The Dynamics of Thermodynamics *

J. Kumičák

Department of Thermodynamics, Technical University,
041 87 Košice, Slovakia.

X. de Hemptinne

Department of Chemistry, Catholic University of Leuven
B-3001 Heverlee, Belgium

Thermodynamic relations are derived from first principles of mechanics for non-equilibrium processes. Since the key role herein is played by the law of increase of entropy, the latter is analyzed at first. It is shown that its derivation for isolated systems does not allow one to say too much about thermodynamic properties in non-equilibrium conditions. From there on, the notion of quasi-isolated systems is introduced, for which it is possible to describe the state of macroscopic systems by a collection of intensive variables. The latter are the differentials of the entropy with respect to the given set of extensive constraints. Arguments are developed showing that the dynamics of irreversible relaxation of non-equilibrium systems consists of two qualitatively different steps. The theory is applied and verified by describing transport processes and calculating the corresponding coefficients. Structure formation and transition to turbulence are equally formalized in the thermodynamic framework.

*Presented at the Workshop on Time-Reversal Symmetry in Dynamical systems, Warwick, U.K., 9th–20th December 1996.
I. INTRODUCTION

Contemporary mathematical literature assigns an abstract meaning to the concept of dynamical systems. They are most often considered as substrates for particular problems in applied mathematics. Physics, by contrast, prefers thinking of dynamical systems as being macroscopic objects with time-dependent properties, consisting of microscopic particles responding to the laws of mechanics. The goal here is to establish links between observable macroscopic properties and the more or less predictable motion or trajectories of the system’s elements. By quoting formally fluid dynamics and statistical physics in the workshop’s announcement as topics to be covered, the physicist’s definition is implicitly included in the general debate. This implies possible confrontation with the experimental reality for validation of the conclusions. The present review has the latter aspect of the problem of dynamical systems in mind.

The general discussion concerns time-reversal properties. With physical systems, not considering (or excluding) possible external action, the microscopic laws of mechanics governing the motion of the particles are Hamiltonian and therefore time-reversible. Macroscopic time-dependent properties show however a high degree of irreversibility. Apparent contradiction between the symmetry properties of the microscopic laws and the experimentally verified macroscopic behaviour of dynamical systems remains a controversial subject of debate.

Macroscopic time-dependent phenomena shown by physical systems include relaxation of disturbances, transport effects like friction and others and bifurcations to more or less ordered dissipative structures. The last item has been quoted explicitly in the list of dynamical phenomena to be covered by the present general discussion. Considering the many connections prevailing between this item and the other time-dependent effects mentioned above, a general discussion including relaxation and transport effects is justified.

In this review it will be proven that next to the internal Hamiltonian laws of motion, observable physical systems rely on interactions with the external world for their global dynamics. Depending on the conditions, the step that controls the relevant time-dependent
phenomenon and defines the observed degree of time symmetry may depend either on internal or external effects. In all cases a correct formalism is required for expressing the properties of the surroundings and their relation to that of the system itself. This is achieved by extending the principles of thermodynamics to conditions removed from equilibrium. A review of paradigms and assumptions supporting the time-reversal symmetry problem in statistical physics will be given first. They will be critically analyzed and a new approach will be suggested based on analysis of Joule’s experiment. The necessary thermodynamic tools will then be developed. The thermodynamic formalism will be applied for predicting and discussing selected topics in fluid dynamics. In a first step, the transport coefficients are considered. Structure formation and transition to turbulence are developed from there on.

II. CONTROVERSIES

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 conservative Hamiltonian systems. Conflict between the time asymmetric behaviour of macroscopic relaxation and the strict reversible nature of microscopic dynamics of conservative systems has been the subject of discussions over nearly a century [1,2].

Results published in recent decennia in applied mathematics concerning 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 is meant to express dissemination of the system’s parameters throughout the available space towards homogeneous and statistically independent distributions. It associates irreversibility to an infinite Poincaré recurrence time for most initial fluctuations. Furthermore, progress obtained in characterizing deterministic chaotic motion (Lyapounov exponents) spurs theoretical research towards
relating the relevant numbers to transport properties associated with irreversible relaxation dynamics. In this context chaotic scattering of particles on hard disks (Lorentz gas) is used as a model for describing irreversible diffusion in agreement with reversible microscopic dynamics [5–8].

Using the language of functional analysis one arrives at a rigorous formulation of the fundamental difference between reversible and irreversible evolutions. The reversible evolution of dynamical systems is expressed by a group of isometric operators, whereas the irreversible one is described by a semigroup of strictly contractive ones. As microscopic laws are time-reversible, the evolution they cause must be formulated by isometric groups. By contrast, macroscopic irreversible processes can be described only by contractive semigroups. We are thus faced with the question of how this transition from a group to a semigroup can be justified. The presently most popular answer is proposed by the Brussels school associated with the name of I. Prigogine [9]. This school’s interpretation rejects formally the role of loss of information in deriving the second law of thermodynamics. It has been subjected to criticism in [10] on the basis of mathematical results of G. Braunss [11].

Aforementioned research trends assume explicitly that irreversible processes would occur in systems isolated from the environment. The statistical properties of the time dependent random forces acting on the particles are supposed to be completely determined by the initial conditions and by the dynamics of the system [1]. Rescaling is said to make phenomenological parameters (e.g. viscous drag controlling the motion of Brownian particles) converging to genuine irreversible properties of the system. Dissipative coupling with a reservoir is therefore explicitly rejected, as “artificial and unnecessary” [2].

Contrasting with the latter, some authors still insist on the unavoidable interaction of macroscopic systems with their environment acting as a reservoir or heat bath [12,13]. Stress is laid 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 back-reaction of the environment to the evolution of the system [14,15]. As an example, concerning viscous drag as mentioned above, the relevant dissipative force is said to originate from interaction of the
Brownian particle with the surrounding fluid acting as a reservoir. The time averaged value of this force gives rise to Stokes’ law, on which fluctuations are superimposed.

To anticipate and prevent future ambiguities, we specify the meaning to be given to some important key-words frequently used in the discussion to follow.

By isolated systems are meant systems the dynamics of which is defined in a unique way by time-independent Hamiltonians. They are obviously conservative. Since we are focussing next on systems that are not perfectly isolated, we need to give them an appropriate name. A system will be called quasi-isolated if it exchanges energy but not matter with its surroundings.

Equilibrium refers to any macrostate that is stationary (i.e. time-independent) under the given macroscopic constraints. As an example we may consider that this property holds for a gas contained within walls at different temperatures when it has reached stationary conditions. By approach to equilibrium we denote any observable macroscopic evolution towards equilibrium.

III. ISOLATED DYNAMICAL SYSTEMS

A. The Problem

Consider a system of $N$ identical structureless classical particles constrained to move in volume $V$. The state of the $i$-th particle is in unique way given by the vector of generalized coordinate $\vec{q}_i$ and by the vector of generalized momentum $\vec{p}_i$. Expression $(q,p)$ will denote the state of the collection of $N$ particles, or a point in the system’s phase space $\Gamma$. This system’s dynamics is described by Hamilton’s equations with the time-independent Hamiltonian $H(q,p)$ [16]. The action of the walls is represented by a high repulsive potential (a possible choice being an infinite potential barrier). The solution $(q(t),p(t))$ to these equations for some initial state $(q(0),p(0))$ can be written using a group of dynamical evolution operators $T_t$: 5
\[(q(t), p(t)) = T_t(q(0), p(0)).\]  

(1)

It represents the motion of a point along a trajectory in phase space \(\Gamma\).

Investigation of the evolution of an individual system is apparently not possible and therefore one resorts to statistical methods \[17\]. One considers an ensemble of equivalent systems. The ensemble properties are then described by means of a distribution function \(f(q, p; t)\), giving the probability density of finding a system at point \((q, p)\) in phase space at time \(t\) \[18\].

From the deterministic description defined by the group of operators \(T_t\), one goes over to the statistical description of evolution of the distribution function by introducing a group of operators \(U_t\) defined through relation

\[U_t f(q, p) = f(T_{-t}(q, p)) .\]

(2)

It is easy to show that the statistic evolution operator \(U_t\) is unitary — and thus isometric — if it acts in a Hilbert space \(L^2(\Gamma)\) of square-integrable functions defined on phase space \(\Gamma\) \[19\]. By Stone’s theorem there exists then a self-adjoint operator \(L\) (Liouville operator), such that \(U_t = e^{-iLt}\). Using the Poisson bracket notation it can be easily proved that \(L\) can be expressed by means of the Hamiltonian function as \(L f = i\{H, f\}\).

The Liouville equation,

\[i \frac{\partial f}{\partial t} = L f,\]

(3)

has for solution: \(f(q, p; t) = U_t f(q, p; 0) = e^{-iLt} f(q, p; 0)\), where \(f(q, p; 0) \equiv f(q(0), p(0))\).

