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Thermodynamic pressure in nonequilibrium gases

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We analyze the nonequilibrium thermodynamic pressure which is obtained by differentiation of a generalized nonequilibrium entropy. It is proposed that this nonequilibrium thermodynamic pressure, π, is related to the pressure tensor $\mathbf{P}$ in the presence of a homogeneous heat flux $\vec{q}$ through $\mathbf{P}=\pi\mathbf{U}+\alpha\vec{q}\,\vec{q}$, with α given by the condition $\mathrm{tr}\mathbf{P}=3p$, p being the local-equilibrium pressure. A simple situation illustrating the physical difference between π and p is presented. The nonequilibrium entropy, pressure, and pressure tensor are also analyzed from a microscopic point of view in several systems.

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I. INTRODUCTION

In classical irreversible thermodynamics, equations of state in nonequilibrium states have (locally) the same form as in equilibrium [1,2]. In recent versions of nonequilibrium thermodynamics, which extend the domain of validity of the classical theory towards the high-frequency and short-wavelength regime [3–7], the entropy depends not only on the classical variables but also on dissipative fluxes and, consequently, the equations of state in nonequilibrium differ from the equations of state in equilibrium in that some contributions depend on the fluxes. Recently, the nonequilibrium equation of state for temperature was investigated by Casas-Vázquez and Jou in a series of papers [8–10], which provided an extensive analysis of the concept and an explicit expression for absolute temperature in nonequilibrium steady states.

The aim of this paper is to examine the meaning of thermodynamic pressure in nonequilibrium steady states. This analysis is not a trivial extension of the previous one, but faces new problems, due to the fact that, whereas absolute temperature is a purely thermodynamical quantity, the pressure has both a thermodynamical and a mechanical meaning.

The plan of the paper is as follows. In Sec. II we briefly review the essentials of the thermodynamic basis of our work and draw from it an explicit prediction. In Sec. III we compare the thermodynamic results with the microscopic results following from information theory for ultrarelativistic ideal gases and for photon gases. In Sec. IV, we compare the macroscopic prediction with the results obtained from an information theoretical analysis of a classical ideal gas. Finally, in the concluding remarks we consider the points to which more attention should be paid in the future in order to get an internally consistent extended thermodynamic theory including generalized equations of state beyond the linear regime.

II. THERMODYNAMIC PRESSURE IN A NONEQUILIBRIUM STEADY STATE UNDER A HEAT FLUX

We consider here a system submitted to a steady state heat flux $\vec{q}$, and study the modifications in the equations of state due to its presence. When the heat flux is introduced in the set of independent variables of the entropy s, the nonequilibrium entropy per unit mass takes the form [3–10], up to second order in $\vec{q}$,

$$s(u,v,\vec{q})=s_{\mathrm{eq}}(u,v)-\frac{\tau v}{2\lambda T^{2}}\vec{q}\cdot\vec{q}\ , \tag{1}$$

where τ is the relaxation time of the heat flux, λ the thermal conductivity, v the specific volume, and s_{eq} the specific local equilibrium entropy. For an ideal monatomic gas,

$$\lambda=\frac{5}{2}\frac{k^{2}Tn}{m}\tau\ ,$$

with k the Boltzmann constant, m the particles' mass, $n=1/vm$ their numerical density, and T the local-equilibrium temperature of the system, and (1) may also be written as

$$s(u,v,\vec{q})=s_{\mathrm{eq}}(u,v)-\frac{1}{5}\frac{1}{n^{2}k^{2}T^{3}}\vec{q}\cdot\vec{q}\ . \tag{2}$$

This is the result obtained in Grad's expansion in kinetic theory [11]. If one writes $\vec{q}=-\lambda\vec{\nabla}T$, (2) becomes

$$s(u,v,\vec{q})=s_{\mathrm{eq}}(u,v)-\frac{5}{4}\frac{k^{2}\tau^{2}}{m^{2}T}(\vec{\nabla}T)^{2}\ , \tag{3}$$

which is the result obtained in the Chapman-Enskog expansion in kinetic theory of gases [12]. Therefore the analysis of the consequences of (1) is not a specific topic of a thermodynamic theory but a rather general topic in nonequilibrium analyses aiming to deal with nonlinear effects.

