particular macrostate is defined unambiguously by specifying the complete set of parameters representing the unavoidable constraints, either external or internal, implied by the system’s particular observational state.

4. Thermodynamics.

A. The Entropy:

Any function determined completely by the set of constraints that define the particular macrostate of the system 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.

$$\delta S \geq \frac{\delta Q}{T}, \tag{4}$$

where T is the system's temperature. The equal sign refers to reversible processes. This fundamental experimental definition implies net transfer of heat and therefore interaction of the system with its environment for the entropy to change in reversible conditions.

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. Let us therefore forget the word equilibrium in this context and define a process as reversible when no coherent or collective motion is allowed to be generated by the process or that it has been allowed 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 [18]. It would be the measure of our personal lack of information concerning the system's conditions. This suggestion that personalizes a function of state indicates that profound confusion still prevails concerning the definitions.

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

$$S = k_B \ln[W(A)]. \tag{5}$$

For the inventor, $W(A)$ meant "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 the English "weight of the given observational state or macrostate". The latter is interpreted as the total 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. Let it be noted that equilibrium macrostates are usually defined by their total energy E, particle number of any sort N_r and physical volume V, which are the traditional microcanonical variables. In the literature, extension of the discussion to non-equilibrium macrostates is usually avoided.

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 [19] by taking $W(A)$ as the total number of independent quantum states (quantum state = microstate) compatible with the given macrostate. This is the third law of thermodynamics according to which, if only one microstate is accessible, the entropy is zero.

Using Planck's suggestion, Boltzmann's entropy is now expressed in terms of quantum mechanics. This does not refer directly to phase points or trajectories in phase space as does classical mechanics. In order to return to the usual classical description, the quantum-classic correspondence is addressed. It implies that every global quantum state occupies in the classical phase space a finite region with a $6N$ dimensional phase volume measuring h^{3N}. The number of available classical trajectories respecting the state defining constraints equals then the ratio of the accessible phase space volume to h^{3N}.

For Boltzmann's entropy to be a pertinent function of state, prompt accessibility of all the quantum states or trajectories belonging to the given macrostate is required. In a strictly conservative environment, the dynamics being described by a single multi-particle trajectory in phase space, no matter how intricate (chaotic) this may be, 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 (microstates). Accessibility of still more trajectories increases Boltzmann's entropy.

Accessibility implies prompt incoherent transitions between the trajectories or quantum states during the observation period. This depends on fast uncorrelated action of the environment with fluctuating 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 some averaging over the time. The time resolution linked to the definition of the entropy is the average lifetime of the conservative trajectories. With macroscopic systems, where the impact rate with the boundaries goes to infinity, the average lifetime and the time resolution tend to zero.

In describing equilibrium states (say for a one-component gas), the traditionally mentioned extensive variables are the basic microcanonical constraints E, V and N. In order to specify unambiguously non-equilibrium macrostates, where more 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, where some of the total energy is stored (e.g. the jet or the acoustic motion in above mentioned Joule's experiment). Many other possible distortions with respect to equilibrium may occur, 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 X_r. The entropy is a function of this collection of variables. By differentiating the entropy with respect to the set of X_r, we get by definition the set of conjugate intensive variables or intensities ξ_r.

$$dS = \sum_r \frac{\partial S}{\partial X_r}\, dX_r = -k_B \sum_r \xi_r\, dX_r. \tag{6}$$

The equation may be considered as defining the temperature $(\partial S/\partial E)^{-1}$ and the chemical potential $-T(\partial S/\partial N)$. In non-equilibrium conditions it generalizes the definitions by proposing an intensity to be conjugate to each of the additional non-equilibrium constraints.

Equation (6) is Gibbs' celebrated equation, generalized to non-equilibrium macrostates. In the simplified model of a spontaneously expanding jet as mentioned above (velocity of the collective motion: $\vec{v}$), the new version of Gibbs' equation reads

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN - k_B\, \vec{\sigma} \cdot d\vec{\mathcal{P}}, \tag{7}$$

where $\vec{\mathcal{P}} = Nm\vec{v}$ is the collective momentum and $\vec{\sigma}$ the conjugate intensity. It may be shown [15] that $\vec{\sigma} = \vec{v}/k_B T$. In the last term of equation (7), the differential of the collective or coherent energy is easily recognized. We have therefore equivalently

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN - \frac{1}{T}d(\mathit{coherent\ energy}). \tag{8}$$

Energy conservation throughout the expansion makes $dE = 0$. During the adiabatic dissemination period, the second term (work made available by the expansion) is very exactly balanced by the last contribution (energy stored in the coherent motion), making $dS = 0$, in agreement with Liouville's theorem for isolated conservative motions. Final relaxation involves transformation of the coherent motion into thermal energy. When this has been achieved, thanks to stochastic exchange at every impact with the boundaries, integration of the last term vanishes and the Gibbs equation yields the correct final equilibrium entropy after expansion.