Let \(\varphi\) denote one of the possible equilibrium functions. Since \(\varphi\) does not change with time, \(\partial \varphi / \partial t = 0\), whence \(L \varphi = 0\). From (3) we have obviously \(U_t \varphi = \varphi\). Now, unitarity of \(U_t\) (i.e. the equality \(U_t^* = U_{-t}\)) implies, first of all, invariance of the scalar product in the course of evolution

\[\langle U_t f | U_t g \rangle = \langle f | g \rangle \quad \text{for any} \ f, g \in L^2(\Gamma).\]

(4)

This reduces to \(||U_t g|| = ||g|| = \text{const}\) for \(f = g\). Taking now \(g = f - \varphi\), where \(f\) is any nonequilibrium distribution function, we obtain
\[ \|U_t f - \varphi\| = \text{const} \] \hspace{1cm} (5)

Hence, approach of mechanical systems to equilibrium cannot be described statistically as a strong convergence of the distribution function to an equilibrium function.

**B. BBGKY Hierarchy**

The description of a system on the basis of a distribution function \( f(q, p; t) \) is complete from a statistical point of view. However, solving equation (3) explicitly is apparently not possible. Since the distribution function cannot converge strongly to any equilibrium function, the entropy as defined by Gibbs by relation

\[
S_G = -\int_{\Gamma} f(q, p; t) \ln f(q, p; t) \, dq \, dp \hspace{1cm} (6)
\]

is equally time-independent \([17]\). This drawback is eliminated by introducing so-called *reduced distribution functions* which are obtained by integrating function \( f(q, p; t) \) over a subset of particles. For example, we obtain an \( r \)-particle distribution function \( f_r(q, p; t) \) by integrating \( f(q, p; t) \) over positions and momenta of \( N - r \) particles \((0 < r \leq N - 1)\). Such a function describes statistical properties of a subsystem comprised of \( r \) particles.

It turns out that subsequent integration as above of Liouville’s equation (3) leads to a system of \( N - 1 \) integro-differential equations for a set of \( N - 1 \) reduced distribution functions. The equations have the property that the equation for \( f_r \) \((r < N)\) contains always function \( f_{r+1} \) too \([20]\). This system (or hierarchy) of equations, the *BBGKY hierarchy*, can be solved only if interrupted at some level. To break the hierarchy, say at the \( r \)-th level, means expressing function \( f_{r+1} \) with the help of \( f_r \) in equation for \( f_r \). Such an interruption having been performed, the equation for \( f_r \) is in principle solvable. The solution may subsequently be substituted in the equation for \( f_{r-1} \). The procedure may be continued until we are left over with the only equation for the single-particle distribution function \( f_1 \). This is the *master (kinetic) equation*. 

7
The mathematics leading to an \( f_r \) independent of term \( f_{r+1} \), can obviously not be substantiated rigourously. One relies exclusively on more or less acceptable heuristic semi-quantitative physical assumptions.

The first attempt in this direction was proposed in 1872 by L. Boltzmann, who derived an integro-differential equation for the one-particle distribution function of a gas and proved that its solution proceeds to the equilibrium distribution function as time goes on. Among the assumptions used, the most important one was the so-called molecular chaos hypothesis, according to which particle momenta are independent of their positions [21]. This hypothesis is eventually equivalent to the assertion that the evolution of a system is not fully deterministic and may be regarded as a stochastic process. Hence the derivation of second law of thermodynamics (or H-theorem) from Boltzmann’s equation cannot be considered as the proof for approach of gases to equilibrium. Despite this, Boltzmann’s equation has become the foundation of the kinetic theory of gases. The hypothesis of molecular chaos remained, however, for more than a century the target of either criticism or efforts to find its exact justification [22].

C. Spectral Theory and Approach to Equilibrium

A well-know theorem of functional analysis [23], states that the spectrum \( \sigma(L) \) of any self-adjoint operator \( L \), acting in a space \( L^2(\Gamma) \) of square-integrable functions, can be decomposed in a unique way into three constituents: the pure point spectrum \( \sigma_{pp}(L) \) consisting of eigenvalues of \( L \), the absolutely continuous \( \sigma_{ac}(L) \) and the singular spectrum \( \sigma_{sing}(L) \). Thus

\[
\sigma(L) = \sigma_{pp}(L) \cup \sigma_{ac}(L) \cup \sigma_{sing}(L) .
\] (7)

Let \( \{E_\lambda\} \) be the resolution of identity for operator \( L \) and \( \nu_f = \langle E_\lambda f \mid f \rangle \) the spectral measure generated by a function \( f \in L^2 \). Decomposition (7) of the spectrum implies decomposition of \( L^2 \) in orthogonal subspaces

\[
L^2 = L^2_{pp} \oplus L^2_{ac} \oplus L^2_{sing} .
\] (8)
where $L^2_{pp} = \{ f \in L^2 : \nu_f \text{ is pure point} \}$, $L^2_{ac} = \{ f \in L^2 : \nu_f \text{ is absolutely continuous} \}$ and $L^2_{sing} = \{ f \in L^2 : \nu_f \text{ is singular} \}$. The basis of $L^2_{pp}$ consists of eigenfunctions of $L$. We shall denote $f \in L^2_{pp}$ by $f_{pp}$, $f \in L^2_{ac}$ by $f_{ac}$ and $f \in L^2_{sing}$ by $f_{sing}$. Decomposition (8) means that every $f \in L^2$ can be written in the form

$$f = f_{pp} + f_{ac} + f_{sing} .$$  (9)

It must be stressed that this decomposition is invariant under the action of evolution operator $U_t$, i.e. $U_tL^2_{ac} = L^2_{ac}$, $U_tL^2_{pp} = L^2_{pp}$ and $U_tL^2_{sing} = L^2_{sing}$. This means that each component of $f$ evolves under $U_t$ independently of the other ones. Hence, the components evolve in orthogonal subspaces of $L^2$. The dynamics of the system can be, therefore, decomposed into subdynamics describing qualitatively different types of evolutions.

In view of the above, any component of a distribution function evolves with time independently of the other ones. One can, therefore, investigate the time evolution of each component separately. It turns out that for realistic Hamiltonians (and therefore Liouvillians) $\sigma(L)_{sing} = \emptyset$. Actually, the singular part of the spectrum corresponds to “pathological” Hamiltonians [24]. For $f_{ac}$ it was shown in [25] that $U_t f_{ac}$ tends weakly to zero for $|t| \to \infty$, i.e. in this limit we have $\langle U_t f_{ac} | g \rangle = 0$ for any $g \in L^2$. In an alternative notation, $U_t f_{ac} \overset{w}{\to} 0$. Finally, the evolution of $U_t f_{pp}$ has been proved to be quasi-periodic.

Functions with the property $U_t f = f$ (for any $t$) span obviously a linear subspace. Let us denote the latter by $L^2_{const}$. For each $f \in L^2_{const}$ we get from (3) $L f = 0$, i.e. $f \in \text{Ker} L$. The inverse implication is equally true, so that we have $L^2_{const} = \text{Ker} L$. A solution of equation $U_t f \equiv f$ is an eigenfunction of operator $L$ corresponding to the eigenvalue $\lambda = 0$. This yields $\text{Ker} L = L^2_{const} \subseteq L^2_{pp}$.

Let now $M \subset \Gamma$, $\mu(M) = \varepsilon$, $0 < \varepsilon < \infty$ and let $\chi(M) \in L^2(\Gamma)$ be the characteristic function of the set $M$ (i.e. $\chi(x) = 1$ for $x \in M$ and $\chi(x) = 0$ otherwise). For arbitrarily small $\varepsilon > 0$, the convergence $U_t f_{ac} \overset{w}{\to} 0$ implies

$$\lim_{|t| \to \infty} \langle U_t f_{ac} | \chi(M) \rangle = 0 ,$$  (10)
which is equivalent to
\[
\lim_{|t| \to \infty} \int_M (U_t f_{ac}) \, d\mu = 0 . \tag{11}
\]
This resembles the behaviour of function \(\sin(tx)\) on the finite interval of \(R\) and one can regard convergence \(11\) as the generalization of the Riemann-Lebesgue lemma to functions \(f \in L^2_{ac}\).

The above implies that \(U_t(f_{ac} + f_{const})\) tends weakly to \(f_{const}\). Weak convergence is mathematically a well defined property with physically relevant contents. In physical systems, stress is rather lead on the observables, or expressions like \(\langle U_t f | g \rangle\), where \(g\) represents dynamical or generating functions. Hence, if the Liouville operator acting in \(L^2(\Gamma)\) has an absolutely continuous spectrum and if its only eigenvalue is \(\lambda = 0\), then, for positively definite functions (distribution functions), as \(|t| \to \infty\), \(\langle U_t f | g \rangle\) tends to \(\langle U_t f | f_{const} \rangle\), that is the value of the observable corresponding to an equilibrium state. This result may be regarded as the exact criterion of approach to equilibrium in conservative systems.

The above results show that approach to equilibrium in isolated systems makes sense only for observables, not for distribution functions. Distribution functions themselves change reversibly, and without any apparent tendency to approach equilibrium. Observables related to different distribution functions may tend to the same limit, meaning that the approach to equilibrium is connected to a loss of information caused by the integration leading to \(\langle U_t f | g \rangle\).

D. The Brussels School Theory

As mentioned above, the spectral theory of operators shows that the spectrum of any self-adjoint operator \(L\) is real and that operators defined as \(U_t = e^{-iLt}\), with self-adjoint \(L\), represent a one-parameter group of unitary operators preserving the norm, i.e. \(\|U_t f\| = \|f\|\) for any \(f \in L^2\). Operators preserving the norm are called isometric.