Starting from (1), it is natural to define a nonequilibrium absolute temperature and a nonequilibrium thermodynamic pressure as

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$$\frac{1}{\theta}\equiv\left[\frac{\partial s}{\partial u}\right]_{v,n,\vec{q}}=\frac{1}{T}-\frac{\partial}{\partial u}\left[\frac{\tau v}{\lambda T^2}\right]\vec{q}\cdot\vec{q}\ , \tag{4}$$

$$\frac{\pi}{\theta}\equiv\left[\frac{\partial s}{\partial v}\right]_{v,n,\vec{q}}=\frac{p}{T}-\frac{1}{2}\frac{\partial}{\partial v}\left[\frac{\tau v}{\lambda T^2}\right]\vec{q}\cdot\vec{q}\ . \tag{5}$$

For an ideal monatomic gas and up to the second order in $\vec{q}$ one has

$$\theta=T-\frac{2}{5}\frac{m}{n^2k^3T^2}\vec{q}\cdot\vec{q}\ , \tag{6}$$

$$\pi=p-\frac{4}{5}\frac{m}{nk^2T^2}\vec{q}\cdot\vec{q}\ . \tag{7}$$

Up to now, the definitions (4) and (5) may be seen as purely formal extensions of analogous definitions which are known to be valid in equilibrium. Casas-Vázquez and Jou [8–10] have analyzed the physical consequences of (6) and have proposed a simple physical situation which is illustrative and useful for considering the physical aspects of (4). Here, we will extend their gedanken experiment to cope with the pressure.

We shall consider two systems (Fig. 1). System 2 is in internal equilibrium and system 1 is in a nonequilibrium steady state characterized by a vertical downwards heat flux q_y. Both systems are connected through a thin heat-conducting and movable piston. Both sides of the piston are assumed to have the same local-equilibrium temperature T and the same local-equilibrium pressure p. Therefore, according to the classical theory, one should expect that no heat will flow along the piston and that the piston will not be displaced. However, the generalized theory predicts [8–10] that heat will flow from the equilibrium system towards the nonequilibrium one (even though they are at the same local-equilibrium temperature T) because heat flows according to $\vec{\nabla}\theta$ rather than according to $\vec{\nabla}T$.

Here, we are interested in the study of pressure. The net force to the right experienced by the piston will be

$$F=(\pi_2-\pi_1)A\ . \tag{8}$$

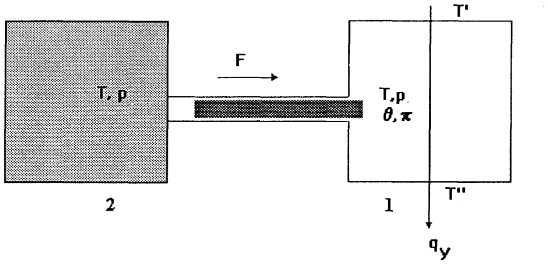

FIG. 1. The system on the left is at equilibrium at temperature T, whereas the system on the right is in a nonequilibrium steady state under a heat flux q_y. A force is expected to occur from the equilibrium gas towards the nonequilibrium one because the nonequilibrium pressure π is lower than the local equilibrium pressure p, according to Eq. (7).

In the classical theory, the force would be zero, because one would consider $F=(p_2-p_1)A$. In contrast, in the nonclassical theory one has $\pi_2=p_2=p$ (because this is an equilibrium system) whereas $\pi_1<p_1=p$, according to (7). In this way, the extended theory predicts that a net force will act on the piston from the equilibrium system towards the nonequilibrium one. In the next section we will analyze the consistency of this prediction from a microscopic point of view.

