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On the (Boltzmann) Entropy of Nonequilibrium Systems

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Abstract: Boltzmann defined the entropy of a macroscopic system in a macrostate M as the log of the volume of phase space (number of microstates) corresponding to M. This agrees with the thermodynamic entropy of Clausius when M specifies the locally conserved quantities of a system in local thermal equilibrium (LTE). Here we discuss Boltzmann's entropy, involving an appropriate choice of macro-variables, for systems not in LTE. We generalize the formulas of Boltzmann for dilute gases and of Resibois for hard sphere fluids and show that for macro-variables satisfying any deterministic autonomous evolution equation arising from the microscopic dynamics the corresponding Boltzmann entropy must satisfy an $\mathcal{H}$-theorem.

Introduction

Thermodynamics associates to isolated equilibrium macroscopic systems with specified

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parameters M an additive, macroscopically well defined, entropy $S(M)$. The second law of thermodynamics then asserts that in any temporal change occurring in such isolated systems (due e.g. to the relaxation of some constraint) the new equilibrium state, with M', must satisfy $S(M') \geq S(M)$. $S(M)$ as well as the second law naturally generalize to an entropy $S_{\text{loc.eq.}}(M) = S_{\text{loc.eq.}}(\{M(\mathbf{x})\})$ for systems in LTE with particle, momentum and energy densities varying slowly (on a microscopic scale) in space and time. $S_{\text{loc.eq.}}(M)$ increases with time when $M(\mathbf{x})$ evolves to $M_t(\mathbf{x})$ according to macroscopic hydrodynamical equations [1,2]. This is reviewed briefly in section 2.

We then discuss in section 3 Boltzmann's microscopic interpretation of $S(M)$ as the log of the volume of phase space associated to M. This not only provides a formula for computing $S(M)$ microscopically, but also explains the origin of the time asymmetric second law in the time symmetric microscopic laws [3, 4]. It shows in particular that if there is a deterministic autonomous equation describing the time evolution of a macrostate M_t be it hydrodynamic or kinetic, e.g. the Boltzmann equation, it must give an $S(M_t)$ which is monotone non-decreasing in t.

Boltzmann's macroscopic formulation leads naturally to a formula for the entropy of dilute gases which may be far from LTE. For such systems the macrostate M may be specified by $f(\mathbf{x}, \mathbf{v})$, the density of gas particles in the six-dimensional one particle phase space. Boltzmann showed that this entropy, $S_{\text{gas}}(f_t)$, increases with time when f_t evolves according to the Boltzmann equation ($\mathcal{H}$-theorem) [3, 4, 5]. This is discussed in section 4.

In section 5 we give a formula for $S(f, E)$ the log of the phase space volume of a general system whose macrostate is specified by $f(\mathbf{x}, \mathbf{v})$ and the total energy E. This reduces to $S_{\text{gas}}(f)$ for a dilute gas and to $S_{hs}(f)$ for a system of hard spheres. $S_{hs}(f)$ was found by Resibois [6] to satisfy an $\mathcal{H}$-theorem when f evolves according to the (modified) Enskog equation for a system of hard spheres. We note that the general argument given by Boltzmann for the origin of the second law suggests that $S(f_t, E)$ should be monotone in time even if f does not satisfy an autonomous evolution equation.

Section 6 consists of some remarks comparing and contrasting Boltzmann's definition of the entropy of a macroscopic system with other definitions of entropy. We raise, but do not resolve, the question of the appropriate choice of macrostates for general nonequilibrium systems.

The article is written in an informal style describing the ideas and facts (not necessarily in the right historical order) we think important for understanding the notion of the entropy of a macroscopic system, made up of a very large number of atoms or molecules. We restrict ourselves to classical systems, assume familiarity with the basic notions of thermodynamics and statistical mechanics, and omit many details (including units, boundary conditions, etc.). We refer the interested reader to [7] and references there.

2. Clausius' Macroscopic Entropy

Rudolf Clausius' 1865 paper [8] concludes with his celebrated "two fundamental theorems of the mechanical theory of heat": 1. The energy of the universe is constant. 2. The entropy of the universe tends to a maximum. These express in succinct form what is generally referred to as the first and second law of thermodynamics; see [3, 4] for their interesting history.

The first law needs no elaboration. The existence of a conserved energy for isolated systems goes back to Newton for mechanical systems. The experiments of Joule then showed, that thermal phenomena are subject to the same mechanical laws.

The second law, on the other hand, which contains the newly coined word entropy, does need elaboration. Let us quote Lars Onsager [9]: "The second law of thermodynamics forbids perpetual motion of the second kind and implies the existence of a definable entropy for any system in a state that can be reached by a succession of reversible processes. These "thermodynamic" states are typically defined as states of "equilibrium" under specified restraints on composition, energy, and external boundary conditions, in the sense that no spontaneous change can occur in the system as long as the constraints remain fixed." The implicit "restraints" exclude chemical or nuclear reactions which would change the species present, etc..

As put in the textbooks [1]: given an equilibrium system with energy E and mole (or particle) numbers $\mathbf{N}$ in a spatial region V, with a volume which we shall also denote by V, there exists a function $S(E, \mathbf{N}, V)$ such that in a reversible process

$$dS = [dE + pdV - \sum \mu_j dN_j]/T \tag{1}$$

where T is the absolute temperature, p the pressure and μ_j the chemical potentials. The terms in the square bracket just give the amount of heat added to the system in a reversible process.

