Nonequilibrium entropy of a gas

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The Boltzmann entropy of a dilute gas under uniform shear flow is analyzed. The entropy variation associated with viscous heating is evaluated and compared with the local equilibrium expression. For interaction potentials other than the Maxwell potential, significant discrepancies are found that can be related to the difference between thermodynamic quantities, defined from the entropy, and kinetic quantities, defined by means of local equilibrium. The discrepancies change, but remain relevant, when artificial external forces are introduced in order to create an ideal stationary state.

I. INTRODUCTION

The extension of thermodynamic ideas to far-from-equilibrium systems appears as a fundamental and necessary step toward the development of a general body of theory for those systems. From a formal point of view, it may be expected that this would open the possibility of looking for general relations similar to the ones existing at and near equilibrium. These relations would apply to a wide range of states, for instance stationary states. But, beyond the above possibility, there is a basic problem that must be solved for any theory in order to connect with what is actually observed and measured in the real world: the temperature of far-from-equilibrium states must be defined in some way. It must be noticed that, conceptually, one could avoid the use of the temperature, both in theory and experiments, by employing the energy density instead. Nevertheless, experimentalists have found it fruitful to characterize and classify their results by means of the temperature, whatever its meaning may be.

In most of the existing theories, the temperature is introduced by assuming some kind of local equilibrium, but this assumption is quite dubious in far-from-equilibrium situations. In fact, it is known that in strict local equilibrium there is no transport. A more-consistent definition of nonequilibrium temperature could be given if the definition of some thermodynamic potential, for instance the entropy, had been previously extended. The above comments can also be applied to the pressure.

In spite of the great deal of work devoted to it, no general microscopic formulation of the entropy, having the minimal requirements to deserve such a name, has been found for nonequilibrium states. An exception refers to dilute gases obeying the Boltzmann equation (BE). In this case, a nonequilibrium entropy $S(t)$ can be defined in terms of the one-particle distribution function, $f(\mathbf{r},\mathbf{v},t)$, as

$$S(t) = -k_B H(t) + \text{const} , \qquad (1.1)$$

where k_B is the Boltzmann constant, $H(t)$ is the quantity

$$H(t) = \int \int d\mathbf{r}\, d\mathbf{v}\, f(\mathbf{r},\mathbf{v},t) \ln f(\mathbf{r},\mathbf{v},t) , \qquad (1.2)$$

and the constant is simply proportional to the number of particles in the system. By using the symmetry properties of his equation, Boltzmann himself was able to prove the H theorem, stating that any initial distribution approaches equilibrium. Besides, the entropy $S(t)$ grows monotonically in time, reaching its maximum value in the equilibrium situation [1]. The theorem holds for constant-external-potential fields, including the wall interactions, which are velocity independent [2]. A very interesting stronger version of the theorem has been given by Dorfman and van Beijeren [9]. For boundary conditions satisfying a thermostat condition, they proved a generalization of Clausius's formula relating the change of entropy and the heat interchange of the system through the walls.

From knowledge of $S(t)$ it is possible to study near-equilibrium states [4], but to the best of our knowledge no useful connection has been established between Boltzmann's entropy and the quantities characterizing far-from-equilibrium states. Here it will be seen that this is not a trivial task, even for very simple situations.

The evaluation of $S(t)$ from Eqs. (1.1) and (1.2) for a given state requires the knowledge of the distribution function for the state; i.e., one has to solve the nonlinear BE. The only exact solutions we are aware of correspond to homogeneous systems [5] or to dilational flows not directly related to transport problems [6]. There are other cases where the distribution function is not known, but partial information has been obtained by computing a finite number of its moments. They are restricted to Maxwell's interaction and correspond to uniform shear flow [7], steady heat flow [8], and color conductivity [9].

In the last years, a number of exact solutions of the Bhatnagar-Gross-Kook (BGK) model kinetic equation [1] describing a variety of interesting physical situations have been derived [10,11]. The BGK equation can be

considered as a model of the BE with the collision term replaced by a single-time relaxation towards local equilibrium. It keeps some of the main physical properties of the BE, namely the conservation laws and the H theorem.

A definition of entropy for nonequilibrium steady states has recently been proposed by Evans [12]. In the low-density limit it reduces to Boltzmann's entropy. Using molecular-dynamics simulation, Evans computed the entropy of a low-density gas of soft disks under uniform shear flow. In principle, this state is not steady due to viscous heating [13], but a thermostat force is introduced in Ref. [12] in order to keep the energy constant. From the entropy data, Evans evaluated thermodynamic temperatures and pressures, finding significant discrepancies with the values of the corresponding kinetic quantities, the latter being defined from the equipartition of energy and the pressure tensor, respectively.