First of all, though, we should remember, as we have pointed out in the Introduction, that, whereas temperature is a purely thermodynamic quantity, pressure has also a mechanical aspect. In equilibrium, both aspects coincide, but it is not so obvious that this assumption holds in nonequilibrium situations.

For a gas at rest, the pressure tensor must satisfy

$$\mathrm{tr}\mathbf{P}=3p \tag{9}$$

as the kinetic theory of gases demands [13]. Therefore the nonequilibrium pressure π must not be related to the trace of the pressure tensor. Instead we proposed the following expression for the pressure tensor in a nonequilibrium state characterized by a homogeneous heat flux $\vec{q}$:

$$\mathbf{P}=\pi\mathbf{U}+\alpha\vec{q}\vec{q}\ , \tag{10}$$

with $\mathbf{U}$ the unit tensor and with α determined by the requirement (9), i.e., by the relation

$$3\pi+\alpha q^2=3p\ . \tag{11}$$

Note that an expression of the form (10) is not surprising from a purely algebraic point of view, since the most general tensor that may be formed in the presence of the vector $\vec{q}$ has the form $a(q^2)\mathbf{U}+b(q^2)\vec{q}\vec{q}$. *The physical idea that we have introduced in (10) is that the coefficient multiplying* $\mathbf{U}$ *is directly related to the derivatives of a nonequilibrium entropy.* That this idea has not been proposed before is not strange, for the analysis of the entropy in nonequilibrium systems has usually received little attention, due to the success of the local-equilibrium hypothesis in most common situations. Note also that an expression similar to (10) is usually found in the description of plasmas under an external magnetic field $\vec{B}$, where $\mathbf{P}=p_\perp\mathbf{U}+(p_\parallel-p_\perp)(\vec{B}\vec{B}/B^2)$, $p_\perp$ being the pressure transverse to $\vec{B}$ and $p_\parallel$ the pressure in the direction parallel to $\vec{B}$. Of course, since $\vec{B}$ exerts a force on the particles, this expression for $\mathbf{P}$ is not surprising in the presence of $\vec{B}$, but it is new for $\vec{q}$. This does not mean, of course, that $\vec{q}$ exerts a force on the particles: in this case, the effect is more subtle, as it is related to the anisotropy of the distribution function in the presence of $\vec{q}$.

Throughout this paper we consider $\vec{q}=q_y\vec{j}$ and so the component of the pressure tensor responsible for the force throughout the piston, P_{xx}, is simply π, in accordance with (8).

III. NONEQUILIBRIUM PRESSURE IN ULTRARELATIVISTIC GASES. MICROSCOPIC INTERPRETATION

To have a microscopic understanding of the hypothesis (10) we first consider ultrarelativistic gases, for which the extension of the pressure tensor to the nonequilibrium case has been thoroughly studied. This is due to the fact that heat fluxes can be extremely high in astrophysical plasmas, for instance, and a nonequilibrium pressure tensor is necessarily used. However, the corresponding nonequilibrium entropy has not received much attention, so that the connection (10) between **P** and the entropy has never been mentioned in the literature.

To obtain an explicit expression for the entropy, we start from the distribution function for an ideal relativistic gas with mean internal energy U and mean energy flux $\vec{J}$, which can be found exactly in the framework of information theory [14]. According to the methods of the maximum entropy principle, the distribution function is given by [15]

$$f=\frac{1}{Z}\exp\left[-\beta\sum_i p_i c-\vec{I}\sum_I p_i c\vec{c}_i\right] . \tag{12}$$