Thermodynamics further states that the entropy of two isolated macroscopic systems, each in equilibrium, with their own energies, mole numbers and volumes, is the sum of their individual entropies, i.e.

$$S_{1,2}(E_1, \mathbf{N}_1, V_1.E_2, \mathbf{N}_2, V_2) = S_1(E_1, \mathbf{N}_1.V_1) + S_2(E_2, \mathbf{N}_2, V_2) \tag{2}$$

Suppose now that these two systems are permitted to interact and exchange energy over some period of time after which they are again isolated. Then, according to the first law, their new energies E'_1 and E'_2 will satisfy $E'_1 + E'_2 = E_1 + E_2$. If we now wait until each of the systems comes to equilibrium then, according to the second law, their combined new entropy must satisfy the inequality,

$$S'_{1,2} = S_1(E'_1, \mathbf{N}_1, V_1) + S_2(E'_2, \mathbf{N}_2, V_2) \geq S_{1,2} = S_1(E_1, \mathbf{N}_1, V_1) + S_2(E_2, \mathbf{N}_2, V_2). \tag{3}$$

Similar inequalities hold when relaxing other constraints. As an extreme example imagine that initially system 1 contained a mixture of hydrogen and oxygen at a low temperature T_1, with an implicit constraint prohibiting their chemical reaction, while system 2 was at a high temperature T_2. The final state could now be very hot steam in system 1, with a temperature T_1' higher than the temperature T_2' in system 2, e.g. $T_1' > T_2' > T_2 > T_1$.

In all cases, *if the two systems have come to a joint equilibrium* at the end of this period of interaction, with possibly new $\mathbf{N}'$, then E_1' and E_2' must be such that the new entropy satisfies

$$S_1'(E_1', \mathbf{N}_1', V_1) + S_2'(E_2', \mathbf{N}_2', V_2) = S_{1,2}' = \sup_{U_1, U_2} \{S_1(U_1, \mathbf{N}_1', V_1) + S_2(U_2, \mathbf{N}_2', V_2)\} \quad (4)$$

subject only to energy conservation, $U_1 + U_2 = E_1 + E_2$. This implies

$$T_1' \equiv \left[\frac{\partial S_1}{\partial E_1'}(E_1', \mathbf{N}_1', V_1)\right]^{-1} = T_2' \equiv \left[\frac{\partial S_2(E_2', \mathbf{N}_2', V_2)}{\partial E_2'}\right] \quad (5)$$

Similar relations hold when there can be an exchange of matter or volume between the systems.

Using the fact that for macroscopic systems surface areas (multiplied by a suitable microscopic length) and surface energies are negligible compared to the corresponding bulk quantities, the additivity of the entropy, expressed by (2), also gives extensivity. That is, for systems uniform in the bulk,

$$S(E, \mathbf{N}, V) = V s(e, \mathbf{n}). \tag{6}$$

The thermodynamic entropy can now be extended to a system in LTE [1, 2]: a system in a volume V which can be considered, to a good approximation, as being locally in equilibrium with energy density $e(\mathbf{x})$, particle density $n(\mathbf{x})$ and hydrodynamic velocity $\mathbf{u}(\mathbf{x})$: for a precise definition see [10]. For such systems we can, by extension of (6), write

$$S_{\text{loc.eq.}}(n, \mathbf{u}, e) = \int_V s(e(\mathbf{x}) - \frac{1}{2} m n(\mathbf{x}) \mathbf{u}^2(\mathbf{x}), n(\mathbf{x})) d\mathbf{x} \tag{7}$$

where m is the mass (per mole) and we consider just one component for simplicity, [1–12]. (The "mechanical" energy associated with $\mathbf{u}(\mathbf{x})$ does not contribute to S until it is dissipated and we always take $\int_V n(\mathbf{x}) u(\mathbf{x}) d\mathbf{x} = 0$).

Eq. (7) clearly agrees with (6) when the system is in true equilibrium, $\mathbf{u} = 0$, and e and n are independent of $\mathbf{x}$. Furthermore if a LTE state evolves in time according to macroscopic equations then $S_{\text{loc.eq.}}$ must increase (or at least not decrease) as a function of t. Consider for example an isolated system in LTE (with $\mathbf{u} = 0$ and n constant) with an energy density profile $e_0(\mathbf{x})$ and corresponding temperature profile $T_0(\mathbf{x})$ for which we have, using an extension of (1) to continuous time

$$\frac{\partial s}{\partial t} = -\frac{\nabla \cdot \mathbf{J}}{T} = -\nabla \cdot (\mathbf{J}/T) + \mathbf{J} \cdot \nabla(1/T) \tag{8}$$

where $\mathbf{J}$ is the heat flux, $\mathbf{J}/T$ is the entropy flux, and $\mathbf{J}\cdot\nabla(1/T)$ is the entropy production. According to Fourier's law, $\mathbf{J} = -\mathcal{K}(T)\nabla T$ so (8) can be written in the more familiar form as

$$C_V(T)\frac{\partial}{\partial t}T(\mathbf{x},t) = \nabla\cdot[\mathcal{K}(T)\nabla T] \tag{9}$$

where $C_V(T) = T^{-1}\frac{ds(T)}{dT}$ is the specific heat and $\mathcal{K}$ is the heat conductivity. Eq. (9) is to be solved, for $t > 0$, subject to no heat flux, or $\nabla T = 0$, at the surface of V. Integrating (8) or (9) then yields,

$$\frac{dS_{\text{loc.eq.}}}{dt} = \frac{d}{dt}\int_V s d\mathbf{x} = \int_V \mathbf{J}\cdot(\nabla\frac{1}{T})d\mathbf{x} = \int_V \mathcal{K}T^2(\nabla\frac{1}{T})^2 d\mathbf{x} \geq 0. \tag{10}$$

As $t \to \infty$, $T(\mathbf{x},t) \to \bar{T}$, for all $\mathbf{x} \in V$, with $\bar{T}$ determined by energy conservation and $S_{\text{loc.eq.}}$ approaches its maximum (equilibrium) value $Vs(\bar{e},n)$.