Unitary group \(U_t\) is defined for any real \(t\) and — if such a group describes the evolution of distribution functions — this means, if an evolution is possible for \(t > 0\), then the evolution
for $t < 0$ is equally possible. Hence, the unitary group describes a reversible evolution, expressed explicitly by $U_{-t}(U_t f) = f$.

Irreversible evolution can be described only by semigroups (which cannot be continued into groups), i.e. sets of operators defined e.g. only for $t \geq 0$, not for $t < 0$. Let us denote such a semigroup by $W_t$. The impossibility to define a semigroup for any real $t$ follows from the spectral properties of its generator $K$: $W_t = e^{-iKt}$. If the spectrum of $K$ contains points with negative imaginary components, the semigroup is strictly contractive, i.e. $\|W_t f\| < \|f\|$, so that it is not isometric and it cannot be continued into a group [26].

The reversible evolution is expressed by a group of isometric operators, the irreversible one, on the contrary, by a semigroup of strictly contractive operators. The most popular answer to the question of how such a transition from a group to semigroup occurs when going from the microscopic level to the macroscopic one is given by the Brussels school. The short formulation of this viewpoint might run as follows. Suppose that for a given system there exists a nonunitary operator $\Lambda$ such that

(a) $W_t = \Lambda U_t \Lambda^{-1}$ is a strictly contractive semigroup for $t \geq 0$,

(b) $W_t$ is positivity preserving, i.e. $f(\omega) \geq 0$ for almost all $\omega \in \Gamma$ implies $W_t f(\omega) \geq 0$ for almost all $\omega$ too, and

(c) $W_t f_{\text{const}} = f_{\text{const}}$.

The dynamics $U_t$ of the system is then said to be inherently stochastic, meaning roughly that the microscopic behaviour of the system is deterministic, while it behaves as if it was really stochastic. That is why it is appropriate to describe the dynamics using statistical methods [27]. Under the above conditions it is claimed specifically [9], that operator $\Lambda$ converts the deterministic evolution into a Markov process whose transition probabilities can be obtained from the adjoint of $W_t$ by

$$P(\omega, \Delta; t) = W_t^{\ast} \chi(\Delta) ,$$

(12)

where $P(\omega, \Delta; t)$ is the probability of transition from point $\omega$ to domain $\Delta$ of phase space in time $t$ and $\chi(\Delta)$ is a characteristic function of the set $\Delta$. Operator $\Lambda$ is called the system’s
Lyapunov converter.

It is not expected that $\Lambda$ would exist for all dynamical systems (flows). It is shown in [28] that the mixing property is necessary and the condition of $K$-flow sufficient for the existence of a Lyapunov converter $\Lambda$. The close connection between the intrinsic irreversibility of the system, expressed by the existence of $\Lambda$, and the instability of the motion is put forward.

The result of the Brussels school is important in that it divides the systems into two categories: systems in which it makes sense to expect thermodynamic behaviour and systems where this is not the case (trivial examples of the latter are harmonic oscillators). This classification is however used as the basis for derivation of far-reaching consequences which are not always convincing.

The Brussels school does not give any physical interpretation to the action of operator $\Lambda$. It is only stated that stochastic evolution arises from a deterministic one “simply as a result of ‘change of representation’ brought about by (non-unitary) similarity transformation $\Lambda$” [9]. The physical meaning of this transformation is indeed nowhere explained. Moreover, the analysis of the properties of Markov processes shows that the claim, that every semigroup $W_t$ of operators acting on $L^2$ and having the properties $(a)$–$(c)$ (see above) defines a Markov process, is not in general sufficient to prove that the process has time-independent transition probabilities. This condition is necessary for a process to have any physical meaning at all.

The action of $\Lambda$ is equivalent to a change of dynamics of the system from deterministic to stochastic [29]. Such a change can be performed in many ways and the operator $\Lambda$ is constructed precisely in such a way that the transition probabilities do not depend on time. The possibility to change deterministic evolution into a stochastic one does not give any information about the original deterministic evolution, as is demonstrated by the following example [10].

Consider the unitary group of shifts $U_t f(x) = f(x+t)$, $f \in L^2(R; dx)$. Using the operator of differentiation $d/dx$, this group may be written, in the form

$$U_t = e^{t d/dx},$$

(13)
so that the generator of the group is operator \( L = \frac{id}{dx} \). For this group it is possible to construct a Lyapunov converter \( \Lambda \), defined on the subspace of continuous functions with compact support, converting \( U_t \) into the strictly contractive semigroup \( W_t = \exp(t \frac{d^2}{dx^2}) \), \( t \geq 0 \) associated with a one-dimensional diffusion process, like diffusion of heat \([\text{11}]\). The group of shifts \( U_t f(x) = f(x + t) \) lacks obviously any resemblance to a process that could be either random, stochastic, approaching equilibrium, or even irreversible. The only convergence property it has is the weak approach to a function \( \varphi \equiv 0 \).

This example shows clearly that the existence of a Lyapunov converter (be it that converting an isometric group into a strictly contractive one) is not sufficient to prove the approach to equilibrium. Consequently (in view of our comments about the relation between irreversibility and approach to equilibrium) this cannot justify the origin of irreversibility. However, it turns out that the notion of Lyapunov converter is significant in understanding the essence of the method of complex scaling introduced originally for identifying the so-called resonant discrete points in the continuous spectrum of quantum systems \([\text{30,31}]\).

IV. QUASI-ISOLATED DYNAMICAL SYSTEMS

The discussion above was centred on the quest for solutions to irreversible approach to equilibrium on the basis of reversible microscopic laws in perfectly isolated systems. The proposed theories leave us disappointed, being restricted to qualitative results and concerned only with the limiting behaviour for \( t \to \infty \). They are unable to predict finite-time dynamics and experimentally verifiable results.

Contrasting with the above let us not consider the system’s boundaries (walls) as a potential to be added to the Hamiltonian, but instead as the locus for an independent contribution to the particles’ motion. This is the quasi-isolated system’s paradigm.
A. Experimental evidence

Discussion of the 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 long time evolution towards a new equilibrium distribution following rupture of the division is taken to be modelling irreversible behaviour of the global dynamics. Joule repeated Gay-Lussac’s experiment with great accuracy. His purpose was to measure possible heat exchange with an external calorimeter associated with spontaneous expansion. With an ideal gas, if no mechanical work is allowed to be performed during the process, when the system had reached its final state of equilibrium, no net exchange of heat with the surroundings was observed. Joule concluded that the system behaved as if it were isolated. Be it stressed that Joule was considering only the initial and the final conditions, neglecting whatever dynamics was involved in reaching final equilibrium.

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 both cases the excess air contained in the balloon disseminates spontaneously throughout the rooms, never to come back again, compressed in its initial volume, 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 correctly shaped walls, the initial information might 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) assumed usually to be the source of relaxation. The only difference between the two experiments is the nature of the walls. One is therefore forced to conclude that global relaxation dynamics of a spontaneously expanding gas leading to final equilibrium depends on the acoustic (physical) quality of the walls representing the system’s environment.

The experiment suggests convincingly that the global dynamics consists of two independent major steps. According to the coupling efficiency of the system to its surroundings (impedance matching), either step may be rate determining. If coupling is very effective, global dynamics is controlled by slow transport of mechanical properties to the walls (momentum, energy, matter). Transport coefficients like viscosity, thermal conduction etc., are correctly defined only in such non isolated conditions. By contrast, if the system is nearly isolated (quasi-isolation), memory of the initial conditions remains for some time as a collective or coherent motion of the particles (acoustic motion) and full thermodynamic equilibrium is slow to reach. Strict isolation and transport effects are incompatible.

The two steps involved by the scenario are very different in their dynamics. Depending on the system of interest, they may be more or less concomitant. For simplicity, we shall take them next as frankly separated in the time.

In Joule’s experiment, as soon as the membrane has been 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 into the jet. This is subtracted from the initial thermal supply (adiabatic expansion). Loss of thermal energy is equivalent to cooling.

On reaching the wall opposite the puncture, if this is hard, the initial jet is reflected and turns progressively into a compound acoustic perturbation with the same energy. The spectrum and phases of its components are the memory of the initial conditions and of the shape of the reverberating walls (coherence). This is the first step of the general process. When this is done, although the particles are disseminated throughout the whole volume, the system may not be claimed to be at equilibrium (weak irreversibility).

Relaxation of the coherent or collective motion starts now. Every collision with inco-
herently fluctuating wall atoms interrupts the running canonical trajectory. A new one starts, with possibly modified initial conditions\textsuperscript{1}. Earlier correlations are progressively broken, thereby thermalizing the energy accumulated initially in the jet and stored later in the acoustic perturbation. As a result, if the system is an ideal gas (hard spheres allowed), aforementioned transient cooling is progressively neutralized, as is expected by Joule’s result. When final equilibrium has been reached, collective or coherent motion has relaxed and information about the initial conditions is completely lost (strong irreversibility).