In this paper, we will analyze some properties of the Boltzmann entropy for a system under uniform shear flow, using both the BE and the BGK equation. Because the solution of the BE for this state is only known for Maxwell molecules, our results will be much more limited in the case of the BE. Nevertheless, it has been shown by computer simulation that the BGK equation is a quite good approximation of the BE for the uniform shear flow, even at a quantitative level [14]. The distribution function of the idealized steady state of uniform shear flow has been derived in the BGK approximation [15]. Here we obtain the first few terms of the expansion of the entropy in powers of the (reduced) shear rate and compare, at a qualitative level, with the results reported by Evans. As is often the case, Maxwell molecules lead to a peculiar behavior. In particular, the thermodynamic and kinetic temperatures are the same for that interaction. This property is also true when the exact BE is used. To avoid misunderstandings, it is worth mentioning that the role played by the thermostat forces is not neutral, in the sense that the relationship between results obtained from the BE with and without the thermostat is not simple for molecules other than Maxwell molecules.

The plan of the paper is as follows. In the next section, the existence of an entropy function for the uniform shear flow is postulated and thermodynamic temperature and pressure are defined. For a dilute gas, they can be easily written in terms of the distribution function if the Boltzmann definition of entropy is adopted. The case of the BE for Maxwell molecules is explicitly considered. Using a powers-series expansion in the shear rate, the BGK equation is solved in Sec. III, and the thermodynamic quantities are related to the kinetic ones. Also, it is shown that the local equilibrium assumption for the entropy variation is not verified in general. The thermostated flow is discussed in Sec. IV, while the final section is devoted to some comments.

II. NONEQUILIBRIUM ENTROPY IN THE UNIFORM SHEAR FLOW

Macroscopically, the uniform shear flow (USF) is characterized by a constant density n, and by the uniformity of all the hydrodynamic fields except one of the components of the local velocity $\mathbf{u}$ that has a linear profile along a direction perpendicular to it. We will take

$$u_i = a_{ij} r_j, \quad a_{ij} = a \delta_{i,x} \delta_{j,y}, \quad a = \text{const} , \quad (2.1)$$

where a is the shear rate. In the absence of an external thermostat force, work is done on the system so that the state is time dependent.

Let us assume that there exists for this state a nonequilibrium entropy that is an extensive function of the number of particles, the volume, and the internal energy, and parametrically depends on the shear rate. The internal energy is independent of $\mathbf{u}$, and, therefore, the entropy density will be uniform in the system. We can write

$$s = s(n,e,a) , \quad (2.2)$$

where s and e are the entropy and internal energy per particle, respectively. Now, a nonequilibrium thermodynamic temperature T_{th} and a nonequilibrium thermodynamic pressure p_{th} are defined as

$$T_{\text{th}}^{-1} = \left[\frac{\partial s}{\partial e} \right]_{n,a} , \quad p_{\text{th}} = -n^2 T_{\text{th}} \left[\frac{\partial s}{\partial n} \right]_{e,a} , \quad (2.3)$$

i.e., using the same relations as in equilibrium. Of course, one can also introduce a specific nonequilibrium quantity conjugated to the shear rate

$$r_{\text{th}} = -T_{\text{th}} \left[\frac{\partial s}{\partial a} \right]_{n,e} . \quad (2.4)$$

In this way, we arrive at the generalized Gibbs relation [12,16]

$$de = T_{\text{th}} ds + n^{-2} p_{\text{th}} dn + r_{\text{th}} da . \quad (2.5)$$

The validity of the above scheme lies on the existence of an entropy function satisfying some minimal requirements. In particular, it must reduce to the equilibrium value for $a = 0$. Besides, if we want the definitions given in Eqs. (2.3) to be useful, their relation with more standard definitions and with real and computer experiments has to be established.