The second law thus manifests itself for LTE by the requirement that the entropy production $\mathbf{J}\cdot\nabla(1/T)$ be non-negative, i.e. that $\mathcal{K}(T) \geq 0$. The formula for entropy production generalizes to other macroscopic equations [2, 12], e.g. to the compressible Navier-Stokes equations which describe the time evolution of $n(\mathbf{x},t), \mathbf{u}(\mathbf{x},t)$ and $e(\mathbf{x},t)$. The Euler equations, on the other hand, conserve $S_{\text{loc.eq.}}$, in the absence of singularities of the flow. They do not give an approach to equilibrium of an isolated system and thus do not provide a description valid for times over which such an approach takes place. In the presence of shocks, however, the solutions are non-unique and the requirement that $S_{\text{loc.eq.}}$ increase picks out the correct evolution.

3. Boltzmann's Microscopic Entropy

There are many ways to stretch the notion of LTE and apply the second law to processes taking place in systems which are clearly very far from equilibrium, e.g. living organisms [3, 9]. These ad hoc extensions work quite well in the hands of seasoned practitioners [9] but are far from systematic. It would certainly be desirable to find systematic ways for defining and calculating the entropy, expressed as a function of the appropriate macroscopic variables of systems that are not in LTE. This entropy would be monotone in time and coincide with $S_{\text{loc.eq.}}$ for a system in LTE.

This is exactly what was accomplished by Boltzmann's microscopic interpretation of the macroscopic Clausius equilibrium entropy $S(M)$. This interpretation provides a formula for the computation of $S(M)$ from the microscopic Hamiltonian. Even more importantly, it explains the origin of the time asymmetric second law in the time reversible dynamics of the atoms and molecules which are the microscopic constituents of macroscopic matter, and shows its applicability to systems not in LTE. We will be very brief here, c.f. [1–14].

A very good summary of Boltzmann's accomplishment is given by this quote from

Einstein [13]: "On the basis of the kinetic theory of gases Boltzmann had discovered that, aside from a constant factor, entropy is equivalent to the logarithm of the "probability" of the [macro]state under consideration. Through this insight he recognized the nature of the course of events which, in the sense of thermodynamics, are "irreversible". Seen from the molecular-mechanical point of view, however, all courses of events are reversible. If one calls a molecular-theoretically defined state a microscopically described one, or, more briefly, micro-state, then an immensely large number (Z) of states belong to a macroscopic condition. Z then is a measure of the probability of a chosen macro-state. This idea appears to be of outstanding importance also because of the fact that its usefulness is not limited to microscopic description on the basis of mechanics."

Let us make Einstein's remarks more explicit by considering a classical system of N particles in a box V. Its microstate X is given by a point in the $6N$ dimensional phase space which specifies everything about the system, e.g. the energy given by its Hamiltonian $H(X)$, etc.. When N is very large a more appropriate coarse-grained description of the system is provided by its macrostate M. We can specify M, for example, by dividing V into J cubes Δ_k, $J << N$, so that each cube contains a very large number of particles and specifying coarse grained values of the energy, momentum and number of particles in each Δ_k. Let Γ_M be the region of the phase space consisting of all microstates consistent with

M, i.e. the set of all X such that the appropriate phase space function $M(X) = M$. Let $|\Gamma_M|$ be the volume of Γ_M in appropriate units (this is Einstein's Z for a classical system). Boltzmann defined the entropy of a macroscopic system with microstate X, by

$$S_B(X) = k \log |\Gamma_{M(X)}|. \tag{11}$$

Boltzmann then showed that for a gas in an equilibrium macrostate, M_{eq}, which, for the above choice of M, corresponds to a uniform density of the macro-variables in V, S_B agrees (to leading order in N), with the thermodynamic entropy of Clausius. The same is true for LTE states, i.e. if $M(X) = \{n(\mathbf{x}), \mathbf{u}(\mathbf{x}), e(\mathbf{x})\}$ then $S_B(M) = k \log |\Gamma_{M(X)}| = S_{\text{loc.eq,}}(n, \mathbf{u}, e)$. This means that if the entropies $S_B(M) > S_B(M')$ differ by a macroscopic amount the ratio of their corresponding phase space volumes is exponentially large in N. Thus if the system contains one mole of material, the ratio of $|\Gamma_{M_{eq}}|$ to $|\Gamma_M|$, for a macrostate M in which all the particles are in the left half of the box is of order $\exp[10^{20}]$. This is far larger than the ratio of the volume of the known universe to the volume of one proton.

Boltzmann then argued that given this disparity in sizes of Γ_M for different M's, the time evolved $M_t = M(X_t)$ will be such that $|\Gamma_M(X_t)|$ and thus $S_B(X_t)$ will *typically* increase in accord with the second law. By "typically" we mean that for any Γ_M (of the kind described above) the relative volume of the set of microstates X in Γ_M for which the second law is violated by a macroscopic amount, i.e. by an amount proportional to N, during any fixed time period, (no bigger than the age of the universe), goes to zero rapidly (exponentially) in the number of atoms and molecules in the system.

