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Thermodynamic pressure in nonlinear nonequilibrium thermodynamics of dilute nonviscous gases

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In this paper, using extended thermodynamics, we build up a nonlinear theory for a dilute nonviscous gas under heat flux. The fundamental fields are the density, the velocity, the internal energy density, and the heat flux. The constitutive theory is builtup without approximations. We single out the nonlinear complete expressions of the Gibbs equation and of the nonequilibrium pressure. In particular, we determine the complete expressions furnished by the theory for the nonequilibrium pressure tensor and thermodynamic pressure, i.e., the derivative of the nonequilibrium internal specific entropy with respect to the specific volume, times the nonequilibrium temperature. In a second-order approximation these expressions are identical with those obtained in Phys. Rev. E **51**, 158 (1995), using information theory.

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I. INTRODUCTION

The behavior of materials in the presence of high values of heat flux has, in recent years, been the object of many investigations. Extended thermodynamics (ET) [1,2] has been a tool used very frequently in these studies. As is well known, this theory chooses some dissipative fluxes as fundamental fields in addition to the traditional fields of classical thermodynamics. We can say that some fluxes, e.g., the heat flux, must be chosen as independent fields when their evolution times are comparable to the evolution times of the classical variables, i.e., density, velocity, and temperature. Many materials require the use of the heat flux as an independent variable for their description: superfluids, hydrodynamical models for the charge transport inside semiconductors, hydrodynamics of phonons, and photons, plasmas, ultrarelativistic fluids, etc. (see the bibliography in Refs. [1–3]).

Sometimes, in the description of materials where the heat flux must be considered as an independent variable, the approximation of nonviscous fluid may be useful. In classical thermodynamics the absence of viscosity amounts to setting the shear and bulk viscosity coefficients equal to zero. In extended thermodynamics, to assume that a fluid is nonviscous means to set equal to zero the evolution times of the nonequilibrium part of the pressure tensor (both trace and deviator). The two definitions are essentially equivalent as long as a linear theory is considered, but this is not true far from equilibrium.

In this paper we investigate the behavior, far from equilibrium, of a dilute gas whose evolution time of the heat flux is high, while the evolution time of the stress deviator is zero. We will use as fundamental fields the density ρ, the velocity v_i, the internal energy density E, and the heat flux q_i. We will study in detail the expression, far from equilibrium, of the thermodynamic pressure π, defined as the derivative of specific entropy with respect to specific volume times the temperature. In classical thermodynamics, the pressure, as the entropy, depends only on the equilibrium quantities, i.e., temperature and density, and coincides with the scalar part p of the stress tensor p_{ij}:

$$\pi = T\frac{\partial \eta_0}{\partial V} = \frac{1}{3}p_{ll} = p. \tag{1.1}$$

On the contrary, in extended thermodynamics, owing to the lacking of local equilibrium, entropy depends also on the fluxes, and with it also the thermodynamic pressure does. Furthermore, the thermodynamic pressure is no longer equal to the scalar part of the stress tensor.

In Ref. [4] Diminguez and Jou, drawing inspiration from the form of the pressure tensor widely used for anisotropic radiation, suggest that the thermodynamic pressure π, obtained as the derivative of the generalized specific entropy $\eta = \eta(\rho, E, q^2)$ with respect to the specific volume times the nonequilibrium temperature θ, is linked to the pressure tensor through the relation

$$p_{ij} = \pi\delta_{ij} + a q_i q_j. \tag{1.2}$$

As a consequence, they suggest the following relation between π and p:

$$\pi - p = -\tfrac{1}{3} a q^2, \tag{1.3}$$

where the quantity a must be intended as the coefficient of the off-diagonal terms in the expression of the stress tensor. However, as the authors themselves observed, expression (1.3) is not in complete accord with the microscopic theory: in fact, in the case of a dilute gas under heat flux, in a second-order approximation, using information theory, they obtain the following different result:

$$\pi - p = -\frac{5}{9} a q^2. \tag{1.4}$$

This relation has been questioned by Nettleton in Ref. [5]. Successively, Dominguez-Cascante and Faraudo [6] reconsider the problem, providing a new physical basis for the term proportional to q^2 in the pressure, and recalling the necessity of an understanding of this kind of expression in a thermodynamic framework.