Initial dissemination of the particles throughout the system follows conservative Hamiltonian dynamics. No matter how intricate (chaotic) the motion of individual particles may be (Sinai billiards), this part of the motion preserves the memory of the initial conditions. Contrasting with the latter, the correlations removing step, where the particular properties of the walls determine how efficiently the system is coupled to its surroundings introduces in the global motion stochastic non Hamiltonian jumps between the different accessible trajectories. According to whether during the particular impacts the relevant wall atom moves towards the colliding particle or in the opposite direction, transient work is transferred to the system or to the environment. Energy fluctuates about its average value. Only if the thermodynamic requirement is fulfilled that the system and its neighbourhood are at the same temperature does the average energy transfer vanish.

B. Thermodynamics

\textsuperscript{1}It should be obvious that this behaviour is much less stochastic than the one put forward by Boltzmann’s Stoßzahlansatz, according to which stochasticity builds up at every collision between two particles.
1. *Entropy*

Any function determined completely by the set of constraints defining the relevant system’s particular macrostate is a function of state. In 1865 Clausius discovered a function of state called entropy which, for reversible processes, is defined as a differential $\delta S = \delta Q/T$, where $T$ is the system’s temperature. In 1877, Boltzmann derived an expression that links the experimental entropy to the statistical properties of the relevant macroscopic system. This reads

$$S = k_B \ln[W(A)],$$

with $W(A)$ meaning the probability associated to macrostate $A$. The latter is to be interpreted as the total volume accessible to the motion in phase space, given the set of constraints (represented by the collective variable $A$) describing 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 $V$, the traditional microcanonical variables. In the literature, extension of the discussion to non-equilibrium macrostates is avoided. This limitation will be reconsidered below.

In a strictly conservative isolated 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 are not possible. Then, according to the definition, the entropy is zero and it does never change. This conclusion is consistent with Liouville’s theorem claiming conservation of the measure in phase space when the mechanics is conservative.

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. Accessibility means incoherent transitions between the available and accessible 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 resolution linked to the definition of the entropy is the average lifetime of conservative trajectories. With macroscopic systems, where the impact rate with boundaries goes to infinity, the average lifetime and hence the time resolution tend to zero.

Relaxation implies relief of constraints. It opens the way to an enhanced choice of trajectories (microstates). Accessibility of more trajectories increases Boltzmann’s entropy.

In describing equilibrium states, the extensive variables mentioned traditionally are the basic microcanonical constraints \( E, V \) and \( N_r \). 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 the aforementioned Gay-Lussac 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 defining the constraints of a macroscopic system in a particular macrostate be written \( \{X_l\} \). The entropy is a function of this collection of variables. By differentiating the entropy with respect to the set we get by definition the set of conjugate intensive variables or intensities \( \{\xi_l\} \):

\[
\frac{dS}{dX_l} = \frac{\partial S}{\partial X_l} = -k_B \sum_l \xi_l dX_l.
\]

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

Equation (15) is Gibbs’ celebrated equation, generalized to non-equilibrium macrostates. In the simplified model of a spontaneously expanding jet mentioned above (velocity of the collective motion is \( \vec{v} \)), the new version of Gibbs’ equation reads

\[
\frac{dS}{dE} = \frac{\partial S}{\partial E} \frac{dE}{T} + \frac{P}{T} dV - \sum_r \frac{\mu_r}{T} dN_r - k_B \vec{\sigma} \cdot d\vec{P},
\]

(16)
where $\vec{P} = Nm\vec{v}$ represents the collective momentum of the jet and $\vec{\sigma}$ the conjugate intensity.

It may be shown [15] that $\vec{\sigma} = \vec{v}/k_BT$. In the last term of equation (16), the differential of the collective or coherent energy is easily recognized. We have therefore equivalently

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \sum \frac{\mu_r}{T}dN_r - \frac{1}{T}d(coherent\ energy). \quad (17)$$

Energy conservation throughout the expansion makes $dE = 0$ and isolation causes $dN_r = 0$. During the adiabatic dissemination period, the second term (work made available by 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, the integral of the last term vanishes and Gibbs’ equation yields the correct final equilibrium entropy after expansion.

If the contribution regarding the non-equilibrium constraint had been omitted in equations (16) and (17), we would not have been able to describe the thermodynamics of the low entropy non-equilibrium transient state.

2. The generalized Massieu function

The inconvenience of considering the entropy as the leading thermodynamic function is that it is an explicit function of the extensive properties ($X_l$), while the intensities ($\xi_l$) are better measured and controlled by the environment. That is why 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 concerning the entropy, general laws involving the energy do not exist. It is therefore advisable to consider transformations involving the entropy itself. If all the parameters (excepting the system’s physical volume $V$) defining non-equilibrium conditions are included in the transformation, we obtain the generalized Massieu function $\mathcal{M}(\xi_l, V)$:
Unlike Massieu’s original proposal, $\mathcal{M}$ is an explicit function of all the state defining intensities. It may be verified that

$$\frac{\partial \mathcal{M}(\xi_l, V)}{\partial \xi_j} = X_j.$$  \hfill (19)

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 values in the neighbourhood. We might call them strong intensities (e.g. the temperature in an efficiently thermostated system). Dynamics of transient states refers to the intensities of the rate determining 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 generalized 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.

The equations above (18–19) are generally valid. With ideal gases, the expression for the generalized Massieu function takes a very simple form. Individual motions being independent, the global motion may be represented by a swarm of points in a reduced 6-dimensional single-particle phase space ($\Gamma_1$). From here on, $\Gamma$ will represent a one-particle phase space.

Let $f(x)$, $x \in \Gamma$, be the most probable particle distribution: that which maximizes the entropy. Any extensive property $X_j$ is then related to a generating function $\phi_j(x)$ so that

$$X_j = \int_\Gamma \phi_j(x)f(x)d\Gamma \equiv \langle \phi_j|f \rangle.$$  \hfill (20)

In that context, function $f(x)$ is readily known to be

$$f(x) = \exp[\sum_l \xi_l \phi_l(x)],$$  \hfill (21)
where the intensities \( \{ \xi_l \} \) are the Lagrange multipliers used in the maximizing process for
the entropy.

With the latter distribution function, it may be verified that \( \mathcal{M} \) takes the very simple
form
\[
\mathcal{M}(\xi_l, V) = \int_{\Gamma} \exp \left[ \sum_l \xi_l \phi_l(x) \right] d\Gamma.
\] (22)

Its numerical value is the (average) number of particles contained in the system. Through
the integration limits in configuration space it has the system’s physical dimensions \( V \) 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 a
low density approximation when the duration of the inter-particle collisions is negligible
compared to the time separating the collisions (e.g. hard spheres).

**V. TRANSPORT COEFFICIENTS**

The main objective of the theory is to predict transport coefficients from first principles,
to be compared with the experiment. Since Boltzmann’s equation there has been a consid-
erable literature concerning that question [20,32]. Most frequently cited are the traditional
Chapman and Enskog derivations [33] and the more recent Green-Kubo formalism [20].

When referring relaxing systems to their fixed boundaries, the thermodynamic approach
fits best into an Eulerian frame [34,35]:
\[
\frac{df_N}{dt} = \{f_N, H\} + J.
\] (23)

Poisson bracket \( \{f_N, H\} \) expresses implicit deterministic contribution to the motion while the
source/sink term \( J \) describes explicit stochastic action of the environment. If \( df_N/dt \neq 0 \), we
have a transient state. Either implicit or explicit contributions may then be rate determining. If \( df_N/dt = 0 \), \( J \) may still be different from zero, balancing a non-zero \( \{f_N, H\} \). That are stationary states. Steady transport of heat between reservoirs at different temperatures and steady transport of momentum in the Couette flow belong to that class of processes. Stochastic action of the neighbourhood defines a finite life-time to deterministic trajectories. In stationary conditions, flows of extensive properties supported by \( J \) are obtained by integrating the deterministic contribution over this average life-time. For individual particles, this is the average periodicity \( \tau \) of effective relaxing collisions.

In very low density systems, when the mean free path is comparable to the system’s physical dimensions (Knudsen gas), properties picked up by the particle at one wall are transported in a single jump to the opposite one. In the thermodynamic limit (non-Knudsen regime), head-on collisions of identical particles do not hamper transport properties but parallactic or off-axis inter-particle collisions do. They reduce the range of free transport, while information about the reservoir conditions is transferred to the relevant bulk region.

We consider a given extensive property \( X_j \) with generating function \( \phi_j(x) \), \( x \in \Gamma \), and we investigate its flow along the \( z \)- direction. Let \( z^* \) be the ordinate of an arbitrary plane. The basic equation for the relevant flow \( J_j \) through this plane is

\[
J_j = \frac{1}{\tau} \int \int \int (\frac{d^3p}{h^3}) \int_{(z^*-p_z \tau/m)}^{z^*} \phi_j(x) \exp[\sum \xi_l \phi_l(x)] dz.
\]

(24)

The term \( 1/h^3 \) is introduced for the sake of normalization [36].

Equation (24) stresses that free transport of the given property by particles is limited to the life-time of their trajectories. Local thermodynamic conditions at the latter’s onset determine how much of the property is transported. Hence, the lesser the collision frequency, the more effective is the transport. Collisions increase the system’s resistance to flow.

