ENTROPY IN EQUILIBRIUM AND NONEQUILIBRIUM SYSTEMS

by

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Introduction

More than twenty-five years have elapsed since the writing of a number of papers by E. T. Jaynes [23],[24] in which the role played by the entropy in both equilibrium and nonequilibrium states of macroscopic systems was clearly brought into the field of thermophysics. And yet, the message seems to have passed by unnoticed by most of the workers in this field. This paper is a modest attempt to revive the ideas set forth by Jaynes in a slightly different context, stressing the utilization of entropy in nonequilibrium phenomena. The main point which lies in the heart of this subject is related to the simple notion that entropy is strictly related to a set of experiments that one may perform on a given macroscopic system and it may only be defined provided one clearly specifies which are the thermodynamic parameters defining the state of the system. This very simple requirement is almost always completely forgotten, especially when dealing with systems whose states are not in equilibrium.

In the phenomenological attempts which have been made to cope with the study of nonequilibrium phenomena, such as Linear Irreversible Thermodynamics (LIT), the concept of entropy enters into the theoretical framework only in a purely formal way. It serves merely to provide the formalism with a mathematical expression for what Clausius, over one hundred years ago, called the uncompensated heat which appears in any irreversible process. Now under the concept of "entropy production" which allows one to identify which are the effects produced in the system by the causes (forces)

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originating them. But the entropy per se is never sought as a computable variable in the formalism nor is any attempt made to relate it with some well defined set of experiments. Of course, when the entropy production is zero, that means that Clausius' uncompensated heat is not present, the equation containing it reduces to the well known Clausius expression for the second law of thermostatics.

As we move into the more microscopic theories of nonequilibrium phenomena, the above picture does not improve very much. The most well established model for studying time dependent macroscopic processes is that of the dilute monoatomic gas formulated by L. Boltzmann 115 years ago [2],[3],[6],[19],[20]. In this model the molecules of the gas conceived roughly as billiard balls are allowed only to collide pairwise as a consequence of the diluteness and characterized by a scattering cross section which can be computed using the laws of classical mechanics. The bulk motion of the molecules of the gas is described by a time irreversible integrodifferential equation which is closed and nonlinear in f, the single particle distribution function. In terms of this quantity, a time dependent function, the famous H function is defined as the average value of the logarithm of f, with weight f. It may then be shown that the time derivative of H is a nonincreasing monotonic function of time and furthermore it is such that for the equilibrium state of the gas, characterized by a Maxwellian distribution function for the velocities, the negative of its value multiplied by Boltzmann's constant is identical with the expression that one gets

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for the equilibrium value of the entropy of a monoatomic ideal gas. This immediately suggests the identification of (-H) with the nonequilibrium entropy of the gas. Yet, this is completely unjustified. First, as Jaynes has shown [24] the equilibrium value of H is only at grips with the conventional definition of the entropy for an ideal gas. Secondly to actually compute H one needs the full solution to the kinetic equation obeyed by f. This task has never been accomplished for any realistic model. Thirdly, the set of experiments that is required to measure such nonequilibrium functions is also lacking. Since this picture is applicable to all the so far studied approaches to nonequilibrium phenomena under the heading of "master equations", we may conclude at once that for these so called "mesoscopic or coarse-grained" equations used to study the approach to equilibrium of many body systems, the concept of entropy is not well defined for the nonequilibrium states of such systems.

The most fundamental approach that one could conceive to study the problem posed above would be through other equations which govern the motion of the molecules, atoms, or whatever microscopic particles comprise the system. Since these equations are well known to be time reversible; namely, invariant under the operation t → -t, any H-like function constructed from quantities involving the full microscopic dynamics of the system will clearly not serve the purpose of defining an entropy-like function which, as discussed in the previous paragraph, must be in some sense a nondecreasing monotonic function of time. Once more as Jaynes has shown, the form proposed by Gibbs to perform this role is the most convenient one for any arbitrary

system in an equilibrium state since it is compatible with the ordinary definition of equilibrium entropy and it is also the best candidate to define entropy for nonequilibrium states, yet its computation and relationship with a well defined set of experiments is still a program and not a fact.

After this lengthy discussion, it is easy to appreciate that very often we meet statements about entropy which are hard to understand. To speak about this function in systems which are far away from equilibrium states, or to say that entropy is the supreme law of nature, that it plays an important role in the evolution towards complexity, and so on, without ever stopping to define it in terms of the set of variable specifying the state of the system we are dealing with is meaningless.

As we mentioned before, the purpose of this paper is to give an account of the physical basis supporting the ideas contained in the previous paragraphs. For this purpose, it is divided in four sections. The first one is devoted to a brief review of the concept of entropy as used in equilibrium thermophysics. The second one bears directly on the question of using the Boltzmann entropy and the famous H-theorem as the kinetic theoretical justification for the equilibrium entropy and the second law of thermodynamics. In this respect we insist on the different content of the two statements and clearly indicate the up to present limitations on the use of the concept of entropy beyond the local equilibrium state. We also show explicitly that beyond this state the concept of entropy has no significance. In section III we discuss other equally unsuccessful

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attempts to extend the concept of entropy to nonequilibrium states using the basic laws of classical statistical mechanics and finally, the last section contains some remarks on the misuse and abuse of the concept of entropy.

I. Entropy in Equilibrium Systems

In order to set a framework for the discussion on the concept of entropy, we shall briefly summarize in this section the significance of this variable as it is ordinarily presented in the context of thermostatics and equilibrium statistical mechanics. We recall that for any closed (no mass exchange with its surroundings) arbitrary system which undergoes a reversible process between two equilibrium states A and B, where these letters stand for the set of pertinent thermodynamic variables required to specify such states, the difference in their entropy is given by [4],[30],[33],[45]

$$S(B) - S(A) \equiv \Delta S = \int_A^B \frac{dQrev}{T} \qquad (1)$$

where T is the temperature at which the system exchanges the amount of heat dQrev with its surroundings. Regardless of the way we choose to introduce eq. (1) into the theory, it surely provides us with a well defined way of computing ΔS; namely, by measuring dQrev or by using the well known differential forms for this quantity arising from the first law of thermostatics. When the process between A and B is not a reversible one, then eq. (1) becomes, according to Clausius' theorem, an inequality, ΔS being always greater than the integral in the right hand side where dQ now refers to the arbitrary, in general, irreversible process. If further such process occurs in

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an isolated system, then we get the well known inequality [30],[36], [45]

$$\Delta S \geq 0 \qquad (2)$$

It is also imperative to recall that eqs. (1) and (2) are valid in systems for which the acceleration due to the force of gravity is negligible or taken to be equal to zero. For systems which are closed but may exchange energy with their surroundings, eq. (2) still holds true for the thermodynamic universe, uniquely understood to be composed by the system plus its environment (surroundings).

For open systems which are usually conceived as the thermodynamic phases composing a single heterogeneous system, the phases being able to exchange matter through their boundaries, eq. (2) holds true for the whole system provided we introduce the additional assumption stating that the entropy, and in fact, all the exterior thermodynamic properties, are additive. Using this assumption it is then a standard task to prove that the basic differential form for classical thermostatics, namely Gibb's relation, take the form

$$TdS = dU + pdV + \text{other forms of work} - \sum_{i=1}^{r} \mu_i dN_i \qquad (3)$$

where N_i is the number of units of species i in a given phase, μ_i is the chemical potential of species i, and the rest of the symbols are the standard ones. These equations summarize the basic results from which ΔS may be computed for any two equilibrium states of a given arbitrary system.