In fact let us consider the case where M_t satisfies an autonomous deterministic evolution, e.g. equation (9). This means that if that evolution carries $M_{t_1} \to M_{t_2}$, then, the microscopic dynamics Φ_t carries $\Gamma_{M_{t_1}}$ inside Γ_{Mt_2}, i.e. $\phi_{t_2-t_1}\Gamma_{M_{t_1}} \subset \Gamma_{M_{t_2}}$, with negligible error. Now the fact that phase space volume is conserved by the Hamiltonian time evolution (Liouville's theorem) implies that $|\Gamma_{M_{t_1}}| \leq |\Gamma_{M_{t_2}}|$ and thus by (11) that $S_B(M_{t_2}) \geq S_B(M_{t_1})$ for $t_2 \geq t_1$. We have thus derived an "$\mathcal{H}$-theorem" for any deterministic evolution of the macro-variables arising from the microscopic dynamics. The explicit form for the rate of change of $S_B(M_t)$ (including strict positivity) depends on the detailed macroscopic evolution equation. The fact that $\Gamma_{M_{eq}}$ essentially coincides for large N with the whole energy surface $H(X) = E$ also *explains* the evolution towards and persistence of equilibrium in an isolated macroscopic system.

The emergence of definite time asymmetric behavior in the observed evolution of macroscopic systems, despite the total absence of such asymmetry in the microscopic dynamics, is thus a consequence of the great disparity between microscopic and macroscopic scales, together with the fact (or very reasonable assumption) that what we observe in nature is typical behavior, corresponding to typical initial conditions, c.f. [7].

4. Going Beyond LTE: Dilute Gases

As is clear from Eq. (11), the choice of the macro variables M is essential for the computation of $S_B(X)$ although there is a large leeway in choosing the sizes of the boxes Δ_k, if we consider only leading terms in N. For equilibrium systems or those in LTE these are specified by thermodynamics. They are the locally conserved and hence microscopically slowly varying quantities—precisely those for which one has hydrodynamic type autonomous equations.

To obtain useful quantitative information from the second law for systems not in LTE one has to find appropriate macro-variables M for the system under consideration, e.g. those which satisfy autonomous time evolution equations, and for which one can compute $S_B(M)$. A paradigmatic example of where this has been achieved is a dilute gas. Following Boltzmann, we refine the M considered in the last section for a system of N particles in a box V. This is done by noting that the microstate $X = \{\mathbf{r}_i, \mathbf{v}_i\}$, $i = 1, ..., N$, can be considered as a set of N points in six dimensional μ-space, somewhat analogous to positions $\{\mathbf{r}_i\}$ in $V \subset \mathbb{R}^3$. We may then divide up this μ-space space into $\tilde{J}$ "cells" $\tilde{\Delta}_\alpha$, centered on $(\mathbf{r}_\alpha, \mathbf{v}_\alpha)$, of volume $|\tilde{\Delta}_\alpha|$. A "macrostate" $\tilde{M}$ is then specified by the (coarse grained) number of particles in each $\tilde{\Delta}_\alpha$,

$$\tilde{M} = \{N_\alpha\}, \quad \alpha = 1, ..., \tilde{J} << N. \tag{12}$$

For dilute gases one can *neglect*, for typical configurations, the existence of interactions between the particles, although of course they still play a role in the dynamics now described by a succession of collisions between pairs of particles [3, 4, 5]. Under these conditions the coarse grained energy of the system in the state $\tilde{M}$ is given by

$$\frac{1}{2} m \sum_\alpha N_\alpha \mathbf{v}_\alpha^2 = E \tag{13}$$

$$\sum N_\alpha = N \tag{14}$$

We do not therefore need to specify the energy separately and the phase space volume associated with such an $\tilde{M}$ is then readily computed to be [4b]

$$|\Gamma_{\tilde{M}}| = \Pi_\alpha (N_\alpha !)^{-1} |\tilde{\Delta}_\alpha|^{N_\alpha} \tag{15}$$

where we do not distinguish between configurations in which particle labels are interchanged. For large enough N and a judicious choice of the $\{\tilde{\Delta}_\alpha\}$ we can, for almost all X consistent with (13) and (14), use Stirling's formula in (15) and obtain

$$S_B(\tilde{M}) \sim -k\{\sum_\alpha (\frac{N_\alpha}{|\tilde{\Delta}_\alpha|} \log \frac{N_\alpha}{|\tilde{\Delta}_\alpha|}) |\tilde{\Delta}_\alpha| - N\}. \tag{16}$$

Using $\tilde{M}$ we can associate with a typical X a coarse grained density $f_X \sim N_\alpha/|\tilde{\Delta}_\alpha|$ in μ-space, i.e. such that $N_\alpha = \int_{\tilde{\Delta}_\alpha} d\mathbf{x}d\mathbf{v} f_X(\mathbf{x},\mathbf{v})$. Eq. (16) then shows that, up to a constant (depending on N), the Boltzmann entropy $S_B(X)$ is given by the negative of Boltzmann's $\mathcal{H}$-function,

$$S_{\text{gas}}(f) = -k \int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x},\mathbf{v}) \log f(\mathbf{x},\mathbf{v}) \tag{17}$$

where $f = f_X$. (We shall drop the subscript X unless we want to emphasize that f is associated with a given microstate X.) The maximum of $S_{\text{gas}}(f)$ over all f which satisfy the conditions,

$$\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x},\mathbf{v}) = N \tag{18}$$

$$\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} \frac{1}{2} m\mathbf{v}^2 f(\mathbf{x},\mathbf{v}) = E \tag{19}$$

is given by the equilibrium distribution

$$f_{eq} = \frac{N}{V}(2\pi kT/m)^{-3/2} \exp[-m\mathbf{v}^2/2kT] \tag{20}$$

where $kT = 2/3(E/N)$. f_{eq} coincides of course with the density $f_X(\mathbf{x},\mathbf{v})$ obtained for a typical microstate X on the energy surface $H(X) = E$ when N is macroscopic (with deviations going to zero as $N \to \infty$).