When integrated, the effective collision frequency comes in the normalized form \( \tau/(D\sqrt{\beta m}) \). With Knudsen systems (mean free path at least of the order of the system’s physical dimensions), this parameter equals 1. In thermodynamic conditions, the parameter is much less than 1, justifying expanding the integrand to its lowest order in \( \tau \).
In the following, equation (24) will be applied to different types of flows.

A. Single-component gases

1. Viscosity

We consider a fluid bound by a pair of walls distant by 2\(D\), moving in opposite directions (Couette flow). The system’s stationary conditions are defined completely by the set of constraints listed in table I. The intensities under direct control of the surroundings are the particles number, the kinetic energy and the intensity conjugate to the gradient of shear momentum. It may be verified [15] that the velocity of the walls \((y–\text{direction})\) equals \(\pm \sigma_y/\beta\).

| \(X_l\)                  | \(\phi_l(\Gamma)\)                      | \(\xi_l\)        |
|-------------------------|----------------------------------------|-------------------|
| Particles number        | 1                                      | \(\alpha\)       |
| 2nd moment of particle distribution | \([\zeta^2 - 1]\)                       | \(\theta_2\)     |
| Kinetic energy          | \(\sum(p^2/2m)\)                       | \(-\beta\)       |
| 2nd moment of energy distribution | \((\zeta^2 - 1) \sum(p^2/2m)\)             | \(-\gamma_2\)   |
| Gradient of shear momentum | \(\zeta p_y\)                         | \(\sigma_y\)     |
Two variables remain to be determined, namely $\theta_2$ and $\gamma_2$, requiring two independent equations. In stationary conditions, pressure gradients or acoustic perturbation are absent. This is expressed by vanishing $z^*$-dependence of flow of transverse momentum ($p_z$). Likewise, the total flow of energy through the system is zero. By implementing equation (24) with the two relevant generating functions, the conditions $\partial J_{p_z} / \partial z = 0$ and $J_E = 0$ yield together

$$\theta_2 = 0, \quad \frac{5}{2} \frac{\gamma_2}{\beta} = \frac{m\sigma^2}{2\beta}. \quad (25)$$

Flow of the shear component of momentum ($p_y$) is obtained by implementing equation (24) with generating function $p_y$, where $\theta_2$ and $\gamma_2$ are replaced by their values. This yields

$$J_{p_y} = -\frac{\sigma_y}{2\beta D} \frac{n\tau}{\beta}, \quad (26)$$

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

The coefficient of shear viscosity is the ratio of the forces applied to the plates, compensating for transfer of momentum from wall to wall, to the velocity gradient ($\sigma_y/(\beta D)$).

Following equation (26), its value is

$$\eta = n \frac{\tau}{\beta}. \quad (27)$$

2. Thermal conduction

Let us consider now a system in thermal contact with two planar heat reservoirs at different temperatures separated by $2D$. The system’s stationary conditions are completely described by the set of constraints listed in table II. By inspecting the generating function conjugate to the temperature gradient it is clear that $k_B \nabla T = -\gamma_{11}/(\beta D)$.

In the presence of a temperature gradient, particles moving towards the cold wall have been equilibrated with the system upstream in a hotter region at the instant of their last collision and vice-versa. Hence, 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 on the average immobile, collective momentum must be transferred by the container into the system. That is why a generating function for collective motion of the particles perpendicularly to the walls needs to be considered in constructing the expression for flow of heat.

| $X_l$                  | $\phi_l(\Gamma)$ | $\xi_l$ |
|-----------------------|-------------------|---------|
| Particles number      | 1                 | $\alpha$ |
| Gradient of particle distribution | $\zeta$          | $\theta_1$ |
| Kinetic energy        | $\sum(p^2/2m)$   | $-\beta$ |
| Gradient of energy distribution | $\zeta/D \sum(p^2/2m)$ | $-\gamma_1$ |
| Collective momentum   | $p_z$             | $\sigma_z$ |
The intensities under direct control of the surroundings are the particles number, the average kinetic energy and the temperature gradient. Two intensities remain to be determined: $\theta_1$ and $\sigma_z$. This requires two independent equations. One is stationarity. The other equation describes mechanical equilibrium of the system between its walls.

Let $z^*$ be an arbitrary position between the boundaries. The average local density $n$ responds to the equation

$$n(z^*) = \frac{1}{h^3} \int \int \int dp_x dp_y dp_z \exp \{ \sum_l \xi_l \phi_l[(z = z^*), p_x, p_y, p_z] \}. \quad (28)$$

We call $n_+(z^*)$ the partial density of the particles with positive velocity along the $z$–direction. Stationarity implies that this partial density equals the sum of the densities of the particles present at places from where they will be reaching this position without disturbance after one collision period, their velocities being oppositely oriented. Hence

$$n_+(z^*) = \frac{1}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_0^{\infty} dp_z \exp \{ \sum_l \xi_l \phi_l[(z = z^* - \frac{p_z \tau}{m}), p_x, p_y, p_z] \}. \quad (29)$$

This condition yields

$$\left( \theta_1 - 2 \frac{\gamma_1}{\beta} \right) \frac{\tau}{mD} = 2\sigma_z. \quad (30)$$

The second condition expresses position independence of flow of momentum across the system. Equation (24) is used with $p_z$ as the flow defining generating function. Condition $\partial J_{pz}/\partial z = 0$ yields

$$\theta_1 = \frac{5}{2} \frac{\gamma_1}{\beta}. \quad (31)$$

For flow of energy (heat) through the system, the generating function in equation (24) is $\sum (p^2/2m)$. If internal rotation is superimposed on translation (Eucken’s correction [33,37]), the relevant contribution should be added to the generating function. With atomic gases however, the result reads

$$J_E = \frac{15}{8} \frac{\gamma_1}{\beta^2 D} n \frac{\tau}{\beta m}. \quad (32)$$
Heat conductivity ($\lambda$) is the ratio between the sum of the exchanges at either walls ($2J_E$) and the temperature gradient. Hence

$$\lambda = \frac{15}{4} \frac{k_B}{n} \frac{n}{\beta m} \tau.$$  \hspace{1cm} (33)

In equations (27) and (33), the transport coefficients are expressed in terms of the effective collision periodicity $\tau$. For absolute comparison with the experiment, an additional expression is required that relates the latter to the mechanical properties of the colliding species (mass and cross-section) at the given temperature. Without this additional information, only the ratio between viscosity and heat conductivity may be compared with experimental data. This ratio is by definition Prandtl’s number

$$\text{Pr} = \frac{\eta c_p}{m \lambda},$$ \hspace{1cm} (34)

with $c_p$ as the constant pressure heat capacity. Implementation with the results obtained above yields the experimental results identically.

**B. Mixtures of atomic gases**

Let the components of a given mixture be indexed $A$ and $B$, where $A$ points to the substance with the higher mass. Each component may be considered as a separate subsystem, with its own thermodynamic variables, interacting simultaneously with the other one and with the environment. The generalized Massieu function being extensive, we have for the composite system

$$\mathcal{M} = \mathcal{M}_A + \mathcal{M}_B.$$  \hspace{1cm} (35)

With dilute gases or gases interacting as hard spheres, the individual generalized Massieu functions are defined as in equation (22). For each component separately the generating functions to be used are the same as for single-component gases (see tables I and II), excepting for the requirement of indexing the relevant masses in the appropriate generating functions. In stationary or quasi-stationary conditions (see below), for exchangeable properties where
equilibrium between the subsystems prevails, the intensities are the same. In the examples treated below, that is the case for the temperature and its moments and for the intensities conjugate to collective motion. Intensities conjugate to not exchangeable properties and their respective moments will be indexed according to the particular component they refer to.

The collision periodicity has been shown above to be an essential ingredient in the dynamics. In multi-component systems, there is an average collision periodicity for each of the constituents \((\tau_A, \tau_B)\). It measures for each how long the relevant atoms move freely before being halted by the matrix formed by the remaining particles.

In multi-component systems there are homogeneous and heterogeneous collisions. Their frequencies add up. The efficiency for exchange of momentum from a colliding atom to the local thermodynamic bath depends on the masses of the collision partners. When a heavy particle hits a light constituent of the thermodynamic bath, its path is less disturbed and less momentum is transferred than in the opposite case.

We assume a particle with mass \(m_1\) and linear momentum \(\vec{P}\) hitting a stationary matrix particle with mass \(m_2\). If the exit path of the matrix particle forms an angle \(\psi\) with the incident one, momentum transferred to the matrix equals \(2|\vec{P}|\cos(\psi)m_2/(m_1 + m_2)\). Hence, the relative transfer efficiency of heterogeneous collisions is \(2m_2/(m_1 + m_2)\). For the total effective collision frequency of atoms of one sort with respect to the matrix \((1/\tau)\), the latter coefficient is the appropriate scaling factor relating efficiency of heterogeneous collisions to homogeneous ones.

