Journal of Statistical Physics, Vol. 69, Nos. 1/2, 1992

The Kinetic Foundations of Extended Irreversible Thermodynamics Revisited

R. M. Velasco[1] and L. S. García-Colín[1,2]

Received April 3, 1991; final March 3, 1992

Extended irreversible thermodynamics (EIT) has been used mainly to study the short-time behavior of fluids and some other systems. It has also been shown how the structure of the equations of motion constructed for the so-called relaxation variables coincides with those obtained by means of Grad's method in kinetic theory. In this work we calculate the generalized entropy from the one-particle distribution function up to 26 moments. We find that the characteristics of such entropy and the equations of motion for the relaxing variables are supported by the kinetic theory. This is not the case for the hierarchical relaxation hypothesis which is used in the applications of EIT to the generalized hydrodynamic regime.

KEY WORDS: Grad's method; extended irreversible thermodynamics; entropy balance.

1. INTRODUCTION

The main purpose of this paper is to examine critically the physical content of the basic assumptions behind extended irreversible thermodynamics (EIT)(1–4) in the light of results obtained through the one-particle distribution function for a dilute monatomic gas using Grad's moments method.(5–7) The basic difference between these results and the conventional ones is that 26 moments were used in the calculation instead of the 13 moments used in the latter. This means that not only were the heat and momentum fluxes raised to the status of independent variables, but so were also additional variables whose physical meaning will be discussed later. The choice of this number of moments was motivated by the fact that it

---

[1] Department of Physics, Universidad Autónoma Metropolitana Iztapalapa, 09340 Mexico.

[2] On temporary leave at the Universidad Iberoamericana, Mexico. Also at El Colegio Nacional, Mexico.

0022-4715/92/1000-0217$06.50/0

is the lowest approximation which yields frequency- and wavenumber-dependent transport coefficients.(8) The merit of this calculation is that all quantities which appear as undetermined phenomenological coefficients in the macroscopic formulation of EIT are here expressed in terms of collision integrals which may be explicitly evaluated for some intermolecular potentials, thus allowing for a quantitative analysis of many of the so far hidden features of macroscopic EIT.(1–4) Moreover, a more realistic analysis about the physical meaning of the so-called "generalized entropy function" as well as its related entropy production can be readily performed, thus clarifying some of their so far conjectured properties. The orders of magnitude of the relaxation times associated to the nonconserved or fast variables often assumed to obey some kind of hierarchical order can be explicitly calculated showing clearly how this hypothesis seems to be untenable.(9,11)

Finally, some insight is obtained regarding the balance equation for the generalized entropy, namely

$$\rho \frac{DS}{Dt} + \nabla \circ \mathbf{J}_s = \Phi_s \tag{1.1}$$

In order to keep such an equation in some way consistent with the Clausius–Duhem inequality, provided of course that the generalized entropy S and its flux $\mathbf{J}_s$ have a well-defined physical meaning, Φ_s is assumed to be nonnegative by many practitioners of EIT.(1) This assumption, as essential or not to the EIT development, has raised many questions about both the full significance of the entropy balance equation and the identification of Φ_s as an entropy production term. Here some rather concrete results are obtained which support the usual interpretation of Eq. (1.1) as is done in linear irreversible thermodynamics(13) regardless of whether this assumption is taken to hold or not in EIT. Since there are a number of recent papers concerning the basic ideas behind EIT,(1–4) we shall not go into this matter here.

The structure of the paper is as follows. In Section 2 we give the basic results obtained for the distribution function for a dilute monatomic gas using Grad's moment method and extending it to include up to 26 moments. Such results include the explicit calculation of the time rate of change of the so-called nonconserved variables, the generalized entropy, entropy flux, and entropy source as defined in kinetic theory. We also compute the relaxation times associated to such fluxes. Finally in Section 3 we discuss the significance of these results under the framework of EIT and analyze the ensuing conclusions.