Now we adopt a kinetic-theory standpoint and consider a system described by the BE. The existence of the USF state is consistent with the BE [6,7,13,14] and also with the BGK equation [10,15]. The distribution function of a gas under USF is a function of the form $f(\mathbf{V},t)$, where

$$\mathbf{V} = \mathbf{v} - \mathbf{u} , \quad (2.6)$$

i.e., all the position dependence occurs through the peculiar velocity with respect to the local flow velocity [7,13]. The internal energy density is given by

$$ne = \int d\mathbf{V} \tfrac{1}{2} m V^2 f , \quad (2.7)$$

and coincides with the kinetic energy density in the Lagrangian frame. Furthermore, the kinetic temperature T_k is defined as proportional to e by means of the local equilibrium relation

$$\tfrac{3}{2} k_B T_k = e . \quad (2.8)$$

Let us introduce the dimensionless velocity

$$\mathbf{V}^* = \left[\frac{2k_B T_k}{m}\right]^{-1/2} \mathbf{V} \qquad (2.9)$$

and the corresponding distribution

$$f^* = \frac{1}{n}\left[\frac{2k_B T_k}{m}\right]^{3/2} f \ . \qquad (2.10)$$

In terms of these, the Boltzmann entropy, Eq. (1.1), for the USF reads

$$s = \frac{S}{N} = k_B\left[\ln\frac{(2k_B T_k/m)^{3/2}}{n} - h^*\right] + C \ , \qquad (2.11)$$

where N is the number of particles, C is a constant, and

$$h^* = \int d\mathbf{V}^* f^* \ln f^* \ . \qquad (2.12)$$

As long as there is a normal solution of the BE for the USF, Eq. (2.11) provides an expression for the entropy that has the dependence assumed in the thermodynamic description. Notice that the use of T_k is a matter of convenience, since it can always be eliminated in favor of e by using Eq. (2.8). From Eqs. (2.3) and (2.11) we have

$$T_{th} = T_k\left[1 - \tfrac{2}{3}T_k\frac{\partial h^*}{\partial T_k}\right]^{-1} \ , \qquad (2.13)$$

$$p_{th} = nk_B T_{th}\left[1 + n\frac{\partial h^*}{\partial n}\right] = p_k\frac{1 + n\partial h^*/\partial n}{1 - \tfrac{2}{3}T_k\partial h^*/\partial T_k} \ , \qquad (2.14)$$

where in the last equality of Eq. (2.14) the kinetic pressure is defined as one-third the trace of the pressure tensor, i.e., $p_k = nk_B T_k$. It follows that the thermodynamic temperature is equal to the kinetic temperature if and only if $\partial h^*/\partial T_k = 0$. If in addition it is $\partial h^*/\partial n = 0$, there is also agreement between the thermodynamic pressure and the kinetic pressure. From a mathematical point of view, $p_{th} = p_k$, even if $T_{th} \neq T_k$, if h^* is a function of the scaled variable $n/T_k^{3/2}$.

For Maxwell molecules, a solution of the BE corresponding to the USF state has been found using the moment method [7,13]. Although the explicit form of f^* has not been determined, it is known that it does not depend on time explicitly. In fact, f^* obeys the equation [13]

$$-\gamma\frac{\partial}{\partial \mathbf{V}^*}\cdot(\mathbf{V}^* f^*) - aV_y^*\frac{\partial}{\partial V_x^*}f^* = n\,J[f^*, f^*] \ , \qquad (2.15)$$

where J is the Boltzmann collision operator and

$$\gamma = \tfrac{2}{3}\lambda n \sinh^2\{\tfrac{1}{6}\cosh^{-1}[1 + 9(a/\lambda n)^2]\} \ , \qquad (2.16)$$

λ being a constant. Since e (or T_k) is the only time-dependent parameter in the USF, h^* cannot depend on T_k. Therefore, for Maxwell molecules $T_{th} = T_k$. The dependence of h^* on the density is not known in detail, but Eq. (2.15) shows that it is coupled to the dependence on a through the scaled variable a/n. It follows that p_{th}

is different from the kinetic pressure p_k. More specifically,

$$\frac{p_{th}}{p_k} = 1 - \frac{na}{p_k}r_{th} \ . \qquad (2.17)$$

The above discussion can be put in a different but closely related form. The time derivative of the Boltzmann entropy for the USF is from Eq. (2.11)

$$\frac{ds}{dt} = \tfrac{3}{2}k_B\frac{d(\ln T_k)}{dt} - k_B\frac{dh^*}{dt}$$

$$= \tfrac{3}{2}k_B\frac{T_k}{T_{th}}\frac{d(\ln T_k)}{dt} \ , \qquad (2.18)$$

which for Maxwell molecules reduces to

$$\frac{ds}{dt} = \tfrac{3}{2}k_B\frac{d(\ln T_k)}{dt} \ . \qquad (2.19)$$

This is the expression assumed by the local equilibrium hypothesis. Therefore, although the Boltzmann entropy does not have the functional form assumed by local equilibrium, the latter correctly reproduces its time variation in the USF.