The microscopic interpretation of these results is well accounted for through the Gibbs-Einstein formulation of equilibrium

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statistical mechanics [33],[1],[18]. Recalling that the microcanonical ensemble is the one suitable to represent an isolated system whose thermodynamic states are necessarily described through extensive variables; namely, its energy, its volume and perhaps an extra set of extensive parameters, then if we denote in classical statistical mechanics $\Omega(E,V,\{Yi\})$ the region in phase space corresponding to that determined by a given set of numerical values of such macroscopic, measurable variables, the entropy of the system as a function of E, V and $\{Yi\}$ is given by the well known formula, [33],[18],[21],[38]

$$S(E,V,\{Yi\}) = k \ln \Omega (E,V,\{Yi\}) \tag{4}$$

where k may be shown to be the Boltzmann constant $k = \mathcal{R}/N_O$ where $\mathcal{R}$ is the universal gas constant and N_O is Avogadros' number. Eq. (4) is the basic equation of equilibrium statistical mechanics. Given a Hamiltonian function describing the microscopic properties of the system, Ω may be in principle computed and after identifying E with the internal energy of the system, one gets an explicit form for the thermodynamic potential S in the energy representation. Thereafter, all the thermodynamic properties of the system may be obtained through simple straight forward algebraic operations. If the system is not isolated but in thermal contact with its surroundings, one may easily show that the appropriate representative ensemble is Gibbs' canonical ensemble for which the corresponding thermodynamic potential is Helmholtz's free energy F which is now a function of T,V and $\{Yi\}$. The calculation of F is now easily performed by computing the partition function in the standard way. It should be emphasized

here that provided that the fluctuations in the energy arising from the interaction between the system and its bath (surroundings) are normal, that is to say that the root mean square derivation is of the order of $(\sqrt{N})^{-1}$ where N is the number of particles in the system (N ~ 10^{23}) eq. (4) remains essentially valid (although its mathematical structure might change a little). The same comments apply to the case of an open isothermal system exchanging both matter and energy through its boundaries with its surroundings. The appropriate representative ensemble is the grand canonical ensemble, (-pV) turns out to be the corresponding thermodynamic potential and eq. (4) remains a valid expression for the entropy provided the fluctuations in the energy and in each of the number of species are normal.

In essence, what classical (and quantum) statistical mechanics teaches us is that as long as we are not dealing with small systems (N<<10^{23}), with the behavior of systems near critical points and with a few other situations in which fluctuations of the extensive variables E, V, N, etc. are not normal, eq. (4) provides us with the link between the microscopic and the macroscopic nature of our system. Or, rephrasing this statement, for sufficiently small fluctuations characteristic of thermostatic equilibrium, all the various representative ensembles are equivalent. Since the macroscopic entropy defined in eq. (1) may be computed from calorimetric measurements, we may refer to it as the calorimetric entropy. On the other hand, the entropy computed from eq. (4) requires the knowledge of molecular parameters usually provided by spectroscopic measurements so we may refer to it as the spectroscopic entropy.

Agreement in the values thus obtained for these two quantities is thus considered as a satisfactory proof of the relationship between the macroscopic and the microscopic description of a given system in a state of equilibrium. (11),[34]

Such an agreement, however, does not always occur. There are many systems for which at a given temperature (usually the boiling point) the spectroscopic entropy is smaller than the calorimetric value. This discrepancy is closely connected with the Nernot principle which entails us with a prescription to compute the values of S as the temperature is lowered toward the absolute zero. [43], [11] The excess entropy manifested in these cases is then interpreted as a measure of the residual entropy that the system possesses due to some internal degrees of freedom which, in the process of cooling, never reached their true equilibrium state. Thus, it is also referred to as the "degree of disorder" that the system exhibits compared to the case of a perfect crystal for which at absolute zero, the entropy is equal to zero. Space forbids a more profound discussion of this rather still controversial point about using this criterium to endow S with the property of measuring the "degree of disorder" in a macroscopic system. [11],[33],[34],[43]

The final point to be stressed in this introduction is that eqs. (1) and (4) are operative expressions which allow us to compute ΔS in the macroscopic world and in the microscopic world, respectively, for a given well defined set of measurable parameters. Entropy is thus a well defined property for any closed or open thermostatic system

which is in a state of equilibrium, regardless of what interpretation we want to adopt for it. [23],[24],[38]

II. Entropy in Nonequilibrium Systems

In the previous section we have simply reminded the reader of the indisputable fact that entropy, regardless of the physical interpretation we wish to attach to it, is a well defined computable property for any system in thermodynamic equilibrium. This section is devoted to the discussion of whether or not, and how in the affirmative case, one can define and compute entropy in a system which is not in a state of equilibrium. Since Higatsburger [22] in an accompanying article in this volume has undertaken the task of following the historical development of the concept of entropy, we shall follow here a rather logical order discussing first the macroscopic approach to the question and afterwards touching on some of the efforts made to cope with it on more microscopic bases.

The first and perhaps the only well structured approach to extend the framework of thermostatics to nonequilibrium systems is based on the ideas of Onsager, Casimir, de Donder and others (7),(5),(26),(29),[5],[7],[28],[31] which date back no more than six decades or so. The ensuing formalism, now referred to as Linear Irreversible Thermodynamics (LIT) is based on four assumptions which are outlined in what follows. They are:

(a) The local equilibrium assumption which states that for any system whose properties are space and time dependent, around each point in space and at any given time we may conceive a local state of equilibrium. This state is specified by assuming that the entropy

density $S(\vec{r},t)$, or any other variable as well, may be defined by regarding it as having the same functional dependence with the relevant independent variables, as it has in thermodynamic equilibrium. For a fluid for instance, if we take the mass density $\rho(\vec{r},t)$ and the internal energy density $e(\vec{r},t)$ as two independent local variables, then $S(\vec{r},t)$ has the same functional dependence with ρ and e as the equilibrium entropy has with the internal energy and the mass of the system. Notice should be taken that although the functional relationship is claimed to be the same, this is not so for the numerical values of the local quantities. In short, what we are stating in this example is that the local entropy is a functional of $\vec{r}$ and t through e and ρ only. As an example of this statement, consider the case of an ideal gas. The relationship between its state variable at any given point in space and any arbitrary time is $p(\vec{r},t) = \rho(\vec{r},t)\ T(\vec{r},t)$, where p, ρ and T are the local pressure, density and temperature, respectively. This is the local equation of state where the numerical values for each of the three local state functions appearing therein are to be obtained from the solutions to the Euler equations of hydrodynamics for an ideal fluid under specified initial and boundary conditions.

(b) Due to the nature of assumption (a) one may compute the total time derivative of $S(\vec{r},t)$ in terms of the time derivatives of the independent variables. In the case of $\rho(\vec{r},t)$ and $e(\vec{r},t)$ such derivatives are known through the conservation equations. In turn, one can manipulate the results in such a way that the time rate of change of $S(\vec{r},t)$ is written as a balance equation

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characterized by a flow and a source term. This latter one may <u>always</u> be expressed as a sum of products, each product containing a flux or current characterizing the nonequilibrium state (heat flux, etc.) and the gradient of the intensive variable producing such a flux (temperature gradient, etc.) which is identified as the conjugate force. This source term known as the entropy production is assumed to be non-negative. This assumption, the second one in the theory process is the logical generalization of eq. (2) both for closed and open systems. [7],[31]

Before we move to the content of the third postulate, its rationale should be clearly understood. The main goal to be achieved by any macroscopic theory of matter (and radiation as well) is to establish a well defined set of differential equations for the selected independent variables which may be solved with a minimum of additional information to disclose all the properties of the system under study. This is precisely the status of eq. (3) in thermostatics. In LIT it turns out that the conservation equations for the locally conserved densities when chosen as independent variables, are outnumbered by the number of unknowns among which the fluxes are included. Thus, additional information is required to relate such unknowns to the state variables themselves. This is accomplished through the introduction of the so-called constitutive equations, and their structure forms the main body of the third assumption. Hence,

(c)   For any isotropic systems (this restriction is easily removed) in which there are n fluxes of a given tensorial character

associated with an equal number of forces of the same tensorial character we assume that the coupling of any given flux, say J_i, depends linearly on all the n forces. Shortly,

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \quad i = 1, \ldots, n \tag{5}$$

Here, the coefficients L_{ij} depend only on the equilibrium values of thermodynamic quantities such as the density and the temperature. The matrix $\underline{L}$ whose elements are L_{ij} is known as the "transport matrix". Fourier's equation, Fick's equation, Navier-Newton's equation, etc., are typical examples of eq. (5).