When $f \neq f_{eq}$ then f and consequently $S_{\text{gas}}(f)$ will change in time. The microscopic version of the second law, discussed in section 3, now says that typical $X \in \Gamma_{\tilde{M}}$ at the initial time $t = 0$, will have an $\tilde{M}_t = \tilde{M}(X_t)$ with the property that $S_B(\tilde{M}(X_t)) \geq S_B(\tilde{M}(X_{t'}))$, for $t \geq t'$. This means that $f_{X_t}(\mathbf{x}, \mathbf{v}) = f_t(\mathbf{x}, \mathbf{v})$ has to be such that $S_{\text{gas}}(f_t) \geq S_{\text{gas}}(f_{t'})$, for $t \geq t'$. This is exactly what happens for a dilute gas for which the time evolution of $f_t(\mathbf{x}, \mathbf{v})$ is well described by the Boltzmann equation (BE) [3–5] which we shall not write out here: see [14] for a rigorous derivation of the BE under suitable conditions. As shown by Boltzmann, in his famous $\mathcal{H}$-theorem, it indeed follows from the BE that $\frac{d}{dt} S_{\text{gas}}(f_t) \geq 0$, with equality holding only when $f(\mathbf{x}, \mathbf{v})$ is a local Maxwellian $\hat{f}(\mathbf{v}; n, \mathbf{u}, T)$, [5]

$$\hat{f} = n(\mathbf{x})[\frac{2\pi kT(\mathbf{x})}{m}]^{-3/2} \exp\{\frac{-m[\mathbf{v} - \mathbf{u}(\mathbf{x})]^2}{2kT(\mathbf{x})}\}, \tag{21}$$

Eq. (21) defines LTE for a dilute gas with the $n(\mathbf{x}), \mathbf{u}(\mathbf{x})$ and $e(\mathbf{x})$ obtained from f in the usual way, $n = \int_{\mathbb{R}^3} f d\mathbf{v}, \mathbf{u}(\mathbf{x}) = \int \mathbf{v} f d\mathbf{v}/n$, $kT(\mathbf{x}) = \frac{2}{3}[e(\mathbf{x}) - \frac{1}{2}mn(\mathbf{x})\mathbf{u}^2(x)]/n(\mathbf{x})$. When (21) is substituted into (17) we obtain

$$S_{\text{gas}}(\hat{f}) = \int_V d\mathbf{x} s_{\text{gas}}(e, n) \tag{22}$$

with

$$s_{\text{gas}}(e, n) = k\Big\{\frac{3}{2} n \log(kT) - n(\log n - 1)\Big\} + \text{Const.}, \tag{23}$$

the Clausius entropy density given in (7),for a gas in LTE. Since $\hat{f}$ is not stationary unless n, e and $\mathbf{u}$ are uniform in the whole box, i.e. $\hat{f} = f_{eq}$, it is expected and partially proven [5, 15], that starting with an initial $f_0(\mathbf{x}, \mathbf{v})$, which can be far from a local Maxwellian,

$f_t(\mathbf{x}, \mathbf{v})$ will "rapidly" approach an f which is close to $\hat{f}(\mathbf{v}; n, \mathbf{u}, T)$ and will stay close to it while the local variables $n, \mathbf{u}$ and e change on a slower time scale. As the gradients become smaller this evolution will be hydrodynamic, i.e. $n, \mathbf{u}, e$ will evolve according to the compressible Navier-Stokes equations, which will then bring the gas to equilibrium with $S_{\mathrm{loc.eq.}}$ increasing with time.

Note that f satisfies the requirements for macro-variables discussed in the beginning of this section so that $S_{\mathrm{gas}}(f)$ is indeed a useful entropy functional. The non-decrease of $S_{\mathrm{gas}}(f_t)$ for f_t a solution for the BE is, as already noted, a consequence of Boltzmann's interpretation of the second law. As put by Boltzmann: "In one respect we have even generalized the entropy principle here, in that we have been able to define the entropy in a gas that is not in a stationary state" [4b, p. 75].