In this expression $\sum_i p_i c$ is the Hamiltonian of the system (p_i is the modulus of the momentum of particle i and c is the speed of light), $\sum_i p_i c\vec{c}_i$ is the microscopic expression for the energy flux, β and $\vec{I}$ are the corresponding Lagrange multipliers related, respectively, to the restrictions on the energy and the energy flux, and Z is the partition function. The corresponding results for β and $\vec{I}$ are

$$\beta=\frac{3N}{U}\left[\left[4-\frac{3J^2}{c^2U^2}\right]^{1/2}-1\right]^{-1}=\frac{3N}{U}\frac{1}{x-1} , \tag{13}$$

$$\vec{I}=-\frac{9N\vec{J}}{c^2U^2}\left[2-\frac{3J^2}{c^2U^2}+\left[4-\frac{3J^2}{c^2U^2}\right]^{1/2}\right]^{-1}$$
$$=\frac{3N\vec{J}}{J^2}\frac{x-2}{x-1} , \tag{14}$$

and the nonequilibrium entropy, defined by

$$S=-\frac{k}{h^{3N}N!}\int f\ln f\,d\Gamma , \tag{15}$$

is found to be

$$S=S_{\mathrm{eq}}+Nk\ln\left[\frac{(x-1)(x+2)^2}{16}\right] , \tag{16}$$

where

$$x\equiv\left[4-\frac{3J^2}{c^2U^2}\right]^{1/2} . \tag{17}$$

Note that, since the energy flow $\vec{J}$ in a system cannot be higher than the internal energy U in this system times the speed of light c, because this is the maximum speed that the particles in the system may achieve, it follows that $J^2\le c^2U^2$. According to (17) this implies that $x\ge 1$, i.e., that β in (13) is positive.

On the other hand, expression (16), in contrast to (1), is not limited to second order in $\vec{q}$ and it is immediately seen that

$$\frac{\pi}{\theta}=\left[\frac{\partial S}{\partial V}\right]_{U,N,\vec{J}}=\frac{p}{T}=\frac{N}{V}k \tag{18}$$

because the nonequilibrium part does not depend on V under fixed U, N, $\vec{J}$. Here, $\theta=(\partial S/\partial V)_{V,N,\vec{J}}=1/k\beta$, which follows from (16) and which is a generalization of the equilibrium expression $T=1/k\beta$.

Now, according to (18) and (13) we have for the generalized thermodynamic pressure π,

$$\pi=\frac{U}{3V}[x-1] . \tag{19}$$

On the other side, the pressure tensor may be obtained independently of the entropy as

$$\mathbf{P}=\frac{1}{N!h^{3N}}\int p\vec{c}\vec{c}f\,d\Gamma , \tag{20}$$

with f given by (12). It is straightforward, then, to see that

$$\mathbf{P}=\pi\mathbf{U}+9\frac{\pi}{(x-1)(x+2)}\frac{\vec{J}\vec{J}}{c^2U^2}$$
$$=\frac{U}{3V}\left[(x-1)\mathbf{U}+\frac{9}{x+2}\frac{\vec{J}\vec{J}}{c^2U^2}\right]$$
$$=\frac{U}{3V}\left[(x-1)\mathbf{U}+3(2-x)\frac{\vec{J}\vec{J}}{J^2}\right] . \tag{21}$$

Thus the coefficient which is multiplying **U** is indeed the nonequilibrium pressure π obtained by differentiation of the nonequilibrium entropy.

We recall that the pressure tensor for radiation under an energy flux is usually written in radiation thermodynamics as [16–22]

$$\mathbf{P}=\frac{U}{V}\left[\frac{1-\chi}{2}\mathbf{U}+\frac{3\chi-1}{2}\frac{\vec{q}\vec{q}}{q^2}\right] , \tag{22}$$

where χ is the so-called Eddington factor. Hence, comparing expressions (21) and (22), the Eddington factor turns out to be given by

$$\chi=\frac{5}{3}-\frac{2}{3}\left[4-\frac{3J^2}{c^2U^2}\right]^{1/2}=\frac{5-2x}{3} . \tag{23}$$

This expression is usually found in the literature [16,19–21].

We can note the following relation between the Eddington factor and the generalized pressure:

$$\pi=\frac{U}{V}\frac{1-\chi}{2} , \tag{24}$$

which means that we can choose any of both parameters π or χ to identify unequivocally the pressure tensor. The advantage of the generalized pressure π is that it can be easily calculated if the entropy of the system is known and that it has a more precise meaning that the Eddington factor, although this latter has been widely used.