With hard spheres, the traditional expression for the collision periodicity between identical particles with collisional cross-section \(d\) is known to be \[33\]

\[
\tau = \frac{5}{16} \frac{\sqrt{\pi m \beta}}{n \pi d^2}.
\] (36)

Let now the collision cross-sections be respectively \(d_{AA}, d_{BB}, d_{AB}\). Using the efficiency parameter defined above and adding for either constituents the homogeneous and the heterogeneous contributions, the total effective collision periodicities read
\[
\tau_A = \frac{5}{16} \sqrt{\frac{\beta}{\pi}} \left( \frac{n_A d_{AA}^2}{\sqrt{m_A}} + \frac{2m_B}{m_A + m_B} n_B d_{AB}^2 \sqrt{\frac{m_A + m_B}{2m_A m_B}} \right)^{-1}, \tag{37}
\]
\[
\tau_B = \frac{5}{16} \sqrt{\frac{\beta}{\pi}} \left( \frac{2m_A}{m_A + m_B} n_A d_{AB}^2 \sqrt{\frac{m_A + m_B}{2m_A m_B}} + \frac{n_B d_{BB}^2}{\sqrt{m_B}} \right)^{-1}. \tag{38}
\]

From here on it is advisable to replace \( n_A \) by \( xn \) and \( n_B \) by \((1 - x)n\).

With hard spheres we have \( d_{AB} = (d_{AA} + d_{BB})/2 \). It appears that the published data on the viscosity of mixtures of atomic gases is accurate enough to allow the heterogeneous hard sphere cross-section to be corrected by a factor \( \epsilon \) close to 1.

1. Viscosity

With Couette flow conditions, the intensities under direct control of the surroundings are the intensities conjugate to the particle numbers of either substances (\( \alpha_A, \alpha_B \)), the temperature (or better \( \beta \)) and the intensity conjugate to the linear moment of shear velocity \( \sigma_y \) (see table I). Three intensities need still to be determined, namely the quadratic moment of the temperature (or better \( \gamma_2 \)) and the quadratic moments of the particle distributions for A and B (\( \theta_2, A, \theta_2, B \)).

The three additional relations required for completing the thermodynamic description of the system are of the same vein as those used for Couette flow in single component gases. For symmetry reasons, it is easy to show that flow of shear momentum is independent of the particular values of three missing intensities. The principles involved in their determination will be therefore skipped.

Flow of momentum is supported by either components. For each, the contribution is given according to equation (24), where the generating function to be implemented as \( \phi_j \) is \( p_y \). Integration yields

\[
J_{p_y} = -n \frac{\sigma_y}{2\beta^2 \nu} \left[ x\tau_A + (1 - x)\tau_B \right] \tag{39}
\]

The viscosity of the mixture is therefore

\[
\eta_{mix} = \frac{n}{\beta} \left[ x\tau_A + (1 - x)\tau_B \right], \tag{40}
\]
where $n/\beta$ is the total pressure.

The result of equation (40) is plotted in figure 1 for a mixture of Xe in He. Experimental results at 291 K [38] are indicated on the same graph (experimental uncertainties $\approx \pm 1\%$). Correction factor $\epsilon$ for heterogeneous collisions may be estimated by fitting the curve to the experimental results. That obtained without the correction factor is displayed as a dotted curve. The fit performed on the ten mixtures of atomic gases leads to the values of $\epsilon$ in the range 1.03 – 0.98, the highest values being for mixtures with a light component (He). Results for the ten mixtures of atomic gases are listed in [39].

**FIG. 1.** Predicted and experimental viscosity of a mixture of Xe in He at 271 K. The smooth curve is for $\epsilon = 0.98$, the dotted curve for $\epsilon = 1$.

2. **Diffusion and thermal conduction**

For a binary system enclosed between two reservoirs at different temperatures separated by a distance $2D$ ($x$: mole fraction of the heavier substance ($A$)), stationary conditions are completely described by the set of constraints listed in table[1], the intensities being indexed
accordingly.

The intensities conjugate to the particle numbers of either substances \((\alpha_A, \alpha_B)\), the temperature (or better \(\beta\)) and its gradient (or better \(\gamma_1\)) are under direct control of the surroundings. Thermal interaction between the subsystems removes the necessity for indexing the latter two intensities.

Three intensities remain to be determined, namely the two gradients of the particle distributions \((\theta_{1,A}, \theta_{1,B})\) and the intensity conjugate to collective momentum from wall to wall \((\sigma_z)\). Hence, three additional conditions or equations are required. Two are identical to the conditions discussed for single component systems: mechanical equilibrium and global stationarity.

Mechanical equilibrium of the system between its walls implies vanishing total pressure gradient. It does not require \textit{per se} vanishing partial pressure gradient for either substances separately. A possible pressure gradient of \(A\) is indeed neutralized by an opposite gradient for \(B\). By stating that the sum of the contributions of either substances to flow of momentum between the boundaries is position independent, the following equation is derived (compare equation (31))

\[
x \left( \theta_{1,A} - \frac{5\gamma_1}{2\beta} \right) + (1 - x) \left( \theta_{1,B} - \frac{5\gamma_1}{2\beta} \right) = 0.
\]  

(41)

The condition for global stationarity is defined along the same lines as above (equations (28)–(30)), where the density \(n_+(z^*)\) is now understood as the sum for the two components. As a result, the relation for internal collective motion \((\sigma_z)\) becomes (see equation (30))

\[
x \sqrt{m_A} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,A} - 2\frac{\gamma_1}{\beta} \right) \frac{\tau_A}{m_AD} \right] \\
+ (1 - x) \sqrt{m_B} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,B} - 2\frac{\gamma_1}{\beta} \right) \frac{\tau_B}{m_BD} \right] = 0.
\]  

(42)

The last condition to be considered concerns mutual diffusion or motion of the subsystems with respect to each other. By implementing equation (24) with the generating function \(\phi_j = 1\), the particle flow of either subsystems is obtained. According to whether the named parameters are indexed \(A\) or \(B\), the results are
\[ J_A = \frac{x m}{\beta} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,A} - \frac{5 \gamma_A}{\beta} \right) \frac{x_A}{m_A D} \right], \]

\[ J_B = \left( 1 - x \right) \frac{n}{\beta} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,B} - \frac{5 \gamma_B}{\beta} \right) \frac{x_B}{m_B D} \right]. \] (43)

The first contribution in either equations (that proportional to \( \sigma_z \)) represents collective drag generated in the fluid by correlated effect of the walls. This acts on the two subsystems alike. Therefore it does not drive diffusion of the subsystems with respect to each other. By contrast, diffusion is related to the second part of the flow equations. As it may be verified, this is driven by the relevant partial pressure gradients.

Diffusive stationarity is reached by differential displacement of the subsystems with respect to each other. Then we have for either subsystems vanishing partial pressure gradients. This is the remaining constraint for complete thermodynamic description of the system. In experimental conditions, the question is however whether diffusive stationarity has been reached in practical cases when thermal conductivity of multi-component mixtures is measured.

For measuring thermal conductivity, an appropriate binary mixture is prepared in a conventional thermostat. The walls are then brought at different temperatures. When possible acoustic perturbations have relaxed, the total pressure distribution is flat (equation (41)). Nevertheless, on establishing the temperature gradient, pressure gradients of the individual constituents are created, forcing the particles to segregate. If the mixture consists of particles with different mobility, final stationary conditions are slow to reach. The slower moving particles tend to remain distributed homogeneously, as they were before the temperature gradient was created. The partial pressure gradient of the faster moving subsystem compensates for resulting unbalance. Final equilibrium requires that the migration of the slower particles have taken place, cancelling all partial pressure gradients.

The published experimental data that have been considered do not mention whether (or how much) the system has been allowed to relax the initially created individual partial pressure gradients. Let us assume this would not have occurred at all. The state is then pseudo-stationary as it continues to change slowly in time while the constituents still migrate.
with respect to each other. The two subsystems should then be considered as acting independently for all the properties concerning the particle distributions. They remain however tightly coupled for the properties that are promptly interchanged. In particular, they share the same $\beta$ and $\gamma_1$. The intensity $\sigma_z$ conjugate to the collective momentum generated by the temperature gradient is also common to the two subsystems. Concerning the latter, its relation to the other intensities and to the collision periodicities is given by (30). Instead of (42) we have now two relations, namely

$$\left( \theta_{1,A} - \frac{2 \gamma_1}{\beta} \right) \frac{\tau_A}{m_A D} = 2\sigma_z,$$
$$\left( \theta_{1,B} - \frac{2 \gamma_1}{\beta} \right) \frac{\tau_B}{m_B D} = 2\sigma_z.$$  \hspace{1cm} (44)

By combining (41) with the two latter ones, an expression for the gradients of the individual partial pressures may be derived. Writing

$$R = \frac{\tau_A/m_A}{\tau_B/m_B},$$  \hspace{1cm} (45)

this relation reads

$$\theta_{1,A} - \frac{5 \gamma_1}{2 \beta} = \frac{1}{2} \left( 1 - R \right) \left( 1 - x \right) \frac{\gamma_1}{\beta}.$$  \hspace{1cm} (46)

In practical cases, depending on the mixture to be considered, when heat conductivity is measured, the system may be somewhere between the two extreme conditions. The uncertainty concerning how close diffusion has reached stationarity in the experimental conditions where the measurements have been performed, explains why thermal conduction data of mixtures are difficult to reproduce. Let us express the uncertainty by a coefficient $c$, to multiply the right-hand side of equation (46). When discussing a homogeneous set of data with varying compositions $x$, we assume for simplicity that the same coefficient is valid. Equilibrium for diffusion implies $c = 0$. 