2. GRAD'S MOMENT METHOD

The Boltzmann equation for a dilute monatomic gas as well as its solution using the 13-moment method devised by H. Grad 40 years ago are thoroughly discussed in the literature,(5,6) so that we shall not enter into any unnecessary details. The gist of the method lies in developing the single-particle distribution function describing the states of the gas in the six-dimensional phase space (μ) around a local Maxwellian distribution function. The first five moments of this distribution define the five locally conserved variables in such a way that the usual conservation equations are valid. Just for the sake of completeness we recall here the kinetic definitions for the macroscopic variables we will use as relevant to the description of the system. The mass density is given by $\rho = nm$, m being the mass of a molecule and

$$n(\mathbf{x}, t) = \int f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.1}$$

the numerical density, $\mathbf{c}$ denoting the molecular velocity. The hydrodynamic velocity is defined as

$$\mathbf{v}(\mathbf{x}, t) = \frac{1}{n} \int \mathbf{c} f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.2}$$

and the internal energy

$$ne(\mathbf{x}, t) = \tfrac{3}{2} nKT(\mathbf{x}, t) = \int \tfrac{1}{2} mC^2 f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.3}$$

K being the Boltzmann's constant, and $\mathbf{C} = \mathbf{c} - \mathbf{v}(\mathbf{x}, t)$ is the chaotic or random velocity.

The ordinary fluxes appearing in the conservation equations now have a well-defined kinetic meaning, namely

$$\mathbf{q} = \int \tfrac{1}{2}(mC^2 - 5KT)\, \mathbf{C} f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.4}$$

is the heat flux, and

$$\overset{\circ}{P} = \int m(\mathbf{CC})^{\circ} f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.5}$$

is the traceless viscous tensor. Equations (2.1)–(2.5) provide the first 13 moments for the distribution function. The additional variables required for our calculation are now defined as

$$s_{ijk} = \mathbb{S}_{ijk} - \tfrac{2}{5}(q_i \delta_{jk} + q_j \delta_{ik} + q_k \delta_{ij}) \tag{2.6}$$

is a symmetric traceless third-order tensor, where

$$\mathbb{S}_{ijk} = \int mC_iC_jC_k f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.7}$$

is the usual third-order moment of the distribution function. Also the contraction of the fourth moment will be taken as a relevant variable

$$\mathscr{J}_{ij} = \int \tfrac{1}{2}(mC^2 - 5KT)\, C_iC_j f(\mathbf{c}, \mathbf{x}, t)\, d\mathbf{c} \tag{2.8}$$

In a qualitative way these tensors can be seen to correspond physically to the flux of the momentum flux $\overset{\circ}{P}$ and the flux of the heat flux $\mathbf{q}$, respectively. Equations (2.1)–(2.8) define the set of 26 independent moments which will be taken as the variables describing the states of the gas. Notice should be made that the variables we have chosen as relevant are not the only ones. In fact, we can construct different approximations to the distribution function according to the quantities we choose to be zero in Grad's expansion. Here we obtain the 13-moment approximation by taking $s_{ijk} = 0$ and $\mathscr{J}_{ij} = (KT/m)\, \overset{\circ}{P}_{ij}$, whereas the 20-moment approximation is worked out with the assumption that

$$a^{(4)}_{ijkl} = \frac{2}{p}\left(\frac{m}{KT}\mathscr{J}_{ij} - \overset{\circ}{P}_{ij}\right) = 0$$

The moment $a^{(4)}$ is the trace of the fourth-order moments in the multidimensional Hermite polynomials. The 26-moment approximation we will describe here in full detail is obtained when the traceless fourth-order moment q_{ijkl} of the distribution function is zero.

The distribution function we will use can be straightforwardly written as

$$\begin{aligned} f(\mathbf{c}, \mathbf{x}, t) = f^{\circ} \Bigg\{ & 1 + \frac{m}{2KT}(\mathbf{CC})^{\circ} : \frac{\overset{\circ}{P}}{p} + \frac{2}{5p}\frac{m}{KT}\left(\frac{mC^2}{2KT} - \frac{5}{2}\right)\mathbf{C} \circ \mathbf{q} \\ & + \frac{1}{6p}\left(\frac{m}{KT}\right)^2 C_iC_jC_k : s_{ijk} + \frac{1}{7p}\left(\frac{m}{KT}\right)^2 \left(\frac{mC^2}{2KT} - \frac{7}{2}\right) \\ & \times (\mathbf{CC})^{\circ} : \left(\overset{\circ}{\mathscr{J}} - \frac{KT}{m}\overset{\circ}{P}\right) + \frac{m}{30pKT}\left[\frac{mC^2}{KT}\left(\frac{mC^2}{2KT} - \frac{7}{2}\right)\right. \\ & \left. - 3\left(\frac{mC^2}{2KT} - \frac{5}{2}\right)\right] \mathscr{J}_{rr} + \frac{m}{24pKT} q_{ijkl}\mathscr{H}^{(4)}_{ijkl} \Bigg\} \end{aligned} \tag{2.9}$$