For interaction potentials other than Maxwell potential, no solution of the BE has been found for the USF. Furthermore, the transformation properties of the Boltzmann collision operator show that h^* is expected to depend explicitly on time [13]. However, realistic estimates can be carried out using the BGK model kinetic equation. This is done in the next section.

III. UNIFORM SHEAR FLOW FROM THE BGK MODEL

The BGK equation for the USF is [15]

$$\frac{\partial f^*}{\partial t} - \frac{1}{2}\frac{d(\ln T_k)}{dt}\frac{\partial}{\partial \mathbf{V}^*}\cdot(\mathbf{V}^* f^*) - aV_y^*\frac{\partial f^*}{\partial V_x^*}$$

$$= -\zeta(f^* - f_0^*) \ , \qquad (3.1)$$

where f_0^* is the dimensionless Maxwellian distribution

$$f_0^* = \pi^{-3/2}\exp(-V^{*2}) \qquad (3.2)$$

and ζ is an effective collision frequency that is linear in the density. The only other dependence of ζ is on the temperature. Here we will take $\zeta \propto T_k^\alpha$ with $0 \leq \alpha \leq \tfrac{1}{2}$, which corresponds to purely repulsive power-law potentials, including Maxwell molecules ($\alpha = 0$) and hard spheres ($\alpha = \tfrac{1}{2}$) as limit cases. Taking into account that T_k increases monotonically due to viscous heating, the time dependence of f^* can be accounted for through the reduced shear rate

$$a^* = \frac{a}{\zeta} \ , \qquad (3.3)$$

and Eq. (3.1) becomes

$$-\frac{1}{\zeta}\frac{d(\ln T_k)}{dt}\left[\alpha a^*\frac{\partial f^*}{\partial a^*}+\frac{1}{2}\frac{\partial}{\partial \mathbf{V}^*}\cdot(\mathbf{V}^*f^*)\right]$$
$$-a^*V_y^*\frac{\partial f^*}{\partial V_x^*}=-f^*+f_0^* \ . \qquad (3.4)$$

In order to close this equation we need an expression for the evolution of T_k. This can be easily achieved by taking moments in the equation itself. Since the details have been already given elsewhere [15], we merely quote the results. One finds

$$\frac{1}{\zeta}\frac{d(\ln T_k)}{dt}=\frac{2}{3}a^{*2}\eta^*(a^*) \ , \qquad (3.5)$$

with

$$\eta^*(a^*)=-\frac{P_{xy}}{nk_BT_ka^*} \ , \qquad (3.6)$$

where P_{xy} denotes the component of the pressure tensor. The function $\eta^*(a^*)$ is a generalized shear viscosity that verifies a closed nonlinear second-order differential equation (see Eq. (4.1) in Ref. [15]). The solution of this equation corresponding to the hydrodynamic regime, i.e., in the long-time limit, can be constructed numerically for all values of a^* [15]. Here we will restrict ourselves to the first few terms of the expansion in powers of a^*:

$$\eta^*(a^*)=1-\frac{2}{3}(2-\alpha)a^{*2}+\frac{4}{9}(7-13\alpha+4\alpha^2)a^{*4}+\cdots \ .$$
$$(3.7)$$

This series has been shown to be only asymptotic for any value of α other than zero [15]. In the case of Maxwell molecules ($\alpha=0$), Eq. (3.4) reduces to

$$-\frac{\gamma}{\zeta}\frac{\partial}{\partial\mathbf{V}^*}\cdot(\mathbf{V}^*f^*)-a^*V_y^*\frac{\partial}{\partial V_x^*}f^*=-f^*+f_0^* \ , \qquad (3.8)$$

where

$$\gamma/\zeta=\gamma^*=\frac{1}{3}a^{*2}\eta^*(a^*)=\frac{2}{3}\sinh^2[\frac{1}{6}\cosh^{-1}(1+9a^{*2})] \ .$$

Notice the similarity between Eqs. (2.15) and (3.8). Although the solution of Eq. (3.8) is known [15], it will not be needed here.