If the contribution relating to the non-equilibrium constraint had been omitted in equations (7) and (8), we would not have been able to describe the thermodynamics of the low entropy non-equilibrium transient state.

B. The generalized Massieu function:

The inconvenience when considering the entropy as the leading thermodynamic function is that this is an explicit function of the extensive properties (X_r), while the intensities (ξ_r) are better measured and controlled by the environment. For that reason, thermodynamics makes widely use of potentials and other Massieu-Planck functions, obtained from the entropy or the energy by Legendre transformations.

Most popular are free energy transformations. However, contrasting with the second law for the entropy, general laws involving the energy do not exist. It is therefore advisable to consider transformations involving the entropy itself. If the additional parameters defining non-equilibrium conditions are included in the definition we obtain the generalized Massieu function (the volume is not included in the transformation) $\mathcal{M}(\xi_r, V)$:

$$\mathcal{M}(\xi_r, V) = \frac{S}{k_B} + \sum_r \xi_r X_r. \tag{9}$$

Unlike Massieu's original function, $\mathcal{M}$ is an explicit function of all the state defining intensities. It may be verified that

$$\frac{\partial \mathcal{M}(\xi_r, V)}{\partial \xi_r} = X_r. \tag{10}$$

The advantage of referring to a state function depending explicitly on intensities is that, with promptly exchangeable properties, the relevant intensities of the system of interest remain at all times equal to their value in the neighbourhood. We might call them strong intensities (e.g. the temperature in an efficiently thermostated system). Investigation concerning transient states refer to the intensities of the slowly exchanging or soft properties.

The Legendre transformation changes the maximum entropy condition with respect to fluctuations of the extensive variables into a minimum of the extended Massieu function with respect to the intensities relating to non-exchangeable properties (e.g. particle numbers and their distribution in closed systems). With transient effects, this fundamental property defines the path followed by the system during relaxation. It gives a key for treating coupled flows.

With ideal gases, when the collision time is very much shorter than the time spent by the particles between individual collisions (hard spheres approximation), the expression for the generalized Massieu function takes a very simple form. Individual motions being practically independent, representation of the global motion may be approximated as a swarm of points moving in a reduced 6-dimensional single-particle phase space (Γ). Indeed, let $f(\Gamma)$ be the most probable particle distribution: that which maximizes the entropy. Every extensive property X_r is then related to a particular generating function $\phi_r(\Gamma)$ so that

$$X_r = \int_\Gamma \phi_r(\Gamma) f(\Gamma) d\Gamma. \tag{11}$$

For the traditional microcanonical extensive properties N and E, the relevant generating functions are respectively $\phi_N = 1$ and $\phi_E = (p_x^2 + p_y^2 + p_z^2)/2m$. For a fluid moving in the z-direction with average total momentum P_z, the generating function $\phi_p = p_z$ is the link between the distribution function and the relevant extensive property.

With the appropriate set of generating functions, function $f(\Gamma)$ is readily known to be [15]

$$f(\Gamma) = \exp[\sum_r \xi_r \phi_r(\Gamma)]. \tag{12}$$

The intensities ξ_r are the Lagrange multipliers in the maximizing process. It may then be verified that $\mathcal{M}$ takes the very simple form

$$\mathcal{M}(\xi_r, V) = \int_\Gamma \exp[\sum_r \xi_r \phi_r(\Gamma)] d\Gamma. \tag{13}$$

Its numerical value equals the (average) number of particles contained in the system. Through the integration limits in configuration space it has the system's physical dimensions (volume) as one of its independent variables. By restricting the integration to the only momentum coordinates, a local generalized Massieu function is obtained, the value of which represents the average local density in configuration space.

With real gases, the generalized Massieu function is modified due to the interaction potential between the particles. The simplified formulation is however still useful as an approximation at low density, when the duration of the inter-particle collisions is negligible compared to the time separating collisions.

5. Transport coefficients.

One of the main objectives of the theory of non-equilibrium dynamics is prediction of the transport coefficients from first principles. Comparison between the predicted and experimental results is often considered as a test for the validity of the relevant approach.