(d) For many systems eq. (5) is not enough to provide the necessary number of equations that may lead to a closed set of equations for independent variables. The fourth assumption of the theory makes sure that this is the case and states that $\underline{L}$ must be a symmetric matrix; namely, $L_{ij} = L_{ji}$ for all i and j. This property was actually derived by L. Onsager in 1931 from strictly microscopic considerations, the invariance of the dynamical equations of motion under time reversal ($t \rightarrow -t$). [25],[44],[33]

When assumptions (c) and (d) are combined with the local equilibrium assumption (a) together with the conservation equations, one is led to a complete set of nonlinear differential equations for the local state variables which may be solved in principle for given initial and boundary conditions provided the coefficients L_{ij} are known, either from experiment or from microscopic models. Emphasis has to be placed here on the role played by the conceptualization of the entropy in the theory. Except for the fact that throughout the entropy balance equation, in particular the entropy source term, one

gets to perceive the relationship between fluxes and forces and further because the non-negativeness of this term connects us with equilibrium thermostatics, the calculation of $S(\vec{r},t)$ as such is entirely secondary and, in fact, assumption (b) is not needed to accomplish the goal of the theory. In short, we have no prescription to compute $S(\vec{r},t)$ and even the less to compare it with experiment. Thus, the very tangible concept of entropy in thermostatics falls here behind a mask through which we may sense its general features but it is not accessible to us in its full meaning. This does not imply that LIT is not a useful or successful theory, which indeed it is, [27] it only indicates that the extrapolation of the concept of entropy as used in thermostatics loses, if not all, certainly a great deal of its objectivity.

One might turn his head around seeking enlightenment to this question through a more microscopic theory. Yet, contrary to the case of thermostatics, this effort becomes rather frustrating. In fact, up to date and especially along the issue of clarifying the concept of entropy for nonequilibrium states, the only more microscopic interpretation we have on LIT is through the kinetic theoretical model for a dilute gas proposed by Boltzmann over 100 years ago. (2),(3) This model generates the time evolution equation for the single particle distribution function of a monoatomic gas known as the Boltzmann equation. This is not the place to enter into a full discussion about the origin and nature of this equation [2],[6],[20],[33],[39]. Let us just remind the reader that in the six dimensional space in which the molecules, pictured as point masses,

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are described through their position vectors $\vec{r}_i$ and velocities $\vec{v}_i$ (i = 1,...,N; N ~ 10^{23}) we may define a function $f(\vec{r},\vec{v},t)$ such that if it is multiplied by a six dimensional volume element $d\vec{r}\,d\vec{v}$, the product is a measure of the number of molecules which at time t are found to lie in $d\vec{r}\,d\vec{v}$. The Boltzmann equation (BE) simply states that the flow of particles through the boundaries of any such volume element has to be compensated by the number of particles which enter or leave the element on account of binary molecular collisions. In symbols, in the absence of external forces,

$$\left(\frac{df}{df}\right)_{drift} \equiv \frac{\partial f}{\partial t} + \vec{v} \cdot \left(\frac{\partial f}{\partial \vec{r}}\right) = \left(\frac{df}{dt}\right)_{collisions} \qquad (6)$$

With a master stroke of genius, Boltzmann proposed an explicit form for the right hand side of eq. (6) converting it into an intergrodifferential nonlinear equation in f. Such an equation may in principle be solved for $f(\vec{r},\vec{v},t)$ for given initial conditions $f(\vec{r},\vec{v},o)$ and suitable boundary conditions in the six dimensional $(\vec{r},\vec{v})$ space. The most important question about the (BE) is if for arbitrary $f(\vec{r},\vec{v},o)$ the gas will reach in time its equilibrium state. The answer to this question represents a formidable task which would require knowing in complete detail the existence conditions and properties of the solutions [19] to a class of nonlinear integro-differential equations, for almost arbitrary initial conditions. This program is unavailable to us even today. Here again Boltzmann gave way to his genius and found an answer to this question without having to solve the equation itself.

Let us assume that the solution to the BE exists for a large (unrealistic) class of initial conditions $f(\vec{r},\vec{v},o)$. Furthermore, let us assume that all integrals of $f(\vec{r},\vec{v},t)$ in $(\vec{r},\vec{v})$ space converge. Then if we define a quantity

$$H = \iint d\vec{r}\ d\vec{v}\ f\ \ell n\ f \tag{7}$$

it may be shown that [2],[3],[7],[39],

$$\frac{dH}{dt}\ \leq 0 \tag{8}$$

the function H is a monotonic nonincreasing function of time. This is the content of the celebrated H-theorem which is at the heart of all discussions about the nonequilibrium interpretations of entropy as we shall further see. Once the property defined by eq. (8) is established, one can also prove that the thermodynamic equilibrium state is <u>always</u> reached given that the external forces acting on the gas satisfy some specific conditions. In the absence of an external force, the equilibrium state is uniquely described, as it is well known from elementary kinetic theory [33] by the well known Maxwell-Boltzmann distribution function; namely,

$$f^{(eq)}(n,T) = n\ \left(\frac{m}{2\pi kT}\right)^{3/2}\ \exp\left(-\frac{mv^2}{2kT}\right) \tag{9}$$

where $n = N/V$ is the number density, T the equilibrium temperature, m the mass of the molecules and k, Boltzmann's constant.

The remarkable feature about this theorem pertinent to the subject of this paper is that when eq. (9) is substituted into eq. (7), one finds after a very elementary calculation that $H^{eq} = -k^{-1} S^{(id)}(n,T)$ where $S^{(id)}(n,T)$ is the equilibrium entropy for a

monoatomic ideal gas as derivable from eqs. (2) and (4). This immediately suggests the identification

$$S = -k \, H \tag{10}$$

as the general definition of entropy including nonequilibrium states. Furthermore, eq. (8) then implies that $\frac{dS}{dt} \geq 0$, the entropy can never be a nondecreasing function of time and joyfully we may thus claim that we have a kinetic theoretical proof of the second law of thermodynamics. A word of caution is nevertheless pertinent at this stage because the contents of eqs. (2) and (10) are virtually different. Eq. (2) states that the change in entropy for any isolated system in a process occurring between two equilibrium states can never decrease. On the other hand, eqs. (8) and (10) state that for a dilute monoatomic gas which at some time t=0 is characterized by some unspecified value of the distribution function $f(\vec{r}, \vec{v}, o)$ associated to a nonequilibrium state, the gas evolves towards its equilibrium state in such a way that for all times, S defined as such is always a nondecreasing function of time. Once the equilibrium state is reached, then S^{eq} has precisely the same mathematical form as that predicted by the equilibrium theories. Therefore, the attempt of identifying the H function with the entropy of a dilute monoatomic gas is valid only for the equilibrium state [23],[24].