As the next step of our calculation, we now wish to consider the computation of the kinetic entropy function. Although this is straightforward as far as algebraic details are concerned, this calls for some precautions. We recall that by an appropriate mathematical transformation(5, 12–14) the Boltzmann equation may be rewritten in the same form as Eq. (1.1) if we identify the entropy density S as

$$\rho S = -K \int f(\ln f - 1)\, d\mathbf{c} \tag{2.10}$$

the entropy flux $\mathbf{J}_s$ as

$$\mathbf{J}_s = -K \int f(\ln f - 1)\, \mathbf{C}\, d\mathbf{c} \tag{2.11}$$

and the entropy source Φ_s as

$$\Phi_s = -K \int (\ln f - 1)\, J(f, f)\, d\mathbf{c} \tag{2.12}$$

where $J(f, f)$ is the collision term. Equations (2.10)–(2.12) are devoid of any physical meaning whatsoever until we specify the explicit form for $f(\mathbf{c}, \mathbf{x}, t)$. Indeed, if we want to recover the usual balance equation for the entropy density for a closed system according to LIT, and identify Eq. (2.10) with the entropy, as used in this formalism,(13, 28) something else will have to be said about $f(\mathbf{c}, \mathbf{x}, t)$, since direct substitution of a solution to Boltzmann's equation in Eq. (2.10) would yield a function depending on $\mathbf{x}$ and t but not of the state variables for the system as thermodynamics requires. Analogously, in Eq. (2.11) we must be able to prove that $\mathbf{J}_s = \mathbf{q}/T$, where $\mathbf{q}$ is the heat flux, and in Eq. (2.12) that Φ_s be nonnegative. We remind the reader that all these requirements are accomplished when f is taken as the solution first order in the gradients to the Boltzmann equation by the Chapman–Enskog method.(12–14) If one uses the solution to the Boltzmann equation obtained with Grad's 13-moment, method the main assumptions of EIT are recovered,(1, 7) but not enough information is available to carry out a deeper analysis of the relaxation times involved in the equations of motion. Also, the entropy balance equation needs a somewhat careful analysis when we are in the short-wavelength and frequency regime.

When Eq. (2.9) is substituted into Eqs. (2.10)–(2.12) the problem arises as to how to evaluate $f(\ln f - 1)$. Here, as in the cases mentioned above, one turns to an approximation, namely, to regard f as $f^{(0)}(1 + X)$, where X can be identified in Eq. (2.9). Assuming that X is a number small compared with one and using the series expansion in powers of X, we retain in the product only those terms which are at most bilinear in the relevant variables. Notice should be made that this approximation is the kinetic analog of the expansion around local equilibrium made by the Barcelona school to construct the entropy balance equation.(1) This procedure will have a strong effect on the final forms of both ρS and $\mathbf{J}_s$, which in turn will be reflected in their comparison with the corresponding phenomenological coefficients. One obtains for the entropy that

$$\begin{aligned}\rho S = \rho S_0 &- \frac{1}{4pT} \mathring{P}_{ij} \mathring{P}_{ij} - \frac{m}{5pKT^2} q_i q_i - \frac{m}{12pKT^2} s_{ijk} s_{ijk} \\ &- \frac{1}{60pT} \left(\frac{m}{KT}\right)^2 \mathscr{J}_{rr}^2 - \frac{1}{14pT} \left(\frac{m}{KT}\right)^2 \left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m} \mathring{P}_{ij}\right) \\ &\times \left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m} \mathring{P}_{ij}\right)\end{aligned} \tag{2.13}$$

where S_0 is the local equilibrium entropy. Equation (2.13) shows an explicit dependence of the generalized entropy with the fluxes chosen as macrovariables for the system, thus implying that the gas is no longer in a local equilibrium state, as defined in LIT.(13,28)