Since Boltzmann first proposed his kinetic equation there has been a considerable literature concerning the calculation of the transport coefficients [10,23]. Most frequently cited are the traditional Chapman and Enskog derivations [24] and the Green-Kubo formalism.

It has been stressed above that, for all but perhaps a few mechanical properties, exchange occurs readily with the surroundings, tending to equalize the conjugate intensities to the reservoir values. This justifies the use of thermodynamic expressions based on intensities. When intensities conjugate to exchangeable properties are different from the reservoir values, we have transient conditions from where the system tends to relax. By contrast, if the system of interest is connected to a surroundings that is not at equilibrium, like a couple of thermostats at different temperatures separated by some distance, the system reaches and remains in a stationary state out of equilibrium. This is the condition we shall focus on now.

If the system is interacting with two reservoirs at different temperatures separated by some distance (here: $2D$), the conditions of the surroundings define and dictate to the system the genuine non-equilibrium intensity “temperature gradient”. Similarly in the Couette flow problem, the externally imposed gradient is caused by a couple of walls moving in opposite directions. This generates in the system a non-equilibrium intensity “gradient of shear momentum”. Asymmetric exchange with the two reservoirs produces flows. In this section, the relevant transport coefficients will be examined using a thermodynamic description. For simplicity, the discussion will however be limited to hard sphere atomic gases.

In very low density systems, where the mean free path is comparable or longer than the system's physical dimensions (Knudsen gas), properties picked up by any particle from one wall are transported in a single jump to the opposite wall. Transport is very efficient indeed. In the thermodynamic limit (non-Knudsen regime), head-on collisions of like particles do not slow down the transport properties. By contrast, parallactic or off-axis inter-particle collisions do. Their effect is one of reducing the range of free transport, while information about the conditions of the external reservoir available at the boundaries is transferred to the relevant region of the bulk. In the same time, the local values of the thermodynamic properties are justified. The flow rates depend therefore on the average periodicity τ of the latter perturbing collisions.

Let us consider an arbitrary property X_r with generating function $\phi_r(\Gamma)$. This may be any one of the generating functions defined above. Still other generating functions are listed in the tables concerning the applications discussed below. We assume that the property flows in the z-direction. Furthermore, let us consider a plane positioned at coordinate z^*. The basic equation for the flow J_r of the relevant property through this plane is

$$J_r = \frac{1}{\tau} \int\int\int (\frac{d\vec{p}}{h})^3 \int_{(z^* - p_z\tau/m)}^{z^*} \phi_r(\Gamma) \, \exp[\sum_l \xi_l \phi_l(\Gamma)] \, dz. \tag{14}$$

The symbol $(d\vec{p})^3$ is a short form for $dp_x dp_y dp_z$. Integration limits in momentum space are $-\infty \to \infty$. As recalled above, Plank's constant is the norm in phase space. In the subsections to follow, this equation will be applied to different types of flow.

It may be useful to stress the difference between equation (14) and that proposed elsewhere, in its own different context, for flows of extensive properties [24,23]:

$$J_r = \int\int\int \frac{p_z}{m} \, \phi_r(\Gamma) \, \exp[\sum_l \xi_l \phi_l(\Gamma)] \, (\frac{d\vec{p}}{h})^3. \tag{15}$$

Equation (14) confirms that transport occurs during the free motion time separating relaxing collisions. The lesser the collision frequency, the more effective is the transport. Collisions do not activate transport but they increase resistance to transport.

A. Viscosity:

We consider a fluid bound by a pair of walls moving in opposite directions (Couette flow). Excepting negligible higher order corrections (proportional to $\tau^2(\beta m D^2)^{-1}$), the system's conditions are defined completely (at the lowest order in τ) by the set of constraints listed in table I, where the symbols used for the relevant intensities are given.

The intensities under direct control of the surroundings (exchangeable properties) are the particles number, the kinetic energy ($k_B T = \beta^{-1}$), and the intensity conjugate to the gradient of shear momentum. It may readily be verified that the velocity of the walls (y-direction) equals $\pm\sigma_y/\beta$. Two variables remain to be determined, namely θ_2 and γ_2. They require two independent equations.