It is important to distinguish between $f_{X_t}(\mathbf{x}, \mathbf{v})$ and another object with the same name, the marginal one particle (probability) distribution $F_1(\mathbf{x}, \mathbf{v}, t)$ obtained from an N-particle ensemble density evolving according to the Liouville equation. We mention here an instructive example in which $F_1(\mathbf{x}, \mathbf{v}, 0) = f_{X_0}(\mathbf{x}, \mathbf{v})$ but $F_1(\mathbf{x}, \mathbf{v}, t) \neq f_{X_t}(\mathbf{x}, \mathbf{v})$ so that $F_1(\mathbf{x}, \mathbf{v}, t)$ does not give an adequate description of the macrostate of the system. Consider a macroscopic system of N noninteracting point particles, moving among a periodic array of scatterers in a macroscopic volume V, [7,10]. Starting with an initial nonuniform density

$f_{X_0}(\mathbf{x},\mathbf{v})$ the time evolved $f_{X_t}(\mathbf{x},\mathbf{v})$ will approach an f which depends only on $|\mathbf{v}|$ and which will have a larger $S_{\rm gas}(f)$. Since, however, $F_1(\mathbf{x},\mathbf{v},t)$ evolves according to the one particle Liouville equation $\int\int F_1 \log F_1 d\mathbf{x}d\mathbf{v}$ remains constant in time. What is crucial here is that what one might have regarded as the obvious evolution equation for f_{X_t} for this system, namely the one particle Liouville equation, in fact, does not describe the evolution of f_{X_t} for times after which $F_1(\mathbf{x},\mathbf{v},t)$ has developed structure on the microscopic scale.

5. The Boltzmann Entropy of Dense Fluids Not in LTE

As already noted, it is very important for the microscopic derivation of the second law and ipso facto for the increase of $S_{\rm gas}(f_{X_t})$ that the initial microstate X_0 of the system under consideration be typical of Γ_{M_0}. Consider now the case when the interaction potential energy between the particles is not negligible so that (19) is just the kinetic energy K rather than the total energy E. The region $\Gamma_{\tilde{M}}$ will then include phase points with widely differing total energies. The set of microstate X of a system with a specified energy, $H(X)=E$ will then correspond to a small fraction of $\Gamma_{\tilde{M}(X)}$ unless E is such that almost all of the points in $\Gamma_{\tilde{M}(X)}$ are also in the energy shell around E.

This illuminates the example considered by Jaynes [16]: One starts with a nonequilibrium system with energy E in which the kinetic energy K is larger than what it would be for an equilibrium system with the same energy E. The system will evolve towards equilibrium with a Maxwellian velocity distribution at temperature $T_\infty = \frac{2}{3k} K_E$ where K_E is the equilibrium kinetic energy corresponding to E. Assuming that f_0 is a Maxwellian with temperature T_0 we will have $T_\infty < T_0$ and so $S_{\rm gas}(f_\infty) < S_{\rm gas}(f_0)$. Since the microstates corresponding to the initial situation just described are not typical for the macrostates Γ_{f_0}, this example does not contradict the typical second law behavior of $S(f_t)$.

To properly describe non LTE macrostates for dense fluids let us suppose now that both $f(\mathbf{x}, \mathbf{v})$ and E are used to specify the macrostate M for a fluid with Hamiltonian H

$$H = \sum \frac{1}{2} m \mathbf{v}_i^2 + \sum \phi(\mathbf{r}_i - \mathbf{r}_j) = K + \Phi \tag{24}$$

in which interactions are important. We expect then that the evolution of a typical initial $X_0 \in \Gamma_{M_0}$, with $H(X_0) = E$ and $f_{X_0}(\mathbf{x}, \mathbf{v}) = f_0(\mathbf{x}, \mathbf{v})$, will indeed be such that $S_B(M(X_t)) = S(f_t, E)$ will increase with time in an actual system *even* if there is no autonomous evolution law for f_t.

To compute $S_B(f, E) = \log |\Gamma_{f,E}|$, let us consider first the case where the macrostate M is specified by both $f(\mathbf{x}, \mathbf{v})$ and the local energy density $e(\mathbf{x})$. The particle, kinetic and potential energy densities $n(\mathbf{x})$, $K(\mathbf{x})$ and $\psi(\mathbf{x})$ are determined from f and e,

$$n(\mathbf{x}) = \int_{\mathbb{R}^3} f(\mathbf{x}, \mathbf{v}) d\mathbf{v}, \quad K(\mathbf{x}) = \frac{1}{2} m \int \mathbf{v}^2 f d\mathbf{v}, \quad \psi(\mathbf{x}) = e(\mathbf{x}) - K(\mathbf{x}) \tag{25}$$

It is easy to see that the entropy corresponding to M can be split into momentum space and configuration space contributions

$$S_B(f, e) = S^{(m)}(f) + S^{(c)}(n, \psi) \tag{26}$$

The momentum contribution $S^{(m)}$ can be readily computed along the lines of formulas (15)–(17),

$$S^{(m)}(f) = -\int_V d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{v} f(\mathbf{x}, \mathbf{v}) \log[f(\mathbf{x}, \mathbf{v})/n(\mathbf{x})] \tag{27}$$

while $S^{(c)}(n, \psi)$ is the configurational local equilibrium entropy corresponding to the density $n(\mathbf{x})$ and the potential energy density $\psi(\mathbf{x})$. $S^{(c)}$ is clearly the same as the configurational part of $S_{\text{loc.eq.}}$ computed at the energy density $e'(\mathbf{x})$ that corresponds to $\psi(\mathbf{x})$ in LTE, i.e.

$$S^{(c)}(n, \psi) = S_{\text{loc.eq.}}(n, 0, e') - \frac{3}{2}k \int_V n(\mathbf{x}) \log(\frac{3}{2}K'(\mathbf{x}))d\mathbf{x} \tag{28}$$

where $K'(\mathbf{x})$ is the kinetic energy density corresponding to $e'(\mathbf{x})$. $S_{\text{loc.eq.}}$ is defined in (7) using the equilibrium $s(e, n)$ and the subtracted kinetic term corresponds to the first term on the right side of (23).