Finally, we consider the case of a quantum photon gas, in order to compare the results with those obtained previously for a classical ultrarelativistic gas.

For this system, the following distribution function is employed:

$$f = A \left[\exp \left[-\beta \sum p_i c - \vec{I} \cdot \sum p_i c \vec{c}_i \right] - 1 \right]^{-1} \tag{25}$$

instead of (12). This generalizes the usual Planck distribution function to the case where there is a nonvanishing energy flux. Here, β and $\vec{I}$ are, as in (12), Lagrange multipliers related to the restrictions on U and $\vec{J}$. The corresponding expression for the nonequilibrium entropy is [19,21]

$$S = \tfrac{2}{3} a^{1/4} U^{3/4} V^{1/4} (2+x)^{1/2} (x-1)^{1/4} , \tag{26}$$

where a is the Stefan constant (i.e., it relates U with the local-equilibrium temperature as $U = aT^4 V$) and x has the same meaning as in (17). By differentiation of S with respect to U and W we can obtain the nonequilibrium absolute temperature and pressure of this system, which are, respectively, given by

$$\theta = T \frac{2(x-1)^{3/4}}{(2+x)^{1/2}} , \tag{27}$$

$$\pi = \frac{U}{3V}(x-1) . \tag{28}$$

It may be found that for the photon gas the pressure tensor is also given by (22) and (23). Thus, also in this case the relation between π and $\mathbf{P}$ proposed in (10) is satisfied.

It is important to insist that, although expression (22) is well known in the literature, the identification of the coefficient of the term proportional to $\mathbf{U}$ with the nonequilibrium pressure obtained from the entropy had not previously been considered.

IV. MICROSCOPIC INTERPRETATION IN CLASSICAL IDEAL GASES

In this section we apply information theory to obtain the entropy and the pressure tensor of the nonrelativistic gas at rest up to second order in the heat flux.

The reason to have restricted ourselves up to second order is that the full generalized partition function that one should obtain by the maximization of the information theory entropy function would diverge for the classical gas, because the operator related to the heat flux is $\frac{1}{2}mc^2\mathbf{c}$, which is dominant with respect to $\frac{1}{2}mc^2$ and which may be either positive or negative. We can cope with this problem assuming that the heat flux is weak enough to allow us to consider only the development of the distribution function up to second order. Likewise, the macroscopic theory we are considering is also restricted up to second order, so, anyway, we should be able to find a complete analogy between them.

In the concluding remarks we will comment on the reason why we have preferred to use information theory rather than kinetic theory for our analysis.

As in the previous situation we assume that the mean values of the energy and the heat flux are fixed. Then, instead of (12) we have

$$f = \frac{1}{Z} \exp \left[-\beta \frac{1}{2} mc^2 - \left[\frac{1}{2} mc^2 - \frac{5}{2\beta} \right] \boldsymbol{\gamma} \cdot \mathbf{c} \right] , \tag{29}$$

where $\mathbf{c}$ is the velocity of the particle. Here, $\frac{1}{2}mc^2$ is the energy of the particle and $\frac{1}{2}mc^2\mathbf{c}$ is its contribution to the heat flux; β and $\boldsymbol{\gamma}$ are the Lagrange multipliers corresponding to the mean internal energy and the mean heat flux, respectively. The term $(5/2\beta)\boldsymbol{\gamma}\cdot\mathbf{c}$ follows from the requirement that the gas is at rest, that is $\langle \mathbf{c} \rangle = 0$. Near equilibrium, this last term, $(5/2\beta)\mathbf{c} \approx (5kT/2)\mathbf{c}$, which is the convective flow of enthalpy.