In stationary conditions there is no local accumulation of the transverse component of momentum (p_z) (no pressure gradient, no acoustic perturbation). The relevant flow is therefore independent of z^*. Likewise, the total flow of energy through the system is zero. By implementing equation (14) with the two relevant generating functions, the conditions $\partial J_{p_z}/\partial z = 0$ and $J_U = 0$ yield together

$$\theta_2 = 0, \qquad\qquad \frac{5}{2}\,\frac{\gamma_2}{\beta} = \frac{m\sigma^2}{2\beta}. \tag{16}$$

The flow of the shear component of momentum may now be determined by implementing equation (14) with the generating function $\phi_p = p_y$, where θ_2 and γ_2 have been replaced by their values given above. This yields

$$J_{p_y} = -\frac{\sigma_y}{2\beta D}\,\frac{n\tau}{\beta}, \tag{17}$$

where $n = \mathcal{M}/V$ represents the particle density.

The phenomenological reaction at the plates' level compensating for transfer of momentum from wall to wall is friction. Shear viscosity is the ratio of the sum of the forces applied to the two plates to the velocity gradient ($\sigma_y\,(2\beta D)^{-1}$). Following equation (17), its value is

$$\eta = n\,\frac{\tau}{\beta}. \tag{18}$$

B. Thermal conduction:

Now we consider a system in thermal contact with a couple of heat reservoirs at different temperatures separated by a distance $2D$. The system's stationary non-equilibrium conditions are completely described (at the lowest order in τ) by the set of constraints listed in table II, where again the symbols used for the relevant intensities are given. By inspecting the definition of the generating function conjugate to the temperature gradient it is clear that $k_B \nabla T = -\gamma_1 \, (\beta^2 D)^{-1}$.

Knowing that the system is bound by a pair of impervious walls it may look strange that collective motion of the particles perpendicularly to the walls needs to be foreseen in constructing the expression for the most probable non-equilibrium distribution function f (equation 12).

In a system controlled by two heat reservoirs at different temperatures, kinetic energy is not uniformly distributed among the particles. Those moving towards the cold wall have been equilibrated with the system upstream in a hotter region at the instant of their previous collision and vice-versa. In moving from the hot wall to the cold one, particles travel on the average faster than in their return cycle. If the particles are to change their average kinetic energy in a correlated fashion on impact with either walls, while the container (the pair of walls) is to remain immobile, collective momentum is indeed transferred by the container to the system.

The intensities under direct control of the surroundings (exchangeable properties) are the particles number, the average kinetic energy and the temperature gradient. Two intensities remain to be determined: θ_1 and σ_z. This requires two independent equations. One is stationarity. The other equation describes mechanical equilibrium of the system between its walls.

According to the local description, at any point in the bulk of the system, the average particles density n responds to the equation

$$n(z^*) = \frac{1}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp\{\sum_r \xi_r \, \phi_r[(z = z^*), p_x, p_y, p_z]\}. \tag{19}$$

We consider at any position z^* the partial density $n_+(z^*)$ of the only particles with positive velocity along the z-direction. Stationarity implies that this partial density equals the sum of the densities of the particles in regions from where they will be reaching this position without disturbance after one collision period, their velocities having opposite orientation. Hence

$$n_+(z^*) = \frac{1}{h^3}\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{0} dp_z \\ \exp\{\sum_r \xi_r\,\phi_r[(z = z^* - \frac{p_z\tau}{m}), p_x, p_y, p_z]\}. \tag{20}$$

This equation yields to the lowest order in τ

$$(\theta_1 - 2\frac{\gamma_1}{\beta})\,\frac{\tau}{mD} = 2\sigma_z. \tag{21}$$

The second equation expresses position independence of flow of momentum across the system. In other words, there are no pressure gradients. Equation (14) is used with $\phi_p = p_z$ as the flow defining generating function. The condition $\partial J_{p_z}/\partial z = 0$ yields

$$\theta_1 = \frac{5}{2}\frac{\gamma_1}{\beta}. \tag{22}$$

Flow of energy (heat) through the system is given by this same general equation (14) where the flow defining generating function is now $\phi_E = \sum(p^2/2m)$. For particles associated with internal rotational motion (Eucken correction [24,20]), the relevant contribution to the energy should be added to the latter generating function. With atomic gases the result reads

$$J_U = \frac{15}{8}\,\frac{\gamma_1}{\beta^2 D}\,n\,\frac{\tau}{\beta m}. \tag{23}$$

Heat conductivity (λ) is the ratio between the sum of the rates of heat exchange at either walls ($2J_U$) and the temperature gradient. Hence

$$\lambda = \frac{15}{4}\,k_B\,n\,\frac{\tau}{\beta m}. \tag{24}$$

In equations (18) and (24) the transport coefficients are expressed in terms of the effective collision periodicity τ. For comparison with experimental results, an additional expression is required that relates the collision periodicity to the mechanical properties of the colliding species (mass and cross-section) at the given temperature. Only the ratio between viscosity and heat conductivity is independent of the particular collisional dynamics. This ratio is given by Prandtl's number

$$\mathrm{Pr} = \frac{\eta\, c_p}{m\, \lambda}, \tag{25}$$

with c_p as the constant pressure heat capacity. By implementing this definition with the results obtained above, the experimental values are obtained identically, thereby confirming the general model.