The above discussion poses an immediate question; namely, can we really compute the values of H (or S) for any arbitrary nonequilibrium state of the gas? This bluntly posed question requires an equally drastic reply; namely, to perform such a calculation, we must solve the BE. But this has never been achieved

in general except for a system of homogeneous rigid spheres and a few other models of little physical significance, if any. For the dilute monoatomic gas there are two well defined methods of solution which we shall discuss with certain detail because they bear heavily on the above question. The first of these methods can be understood under the following basis. [7],[39] Let us recall that our system is a fluid which from the standpoint of hydrodynamics may be described through the values of five local variables which we choose to be the locally conserved densities, mass $\rho(\vec{r},t)$, momentum $\rho(\vec{r},t)\vec{u}(\vec{r},t)$ and energy $e(\vec{r},t)$, where $\vec{u}(\vec{r},t)$ is the hydrodynamic velocity of a fluid element at $\vec{r}$. From the manifold of possible solutions to the BE we want to choose those which are consistent with the hydrodynamic description. They are the so-called "normal solutions". [19] Notice here that whereas the full information contained in $f(\vec{r},\vec{v},t)$ is needed to understand the time evolution of the gas in $(\vec{r},\vec{v})$ space only five local quantities are needed to understand its hydrodynamic status. This means that in some, not yet specified way, we must perform a contraction in the information required to go from the full kinetic to the more structured hydrodynamical language. The method used to sort out the normal solutions of the BE was originally devised by Hilbert [6],[19] and adapted specifically to the BE by Chapman [6] and independently by Enskog [3]. The now called Chapman-Enskog method relies on two basic assumptions; namely

(a) For times long enough compared with the mean collision time, we assume that the distribution function $f(\vec{r},\vec{v},t)$ is governed in its time behavior only through the hydrodynamic variables $\rho(\vec{r},t)$,

$\vec{u}(\vec{r},t)$ and $T(\vec{r},t)$, where the local temperature $T(\vec{r},t)$ is related to the internal energy density $e(\vec{r},t)$ through the relationship $e(\vec{r},t) = \frac{3}{2} kT(\vec{r},t)$. Notice should be made of the fact that this assumption which essentially states that the time evolution of the gas is governed by the time evolution equations of the slow or conserved densities is equivalent to the local equilibrium assumption of LIT (see (a) p. 11.)

(b)   The single particle distribution function $f(\vec{r},\vec{v},t)$ under the restriction imposed by (a), may be expanded around a local equilibrium state in power series of a uniformity parameter, say μ, which is a measure of the magnitude of the macroscopic gradients present in the system. The local equilibrium state is one characterized by a Maxwell-Boltzmann distribution function [cf. eq. (9)] in which the equilibrium variables are replaced by their local values (see Appendix B).

Without going into any of the mathematical details of the procedure [6],[19],[20],[21],[39], we can now analyze the outcome of using these assumptions in the BE emphasizing both the structure of LIT and the role of entropy in nonequilibrium states. If the zeroth order term in μ is taken in the expansion referred to in (b); namely, the local equilibrium state, it follows immediately, as shown in Appendix B that the corresponding hydrodynamic equations are those of a Euler (inviscid) fluid whose local hydrostatic pressure obeys precisely the local equation of state for an ideal gas, $p(\vec{r},t) = \rho(\vec{r},t) \mathcal{R} T(\vec{r},t)$ (see assumption (a) p. 11. Furthermore, the entropy of the gas computed from the local version of eq. (10) is identical

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in structure to that of an ideal gas and it is conserved along the streamlines of the flow. In other words, to this order of approximation, the flow of the gas is adiabatic. These results simply confirm the fact stated in assumption (a) above; namely, that the local equilibrium assumption has already been introduced into the method.

To first order in the parameter μ, as also indicated in Appendix B, the set of hydrodynamic equations corresponds precisely to those obtained from the general conservation equations for momentum and energy when the linear relationship indicated in eq. (5), explicitly written as Fourier's equation for heat conduction and Navier-Newton's equation for the stress tensor are used. In this calculation one obtains explicit forms for the heat conductivity and the shear viscosity in terms of the solutions of well defined linear integral equations which may be solved once the specific intermolecular potential is chosen. Furthermore, the calculation of the entropy according to eqs. (7) and (10) turns out to be identical to the one in the μ = 0 approximation so that the local equilibrium assumption is once more fulfilled. And even more, it may be shown that, by an appropriate mathematical manipulation of the BE the entropy balance equation referred to in assumption (b) p. 12 is obtained with a non-negative expression for the entropy production. This equation, which is a general property of the BE, can also be shown to hold true if the solution for $f(\vec{r},\vec{v},t)$ up to first order in μ is used to evaluate the various contributions involved in it [7]. Finally, when a multicomponent mixture of inert dilute gases is considered under this

first approximation in the parameter μ, one can show that the Onsager reciprocity relations $L_{ij} = L_{ji}$ are also satisfied [7],[25]. In this sense, one may therefore claim that the basic assumptions of LIT find their kinetic justification as a consequence of solving the BE with the Chapman-Enskog method provided that in this solution we keep only those contributions which are at most of the first order in the macroscopic gradients.

This rather attractive panorama is completely disrupted when we go one order further in μ; namely, we include $f^{(2)}$ in the solution. A set of hydrodynamic equations may still be obtained, the so-called Burnett equations, for which eq. (5) is violently violated [7]. And what is more disturbing is that the entropy of the system is no longer at grips with the local equilibrium assumption since it now becomes a function of the gradients themselves! Also, the Onsager relations do not hold true, and the whole picture provided to us by LIT breaks down completely. The reasons behind this catastrophe, which grows worse as we go higher and higher in μ, is a rather subtle point, too technical to be discussed here. The interested reader is referred to the original sources for further information [12-14]. Let us just state that beyond the terms in assumption (b), linear in μ, the Chapman-Enskog solution is no longer compatible with the assumptions of LIT. And moreover, the function H (or S for the matter being) looses its potentiality as one capable of clarifying the concept of entropy for a nonequilibrium state.

The above analysis clearly points out two of the still open questions underlying the definition of S for nonequilibrium states.

The first one is that in the case of the BE, the method of seeking normal solutions is only compatible with the phenomenological theory, LIT, only if small deviations from local equilibrium are considered. This implies neglecting all terms of order μ^n (n>2) in the expansion in parameter μ. Not much insight is gained in clarifying the concept of entropy since to this approximation the local equilibrium assumption is justified. The second question is that the above analysis is valid only for a dilute gas. Since we lack kinetic equations amenable to analytical treatment for other realistic systems, we are unable to extrapolate the true significance of eqs. (8) and (10). We shall come back to this question later on in a different context.

Before leaving kinetic theory, it is important to mention that among other attempts to solve the BE, there is one devised by H. Grad in 1949 which seeks general instead of normal solutions [19],[20]. The main gist of the method is to transform the full nonlinear integrodifferential equation into an infinite set of coupled nonlinear differential equations for an equal number of quantities which depend on the position $\vec{r}$ and time t.[19],[20] These quantities play the role of the local variables of the previous method and, in fact, the first five moments of $f(\vec{r},\vec{v},t)$ appear among them. If one now arbitrarily truncates the set of equations and keeps say n>5 moments (Grad chose n = 13), one finds, for specific models of molecular interactions, that the distribution function depends on such n quantities. This means that besides $\rho(\vec{r},t)$, $\vec{u}(\vec{r},t)$ and $T(\vec{r},t)$ on the remaining n-5, moments are raised to the status of independent

state variables. Physically, this means that there are fluids (unfortunately not ordinary gases) which, under certain conditions, would require more than the five hydrodynamic densities to describe their states. The resulting enlarged space of state variables thus contains additional variables whose time evolution equations turn out to be of the relaxation type equations. But the most important issue of this method in the context of this paper is that although the function H may be formally defined, it is a property associated to the BE. The ordinary concept of entropy has absolutely no room in the formalism and the whole question of defining this function for nonequilibrium states <u>beyond local equilibrium</u> loses all its meaning.