In this paper, this question is further analyzed using a nonlinear thermodynamic theory with eight fields, able to describe a nonviscous gas in the presence of high heat flux. In particular, we will determine the complete expressions furnished by the theory for the nonequilibrium pressure tensor and thermodynamic pressure.

This investigation not only has a conceptual interest, but it may also have practical interest for systems with high heat flux, as it happens, for instance, in astrophysical plasmas. In fact, inside the stars, the energy flux can be extremely high, and the value of π may differ considerably from its equilibrium counterpart p. Because in astrophysical plasmas there must be a tradeoff between the force of pressure and the force of gravity, the dependence of the pressure on the heat flux may significantly modify the field equations.

The plan of this paper is the following: In Sec. II the mathematical consequences of the hypothesis of nonviscosity for an ideal gas are analyzed and the constitutive theory for a set of eight fundamental fields is built up without approximations. In Sec. III the complete nonequilibrium expressions of the chemical potential, thermodynamic pressure, and Gibbs equation are written. The results obtained are compared in Sec. IV with those obtained using the informational approach [4]; in a second-order approximation we obtain complete equivalence.

II. EXTENDED THERMODYNAMICS OF A NONVISCOUS DILUTE GAS

In ET, the behavior of a dilute gas is described by the following balance equations:

$$\frac{\partial \rho_A}{\partial t}+\frac{\partial \rho_{Ak}}{\partial x_k}=P_A \quad (A=\ldots,i,ij,ijk,\ldots), \tag{2.1}$$

where ρ_A are the moments of various order of the phase density of the kinetic theory of gases [7], ρ_{Ak} are the fluxes of the fields ρ_A, which are just the moments of successive order, and P_A are the productions that take into account both the effect of external forces and of the collisions.

In ET of ideal and real gases, the central moments are often chosen as independent fields instead of complete moments. Denoting with f the phase-density function, with m the atomic mass, with u_i the velocity, and with c_i the peculiar velocity, the total and the central moments ρ_{ijkl} and $\hat{\rho}_{ijkl}$ are defined as

$$\rho_{ijkl}=\int m u_i u_j u_k u_l f d\mathbf{c}, \quad \hat{\rho}_{ijkl}=\int m c_i c_j c_k c_l f d\mathbf{c}. \tag{2.2}$$

In particular, ρ is the mass density, $\rho_i=\rho v_i$ the momentum density, ρ_{ij} the momentum flux density, and ρ_{ijj} the energy flux density.

In the following we will denote with p_{ij} the stress tensor $\hat{\rho}_{ij}$; with $E=\frac{1}{2}p_{ll}$ the internal energy density, with $p_{\langle ij\rangle}$ the deviatoric part of the stress tensor p_{ij}, and with $q_i=\frac{1}{2}\hat{\rho}_{lli}$ the heat flux. We will suppose also the gas in an inertial frame and in the absence of external forces; as a consequence of mass, momentum, and energy-conservation laws we obtain $P=0,\ P_i=0,\ P_{jj}=0.$

Let us now suppose that the gas is nonviscous. In a recent work [8], it was shown that, under the only hypothesis that the entropy is a convex function of the field variables, we can formulate a nonlinear theory, able to describe the behavior of a nonviscous gas even in the presence of highly nonlinear phenomena, which takes only ρ, v_i, E, and q_i as independent fields. In Ref. [8] it has been shown that the evolutions equations for these fundamental fields can be easily obtained, solving the first 13 balance equations (2.1) with respect to the material derivatives of the central moments, and neglecting the evolution equation of the stress deviator $p_{\langle ij\rangle}$, we obtain