The generalized entropy flow turns out to be

$$\begin{aligned}J_{s_i} = \frac{q_i}{T} &- \frac{2}{5pT} \left(\frac{m}{KT}\right) q_j \mathring{\mathscr{J}}_{ij} - \frac{5}{14pT} s_{ijk} \mathring{P}_{jk} \\ &- \frac{1}{7pT} \left(\frac{m}{KT}\right) s_{ijk} \mathring{\mathscr{J}}_{jk} - \frac{2}{15pT} \left(\frac{m}{KT}\right) \mathscr{J}_{rr} q_i\end{aligned} \tag{2.14}$$

The first term in Eq. (2.14) corresponds precisely to the form required by LIT, whereas the other terms arise from the fast or relaxing variables. The appearance of these terms is highly dependent on the 26-moment approximation, since in general the flux depends on higher-order momenta which are approximated by their expression consistent with the choice of the specific set of 26 variables. A virtue of both Eqs. (2.13) and (2.14) is that when the fluxes cease to perform as independent variables, both the generalized entropy S and the entropy flux $\mathbf{J}_s$ reduce to their respective forms as required by LIT.

The calculation of the generalized entropy source term uses the same approximation in the computation of $\ln f$, which has to be multiplied by the collision term $J(f, f)$, which is bilinear in f. Retaining only the quadratic terms in the fluxes, one obtains that

$$
\begin{aligned}
\Phi_s = {} & \frac{1}{\lambda_0 T^2} q_i q_i + \frac{1}{\lambda_s T^2} s_{ijk} s_{ijk} + n^2 K \left(\frac{m}{30pKT}\right)^2 \Gamma_3 \mathscr{J}_{rr}^2 \\
& + \frac{1}{2\eta_0 T} \mathring{P}_{ij} \mathring{P}_{ij} + \frac{8}{7(15)\,KT^2} \left(\frac{m}{KT}\right) \Gamma_1 \mathring{P}_{ij} \left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m} \mathring{P}_{ij}\right) \\
& + \frac{8\Gamma_2}{49(15)\,KT^2} \left(\frac{m}{KT}\right)^2 \left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m} \mathring{P}_{ij}\right)\left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m} \mathring{P}_{ij}\right)
\end{aligned} \qquad (2.15)
$$

where λ_0, η_0, λ_s, and the $\Gamma_i\,(i = 1, 2, 3)$ are given in terms of the collision integrals $\Omega^{(r,s)}$, which depend on the intermolecular potential,(12) whose explicit values are given in Table I. Notice should be taken that these integrals are also obtained through very specific measurements, so their values are known in a rather precise way.(16)

Equation (2.15) formally agrees with the LIT calculation, in the sense that it is a bilinear form in the fluxes. However, it is important to remark that we are not invoking the local equilibrium hypothesis and we do not have any evidence for a positive-definite entropy source. We also recall that the total entropy source is the integral of Φ_s over the entire volume of the system and the positiveness of this total entropy production is the property required by the second law of thermodynamics.

The equations of motion corresponding to the nonconserved variables are now obtained by a straightforward substitution of Eqs. (2.13)–(2.15) into Eq. (1.1). In fact we have followed the same procedure as in EIT to construct the equations of motion for those variables, our main contribution being to provide the kinetic expression of all coefficients which

Table I. Relation Between the Coefficients in Eq. (2.15) and the Usual $\Omega^{(r,s)}$ Integrals

$$\eta_0 = \frac{5}{8} \frac{KT}{\Omega^{(2,2)}}$$

$$\lambda_0 = \frac{75}{32} \frac{K^2 T}{m\Omega^{(2,2)}}$$

$$\lambda_s = \frac{9(35)}{16} \frac{K^2 T}{m\Omega^{(2,2)}}$$

$$\Gamma_1 = -\frac{3}{2} (7\Omega^{(2,2)} - 2\Omega^{(2,3)})$$

$$\Gamma_2 = \frac{3}{2} \left(\frac{301}{12} \Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}\right)$$

$$\Gamma_3 = \frac{24}{7} \left(\frac{217}{12} \Omega^{(2,2)} - 5\Omega^{(2,3)} + \Omega^{(2,4)}\right)$$

otherwise remain unknown. For their explicit evaluation we have a molecular model to work with.