These ideas, kinetically valid for dilute gases only, when used on a phenomenological context to describe other arbitrary systems beyond their local equilibrium states have given rise to Extended Irreversible Thermodynamics [15],[16],[32]. This rather recent approach to macroscopic nonequilibrium phenomena, with its present scope and limitations, has proved to be very useful in systematizing a number of results so far disconnected among each other. The important feature of this theory, however, is that entropy or, as a matter of fact, any thermodynamic potential is, so far, completely foreign to the formalism. We thus reach a stage at which a challenging equation ought to be raised: is entropy a concept associated to a variable which may be defined in a clear and unequivocal operative way beyond local equilibrium? To the author's knowledge, a reasonable answer does not yet exist [8],[9],[25].

III. <u>Other Nonequilibrium Aspects of Entropy</u>

As we have shown in the previous section, kinetic theory of gases throws a tiny bit of light on clarifying the possibility of extending the definition of entropy to nonequilibrium states. Yet, one could object to this approach arguing that after all it is not the most general way of formulating the problem. Instead, one should really go to the basic postulates of statistical mechanics to search for the appropriate answer. Moreover, since microscopic dynamics belongs to the realm of quantum physics, one should then appeal to quantum statistical mechanics. We shall dispense here with this last requirement. First for pedagogical reasons, and second because the basic ideas underlying the physical nature of the question are essentially the same in both classical and quantum mechanics [29],[35],[37].

Consider any system of N degrees of freedom, where N is very large ($N \sim 10^{23}$). Think of an N dimensional space in which each point characterizes completely any dynamical state of the system obtained assigning a numerical value to each of the N independent coordinates. Following Gibbs, to cope with all possible initial conditions compatible with the few macroscopic constraints defining the system, the only ones we can control in the laboratory, we introduce a "representative ensemble" composed of an arbitrarily large number (an infinite number in fact) of identical macroscopic replicas of our system, so that the equally large (infinite) number of points in such N-space is actually represented by a continuous distribution. Such a space denoted by Γ is known to us as the phase space for the system.

Let $\rho(\Gamma,t)d\Gamma$ be the number of representative points which at time t are found to be in the N-dimensional volume element $d\Gamma$. The laws of classical mechanics then require that the motion of such points in the course of time behave as an incompressible fluid. $d\Gamma$ may be thought of as an amoeba which changes its shape as it moves so that all points which are initially contained therein, remain within; and no points from the outside can enter $d\Gamma$. This is the physical content of Liouville's theorem [18],[38],[39]. Now imagine a system which at t = 0 is prepared in a nonequilibrium state described by a distribution function $\rho(\Gamma,t)$ which is zero everywhere in Γ space except for a small region whose extension is determined by the number of constraints imposed upon the system in such a state. The next question that comes to mind is to inquire how $\rho(\Gamma,t)$ will evolve in time and, in particular, under which conditions if any it eventually will reach the equilibrium distribution $\rho^{eq}(\Gamma)$. Thus, the question is connected with the possibility of proving the analog of the H-theorem of kinetic theory of gases but now for $\rho(\Gamma,t)$ instead of $f(\vec{r},\vec{v},t)$. Since $\rho(\Gamma,t)$ contains now all the dynamical information about the representative ensemble for our system, one is tempted to define, in analogy with eq. (7), a quantity H of the form [18],[35],[24].

$$H = \int_{\Gamma \text{ space}} \rho(\Gamma,t) \, \ln \rho(\Gamma,t) \, d\Gamma \tag{11}$$

However, the inequality expressed by eq. (8) does not exist for this function. This, however, should not surprise us. In fact, $\rho(\Gamma,t)$ obeys a time evolution equation equivalent in content to Hamilton's equation of motion for the N dynamical variables

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associated with the degrees of freedom. As it is well known from classical mechanics, these equations are invariant under time reversal ($t \to -t$). No privileged direction in time is associated with them so that the "irreversibility" property exhibited by eq. (8) has no place here. Therefore, eq. (11) can hardly be identified with the concept of a nonequilibrium entropy. On the other hand, it is a well known fact [27] that if in this eq. (11) we substitute the equilibrium value of $\rho(\Gamma)$ for any of the standard representative ensembles, we recover the equilibrium value of the entropy $S^{eq} = - kH^{eq}$ where S^{eq} is precisely the same quantity defined in eq. (5). Not much progress is thus achieved by resorting to the microscopic equations of motion as a possible source for clarifying the concept of entropy for nonequilibrium states [24].

The reason why the inequality expressed by eq. (8) could be derived from the BE is essentially that this equation is already irreversible in time. It is no longer invariant under time reversal. One may thus wonder if by contracting information from the exact time evolution equation for $\rho(\Gamma,t)$ one could be led to a class of irreversible equations for which the analog of eqs. (7) and (8) could be derived. That this is indeed the case, was first shown by Pauli in 1927 [38],[40],[44], when by an application of successive random approximations he managed to obtain what is now referred to as a "master equation". Since the underlying ideas are relatively simple to explain, let us proceed to discuss them in the realm of classical mechanics [38],[40].

Imagine that the region in phase space Γ available to the representative points of the systems belonging to the ensemble are divided into cells whose extension is large enough to contain a very large number of points but small compared with the region as a whole. This is basically the coarse graining idea of Ehrenfest [8],[10]. Now imagine that the initial state of the system is such that it may be represented by a uniform distribution of points in a single cell, call it J. Thus $\rho(\Gamma,0)$ = const if a point is in J and is zero otherwise. After a time t has elapsed, long enough compared with a microscopic time, the points in J will have spread out into the neighboring cells so one can speak of the fraction of points in a different cell, say J'. Thus we are led to raise the question of what is the probability of finding a point in cell J' at time t if at initial time t = 0 it lay in J. After such time interval t has elapsed, we look into all neighboring cells containing points, smear them all throughout the cell J,J', etc. and repeat the question about finding points in other cells J'' after a time 2t has elapsed, etc. After this has been done a number of times, one finds that the migration of the representative points along the cells is of a diffusive type which is governed by a differential equation characteristic of a class of stochastic processes known as Markoff processes [17],[40],[41]. This is the so-called master equation [37]. Its mathematical structure is also easy to understand since it reflects the fact that the time rate of change of the probability of finding a point in a given cell at a given time is merely the result of a gain-loss process. The main issue now is that one can define a

quantity H identical in structure to the previous two, eqs. (8) and
(11), as follows:

$$H = \sum_J P_J(t) \, \ell n \, P_J(t) \qquad (12)$$

where $P_J(t)$ is the probability of finding a system in cell J at time
t. From eq. (12) and the master equation governing the time rate of
change of $P_J(t)$, it is easy to show [41],[44] that this H function
satisfied the inequality given by eq. (8). Moreover, if the
equilibrium solution to the master equation $P_J(eq)$ is substituted
into eq. (12), then one recovers once more the equilibrium value for
the entropy as expressed by eq. (10). Thus, we find ourselves in a
situation rather similar to that found in kinetic theory; namely,
only for equilibrium states H and S are related among themselves and
the inequality expressed by eq. (8) exists with a different
interpretation than eq. (2). Moreover, to compute H given in eq.
(16) for nonequilibrium states, one requires a full knowledge of
$P_J(t)$ which is tantamount to solving the master equation, a task that
has been accomplished in some restricted cases [17],[41]. We then
reach the unhappy conclusion that eq. (12) is doubtfully identifiable
with a nonequilibrium entropy.