$$\begin{cases} \dot{\rho}+\rho\dfrac{\partial v_k}{\partial x_k}=0 \\ \rho\dot{v}_i+\dfrac{\partial p_{ik}}{\partial x_k}=0 \\ \dot{E}+E\dfrac{\partial v_k}{\partial x_k}+\dfrac{\partial q_k}{\partial x_k}+p_{ik}\dfrac{\partial v_i}{\partial x_k}=0 \\ \dot{q}_i+q_i\dfrac{\partial v_k}{\partial x_k}+q_k\dfrac{\partial v_i}{\partial x_k}+\hat{\rho}_{ijk}\dfrac{\partial v_j}{\partial x_k}+\dfrac{1}{2}\dfrac{\partial \hat{\rho}_{ijjk}}{\partial x_k}-\dfrac{3}{2\rho}p_{(ij}\dfrac{\partial p_{j)k}}{\partial x_k}=\dfrac{1}{2}\hat{P}_{ill}. \end{cases} \tag{2.3}$$

The constitutive equations for the nonfundamental fields $p_{\langle ik\rangle}$, $\hat{\rho}_{ijk}$, and $\hat{\rho}_{ijjk}$, as a consequence of the material objectivity principle, can be expressed in the form

$$p_{ij}=\tfrac{2}{3}E\delta_{ij}+a(\rho,E,q^2)q_{\langle i}q_{j\rangle}, \tag{2.4}$$

$$\hat{\rho}_{ijk}=\tfrac{2}{5}(q_i\delta_{jk}+q_j\delta_{ki}+q_k\delta_{ij})+\chi(\rho,E,q^2)q_{\langle i}q_j q_{k\rangle}, \tag{2.5}$$

$$\hat{\rho}_{ijjk}=\beta(\rho,E,q^2)\delta_{ik}+\nu(\rho,E,q^2)q_{\langle i}q_{k\rangle}. \tag{2.6}$$

As we see, in this theory, the trace of the stress $3p$ is linked to the internal energy density E by the relation $3p=2E$.

Further restrictions on these constitutive relations are obtained imposing the validity of the entropy principle, applying the Liu method of Lagrange multipliers [9]. This method requires the existence of a scalar function h and a vector function Φ_k of the fundamental fields, namely, the entropy density and the entropy flux density, respectively, such that the following inequality is satisfied for arbitrary fields ρ, v_i, E, and q_i:

$$\begin{aligned}&\dot{h}+h\frac{\partial v_k}{\partial x_k}+\frac{\partial \Phi_k}{\partial x_k}-\hat{\Lambda}\left[\dot{\rho}+\rho\frac{\partial v_k}{\partial x_k}\right]-\hat{\Lambda}_i\left[\dot{v}_i+\frac{1}{\rho}\frac{\partial p_{ik}}{\partial x_k}\right]\\&-\hat{\Lambda}_E\left[\dot{E}+E\frac{\partial v_k}{\partial x_k}+\frac{\partial q_k}{\partial x_k}+p_{ik}\frac{\partial v_i}{\partial x_k}\right]-\hat{\lambda}_i\left[\dot{q}_i+q_i\frac{\partial v_k}{\partial x_k}\right.\\&+q_k\frac{\partial v_i}{\partial x_k}+\hat{\rho}_{ijk}\frac{\partial v_j}{\partial x_k}+\frac{1}{2}\frac{\partial \hat{\rho}_{ijjk}}{\partial x_k}-\frac{3}{2\rho}p_{(ij}\frac{\partial p_{j)k}}{\partial x_k}\\&\left.-\frac{1}{2}\hat{P}_{ill}\right]\geqslant 0. \qquad (2.7)\end{aligned}$$

In this inequality, $h=h(\rho,E,q^2)$ and $\Phi_k=\phi(\rho,E,q^2)q_k$ are objective functions of the fundamental fields. The quantities $\hat{\Lambda}$, $\hat{\Lambda}_i$, $\hat{\Lambda}_E$, and $\hat{\lambda}_i$ are the nonconvective parts of the Lagrange multipliers, which are also objective functions, so that we can write $\hat{\Lambda}=\hat{\Lambda}(\rho,E,q^2)$, $\hat{\Lambda}_i=\hat{\Lambda}_v(\rho,E,q^2)q_i$, $\hat{\Lambda}_E=\hat{\Lambda}_E(\rho,E,q^2)$, and $\hat{\lambda}_i=\hat{\lambda}_q(\rho,E,q^2)q_i$.