Following the standard procedure,(1,2) the balance equation is factorized in the fluxes considered as independent, and equating the corresponding coefficients we obtain the following set of equations:

$$\frac{\partial q_i}{\partial t} = -\frac{1}{\tau_q}(q_i + \lambda_0 \nabla_i T) - \frac{1}{3}\nabla_i \mathscr{J}_{rr} - \nabla_j \mathring{\mathscr{J}}_{ij} \tag{2.16}$$

for the heat flux and

$$\frac{\partial s_{ijk}}{\partial t} = \frac{2}{7\tau_q} s_{ijk} - \frac{5KT}{7m}(\nabla \mathring{P})^{\circ}_{ijk} - \frac{2}{7}(\nabla \mathring{\mathscr{J}})^{\circ}_{ijk} \tag{2.17}$$

for the third-order tensor s_{ijk}, with $(\nabla \mathring{P})^{\circ}$ and $(\nabla \mathring{\mathscr{J}})^{\circ}$ being symmetric traceless third-order tensors. The trace $\mathscr{J}_{rr}$ obeys an equation given by

$$\frac{\partial \mathscr{J}_{rr}}{\partial t} = -\frac{4KT}{m}(\nabla \circ \mathbf{q}) - \frac{n\Gamma_3}{30}\mathscr{J}_{rr} \tag{2.18}$$

The equations for the viscous tensor and the second-order tensor associated with the flux of $\mathbf{q}$ are strongly coupled and are given by

$$\begin{aligned}\frac{\partial \mathring{P}_{ij}}{\partial t} = &-\frac{1}{\tau_p}(\mathring{P}_{ij} + 2\eta_0(\nabla \mathbf{u})^{\circ}_{ij}) - \frac{8nm}{7(15)KT}\\ &\times \Gamma_1\left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m}\mathring{P}_{ij}\right) - \frac{4}{5}(\nabla \mathbf{q})^{\circ}_{ij} - \nabla_k s_{kij}\end{aligned} \tag{2.19}$$

$$\begin{aligned}\frac{\partial \mathring{\mathscr{J}}_{ij}}{\partial t} = &-\frac{p}{m}\left(\frac{KT}{\eta_0} + \frac{4}{15}\Gamma_1\right)\mathring{P}_{ij} - \frac{2pKT}{m}(\nabla \mathbf{u})^{\circ}_{ij} - \frac{8n}{7(15)}(\Gamma_2 + \Gamma_1)\\ &\times\left(\mathring{\mathscr{J}}_{ij} - \frac{KT}{m}\mathring{P}_{ij}\right) - \frac{18KT}{5m}(\nabla \mathbf{q})^{\circ}_{ij} - \frac{2KT}{m}\nabla_k s_{kij}\end{aligned} \tag{2.20}$$

Equations (2.16)–(2.20), together with the conservation equations for the conserved variables, which we have not written here explicitly, are the set of equations that must be compared with their macroscopic analogs. We present the details of this discussion in the following section.

3. DISCUSSION OF THE RESULTS

Since the structure of the conservation equations remains unaltered in all this treatment, we first concentrate on the time evolution equations for the nonconserved quantities, the fluxes. Their phenomenological form, which follows from the premises of EIT, has been explicitly given elsewhere,(17) whereas their form as obtained from kinetic theory is given in Eqs. (2.16)–(2.20). A term-by-term comparison shows that both sets are identical and the undetermined coefficients appearing in the EIT calculation may now be expressed in terms of local equilibrium variables and collision integrals.