In the literature there are different expressions for the effective collision periodicity τ for different more or less realistic atomic models and for the simple hard sphere model [24,23]. Depending on the author and the procedure used to estimate the collision periodicity, the simple hard sphere result differs by some minor correcting factor. When the relevant data is imported in the expressions for the transport coefficients, the same correcting factor holds, expressing the efficiency of the inter-particles collisions with respect to transfer to the bulk of thermodynamic information available at the boundaries.

6. Conclusions.

The main conclusion to be drawn from the discussion above is that, contrasting with a widely adopted paradigm [10], the proposal according to which dissipation of the non-equilibrium constraints of macroscopic systems involves interaction with the outside world is strictly compatible with the experiment.

The word "irreversibility" is ambiguous. If it is understood in the sense of non-recurrent change in the course of time, conservative Hamiltonian dynamics of many-particles systems may indeed belong to that class of phenomena. This weak form of irreversibility does however not lead to thermodynamic equilibrium. Memory of the initial conditions is indeed still present under hidden form (momentum space). By contrast, the opening of the system to a broad choice of new accessible conditions by exchange with the environment ensures the strict or strong irreversible character of true dissipation.

An objection sometimes raised against the privileged role of the neighbourhood is that the proposal merely moves the difficulty stepwise further, while it is often assumed that the universe itself should be isolated. To this it must be answered that extrapolating conclusions valid at our observational level without proof to the whole universe, of which we know almost nothing, is illegal. Our first goal remains understanding the facts that are directly accessible to the experiment rather than elaborating a theory that is far beyond perceptional reach.

The properties of the environment are crucial in defining the very notion of "state of equilibrium". If the system's container is moving, equilibrium conditions imply that the system moves too. At equilibrium, all the properties of the system and of its 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 therefore not correct to define the equilibrium state on the only basis of the extremum conditions of functions of state [21], without implying the environment.

Boltzmann's dynamic equation

$$\frac{\partial f_1}{\partial t} = -\frac{p}{m}\frac{\partial f_1}{\partial q} + \mathcal{C}(f_1, f_1') \tag{26}$$

had as its objective rationalizing in a single tractable equation the relaxation processes observed in macroscopic systems assumed to be isolated from the outside world. It was obtained from mere intuitive arguments. It describes the conservative flow of a density of points in a single particle phase space, perturbed by an interaction term representing the modification to single-particle trajectories brought about by inter-particle collisions.

Referring to the alleged mixing property of complex Hamiltonian dynamics of many-particles systems [3], confidence in Boltzmann's equation has been enforced in recent years [2]. Contrasting with this standpoint, the present paper asserts that, no matter possible complexity, the global Hamiltonian motion remains conservative and therefore strictly symmetrical with respect to the sign reversal of t, in contradiction with Boltzmann's equation.

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 or hydrodynamics where such coefficients are introduced on intuitive arguments (Navier-Stokes equations, Fokker-Planck equations etc.) all relate to non-isolated systems [22].

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X_r	$\phi_r(\Gamma)$	ξ_r
Particles number	1	α
2nd moment of particle distribution	$[(z/D)^2 - 1]$	θ_2
Kinetic energy ($= U$)	$\sum(\frac{p^2}{2m})$	$-\beta$
2nd moment of energy distribution	$[(z/D)^2 - 1]\ \sum(\frac{p^2}{2m})$	$-\gamma_2$
Gradient of shear momentum	$(z/D)\, p_y$	σ_y

Table I. List of the main constraints for Couette flow (distance between the walls: $2D$)

X_r	$\phi_r(\Gamma)$	ξ_r
Particles number	1	α
Gradient of particle distribution	(z/D)	θ_1
Kinetic energy ($= U$)	$\sum(\frac{p^2}{2m})$	$-\beta$
Gradient of energy distribution	$(z/D)\ \sum(\frac{p^2}{2m})$	$-\gamma_1$
Collective transverse momentum	p_z	σ_z

Table II. List of the main constraints for thermal conduction (distance between the walls: $2D$)