We can now obtain $S_B(f, E)$ by taking the sup of $S_B(f, e)$ over all energy densities $e(\mathbf{x})$ such that $\int_V e(\mathbf{x})d\mathbf{x} = E$.

An alternative way to compute $S_B(f, E)$ is to note that

$$S_B(f, E) = S^{(m)}(f) + S^{(c)}(n, \Phi) \tag{29}$$

where $\Phi = \int_V d\mathbf{x}\psi(\mathbf{x})$. We now observe that $S^{(c)}(n, \Phi)$ must agree with the configurational entropy of a system with a Hamiltonian

$$H' = \frac{m}{2} \sum \mathbf{v}_i^2 + \frac{1}{2} \sum\sum_{i \neq j} \phi(\mathbf{r}_1 - \mathbf{r}_j) + \sum_{i=1}^{N} u(\mathbf{r}_i) \tag{30}$$

in equilibrium at energy E', *when* we choose E' and $u(\mathbf{x})$ in such a way that the equilibrium density is equal to $n(\mathbf{x})$ and the total (coarse grained) internal potential energy has the value Φ, i.e.

$$\frac{1}{2} \sum\sum_{i \neq j} \phi(\mathbf{r}_i - \mathbf{r}_j) = \Phi, \tag{31}$$

as that of our actual system Letting then $S(E', N, V; u)$ be the equilibrium entropy of this system we have

$$S^{(c)}(n, \Phi) = S(E', N, V; u) - \frac{3}{2} Nk \log(kT'), \tag{32}$$

where $T' = \frac{2}{3k}(K_{E'}/N)$ is the temperature corresponding to the energy E' and the right hand side is the configurational part of the equilibrium entropy of system (30) at energy E'. (To actually compute $S(E', N.V; u)$ and find the appropriate $u(\mathbf{x})$ for a specified $n(\mathbf{x})$ and Φ we would have to use the canonical or grand canonical ensembles and the corresponding Gibbs entropies, see section 6.)

These considerations simplify for a system of hard spheres where the interactions do not contribute to the energy, i.e. $E = K$. The phase space domain for a specified f

is then just a direct product of the configurational and momentum space regions. The configuration space itself is modified from what it is for a noninteracting system to exclude all microstates X such that the distance between any pair of particles is less than a, the hard sphere diameter. Eq. (32) now assumes the form

$$S_{hs}(f) = S_{\text{gas}}(f) + \int_V n(\mathbf{x}) \log n(\mathbf{x}) dx + \mathcal{S}^C_{hs}(n) \tag{33}$$

where E is specified by f and $\mathcal{S}^C_{hs}(n)$ is the configurational part of the entropy of an equilibrium system of hard spheres kept at a nonuniform density $n(\mathbf{x}) = \int_{\mathbb{R}^3} f(\mathbf{x}, \mathbf{v}) d\mathbf{v}$ by some external potential $u(\mathbf{x})$. (Of course if $a = 0$ or the gas is very dilute then the second and third terms in (33) cancel each other.)

The entropy function $S_{hs}(f)$ in (33) is the same as that used by Resibois [6] to obtain an $\mathcal{H}$-theorem for the modified Enskog equation (MEE). It is generally believed that the MEE, which is a heuristic extension of the BE, accurately describes the evolution of $f_t(\mathbf{x}, \mathbf{v})$ for a moderately dense hard sphere fluid, say $na^3 \leq .1$, where a is the hard sphere diameter [5, 6]. The remarkable result, proved by Resibois in [6], is that when $f_t(\mathbf{x}, \mathbf{v})$ evolves according to the MEE then

$$\frac{d}{dt} S_{hs}(f_t) \geq 0 \tag{34}$$

with equality holding only when $f = f_{\text{eq}}$. (This is actually a stronger statement about entropy increase than what is given by the BE where collisions alone do not change $S_{\text{gas}}(f)$

when f is a local Maxwellian. The reason for this difference is the non-locality of the collisions in the MEE, see [6]. We still have however $S_{hs}(f) = S_{\mathrm{loq.eq.}}(e, \mathbf{u}, n)$ when $f = \hat{f}(\mathbf{v}; n, \mathbf{u}, T)$ and the hydrodynamic variables change slowly in space.)

Resibois was driven to an expression for S_{hs} equivalent to (33) by the structure of the MEE and argued that it should have an intrinsic significance. Our identification of $S_{hs}(f)$ with the Boltzmann entropy $S_B(f, E)$, i.e. as the log of the phase space volume for such a nonequilibrium system, completely justifies Resibois' intuition. It further shows the necessity of the modification of the original Enskog equation: as we have pointed out repeatedly, any deterministic evolution equation arising from the microscopic dynamics for macro-variables such as f must be such that the corresponding Boltzmann entropy satisfies an $\mathcal{H}$-theorem for that equation. The unmodified Enskog equation apparently does not have that property [5, 6].

6. Concluding Remarks

The entropy of a macroscopic state, defined by Eqs. (1) and (6), is clearly a property of an individual macroscopic system specified by macro-variables M. We neither have nor need ensembles to observe the time asymmetric evolution of the color profile of a glass of water in which we dissolve a capsule of purple ink. The appropriate choice of M for this process is clearly that corresponding to dividing the glass into a suitable large number of little cubes and specifying the coarse grained fraction of ink molecules in each cube as was done in section 3. The exact number of little cubes, as long as it is still small compared to the number of ink molecules, will not affect S_B to leading order in the number of molecules. To this order S_B will coincide with $S_{\text{loc.eq.}}$. The evolution of M_t will be given by the solution to a diffusion equation and $S_B(M_t)$ will satisfy the second law.