IV. <u>Concluding Remarks</u>

Before closing this discussion about the possibility of
extending the concept of entropy beyond equilibrium states, some
remarks on the results presented in the previous sections are rather
pertinent.

Entropy is a well defined thermodynamical variable for systems
which are in their equilibrium states. These states, including long

living metastable states, are uniquely defined both from their microscopic and macroscopic points of view as well. This is essentially why the Gibbs-Einstein algorithm is so successful. To each equilibrium thermodynamic potential, the entropy included, one may uniquely associate a microscopically based partition function in which all the relevant information needed to specify such states is contained. This point is clearly borne out in the two explicit methods we discussed for solving the BE, in connection with the calculation of the function H. As long as we stick to the Maxwell-Boltzmann distribution function, eq. (9) or its local version both already containing the relevant variables required to describe the corresponding equilibrium and local equilibrium states, respectively, we find that eq. (10) is satisfied. This means that the expression for the entropy so obtained is identical to that predicted by the equilibrium theories for a monoatomic gas. However, as we start adding up additional contributions, either through higher contributions in the gradients or via the Grad expansion, contributions containing on the one hand terms of higher order in the gradients, or terms containing additional moments, in both cases representing additional dynamical information and such a relationship ceases to exist. And why not! After all, nonequilibrium states are not uniquely characterized, and we should not be able to expect that their description is feasible in terms of well defined equilibrium-like variables. This is precisely the ultimate nature of the so far available calculations.

The same situation occurs with the definitions of H proposed in eqs. (11) and (12). They only hold true for equilibrium states. It seems then inevitable to conclude that entropy as a well defined and experimentally derivable quantity, regardless of its interpretation in terms of order or disorder, a measure of the degree of constraint of a macroscopic system, a thermodynamic potential, etc., is only acceptable in systems which are in equilibrium. To extrapolate the existence of this variable to nonequilibrium states beyond local equilibrium (LIT), especially through its rather restricted relationship with the function H in any of its versions, is entirely devoid of physical reality. We are unable to compute the values of this function from first principles, nor are we able to compare them with experimental results.

In spite of these stringent restrictions on the use of entropy as a physically measurable quantity, its interpretation in terms of order or disorder has been in the author's opinion boldly extrapolated in the field of nonequilibrium thermal physics as well as in other areas not only of physics but other sciences. This is the case of fields such as cosmology, sociology, economy, ecology, etc., where statements about the variable entropy as playing often a dominant role in describing the characteristics of some relevant phenomena are, if not wrong, completely misleading. Particularly, in the field of nonequilibrium phenomena a rather broad, imprecise language has been introduced with the purpose of dealing with "complex" systems which are in "far away from equilibrium" situations and for which evolution towards complexity is dominated by entropy.

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And, of course, the now fashionable terms of order, chaos, fluctuations and so on also come into the whole scheme making the entire wording glamorous and even fantastic but certainly not precise. One of the first vague concepts is the one associated with far away from equilibrium. What should we understand for such a regime? One which is beyond local equilibrium? Or, is it a local equilibrium state with contributions arising from the gradients of the local variables raised to any arbitrary power? Or, is it a state to which a system is driven by external fields? Once we can agree on a definition, we should also agree on selecting the independent state variables needed to describe that state. Assuming that this is accomplished, we should then give a precise definition of entropy for such a state since, as we have just seen, this variable is meaningless beyond a local equilibrium state. Therefore, for other states, any statements we issue about entropy as a variable associated with their behavior are entirely meaningless. There is no such thing as a universal law of entropy, as it is often claimed beyond the realm of equilibrium thermodynamics, at least for the entropy as we understand it presently.

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Appendix A

We shall illustrate the postulates of LIT with a very simple specific example that will keep the mathematics to a minimum. Consider a rigid heat conductor (ρ = const., $\vec{u}$ = 0) which is in a nonequilibrium state. Only one variable is required to specify its state and that will be taken as the energy density $e(\vec{r},t)$. Then

(a) The local equilibrium assumption states that the entropy density $S(\vec{r},t)$ is given by

$$S(\vec{r},t) = S [\rho = const, \ e(\vec{r},t)]$$

or

$$\frac{dS}{dt} = \frac{\partial S}{\partial t} = \left(\frac{\partial S}{\partial e}\right)_{\rho,} \frac{\partial e}{\partial t} = \frac{1}{T} \frac{\partial e}{\partial t} \qquad (A-1)$$

since $\vec{u}$ grad vanishes in this case. We know from first principles that if $\vec{q}$ is the heat flux, the conservation equation for e reads

$$\rho \frac{\partial e}{\partial t} + div \ \vec{q} = 0 \qquad (A-2)$$

because since $\vec{u}$ = 0 there is no dissipation term.

(b) Combining (A-1) and (A-2) we get that

$$\rho \frac{\partial S}{\partial t} = -\frac{1}{T} div \ \vec{q}$$

or

$$\rho \frac{\partial S}{\partial t} + div \ \frac{\vec{q}}{T} = + q \cdot grad \ \frac{1}{T} \qquad (A-3)$$

Defining the entropy flow as $J_S \equiv \vec{q}/T$ (A-3) is the entropy balance equation

$$\rho \frac{\partial S}{\partial t} + div \ J_S = \sigma$$

where

$$\sigma = \frac{\vec{q}}{T^2} \cdot grad \ T \geq 0 \qquad (A-4)$$

the product of the flow $\vec{q}$ times its force   grad T is assumed to be non-negative.

(c)   Equation (A-2) is undetermined.   There are four unknowns, e and $\vec{q}$ and only one equation. The third assumption now states that the flux must be proportional to its force, so

$$\vec{q} = -\frac{L_q}{T^2} \ \text{grad T} \qquad\qquad\qquad (A-5)$$

which is Fourier's equation and $K = \frac{L_q}{T^2}$ is the thermal conductivity. Using once more the local equilibrium assumption $e(\vec{r},t) = e\ [\rho = \text{const}, T(\vec{r},t)]$

$$\frac{\partial e}{\partial t} = C_v \ \frac{\partial T}{\partial t} \qquad\qquad\qquad (A-6)$$

assuming that C_v is still a function of the local temperature. Combining eqs. (A-2), (A-5) and (A-6) we get that

$$\rho C_v \ \frac{\partial T}{\partial t} = \text{div (K(T) grad T)}$$

If K is assumed to depend only on T^{eq}, defining $D \equiv \frac{K}{\rho C_v}$ as the thermal diffusivity we get finally that

$$\frac{\partial T}{\partial t} = D \ \nabla^2 \ T \qquad\qquad\qquad (A-7)$$

which is the well known "heat equation" which given K may be solved for specified initial and boundary conditions on T and ∇T.

Two remarks are important: The role played by $S(\vec{r},t)$ is completely spurious and its calculation depends explicitly on the solution to eq. (A-7).   On the other hand, the structure of σ serves to indicate in a natural way which are the forces associated with the fluxes present in the system.   If eq. (A-5) is introduced in (A-4), we see that

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$$KT^2 \left[\text{grad } \frac{1}{T} \right]^2 \geq 0$$

which implies that $K \geq 0$ is in complete agreement with experiment. In this simple example the fourth assumption concerning the symmetry of the matrix L is entirely unnecessary.