Up to second order in $\boldsymbol{\gamma}$, we can write (29) as

$$f = A \exp \left[-\beta \frac{1}{2} mc^2 \right] \left[1 - \left[\frac{1}{2} mc^2 - \frac{5}{2\beta} \right] \boldsymbol{\gamma} \cdot \mathbf{c} + \frac{1}{2} \left[\frac{1}{2} mc^2 - \frac{5}{2\beta} \right]^2 (\boldsymbol{\gamma} \cdot \mathbf{c})^2 \right] . \tag{30}$$

The parameter A can be identified by normalization of the distribution function, while β and $\boldsymbol{\gamma}$ are obtained from the conditions

$$\int f \tfrac{1}{2} mc^2 d^3c = u = \tfrac{3}{2} nkT , \tag{31}$$

$$\int f \tfrac{1}{2} mc^2 \vec{c} d^3c = \vec{q} . \tag{32}$$

It follows that, up to second order in $\vec{q}$, one has

$$\beta = \frac{1}{k\theta} = \frac{1}{kT} \left[1 + \frac{2}{5} \frac{m}{p^2 kT} \vec{q} \cdot \vec{q} \right] , \tag{33}$$

$$\gamma = -\frac{2}{5} \frac{m}{pk^2 T} \vec{q} . \tag{34}$$

It may be noted that we have obtained for the generalized temperature θ the value predicted by the macroscopic theory.

Hence, after having identified the distribution function, we can evaluate both the entropy and the pressure tensor, according to their usual microscopic definitions [13,14]. Those are given, respectively, by

$$S = S_{\text{eq}} - N \frac{1}{5} \frac{m}{n^2 k^2 T^3} q^2 \tag{35}$$

and

$$\mathbf{P} = p \left[\left[1 - \frac{6}{25} \frac{m}{p^2 kT} q^2 \right] \mathbf{U} + \frac{18}{25} \frac{m}{p^2 kT} \vec{q}\vec{q} \right] . \tag{36}$$

From the expression for the entropy, we can calculate the thermodynamic pressure, which is given by

$$\frac{\pi}{\theta} = \frac{p}{T} - \frac{2}{5} \frac{m}{pkT^2} q^2 . \tag{37}$$

We can observe that we have obtained for the generalized thermodynamic pressure π the same value that was predicted by the macroscopic extended theory of thermodynamics in (7), up to second order in $\mathbf{q}$.

Inspection of (36) shows that in the presence of a heat flux along the y axis, the component P_{xx}, i.e., the pressure along the x axis, is reduced, as predicted in the macroscopic development in (7). This may be attributed intuitively to the anisotropy of the system in the presence of the heat flux: the microscopic motion should be more ordered along the direction of the flux. However, in this case, the term in **U** in (36) does not coincide exactly with the nonequilibrium pressure. We will comment on this result in the next section.

V. CONCLUDING REMARKS

First of all, the reader should be warned that (10) is the general form of the pressure tensor under a uniform heat flux and in a fluid at rest. If the heat flux were not uniform or in the presence of a velocity field, one would have instead of (10)

$$\mathbf{P}=-2\eta\langle\vec{\nabla}\vec{v}\rangle-\zeta(\vec{\nabla}\cdot\vec{v})+\beta(\vec{\nabla}\vec{q})+[\pi U+\alpha\vec{q}\vec{q}]\ . \tag{38}$$

In the first two terms on the right hand side, η is the shear viscosity and ζ is the bulk viscosity: they are the usual hydrodynamic terms; the third term is relevant; for instance, in the description of phonon hydrodynamics [3]; and the two latter terms are those considered in this paper, for a fluid at rest and under a uniform heat flux.