The constitutive theory is obtained substituting Eqs. (2.4)–(2.6) in Eq. (2.7) and imposing that the coefficients of all derivatives must vanish. In particular, imposing that the coefficients of the time derivatives are equal to zero, we obtain

$$\hat{\Lambda}_v=0, \qquad (2.8)$$

$$dh=\hat{\Lambda}d\rho+\hat{\Lambda}_E dE+\hat{\lambda}_i dq_i. \qquad (2.9)$$

Imposing that zero as the coefficients of space derivatives of velocity vanish, we obtain

$$h-\rho\hat{\Lambda}-\hat{\Lambda}_E(E+p)-\hat{\lambda}_q q^2=0, \qquad (2.10)$$

$$a\hat{\Lambda}_E+\hat{\lambda}_q\frac{9+3\chi q^2}{5}=0. \qquad (2.11)$$

In particular, for the pressure tensor p_{ij}, from Eq. (2.11) we obtain

$$p_{ij}=p\,\delta_{ij}-\frac{\hat{\lambda}_q}{\hat{\Lambda}_E}\frac{9+3\chi q^2}{5}q_{\langle i}q_{j\rangle}. \qquad (2.12)$$

Now, we introduce the following quantity:

$$\theta=\frac{1}{\hat{\Lambda}_E(\rho,E,q^2)}, \qquad (2.13)$$

which, near equilibrium, can be identified with the local equilibrium absolute temperature T. Some authors [1,10,11] have proposed that the quantity θ is the absolute temperature, which is actually measured in nonequilibrium states instead of T. In the following we will choose as a fundamental field the quantity θ, instead of the internal energy density E. In accord with Ref. [1], we will call θ ‘‘nonequilibrium temperature.’’ Using this quantity, the physical meaning of the constitutive functions appearing in this section can be better investigated.

III. NONEQUILIBRIUM CHEMICAL POTENTIAL AND NONEQUILIBRIUM PRESSURE

As observed in Refs. [3,4], in nonequilibrium thermodynamics, as in classical thermodynamics, the entropy must be expressed in terms of extensive variables in order to be a thermodynamic potential. Now, we observe that the variable $J_i=Vq_i$ (where V is the specific volume) is extensive in the following sense: if we have two systems of volume V_1 and V_2 crossed by the same heat flux q_i, the variable Vq_i is additive, i.e., $V_{\mathrm{tot}}q_i=V_1q_i+V_2q_i$, although q_i itself is not additive [3].

In this section, therefore, we will study the nonequilibrium Gibbs equations using the quantity $J_i=Vq_i$ as an independent variable, rather than the heat flux. We consider Eq. (2.9); using the variables ρ, θ, and J_i, and introducing the quantity

$$\mu=-\theta(\hat{\Lambda}+\hat{\lambda}_i J_i), \qquad (3.1)$$

Eq. (2.9) can be written as

$$dh=\frac{1}{\theta}[dE-\mu\,d\rho+\rho\hat{\lambda}_i\,dJ_i]. \qquad (3.2)$$

Consequently, the quantity μ can be interpreted as a nonequilibrium chemical potential.

Now, denoting with ϵ the specific energy, with η the nonequilibrium specific entropy and remembering relation (2.10), the nonequilibrium chemical potential μ can be written in the following way:

$$\mu=\epsilon-\theta\eta+\frac{p}{\rho}+\theta\hat{\lambda}_i J_i. \qquad (3.3)$$

As we see, the nonequilibrium chemical potential is no longer expressed by the quantity $\epsilon-\theta\eta+(p/\rho)$, but it contains an additional term proportional, at the lowest order, to the square of the heat flux. Introducing the quantity

$$\pi=p+\theta\lambda_q q^2, \qquad (3.4)$$

relation (3.3) can be written in the following way:

$$\mu=-\theta\hat{\Lambda}=\epsilon-\theta\eta+\frac{\pi}{\rho}. \qquad (3.5)$$

As we see, in this expression the equilibrium temperature T is substituted, as expected, by the nonequilibrium temperature θ, while the pressure is substituted by the term π, which is the sum of the scalar part p of the stress tensor and of a term proportional to the Lagrange multiplier of the field q_i.