Furthermore, if in Eqs. (2.16)–(2.20) we neglect all the coupling terms among the fluxes, the resulting equations are of the Maxwell–Cattaneo type, which are relaxation-type equations.(1,2) Indeed, a relaxation time can be readily identified in each case and to guarantee the relaxing property of the variable such times must be proven to be positive. Table II shows the value of the relaxation times associated with each flux as well as their explicit form in terms of the conserved variables and an estimation of their order of magnitude using both a hard-sphere model and the experimental data reported in the literature.(16) The interesting outcome of this calculation, never reported before, is that they all turn out to be of the same order of magnitude, clearly revealing the inexistence of a hierarchical relaxation of the fluxes. This result has a strong bearing on several calculations which have been performed in the past using the results of EIT. When applied to explain generalized hydrodynamics,(10,11) a claim is made asserting that the fluxes $\mathscr{J}_{ij}$ and s_{ijk} relax faster than $\mathbf{q}$ or $\overset{\circ}{P}$. The results obtained here cast doubt of such an assertion, although here they have been obtained only for the case of dilute monatomic gases. A theory of generalized hydrodynamics based upon the results of a 26-moment approximation has been published elsewhere.(8)

Let us give a more detailed discussion of the problem stated here. As we know, the Boltzmann equation gives a good description of the behavior

Table II. Relationship Between the Relaxation Times and the $\Omega^{(2,2)}$ Value for the Hard-Sphere Potential, Their Value for Low-Density Argon at 303.5 K, and the Experimental Value at the Same Temperature

Hard spheres (HS)	HS value	Experimental value
$\tau_q = \frac{3}{2}\tau_p = \frac{15}{16n\Omega^{(2,2)}}$	3.89×10^{-10} sec	3.42×10^{-10} sec
$\tau_s = \frac{7}{2}\tau_q$		
$\tau_0 = \tau_j = \frac{135}{217n\Omega^{(2,2)}}$	2.58×10^{-10} sec	2.40×10^{-10} sec

of a dilute monatomic gas. The Chapman–Enskog method to solve such an equation yields a perturbative solution around the local equilibrium state of the system. It is well known(12–15) that this method allows the calculation of the constitutive equations and the corresponding transport coefficients, not only for the Navier–Newton–Fourier regime, but also for the Burnett regime, etc. These approximations are well characterized as expansions in the Knudsen number, which gives the relative magnitude between the terms in the distribution function. The consistency of this expansion with the local equilibrium assumption has also been established.(15) This means that the Chapman–Enskog method does not allow for the calculation of equations of motion for the fluxes, which are the additional variables in EIT. This is the reason one must use Grad's method to solve the Boltzmann equation, since it provides the proper framework to understand the kinetic basis of EIT.(7) We have seen in Section 2 that according to Grad's method, it is possible to choose the same relevant variables as in EIT and the equations of motion have the same structure, all of them being relaxation equations. A problem arises when we ask ourselves about the validity of the expansion procedure. In fact, Grad's method does not have an expansion parameter as provided by the Knudsen number in the Chapman–Enskog method. A truncation procedure is necessary to obtain a closed system of equations and this is done without a clear indication about the order of magnitude of the terms we neglect. This is a shortcoming of the method which has been recently stressed by Van Kampen,(18) but does not interfere with our discussion. To overcome this difficulty, we can say that our interest is concentrated in a generalization of linear irreversible thermodynamics to situations in which the local equilibrium assumption is no longer valid, although we must certainly recover it for hydrodynamic times and distances. If we adopt this point of view, we can make some considerations to overcome the first problem provided we exhibit the existence of well-separated time scales in which the different additional variables (or moments of the distribution function) become important. The existence of time scales has been taken for granted in several calculations using EIT reported in the literature,(10,11) yet Table II raises severe doubts regarding their validity.

The conclusion we draw from the 26-moment calculation clarifies the real situation, showing that at least for a dilute monatomic gas there are no such time scales, so that the times we are interested in are not well separated from the nonsteady behavior of the fluxes we have neglected. It seems that beyond local equilibrium we cannot make a moment expansion based on a hierarchial relaxation for the different variables we would like to consider as relevant. This result bears some resemblance with the conclusions reached by Van Kampen a few years ago.(18) Notice should be taken, however, that in some problems the time scales are given in a natural way, for example, in a disparate-mass binary mixture we do have a hierarchical relaxation and EIT can be applied.(19) Finally, we should stress that our results are only valid for dilute monatomic gases, although there is no reason to believe that they are also valid for dense monatomic gases.