33
FIG. 2. Thermal conductivity of a mixture of Xe in He at 271 K. The smooth curve is for $c = 0.5$

Transport of heat is supported by either components of the mixture. For each, the contribution is given according to equation (32), where the relevant intensities are determined as above. Hence,

$$J_E = \frac{x_n}{\beta^2} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,A} - \frac{7 \gamma_1}{2 \beta} \right) \frac{\tau_A}{m_AD} \right] + \frac{(1 - x)n}{\beta^2} \left[ \sigma_z - \frac{1}{2} \left( \theta_{1,B} - \frac{7 \gamma_1}{2 \beta} \right) \frac{\tau_B}{m_BD} \right]. \quad (47)$$

In comparing the result with experimental data, coefficient $c$ may be taken as an adjustable parameter. Using the data published by E. Thornton and coworkers [40] for 291 K, coefficient $c$ has been found to range between 0 for light–light mixtures (e.g. He–Ne) and 1 for heavy–heavy mixtures (Kr–Xe). Figure 2 is an illustration of the results for the He–Xe mixture, where the value of $c$ optimizes at 0.5. Results for the ten mixtures of atomic gases are listed in [39]. Accuracy is better than the announced experimental precision of 4%.

VI. STRUCTURE FORMATION

A. Bénard-Rayleigh thermal convection

Stable vortices developing in a fluid bound by two horizontal plates at different temperatures in a vertical (gravitational) force field are named after Bénard and Rayleigh. Since their first description in 1900 they have been the subject of an abundant literature, being a typical example of structure formation in dynamic systems. The present discussion aims at developing a set of differential equations based on Liouville’s fundamental equation (23), where Hamiltonian iso-entropic contributions and stochastic irreversible interactions are clearly separated.

When convection develops in a fluid, the simple vertical symmetry defined by the two temperature reservoirs and the external field acting perpendicularly to the walls is broken.
From unidimensional the problem becomes bi- or tridimensional, with increased mathematical complexity. Convective motion stimulated by thermal strain may show many different patterns: rolls, cells, etc. The particular shape adopted by the system depends primarily on lateral boundary conditions. Depending on symmetry, we may want to have the coordinate system transformed. For simplicity we consider generation of rolls, for which Cartesian coordinates are most appropriate. Intensities referring to the different directions in space will be indexed accordingly.

Let the fluid be confined between two parallel plates (distance $2D$, taken as the $z$–direction) at different temperatures. The plates represent a double temperature reservoir defining a given average inverse temperature $\beta$ and a gradient $\gamma_z$.

The temperature gradient ($\gamma_z$) generates a linear moment of the density distribution. This causes a non-vanishing value of $\theta_z$. The relation between $\theta_z$ and $\gamma_z$ depends on conservation of momentum (compare (31)). In the presence of gravity, pressure gradient is balanced by the external force ($-mg$), whence $[15]$:

$$\theta_z - \frac{5 \gamma_z}{2 \beta} = -\beta mg D. \tag{48}$$

In field-free conditions, if $\gamma_z = 0$, the system’s center of mass is located half-way between the plates ($Z = 0$). Thermal strain and the external force displace the center of mass with respect to this neutral position. Expressed as a function of the intensive variables and using (48), the vertical moment of the particle density ($N_z$) is given by (18):

$$N_z = D \left( \frac{\gamma_z}{\beta} - \beta mg D \right). \tag{49}$$

Gravitation orients the gradient of the particle density to the bottom regions but, if the system is heated from below, the distribution may reverse. This situation presents much analogy with the population inversion occurring in laser physics and the conclusions developed below may readily be transferred to the domain of quantum optics $[41,42]$.

With convection, intricate distributions develop, requiring for their description additional or modified generating functions, supporting new intensive variables. The distributions will
be analyzed on the basis of generating functions analogous to the set listed in table II, but extended and generalized to include the additional constraints.

The geometric structure we want to focus on is periodic in the horizontal direction. The macroscopic wavelength is $\lambda$, the rolls turning in alternate directions. Let the $y$-axis connect successive vortices, the $x$-direction being parallel to the motion’s local global angular momentum. We isolate along the $y$-direction a distance $\lambda/2$ in which one vortex fits. This cell will be our system.

Let us focus on the intensities conjugate to the vertical and horizontal moments of the particle density and investigate the role of the source/sink contribution in Liouville’s equation (23). When a vortex is active it perturbs the stationary distributions. The vertical gradients are modified and horizontal gradients develop. Let the vertical gradients dictated by the plates and valid in the absence of a vortex be indexed $z, R$ from now on (e.g. $\theta_{z,R}$). Because of slow relaxation of distortions due to finite transport in the fluid, in the presence of a vortex this changes to $\theta_z$. Thermal diffusivity, a process related to thermal conduction, tends to neutralize the latter change. Relaxation of horizontal gradients (indexed $y$) follows the same mechanism. The above may be summarized in the form of a set of linear dissipation equations:

$$\dot{\theta}_z = -k_z(\theta_z - \theta_{z,R}),$$
$$\dot{\theta}_y = -k_y\theta_y.$$

(50)

with, considering the cell’s geometry:

$$k_z = \left(\frac{\pi}{D}\right)^2 \kappa,$$
$$k_y = \left[\left(\frac{\pi}{2D}\right)^2 + \left(\frac{2\pi}{\lambda}\right)^2\right] \kappa,$$

(51)

($\kappa$: coefficient of thermal diffusivity).

In a second step we investigate the conservative iso-entropic part of (23).

Let $N_z$ and $N_y$ be the vertical and horizontal moments of the particle density. Using (19) and (18) it is clear that $dN_z = \frac{2}{\kappa} d\theta_z$. The same argument holds in the horizontal direction.

By referring to equation (15), considering possible changes of the moments of the particle density, invariance of the entropy leads to:
\[ dS = \beta mgD dN_z - \theta_z dN_z - \theta_y dN_y = 0. \]  
\[ \text{(52)} \]

where \( mgD dN_z \) represents change of the potential energy as the system’s centre of gravity moves vertically. By combining the two first r.h.s. terms as \( \theta^* = \theta_z - \beta mgD \), the constant entropy condition may be rewritten \( (\theta^*_z)^2 + \theta^*_y = \text{constant} \).

With \( \omega \) representing the angular velocity characterizing the vortex, iso-entropic circulation is described by the following set of differential equations:

\[
\begin{align*}
\dot{\theta}^*_z &= -\omega \theta_y , \\
\dot{\theta}_y &= \omega \theta^*_z .
\end{align*}
\]

\[ \text{(53)} \]

By combining the latter set with the equations for dissipation \[ \text{(50)} \], the following set is obtained:

\[
\begin{align*}
\dot{\theta}^*_z &= -\omega \theta_y - k_z (\theta^*_z - \theta^*_z,R) , \\
\dot{\theta}_y &= \omega \theta^*_z - k_y \theta_y .
\end{align*}
\]

\[ \text{(54)} \]

In laser physics, this set is named after Bloch.

Gravitation acting on the horizontal density gradient activates the vortex while friction inhibits the collective motion. Complete balance between the conflicting forces has been elaborated in \[ \text{[15]} \]. Full development cannot be given here. It may however be drafted by:

\[
\dot{\omega} = \frac{2}{5} g D \theta_y - G(\lambda) \nu D^2 \omega ,
\]

\[ \text{(55)} \]

where function \( G(\lambda) \) depends on the form factor of the vortex. \( \nu \) is the viscosity of the fluid. By combining equations \[ \text{(54)} \] and \[ \text{(55)} \], threshold inversion conditions for vortex formation and the relevant form factor at and beyond threshold are easily determined (pitchfork bifurcation). The results are in agreement with the experiment \[ \text{[15]} \]. \textit{Mutatis mutandis}, in laser physics, the corresponding set of equations describes readily, next to the threshold requirements, implications for bifurcations to a variety of unstable and chaotic working conditions.

\textbf{1. Von Karman type turbulence}

In fluid dynamics it is known that the dimensionless number named after Reynolds governs both turbulence in pipes or channels and the von Karman vortex streets produced
in flows past airfoils. This suggests that analogous mechanisms may be at work in the latter different kinds of systems. In order to stress the similarity, label von Karman might be generalized by attaching it to turbulent flows in ducts as well.

The flows listed above have all been treated successfully elsewhere [15] in the same thermodynamic context. The detailed mathematics being however rather cumbersome, only the principles involved will be outlined next.

We consider a fluid flowing in a channel with constant width $2D$ (Poiseuille flow). In laminar conditions the velocity profile through the channel is known to be quadratic. Contrasting with the Couette flow discussed above, the table of generating functions required for the thermodynamic description of the system implies therefore a quadratic function for the collective momentum contribution. For the same reason, the kinetic energy distribution involves a fourth order generating function.

We are interested in the non-laminar regime. Instead of the above, let us suppose therefore that a stream of vortices (with angular velocity $\omega$) fitting exactly within the space between the walls flows down the channel. The purpose is to examine this particular regime’s stability.