In the following, our aim will be to find an expansion for the Boltzmann entropy in powers of the reduced shear rate. Therefore, in the spirit of the Chapman-Enskog procedure we write

$$f^*(\mathbf{V}^*,a^*)=f_0^*(\mathbf{V}^*)+a^*f_1^*(\mathbf{V}^*)+a^{*2}f_2^*(\mathbf{V}^*)$$
$$+a^{*3}f_3^*(\mathbf{V}^*)+\cdots \ . \qquad (3.9)$$

Here we have already taken into account that for $a^*=0$ the solution of Eq. (3.4) is given by Eq. (3.2). Substitution of Eqs. (3.7) and (3.9) into Eq. (3.4) yields

$$f_1^*(\mathbf{V}^*)=-2V_x^*V_y^*f_0^*(\mathbf{V}^*) \ , \qquad (3.10)$$

$$f_2^*(\mathbf{V}^*)=[1-\frac{2}{3}V^{*2}-2V_y^{*2}(1-2V_x^{*2})]f_0^*(\mathbf{V}^*) \ , \qquad (3.11)$$

$$f_3^*(\mathbf{V}^*)=4V_x^*V_y^*[V_y^{*2}(3-2V_x^2)+\frac{2}{3}V^{*2}$$
$$-\frac{1}{3}(5+\alpha)]f_0^*(\mathbf{V}^*) \ . \qquad (3.12)$$

We notice that the value of α only appears after the second-order correction in a^* to the local equilibrium distribution. Once the expansion of f^* is known it is a matter of simple algebra to derive the corresponding expansion for h^* defined in Eq. (2.12). The result is

$$h^*=h_0^*+a^{*2}h_2^*+a^{*4}h_4^*+\cdots \ , \qquad (3.13)$$

with

$$h_0^*=-\frac{3}{2}-\frac{3}{2}\ln\pi \ , \qquad (3.14)$$

$$h_2^*=\frac{1}{2} \ , \qquad (3.15)$$

$$h_4^*=-\frac{1}{4}+\frac{2}{3}\alpha \ . \qquad (3.16)$$

Upon deriving the above expressions use has been made of the properties

$$\int d\mathbf{V}^*f_k^*=0$$

and

$$\int d\mathbf{V}^*f_k^*\ln f_0^*=0 \qquad (3.17)$$

for $k\geq 1$, which follow directly from the normalization of f^* and the expression for f_0^*. The fact that only even powers of a^* are present is a consequence of the symmetry of the problem that implies

$$f^*(V_x^*,V_y^*,V_z^*;a^*)=f^*(-V_x^*,V_y^*,V_z^*;-a^*)$$
$$=f^*(V_x^*,-V_y^*,V_z^*;-a^*) \ . \qquad (3.18)$$

Taking into account that

$$\frac{\partial h^*}{\partial T_k}=\frac{\partial a^*}{\partial T_k}\frac{\partial h^*}{\partial a^*}=-\alpha\frac{a^*}{T_k}\frac{\partial h^*}{\partial a^*} \ , \qquad (3.19)$$

the expression of the thermodynamic temperature, Eq. (2.13), can be rewritten as

$$T_{\text{th}}(a^*)=T_K\left[1+\frac{2}{3}\alpha a^*\frac{\partial h^*}{\partial a^*}\right]^{-1} \ , \qquad (3.20)$$

and substitution of Eqs. (3.13)–(3.16) gives

$$T_{\text{th}}(a^*)=T_kF(a^*) \ , \qquad (3.21)$$

where

$$F(a^*)=1-\frac{2}{3}\alpha a^{*2}+\frac{2}{3}(1-2\alpha)\alpha a^{*4}+\cdots \ . \qquad (3.22)$$

For $\alpha=0$ (Maxwell molecules) it is $F=1$, and one recovers the result found in the previous section for the BE. Although the expansion in Eq. (3.22) is only asymptotic, it clearly shows that for arbitrary interaction potentials there are discrepancies between the kinetic and thermodynamic definitions of temperature. The pressures are studied in a similar way. We have

$$\frac{\partial h^*}{\partial n}=-\frac{a^*}{n}\frac{\partial h^*}{\partial a^*} \ , \qquad (3.23)$$

and therefore Eq. (2.14) reads

$$p_{\text{th}}(a^*)=p_k\frac{1-a^*\partial h^*/\partial a^*}{1+\frac{2}{3}\alpha a^*\partial h^*/\partial a^*} \ . \qquad (3.24)$$