Appendix B

In this appendix we will sketch out how the Chapman-Enskog solution to the BE is related to LIT. The full form for the BE is well known to be [2],[7],[19],[31],[37].

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{r}} = \iint dv_1 d\Omega \; \sigma(\Omega) \; g \; [f(\vec{r},\vec{v}_1,t)f(\vec{r},\vec{v}',t) - f(\vec{r},\vec{v}_1,t) \; f(\vec{r},\vec{v},t)]$$

(B-1)

where $\sigma(\Omega)d\Omega$ is the probability that a particle with initial velocity $\vec{v}$ upon collision with a second particle with velocity $\vec{v}_1$ is scattered into a solid angle $d\Omega$ and $\vec{v}_1'$, $\vec{v}'$ are the final velocities of the two particles, respectively. $g = |\vec{v} - \vec{v}_1|$ is the relative velocity of the incoming or outgoing particles.

Let $\psi(\vec{v})$ be any dynamical quantity associated with the molecules of the gas. Multiplying eq. (B-2) by this quantity integrating over $\vec{v}$, integrating by parts the two terms in the left hand side and successively transforming the right hand side making use of the fact that $d\vec{v}d\vec{v}_1 = d\vec{v}'d\vec{v}_1'$ and that the inverse collision exists, one gets that

$$\frac{\partial}{\partial t} \; \psi \; + \frac{\partial}{\partial \vec{r}} \cdot \overline{(\vec{v}\psi)} = \frac{1}{4} \iint d\vec{v}d\vec{v}_1 \sigma(\Omega) \; g \; C[\psi][(f(\vec{v}_1')f(\vec{v}')-f(\vec{v})f(\vec{v}_1))]$$

(B-2)

where

$$C[\psi] = \psi(\vec{v}_1') + \psi(\vec{v}') - \psi(\vec{v}_1) - \psi(\vec{v}) \qquad \text{(B-3)}$$

and

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$$\psi \equiv \frac{1}{n(\vec{r},t)} \int f(\vec{r},\vec{v},t) \; \psi \; (\vec{v}) \; d\vec{v} \qquad (B-4)$$

$n(\vec{r},t)$ being the local number density obtained from (B-4) when $\psi = 1$. When ψ is one of the five collisional invariants, the mass m, the momentum $m\vec{v}$ or the kinetic energy $\frac{1}{2}mv^2$, according to eq. B-5, $C[\psi] = 0$ and (B-2) then yields the five conservation equations, respectively; namely,

$$\frac{\partial \rho}{\partial t} + \text{div} \; (\rho\vec{u}) = 0 \qquad (B-5)$$

$$\rho \; \frac{\partial \vec{u}}{dt} + \text{div} \; \underset{\sim}{\mathcal{I}}^k = 0$$

$$\rho \; \frac{de}{dt} + \text{div} \; \vec{q} = - \underset{\sim}{\mathcal{I}}^k : \text{grad} \; \vec{u}$$

where

$$\vec{u}^{(\vec{r}.t)} = \frac{1}{n(\vec{r},t)} \int f(\vec{r},\vec{v},t)\vec{v} \; d\vec{v} \qquad (B-6)$$

is the local hydrodynamic velocity and

$$e(\vec{r},t) = \frac{m}{2n(\vec{r},t)} \int f(\vec{r},\vec{v},t) \; c^2 \; d\vec{c} \qquad (B-7)$$

is the local internal energy density since $\vec{c} \equiv \vec{v} - \vec{u}(\vec{r},t)$ is the chaotic, random, or peculiar velocity. Also, the fluxes $\underset{\sim}{\mathcal{I}}^k$ and $\vec{q}$ are given by

$$\underset{\sim}{\mathcal{I}}^k = m \int \vec{c}\vec{c} \; f(\vec{r},\vec{v},t) \; d\vec{c} \qquad (B-8)$$

$$\vec{q} = \frac{1}{2} \; m \int c^2 \; \vec{c} \; f \; (\vec{r}, \; \vec{v},t) \; d\vec{c} \qquad (B-9)$$

Also, if we use the definition for H given in eq. (7), compute $\frac{dH}{dt}$, prove that the contributions arising from the streaming term

vanish after the BE has been substituted in the former result and notice that the collision term can be written as

$$-\frac{1}{4} \iint d\vec{v} d\vec{v}_1 \ln \frac{ff_1}{f'f_1'} (ff_1 - f'f_1') \leq 0$$

using the same steps leading to eq. (B-2), one gets eq. (8). All these results are therefore a property of the full BE provided the intermolecular collisions are of electromagnetic origin to guarantee the existence of the inverse collision.

Furthermore, multiplying eq. (B-1) by $\ln f$, integrating over $\vec{v}$ and performing two well defined integration by parts in the left hand side, assuming that $f(\vec{r}, \vec{v}, t)$ vanishes at the boundaries of $\vec{r}, \vec{v}$ space, we get that

$$\frac{\partial}{\partial t} (\rho_S) + \text{div} (J_S + \rho_S \vec{u}) = \sigma \tag{B-10}$$

where ρ_S is the entropy density defined by

$$\rho_S = -k \int f \ln f \, d\vec{v} \tag{B-11}$$

J_S the entropy flux defined by,

$$J_S = -k \int \vec{c} \, f \ln f \, d\vec{v} \tag{B-12}$$

and σ the entropy production

$$\sigma = -k \int \ln f \, J(ff) \, d\vec{v} \tag{B-13}$$

Furthermore, following the same steps leading to eq. (B-2) and using the same inequality that appeared in the proof of the H theorem, we see that $\sigma \geq 0$ in accordance with assumption (b) of LIT.

We now come to the discussion of the Chapman-Enskog (CE) method for solving the BE. According to assumptions (a) and (b) quoted on p. 11 and 12 of the main text, we may write that

$$f(\vec{r}, \vec{v}, t) = f^{(0)}(\vec{r}, \vec{v}/n, \vec{u}T) + \mu f^{(1)}(\vec{r}, \vec{v}/n, \vec{u}, T) + \mu^2 f^{(2)}(\vec{r}, \vec{v}/n, \vec{v}, T) + \ldots$$

where

$$f^{(0)}(\vec{r},\vec{v}/n,\vec{u},T) = \mathcal{N}(\vec{r},t)\left(\frac{m}{2\pi kT(\vec{r},t)}\right)^{3/2} \exp\left(-\frac{m[\vec{v}-\vec{u}(\vec{r},t)]^2}{2kT(\vec{r},t)}\right)$$

$$(B-15)$$

Recall now that f being a distribution function can be characterized uniquely by the whole set of moments in the variable $\vec{v}$. Also, by definition, the locally conserved densities are given through its first five moments. On account of eqs. (B-14) and (B-15) we now arbitrarily choose that $\underline{all}$ the information about these conserved densities is contained in $f^{(0)}$ instead of depending on the full expression for f. Therefore,

$$\mathcal{N}(\vec{r},t) = \int f^{(0)}(\vec{r},\vec{v},t)\, d\vec{v}$$

$$\vec{u}(\vec{r},t) = \frac{1}{\mathcal{N}(\vec{r},t)}\int f^{(0)}(\vec{r},\vec{v},t)\,\vec{v}\, d\vec{v} \qquad\qquad (B-16)$$

$$e(\vec{r},t) = \frac{1}{\mathcal{N}(\vec{r},t)}\int f^{(0)}(\vec{r},\vec{v},t)\,\frac{1}{2}\,mc^2\, d\vec{v}$$

where $\vec{c} = \vec{v}-\vec{u}(\vec{r},t)$ is the random velocity.