Contrasting with the classical procedure where the walls are taken as immobile, investigating the vortices implies the observer to be running with the fluid at the same average speed ($v_y$). The walls are therefore taken to be moving in the opposite direction.

The general dynamical equations for a vortex have been derived above (54). In the present case there is however no external force field to justify inversion. Symmetry breaking results however from the asymmetric field of collective kinetic energy prevailing between the channel’s walls, caused by the very existence of the vortex superimposed on local average downstream translational motion. Accurate analysis of the relevant distribution of downstream collective kinetic energy indicates that it contains at least a linear contribution (proportional to $z$, the direction perpendicular to the walls). Its gradient is proportional to the product $v_y\omega$.

Following Bernoulli’s theorem, a gradient of collective kinetic energy in a fluid generates
a pressure or a density gradient perpendicularly to the flow. This is equivalent to a force acting on the fluid, here in the $z-$direction. This contains the product $v_y \omega$. It depends also on the form factor of the relevant vortices. The modified set of dynamic equations may therefore be written:

\[
\dot{\theta}_z = -\omega \theta_y - k_z [\theta_z^* - C(\lambda)Dv_y \omega], \quad (56)
\]
\[
\dot{\theta}_y = \omega \theta_z^* - k_y \theta_y,
\]

To the latter set an equation for $\dot{\omega}$ must be added.

The walls are the loci for mechanical interaction of the surroundings on the system. Confining the fluid within its boundaries represents a force exerted by the environment. Its magnitude is the local hydrodynamic pressure. If the system is symmetric with respect to facing boundaries, the forces exerted by the latter are equal and oppositely directed. In the present case, asymmetric collective kinetic energy distribution with respect to the boundaries (linear velocity superimposed on vortex) ensures unequal coupling of the fluid with either walls.

When a particle collides with one of the walls, depending on whether this is the one where the local average velocity gradient is higher or lower, the reinjection trajectory following collision is more or less reoriented. Hence, the force acting by the walls on the system is tangent to the flow at one wall and perpendicular at the other wall. The perpendicular pressure forces at either walls are not antagonistic. The resultant (pressure $= n/\beta$) acts mechanically on the system. If the particle density presents a gradient parallel to the walls ($\theta_y \neq 0$) the resulting moment of the forces activates rotation of the vortex. Hence:

\[
\dot{\omega} = \frac{1}{4\beta mD^2} \theta_y - \frac{G(\lambda)\nu}{D^2} \omega. \quad (57)
\]

In stationary conditions, the dotted functions vanish. By eliminating $\theta_z$ and $\theta_y$ in the resulting set of equations, the following equation for $\omega$ results:

\[
\omega^2 - \frac{k_z C}{8G\beta m} \text{Re} \omega + k_y k_z = 0. \quad (58)
\]

where $\text{Re} = 2Dv_y/\nu$ is Reynold’s number.
Besides the trivial solution ($\omega = 0$), expression (58) is the characteristic equation for vortex stability. It has two roots (limit point bifurcation). Depending on the value of the Reynolds number they may be real or complex. Only real solutions justify stable vortices. The value of the critical Reynolds number separating conditions for stable and unstable vortices depends on their form factor. The lowest value must be retained. It has been calculated in [15] for flow in a channel, in a square section pipe and past an airfoil. Results are in agreement with the experiment.

**VII. CONCLUSIONS**

The present paper reviews the state of affairs for solving the irreversibility paradox. The conflict raises from apparent contradiction between reversibility of microscopic laws of motion and the irreversible behaviour of macroscopic systems. The analysis convincingly demonstrates that attempts based on the assumption that the relevant macroscopic systems are perfectly isolated, cannot justify the law of increase of entropy. Such systems are indeed necessarily conservative, a property that holds for the entropy too. Some of the attempts towards escaping this fundamental symmetry property have been discussed. Their arguments have been shown to be inconclusive. As a result one is forced us to assume that perfect isolation conditions are incompatible with real physical systems.

The notion of quasi-isolation has been introduced, indicating the condition of systems that are allowed to exchange energy fluctuations with their environment. With closed systems, the environment is at least for a part represented by their walls.

The conceptual basis for the theoretical investigation of the dynamics of quasi-isolated systems is furnished by the experimental evidences obtained from the analysis of Joule’s experiment.

---

[1] J. L. Lebowitz and O. Penrose, *Physics Today*, 36 (2), 23–29, February 1973.
[2] J. L. Lebowitz, *Physica A*, 194, 1–27, 1993.

[3] Ya. G. Sinai, *Introduction to Ergodic Theory* (Princeton University Press, Princeton, N.J., 1976).

[4] I. P. Cornfeld, S. V. Fomin and Ya. G. Sinai, *Ergodic theory* (Springer, New York, N.Y., 1982).

[5] H. Spohn, *Rev. Mod. Phys.* 53 (1980) 569–615.

[6] P. Gaspard, *J. Stat. Phys* (1992) 68 (1992) 673–749.

[7] P. Gaspard and F. Baras, *Phys. Rev. E* 51 (1995) 5332–5352.

[8] J. R. Dorfman and P. Gaspard, *Phys. Rev. E* 51 (1995) 28–35.

[9] B. Misra, I. Prigogine and M. Courbage, *Physica* A98 (1979) 1–26.

[10] J. Kumičák and E. Brändas, *Int. J. Quantum Chem.* 32 (1987) 669–683.

[11] G. Braunss, *Acta Applicandae Mathematicae* 3 (1985) 1–21.

[12] H. A. Posch and Wm. G. Hoover, *Phys. Rev. A* 38 (1988) 473–482.

[13] D. J. Evans, E. D. G. Cohen and G. P. Morris, *Phys. Rev. A* 42 (1990) 5990–5997.

[14] K. Lindenberg and B. J. West, *The Nonequilibrium Statistical Mechanics of Open and Closed Systems* (VCH Publisher, New York, N.Y., 1990).

[15] X. de Hemptinne, *Non-equilibrium Statistical Thermodynamics applied to Fluid Dynamics and Laser Physics* (World Scientific, Singapore, 1992).

[16] L. D. Landau and E. M. Lifschitz, *Mechanics* (Pergamon Press, Oxford, 1969).

[17] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Plenum, New York, 1974).

[18] L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon Press, Oxford 1959).

[19] V. I. Arnold and A. Avez, *Ergodic Problems of Classical Mechanics* (W. A. Benjamin, New York, 1968).
[20] R. Balescu, *Equilibrium and Non-equilibrium Statistical Mechanics* (John Wiley, New York, N.Y., 1975).

[21] K. Huang, *Statistical Mechanics* (John Wiley, New York, 1975).

[22] E. G. D. Cohen and W. Thirring, eds., The Boltzmann Equation: Theory and Applications, in: *Proc. Int. Symp. “100 Years Boltzmann Equation*” (Springer-Verlag, Wien, 1973).

[23] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, Vol. 1: Functional Analysis* (Academic Press, New York, 1972).

[24] D. B. Pearson, Spectral properties and asymptotic evolution in potential scattering in: E. Velo, A. S. Wightman, eds., *Rigorous Atomic and Molecular Physics* (Plenum Press, New York, 1981, p. 99–130).

[25] J. Kumičák, *Czech. J. Phys.* **B34**, (1984) 821–831.

[26] T. Kato, *Perturbation Theory for Linear Operators* (Springer-Verlag, Berlin, 1966).

[27] J. P. Dougherty, *Phil. Trans. R. Soc. Lond. A* **346** (1994) 259–305.

[28] B. Misra, *Proc. Natl. Acad. Sci. USA* **75** (1987) 1627–1631.

[29] J. Kumičák, *J. Tech. Phys.* (1996) — in print.

[30] N. Moiseyev, P. R. Certain and F. Weinhold, *Mol. Phys.* **36** (1978) 1613–1630.

[31] E. Brändas, *Int. J. Quantum Chem. Symp.* **20** (1986) 119–127.

[32] J. F. Clarke and M. McChesney, *Dynamics of relaxing gases* (Butterworth, London, second edition, 1976).

[33] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular theory of gases and liquids* (Wiley, New York N. Y. 1954).

[34] I. L. Ryhming, *Dynamique des Fluides* (Presses Polytechniques Romandes, Lausanne, 1985).
[35] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Cambridge, Mass., 1951).

[36] R. K. Pathria, *Statistical mechanics* (Pergamon Press, Oxford, 1972).

[37] A. Eucken, *Physik. Zeitschr.* 14 (1913) 324–332.

[38] Y. S. Touloukian, S. C. Saxena and P. Hestermans, *Viscosity — Thermophysical Properties of Matter, vol 11* (Plenum Press, New York, 1975).

[39] Z. Hens and X. de Hemptinne, *Trends in Chem. Phys.* 4 (1996) 13–21.

[40] Y. S. Touloukian, P. E. Liley and S. C. Saxena, *Thermal Conductivity — Thermophysical Properties of Matter, vol 3* (Plenum Press, New York, 1970).

[41] X. de Hemptinne, *J. Chem. Phys* 79 (1983) 727–735.

[42] X. de Hemptinne, *Phys. Rep.* 122 (1985) 1–56.