As argued in section 3, this behavior can be understood fully from Boltzmann's microscopic interpretation of entropy. This direct explanatory connection between Boltzmann's entropy and the observed behavior of individual macroscopic systems seems lacking in other definitions of entropy in which probability distributions are a key ingredient. The best known of these is the Gibbs entropy,

$$S_G(\rho) = -k \int_\Gamma \rho \log \rho dX \tag{35}$$

where $\rho(X)$ is some given probability (ensemble) density. Clearly if $\rho = \rho_M$

$$\rho_M(X) = \begin{cases} |\Gamma_M|^{-1}, & \text{if } X \in \Gamma_M \\ 0, & \text{otherwise.} \end{cases} \tag{36}$$

then

$$S_G(\rho_M) = k \log |\Gamma_M| = S_B(M) \tag{37}$$

For a system specified by $M(X) = (E, N, V)$, ρ_M corresponds to the microcanonical ensemble. Using the equivalence of equilibrium ensembles for macroscopic systems, Eq.

(37) holds also for the canonical and grandcanonical ensembles, in the thermodynamic limit. In fact S_G is of paramount importance both in the mathematical foundations and practical applications of equilibrium statistical mechanics. On the other hand, as is very well known, S_G, unlike S_B, does not change in time for an isolated system evolving under Hamiltonian dynamics [$S_G(t) = S_G(\rho_t)$, where $\rho_t(X)$ is $\rho_0(X_{-t})$]. It is therefore inappropriate, we believe, to use S_G or quantities like it in "derivations" of the second law without explicitly considering typical behavior. Attempts to remedy this through the use of coarse grained ensembles may be useful mathematically, but conceptually they are just variations on the Boltzmann entropy.

The Boltzmann entropy itself is, as indicated by the use of macro-variables for its very formulation, meaningful only for macroscopic systems. For such systems one can speak of the behavior of the macro-variables M as arising from the evolution of a typical microstate in Γ_{M_0}. It might still be true that a system containing just a few particles exhibits ergodicity, mixing, positive Lyapunov exponents, etc.; this is true e.g. for a particle moving among fixed convex scatterers on a torus (Sinai billiard). But the physical system of one such particle will not exhibit any time asymmetric behavior, corresponding to the diffusion of the purple ink in the glass of water. Unlike the glass of inky water or a very large number of particles moving among such scatterers (see discussion at end of sec. 4) a film of the particle's motion run backwards will look the same as one run forward.

The situation is different when one considers open systems, e.g. systems in contact with thermal reservoirs [17, 18]. The time evolution of the microstate X of such a system is then no longer given by a Hamiltonian since the system is not isolated and $S_G(\rho)$ need no longer be constant in time. It is in fact reasonable in some cases to treat X as a random variable evolving via a stochastic Markovian dynamics. It is then easy to show that when the Markov process has a stationary density $\bar{\rho}(X)$ then the relative entropy

$$S_G(\rho|\bar{\rho}) = -k \int_\Gamma \rho \log(\rho|\bar{\rho}) dX \tag{38}$$

increases monotonically in time.

A different situation, of current interest, in which $S_G(\rho)$ is not constant is that of a closed system evolving under a deterministic non-Hamiltonian thermostated dynamics [19, 20]. Starting with an initial density $\rho(X, 0)$, uniform (or absolutely continuous) with respect to the appropriate Lebesgue measure, the dynamics leads to $\rho(X, t) \to \bar{\rho}$, as $t \to \infty$, with $\bar{\rho}$ singular with respect to Lebesgue measure, ($\bar{\rho}$ is generally an SRB measure), and $S_G(\rho) \to -\infty$ decreasing with time in such a way that,

$$\frac{d}{dt} S_G(\rho) \to -\sigma, \tag{39}$$

with $\sigma > 0$. This σ is frequently interpreted as an "entropy production" and indeed has, in some cases, a form similar to the hydrodynamic entropy production in a stationary open system in which there are currents. The connection between the steady states of systems evolving under the invented thermostated dynamics and those obtained from more realistic models for which the stationary $\bar{\rho}$ is not singular, is still not entirely clear. The same is true for the correct identification of entropy in such systems [18, 19, 20].

Let us mention briefly that the word entropy is used very widely in contexts other than that of macroscopic physical systems. There is the Shannon information entropy which is formally similar to S_G, but is designed for situations which have apparently nothing to do with thermodynamics, the Kolmogorov-Sinai and topological entropies of dynamical systems, etc. These entropies are clearly very useful and clearly different from the Clausius and Boltzmann entropies. Surprisingly there are frequently some unexpected deep connections between these different entropies which are very interesting.

Let us finally discuss the choice of appropriate macro-variables M in terms of which to describe a particular nonequilibrium system of interest in some microstate X which is far from LTE. We do not want to choose too coarse a description: one for which X is not typical of $\Gamma_{M(X)}$. This occurred in the example of Jaynes discussed in section 5; the problem could be remedied there by introducing more refined macrostates, given not just by f but by f and E. We also do not want to use a description more detailed than is relevant to macroscopic behavior.

What we are after is a minimal useful description via macro-variables M, adapted to the situation (corresponding to a microstate X) under consideration. This is always achieved when M is such that (1) M_{X_t} typically obeys an autonomous deterministic evolution law, such as those corresponding to hydrodynamics, the BE, or the MEE, and (2) X is typical in this sense of $\Gamma_{M(X)}$.

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