With this arbitrary choice in the selection of the locally conserved densities, all higher order correction terms of f which appear in eq. (B-14) are enforced to obey a set of conditions known as the subsidiary conditions which are clearly seen to be

$$\int f^{(n)}\left\{\begin{array}{c}1\\\vec{v}\\c^2\end{array}\right\}\, d\vec{v} = 0 \qquad n\geq 1 \qquad\qquad (B-17)$$

We now come to the discussion of how the CE fits into the whole question of defining the entropy for nonequilibrium states. Without writing out explicitly the arguments of each function, eq. (B-14) may be easily recast into the following form

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$$f = f^{(0)}(1 + \mu\phi^{(1)} + \mu^2\phi^{(2)} + \ldots) \tag{B-18}$$

where clearly $f^{(n)} \equiv f^{(0)}\phi^{(n)}$

Substitution of eq. (B-18) into (B-1) and collecting terms of equal powers in μ noticing that due to the functional assumption expressed in eq. (B-14) the left hand side of the BE is always of one order in μ higher than the right hand side

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial n}\frac{\partial n}{\partial t} + \ldots$$

and

$$\frac{\partial f}{\partial \vec{r}} = \frac{\partial f}{\partial n}\frac{\partial n}{\partial \vec{r}} + \ldots, \qquad \frac{\partial n}{\partial t}, \text{ etc.}$$

being given by (B-5) which already contains the gradients, one arrives at the following set of linear integral equations:

Order $\mu = 0$ $\qquad\qquad J(f^{(0)}, f^{(0)}) = 0 \tag{B-19}$

Order $\mu = 1$

$$\frac{\partial f^{(0)}}{\partial t} + \vec{v} \cdot \frac{\partial f^{(0)}}{\partial \vec{r}} = C(\phi^{(1)}) \tag{B-20}$$

where

$$C(\phi) \equiv \int d\vec{v}_1 \sigma(\Omega) d\Omega g[\phi^{(1)}(\vec{v}\,') + \phi^{(1)}(\vec{v}_1{}') - \phi^{(1)}(\vec{v}) - \phi^{(1)}(\vec{v}_1)]f_1^{(0)}$$

$$\tag{B-21}$$

is the linearized Boltzman collision integral, etc.

As eq. (B-19) indicates, the local Maxwellian distribution function is a solution to the homogeneous part of the BE but not of the full equation. When substituted in the streaming term it may be shown [7],[39] to reduce to the equilibrium distribution function, eq. (9), in the text for a large class of external potentials. Thus this function is indeed a solution of the full BE; and as we have insistently indicated in the text, the two functions are compatible with a formula for the entropy.

Now is eq. (B-10) satisfied to each order in μ? To zeroth order it is trivial since on account of eqs. (B-2) and (B-3) and the fact that $\ell n f^{(0)}$ is a linear combination of collisional invariants, $\sigma = 0$, $\vec{J}s = 0$, $\vec{q} = 0$ and $\underset{\sim}{\mathcal{T}}^{\kappa}$, the stress tensor, reduced to $n(\vec{r},t)kT(\vec{r},t)\underset{\sim}{11} \equiv p(\vec{r},t)\underset{\sim}{11}$, p being the local pressure for an ideal gas and $\underset{\sim}{11}$ the unit tensor. Thus eq. (B-10) simply states that $s^{(0)}$ is constant along the lines of flow and through eq. (B-11) we see that it is analytically identical with the entropy for an ideal gas. Eq. (B-5) then becomes the Euler equation for an ideal fluid (div $\underset{\sim}{\mathcal{T}}^{\kappa}$ = grad p).

To first order in μ things are more complicated. The left hand side of eq. (B-11) may be explicitly evaluated and through a well known theorem in linear integral equations [7],[19],[39], the solution to the resulting equation may be shown to be of the form

$$\phi^{(1)} = -\mathcal{A}(c)\vec{c} \cdot \frac{\partial \ell n T}{\partial \vec{r}} - \mathcal{B}(c) \underset{\sim}{c^0 c} : \left(\frac{\partial \vec{u}}{\partial \vec{r}} \right) \tag{B-22}$$

where $\underset{\sim}{c^0 c} = \underset{\sim}{cc} - \frac{1}{3} c^2 \underset{\sim}{11}$ and $\mathcal{A}(c)$, $\mathcal{B}(c)$ two functions obeying the following equations

$$- \left(\frac{5}{2} - \frac{mc^2}{2kT} \right) \vec{c} = \mathcal{C}(\mathcal{A}(c)\vec{c}) \tag{B-23}$$

$$- \frac{m}{kT} \underset{\sim}{c^0 c} = \mathcal{C}(\mathcal{B}(c) \underset{\sim}{c^0 c})$$

where $\mathcal{C}(\phi)$ is defined in eq. (B-21) for arbitrary ϕ. These equations may be solved once the form of the molecular interaction is specified, but this technical question need not bother us here.

We now first notice that when $\phi^{(1)}$ is substituted into eqs. (B-8) and (B-9) and we perform the integration we get that

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$$\underset{\sim}{\tau}^\kappa = -2\eta(\underset{\sim}{D} - \frac{1}{3} \text{ div } \vec{u} \underset{\sim}{1\!\!1})$$ (B-24)

where

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

is the symmetric part of grad $\vec{u}$ and η is the shear viscosity given by

$$\eta = \frac{n}{m} (kT)^2 b_0$$ (B-25)

b_0 being a collision integral whose explicit evaluation requires the explicit introduction of the molecular interaction. Also,

$$\vec{q} = -\mathcal{K} \text{ grad } T$$ (B-26)

where

$$\mathcal{K} = + \frac{5nk^2}{2m} T(_1)$$ (B-27)

is the thermal conductivity, and b_1 another collision integral eq. (B-24), the Navier-Newton equation and (B-26), Fourier's equation are just the linear laws mentioned in eq. (5) in the text. They constitute the body of assumption (c) of LIT.

That eq. (B-10) is satisfied to first order in μ is seen by taking $\ln f = \ln f^{(0)}(1 + \mu\phi^{(1)} = \ln f^{(0)} + \ln(1 + \mu\phi^{(1)}) \simeq \ln f^{(0)} + \mu\phi^{(1)}$. Using the subsidiary conditions on $\phi^{(1)}\rho s^{(1)} = 0$ so that

$$\frac{\partial(\rho_s^{(0)})}{\partial t} + \text{div } \frac{\vec{q}^{(1)}}{T} = \sigma^{(1)}$$ (B-28)

where $\sigma^{(1)} = -\vec{q}^{(1)} \text{ grad } \left(\frac{1}{T}\right) + \underset{\sim}{\tau}^\kappa : \frac{\partial \vec{u}}{\partial \vec{r}}$. Eq. (B-28) is the entropy balance equation as required by LIT; namely

$$J_s^{(1)} = \frac{\vec{q}^{(1)}}{T}$$

a fact that has not been mentioned explicitly in the text.

To second order in μ this analysis breaks down completely so that (B-28) is no longer fulfilled and what is disturbing is the fact that $\rho s^{(2)}$ becomes a function of $(\phi^{(1)})^2$ which means that the entropy depends on the gradients. This feature, as well as the proof of Onsager's relations for a multicomponent mixture, will not be discussed here but the reader is referred to other sources in the literature [7],[26],[27].