In order to single out the physical meaning of this term, we consider again the entropy density differential dh, furnished by Eq. (3.2); using expression (3.3) of μ, we obtain

$$\theta\, d\eta = d\epsilon + \pi\, dV + \theta \hat{\lambda}_i\, dJ_i . \tag{3.6}$$

This relation is a generalization to processes far from equilibrium of the Gibbs equation of thermostatics. From this equation we conclude that, in a stationary and adiabatic process ($dJ_i=0,\ d\eta=0$), as a consequence of a change of volume, not only the equilibrium pressure, but the whole quantity π, which is the sum of p and of $\theta\lambda_q q^2$, contributes to the change of internal energy. We can call the quantity π, in accord with Ref. [4], the nonequilibrium thermodynamic pressure. In a stationary nonequilibrium process, in which $dJ_i=0$, the influence of the term $\theta\lambda_q q^2$ in the expression of π ought to be evidenced.

We conclude this section determining the relation between the quantity π and the functions p and a, which appear in the expression of the stress tensor. Using relations (2.11) and (3.4) we obtain

$$\pi - p = \theta\lambda_q q^2 = -\frac{5}{9+3\chi q^2} a q^2 . \tag{3.7}$$

IV. MICROSCOPIC INTERPRETATION AND CONCLUDING REMARKS

In this section, in order to obtain a microscopic interpretation of the results obtained in this paper, we briefly recall the application made in Ref. [4] of the information theory to a dilute gas under heat flux.

According to the information theory, if a given number of moments ρ_A of the phase density f are known, the distribution function $f_{\max}$, which can be used to evaluate the unknowns moments of f, corresponds to the maximum of the entropy functional subject to macroscopic constraints, which consist just of the known moments.

In the case of a nonviscous ideal gas the constraints are the quantities E and q_i, which are the mean values defined in Eq. (2.2) of the microscopic quantities $m(c^2/2)$ and $mc_i(c^2/2)$:

$$E = \langle m(c^2/2)\rangle, \quad \langle mc_i(c^2/2)\rangle . \tag{4.1}$$

Further, we must impose the additional constraint that the mean of the peculiar velocity is zero:

$$0 = \langle c_i \rangle . \tag{4.2}$$

The application of the maximum entropy principle yields to the following expression, approximate to the second order, for the distribution function f [4]:

$$f_{\max} = \frac{1}{Z}\exp\left[-\tilde{\Lambda}_E \frac{1}{2} mc^2\right] \times \left\{ 1 - \tilde{\lambda}_i c_i \left(\frac{1}{2}mc^2 - \frac{5}{2\tilde{\Lambda}_E}\right) + \frac{1}{2}(\tilde{\lambda}_i c_i)^2 \left(\frac{1}{2}mc^2 - \frac{5}{2\tilde{\Lambda}_E}\right)^2 \right\} . \tag{4.3}$$

In Ref. [4], approximated to the second order in q_i, for the pressure tensor p_{ij} and for the thermodynamical pressure π, the following expressions are found:

$$p_{ij} = p\left[\left(1 - \frac{6}{25}\frac{m}{p^2 k_B T} q^2\right)\delta_{ij} + \frac{18}{25}\frac{m}{p^2 k_B T} q_i q_j\right], \tag{4.4}$$

$$\pi = p - \frac{2}{5}\frac{m}{p k_B T} q^2 ; \tag{4.5}$$

hence, we obtain

$$\pi - p = -\tfrac{5}{9} a q^2 . \tag{4.6}$$

Inspection of Eqs. (4.6) and (3.7) shows that, to the second order in the heat flux, these equations are identical.

We conclude this paper by observing that if, using information theory, we do not choose the stress deviator as a constraint, this implies, at the macroscopic level, the hypothesis that the considered gas is nonviscous. In fact, in this case, the evolution time of the stress deviator $p_{\langle ij\rangle}$ goes to zero and, as shown in Ref. [8], when the values of ρ, E, and q_i are known, the value of $p_{\langle ij\rangle}$ cannot be chosen independently, but must satisfy the relation obtained requiring that its production is zero.

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