Let us now consider the results obtained for the generalized entropy and its source. It is obvious that the structure of the terms given in Eqs. (2.13)–(2.15) is the same as in EIT and the corresponding coefficients may be readily identified. The properties of the entropy source can be explicitly studied in terms of the collision integrals appearing in the Γ coefficients. To do this, we first write the density of the entropy source given in Eq. (2.15) in terms of the collision integrals, namely

$$\begin{aligned}
\Phi_s = {} & \frac{1}{T^2}\left(\frac{32m}{75K^2T}\Omega^{(2,2)}\right)\mathbf{q}\circ\mathbf{q} + \frac{1}{T^2}\left(\frac{16m}{9(35)\,K^2T}\Omega^{(2,2)}\right)s_{ijk}s_{ijk} \\
& + \frac{24}{7}n^2K\left(\frac{m}{30pKT}\right)^2\left(\frac{217}{12}\Omega^{(2,2)} - 5\Omega^{(2,3)} + \Omega^{(2,4)}\right)\mathcal{J}^2_{rr} \\
& - \frac{4}{7(5)\,KT^2}\left(\frac{m}{KT}\right)\left(7\Omega^{(2,2)} - 2\Omega^{(2,3)}\right)\mathring{P}_{ij}\left(\mathring{\mathcal{J}}_{ij} - \frac{KT}{m}\mathring{P}_{ij}\right) \\
& + \frac{4}{49(5)\,KT^2}\left(\frac{301}{12}\Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}\right)\left(\frac{m}{KT}\right)^2\left(\mathring{\mathcal{J}}_{ij} - \frac{KT}{m}\mathring{P}_{ij}\right) \\
& \times\left(\mathring{\mathcal{J}}_{ij} - \frac{KT}{m}\mathring{P}_{ij}\right) + \frac{1}{2T}\left(\frac{8}{5KT}\Omega^{(2,2)}\right)\mathring{P}_{ij}\mathring{P}_{ij} \qquad (3.1)
\end{aligned}$$

It is now clear from Eq. (3.1) that the conditions Φ_s must satisfy to be positive definite are therefore given by

$$\Omega^{(2,2)} \geqslant 0 \qquad (3.2)$$

$$\left(\frac{217}{12}\Omega^{(2,2)} - 5\Omega^{(2,3)} + \Omega^{(2,4)}\right) \geqslant 0 \qquad (3.3)$$

$$\left(\frac{301}{12}\Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}\right) \geqslant 0 \qquad (3.4)$$

$$\Omega^{(2,2)}\left(\frac{301}{12}\Omega^{(2,2)} - 7\Omega^{(2,3)} + \Omega^{(2,4)}\right) - \left(7\Omega^{(2,2)} - 2\Omega^{(2,3)}\right)^2 \geqslant 0 \qquad (3.5)$$

Conditions (3.2)–(3.5) are readily satisfied for the hard-sphere potential, centers of repulsion, and the experimental values for noble gases taken from the literature in the interval of reduced temperatures given by $1.2 \leqslant T \leqslant 10.0$ and low density.(16) In fact they can be taken as a probe for models of intermolecular potential, since their validity is assured by the properties of the collision brackets.(12) This result also agrees with some other calculations(20) in which the entropy production is obtained without a specific form for the single-particle distribution function.

The positiveness of the entropy production Φ_s has been a controversial point in the EIT literature.(21,22) In fact, from the phenomenological point of view, nothing can be said about this property. Here its calculation on the basis of kinetic theory has given us an affirmative answer not only for some models, but also for the available experimental values in noble gases. Yet this assertion has to be taken with some precaution. In the evaluation of Eqs. (2.15) an approximation has been made whereby the logarithm of the full distribution function is expanded in powers of fluxes multiplied by f itself, and bilinear terms in the fluxes are retained. It is this approximate version of Φ_s that we have shown to be nonnegative, and it is the one which in each step is consistent with the EIT calculation. The consequences that this has on the form of the equations of motion have been often discussed in the literature.(1,4,23) Nevertheless, conditions (3.2)–(3.5) at least clarify that for the monatomic ideal gas Φ_s is indeed nonnegative. This result is, however, not to be interpreted as the consistency of Eq. (1.1) with the second law of thermodynamics, since the entropy as exhibited by Eq. (2.13) is not the calorimetric entropy not even in its local version. Nevertheless, some recent evidence(24) indicates that it may be very well related to the information entropy defined by Shannon and extensively used by Jaynes' school(25,26) in dealing with nonequilibrium states for macroscopic systems.