Expressions analogous to (38) have been obtained in kinetic theory of gases. It turns out, however, that for Maxwellian molecules the nonequilibrium contributions to the pressure, quadratic in $\vec{q}$, vanish. This is the reason why, instead of kinetic theory, we have used information theory in our analysis of the gas under a heat flux. In fact, if the Chapman-Enskog development is adopted to solve the Bhatnaghar-Gross-Krook equation $\partial f/\partial t+\vec{c}\partial f/\partial\vec{r}=-(1/\tau)(f-f^{(0)})$ with a relaxation time τ independent of the molecular velocity up to second order, we obtain for the pressure tensor

$$\mathbf{P}=p\mathbf{U}-\tfrac{4}{5}\tau\langle\vec{\nabla}\vec{q}\rangle\ . \tag{39}$$

Therefore one observes no modification in the pressure tensor if the heat flux is uniform. Perhaps this is due to the ansatz that τ does not depend on $\vec{c}$, which, in fact, is only the case of Maxwellian molecules.

To explore the origin of this discrepancy, as well as those observed in the preceding section, we should consider whether $\vec{q}$ or $V\vec{q}$ (with V the volume of the system) should be taken as independent variable in the entropy. Under constant $\vec{q}$, the variable $V\vec{q}$ is extensive, but not $\vec{q}$ itself. In fact, in our analysis of the ultrarelativistic gas and of the photon gas, the variable $\vec{J}=V\vec{q}$ has arisen in a natural way as independent variable of the entropy, rather than $\vec{q}$ itself. In fact, if instead of keeping $\vec{J}$ constant during the differentiation in (18) we had kept **q** constant, we would have been led to

$$\pi'=\theta\left[\frac{\partial S}{\partial V}\right]_{U,N,\vec{q}}=\pi\left[1+\frac{3(x-2)}{x-1}\right]\ . \tag{40}$$

If we had considered this definition for the thermodynamic pressure, the expression obtained for the pressure tensor in terms of π would not have been satisfactory.

If instead of $\vec{q}$, we keep constant $\vec{J}=V\vec{q}$ in (5) or (37), we can obtain

$$\frac{\pi}{\theta}\equiv\left[\frac{\partial S}{\partial V}\right]_{N,U,\vec{J}}=\frac{p}{T} \tag{41}$$

and substituting in the expression for θ, (6), in (41), we obtain explicitly

$$\pi=p\left[1-\frac{2}{5}\frac{m}{p^2kT}\vec{q}\cdot\vec{q}\right]\ . \tag{42}$$

This result is closer than (7) or (37) to the coefficient of **U** in (36). Furthermore, since in the kinetic theory of gases T is the only temperature considered, it is not completely surprising that since, according to (41), $\pi=p\theta/T$, there are not corrections to the pressure in the same way as there are not corrections to the temperature in the standard expansion of kinetic energy. Therefore our results seem to suggest that $\vec{J}=\vec{q}V$ is a more suitable variable than **q** in an extended thermodynamic formalism. Since the same results are obtained for θ if $\vec{J}$ or if $\vec{q}$ are used as independent variables, it is logical that the problem of whether $\vec{q}$ or $\vec{J}$ is most suitable had not arisen before.

The last comment refers to the form we have assumed for the pressure tensor. In expression (10) we can observe that, according to the fact that π is always lower in the value than p, the thermodynamic pressure corresponds to the minimum eigenvalue of the pressure tensor. This is in agreement with the conjecture proposed by Evans [23] for a fluid submitted to a shear rate. Within the completely different context of numerical simulations based on molecular dynamics in nonequilibrium steady states, he also pointed out that the thermodynamic pressure should be given by the minimum eigenvalue of the pressure tensor. This assumption looks clearer if we remember that the entropy is related to the minimum reversible work required to accomplish a virtual volume change, so πdV is the minimum possible work.

In summary, we have seen that there are still many open problems regarding the definition and the measurement of very basic quantities, such as temperature and pressure, in nonequilibrium states, when one goes beyond the local equilibrium hypothesis. Such analysis has not only a conceptual interest, but it may also have practical interest for systems with high fluxes, where the values of π and θ may differ considerably from their equilibrium counterparts p and T. Therefore it may be useful and stimulating to have a thermodynamic formalism which allows a discussion of the points we have dealt with in this paper, and which are completely ignored in the classical theory of nonequilibrium thermodynamics.

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