The first remark is that, even for Maxwell molecules, p_{th} is different from the kinetic pressure $p_k = nk_B T_k$. Using the expansion given by Eq. (3.13) we get

$$p_{th}(a^*) = p_k M(a^*) , \tag{3.25}$$

with

$$M(a^*) = 1 - (1 + \tfrac{2}{3}\alpha)a^{*2} + (1 - 2\alpha)(1 + \tfrac{2}{3}\alpha)a^{*4} + \cdots . \tag{3.26}$$

Applying Eq. (2.18) we find for the rate of change of the Boltzmann entropy density

$$\frac{\partial s}{\partial t} = \tfrac{3}{2}k_B \frac{d(\ln T_k)}{dt} G(a^*) , \tag{3.27}$$

$$\begin{aligned} G(a^*) &= [F(a^*)]^{-1} \\ &= 1 + \tfrac{2}{3}\alpha a^{*2} - (\tfrac{2}{3} - \tfrac{16}{9}\alpha)\alpha a^{*4} + \cdots . \end{aligned} \tag{3.28}$$

Therefore, the local equilibrium assumption for the entropy change is not verified for power-law interaction potentials other than the Maxwell potential. As pointed out before, this is a direct consequence of the difference between T_{th} and T_k. Finally, the parameter r_{th}, defined in Eq. (2.4), becomes

$$r_{th} = \frac{k_B T_{th}}{\zeta}\frac{\partial h^*}{\partial a^*} = \frac{k_B T_k}{\zeta}a^* R(a^*) , \tag{3.29}$$

where

$$R(a^*) = \frac{F(a^*) - M(a^*)}{a^{*2}} = 1 - (1 - 2\alpha)a^{*2} + \cdots . \tag{3.30}$$

The series expansions obtained in this section show qualitatively the influence of both the potential parameter α and the shear rate a^* on T_{th}, p_{th}, and r_{th}. Of course, a more careful analysis would be needed in order to evaluate $F(a^*)$ and $M(a^*)$ beyond the limit of small shear rates.

IV. STATIONARY FLOW

The USF is not a stationary state due to the increase in energy associated with viscous heating. In order to get an isoenergetic shear flow, external drag forces must be added to extract energy uniformly from the gas [17]. More precisely, a homogeneous force F proportional to the peculiar velocity $\mathbf{V}$ of each particle is introduced:

$$F = -m\gamma\mathbf{V} . \tag{4.1}$$

The BGK equation for the USF including this nonconservative force is

$$\begin{aligned} \frac{\partial f^*}{\partial t} - \frac{1}{2}\frac{d(\ln T_k)}{dt}\frac{\partial}{\partial \mathbf{V}^*}\cdot(\mathbf{V}^* f) - aV_y^*\frac{\partial}{\partial V_x^*}f^* \\ - \gamma\frac{\partial}{\partial \mathbf{V}^*}\cdot(\mathbf{V}^* f) = -\zeta(f^* - f_0^*) . \end{aligned} \tag{4.2}$$

The parameter γ is determined from the condition that the internal energy of the system remains constant. This leads to

$$\gamma = -\frac{aP_{xy}}{3nk_B T_k} . \tag{4.3}$$

It can be shown [18] that for any arbitrary initial distribution $f^*(\mathbf{V}^*, 0)$, the solution of Eq. (4.2) approaches a stationary form $f_s^*(\mathbf{V}^*)$ that obeys Eq. (3.8). Thus, the reduced distribution function with thermostat force for arbitrary interaction law is the same as that for Maxwell molecules without a thermostat when both are written in terms of the reduced quantities $\mathbf{V}^*$ and a^*. This is a peculiar property of the BGK equation, and it is not held by the BE [13].

By making $\alpha = 0$ in Eqs. (3.13)–(3.16) we now have

$$h_s^* = -\tfrac{3}{2} - \tfrac{3}{2}\ln\pi + \tfrac{1}{2}a^{*2} - \tfrac{1}{4}a^{*4} + \cdots . \tag{4.4}$$

Applying the same procedure as in the previous section, Eqs. (3.20) and (3.24), one gets

$$T_{th} = T_k F_s(a^*) , \tag{4.5}$$

with

$$F_s(a^*) = 1 - \tfrac{2}{3}\alpha a^{*2} + \tfrac{2}{3}(1 + \tfrac{2}{3})\alpha)\alpha a^{*4} + \cdots \tag{4.6}$$

and

$$p_{th} = p_k M_s(a^*) , \tag{4.7}$$

with

$$M_s(a^*) = 1 - (1 + \tfrac{2}{3}\alpha)a^{*2} + (1 + \tfrac{2}{3}\alpha)^2 a^{*4} + \cdots . \tag{4.8}$$