As a last remark, it is convenient to point out that the forms we have derived for the generalized entropy and its production satisfy the requirements that have been imposed on these quantities in a recent formulation of a nonequilibrium thermodynamic theory with a continued-fraction expansion for the coefficients.(27) The main difference between such a theory and our results lies in the fact that all relaxation times for the fluxes and their higher derivatives can hardly be claimed to be different, since in the language of Jou and Ferrer,(27) the only apparently sensible case is that in which $\tau_1 = \tau_2 = \cdots \tau_n \neq 0$. A detailed discussion of some fine points related to this approach to EIT will be published elsewhere.

REFERENCES

1. D. Jou, J. Casas-Vázquez, and G. Lebon, *Rep. Prog. Phys. Lond.* **51**:1105 (1988).
2. L. S. García Colín, *Rev. Mex. Fis.* **34**:344 (1988) [in English].

3. L. S. García Colín, *Acta Phys. Hung.* **69**:79 (1989).
4. G. Lebon, *Acta Phys. Hung.* **69**:241 (1989).
5. H. Grad, in *Handbuch der Physik*, S. Flûgge, ed. (Springer-Verlag, Berlin, 1958), Vol. 12.
6. H. Grad, *Commun. Pure Appl. Math.* **2**:331 (1949).
7. L. S. García Colín, and G. Fuentes Martínez, *J. Stat. Phys.* **29**:392 (1987).
8. R. M. Velasco and L. S. García Colín, *Phys. Rev. A* **44**:4961 (1991).
9. H. Acuña, Sound absorption and dispersion in non-local hydrodynamics, M.Sc. Thesis, Universidad Autónoma Metropolitana Iztapalapa (1990).
10. D. Jou, C. Pérez García, L. S. García Colín, M. López de Haro, and R. F. Rodríguez, *Phys. Rev. A* **31**:2502 (1985).
11. C. Pérez García, D. Jou, R. F. Rodríguez, M. López de Haro, and L. S. García Colín, *Physica* **135A**:251 (1986).
12. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, 1970); J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
13. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
14. I. Prigogine, *Physica* **15**:242 (1949).
15. L. S. García Colín, *Physica* **118A**:341 (1983).
16. J. Kestin, K. Knierim, E. A. Mason, B. Najafi, S. T. Ro, and M. Waldman, *J. Phys. Chem. Ref. Data* **13**:229 (1984).
17. L. S. García-Colín and R. M. Velasco, *Rev. Mex. Fís.* **38**:92 (1992) [in English].
18. N. G. Van Kampen, *J. Stat. Phys.* **46**:709 (1987).
19. J. Granados and R. M. Velasco, unpublished.
20. C. Delale, *J. Stat. Phys.* **37**:451 (1984).
21. M. López de Haro and R. F. Rodriguez, *J. Nonequilibrium Thermodynam.* **14**:37 (1989).
22. J. A. del Río and M. López de Haro; *J. Nonequilibrium Thermodynam.* **15**:59 (1990).
23. D. Jou, J. Casas-Váquez, J. A. Robles Dominguez, and L. S. García Colín, *Physica* **137A**:349 (1986).
24. A. Vasconcellos, R. Luzzi, and L. S. García-Colín, *Phys. Rev.* **43A**:6622 (1991).
25. B. Robertson, *Phys. Rev.* **144**:151 (1966).
26. E. T. Jaynes, in *Maximum Entropy Formalism*, R. D. Levine and M. Tribus, eds. (MIT Press, Cambridge, Massachusetts, 1978), p. 278.
27. D. Jou and M. Ferrer, *Phys. Lett.* **134A**:400 (1989).
28. L. S. García-Colín and F. J. Uribe, *J. Nonequilibrium Thermodynam.* **16**:89 (1991).