Also, Eq. (3.29) now becomes

$$r_{th} = \frac{k_B T_k}{\zeta}a^* R_s(a^*) , \tag{4.9}$$

with

$$R_s(a^*) = 1 - (1 + \tfrac{2}{3}\alpha)a^{*2} + \cdots . \tag{4.10}$$

The stationary distribution function given by Eq. (4.4) is analytic at $a^* = 0$ [15] and, consequently, all the above series are convergent. Nevertheless, their radius of convergence is not known, although it is presumably the same as that for $\eta^*(a^*)$, namely $|a^*| = \sqrt{2}/3$.

For $\alpha = 0$ (Maxwell molecules) it is $F_s = F = 1$, $M_s(a^*) = M(a^*)$, and $R_s(a^*) = R(a^*)$, i.e., the relationship between the thermodynamic and the kinetic quantities is not affected by the drag force. For any other interaction potential, the relations are different with and without thermostat forces. This is a manifestation of the non-neutral role they play [13].

Although the solution $f_s^*(\mathbf{V}^*)$ of the BGK equation is known for arbitrary shear rates [15], an explicit expression of the corresponding function $h_s^*(a^*)$ does not seem feasible. Nevertheless, we can gain insight into its main qualitative features by using information theory (or the maximum-entropy method [19]) to get a lower estimate. More specifically, we seek the distribution function $f_{s,\mathrm{IT}}^*$ that minimizes the functional h_s^*, subject to the constrain of reproducing the actual pressure tensor. A simple calculation yields
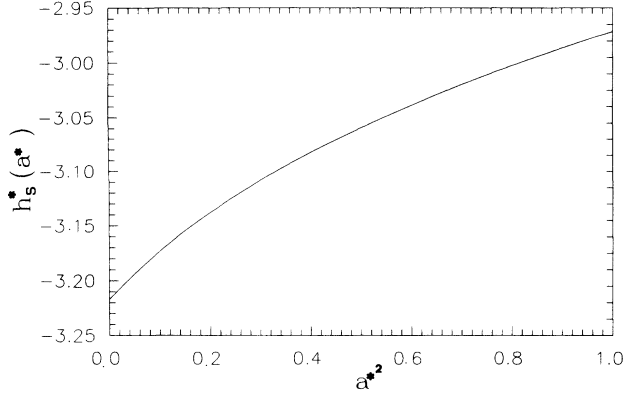
FIG. 1. Reduced entropy function of a gas under stationary uniform shear flow according to information theory by using the results obtained from the BGK equation for the pressure tensor.

$$f^*_{s,\mathrm{IT}}(\mathbf{V}^*) = \pi^{-3/2}(\det P^*_{ij})^{-1/2}$$

$$\times \exp[-(P^{*-1})_{ij} V^*_i V^*_j] \ , \qquad (4.11)$$

$$h^*_{s,\mathrm{IT}}(a^*) = -\tfrac{3}{2} - \tfrac{3}{2}\ln\pi - \tfrac{1}{2}\ln(\det P^*_{ij}) \ , \qquad (4.12)$$

where $P^*_{ij} = P_{ij}/p_k$ is the reduced-pressure tensor. Its determinant is

$$\det P^*_{ij} = \frac{1+3\gamma^*}{(1+2\gamma^*)^3} \ , \qquad (4.13)$$

with γ^* given below Eq. (3.8). The function $h^*_{s,\mathrm{IT}}(a^*)$ is exact up to order a^{*2}, but the coefficient of a^{*4} in the power-series expansion is $-\tfrac{3}{4}$ rather than the exact value $-\tfrac{1}{4}$. Figure 1 shows $h^*_{s,\mathrm{IT}}(a^*)$ in the range $0 \le a^* \le 1$. The curve representing the actual function $h^*_s(a^*)$ would lie above the one plotted in the figure. From $h^*_{s,\mathrm{IT}}(a^*)$ one can get decent estimates for F^*_s, M^*_s, and R^*_s. These functions are plotted in Fig. 2 for hard spheres ($\alpha=\tfrac{1}{2}$). We observe that p_{th} decreases as the shear rate increases more rapidly than T_{th} does. Due to the a^* factor in Eq.
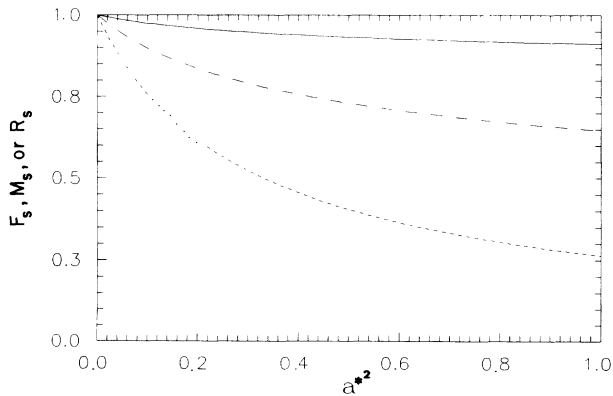

FIG. 2. Information theory estimates of $F_s(a^*)$ (solid line), $M_s(a^*)$ (dashed line), and $R_s(a^*)$ (dotted line) for a gas of hard spheres.

(3.29), the fact that R^*_s monotonically decreases does not mean that so does r_{th}. In fact, information theory shows that r_{th} reaches a maximum at $a^* \simeq 0.79$, decreasing monotonically thereafter.

V. COMMENTS AND DISCUSSION

The Boltzmann definition of entropy seems to be one of the most sensible choices for a dilute gas out of equilibrium. Thermodynamic temperature and pressure can then be defined in terms of the Boltzmann entropy by extending the equilibrium relations. On the other hand, a kinetic temperature is defined as proportional to the internal energy, and a kinetic pressure, describing the internal forces in the fluid, is defined from the trace of the pressure tensor. The results in this paper show that the relationship between thermodynamic quantities, defined in terms of the Boltzmann entropy, and local equilibrium or kinetic quantities is not simple in far-from-equilibrium situations. The complexity is associated with the intricate dependence of the distribution function on the reduced shear rate. Besides, the situation does not improve when artificial forces are introduced to create an ideal stationary state. On the contrary, one has to cope with the added problem of the relationship between quantities measured in systems with and without a thermostat.

Evans [12] performed a molecular-dynamics simulation of a system of soft disks subject to an isoenergetic shear flow. The density of the system was small and he computed the Boltzmann entropy at several shear rates, densities, and energies. Using these data, he obtained values for the thermodynamic temperature and pressure, which he compared with the corresponding kinetic values. The qualitative behavior found in Ref. [12] is quite similar to the one obtained here. In particular, T_{th} and p_{th} were smaller than T_k and p_k, respectively, the discrepancy being bigger in the case of the pressure. Also, the entropy was found to decrease with the shear rate.

However, some qualitative differences must be mentioned. Within the accuracy of his data, Evans got a quasilinear dependence of the entropy density as a function of the shear rate, which apparently extended to the limit of the shear rate going to zero, while the analysis carried out here shows a quadratic dependence in that limit. As pointed out by Evans himself, his simulation values of the shear rate are probably beyond the region where the quadratic behavior is dominant. This fact explains also Evans's observation that r_{th} decreases with the shear rate. Evans also conjectured that the thermodynamic pressure is equal to the minimum eigenvalue of the pressure tensor. On the other hand, our analysis, based in the BGK equation, shows that, in the thermostatted case, the minimum eigenvalue is $p_3 = p_k(1-|a^*|+\tfrac{1}{3}a^{*2}+\cdots)$, which is clearly different from Eqs. (4.7) and (4.8).

It must be stressed that the points addressed in this paper are not merely formal. The meaning of many of the calorimetric measures carried out far from equilibrium is not clear, since they are based on equilibrium relations. It is also important to realize that a certain degree of ambiguity could exist in the definition of nonequilibrium

thermodynamic quantities. This ambiguity is related to several possible choices for the nonequilibrium parameters (such as gradients, external fields, etc.). In the context of the uniform shear flow, if we had chosen to define T_{th} and p_{th} by Eq. (2.3), except that a^* is kept constant instead of a, then we would have obtained $T_{th} = T_k$, $p_{th} = p_k$.

There are some properties that one would like the entropy to have. For instance, one could expect that nonequilibrium stationary states correspond to a maximum of the entropy when the appropriate boundary conditions are imposed. Also, it should be interesting if the entropy would increase uniformly until reaching stationarity. This would be a proof of the stability of the stationary state. We have not been able to prove any of the above properties for the Boltzmann entropy of a dilute gas under uniform shear flow, even in the BGK approximation.

Given the peculiarities of the nonequilibrium states considered here, especially the ideal stationary one, we plan to present in the near future a similar analysis for the steady heat flow.

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