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LETTER TO THE EDITOR

Alternation of derivatives is no criterion for choosing an entropy function

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Abstract. Of the infinity of state functions of a gas given by integrating functionals of the one-particle distribution function over velocity space, it has been conjectured that only one has the property that all successive time derivatives alternate in sign at all times during free thermal relaxation. A function possessing this property in a certain interval is said to be completely monotonic in that interval. Monotonicity of only the first time derivative is known as an H theorem, and is necessary for a state function to be identifiable as entropy. The conjecture continues with a sufficient condition for this identification that the one completely monotonic state function be taken as the entropy. These conjectures are shown to be false: by choosing the initial distribution function and the differential collision cross-section appropriately in velocity space, the second derivative of *any* state function which satisfies an H theorem (and decreases) can be shown to change sign during the relaxation. The rate of decrease of such a state function under these circumstances will initially increase, but then level off as thermal equilibrium is approached: the state function evolves with an inflection. Not only must the criterion therefore be invalid, but worse, it cannot serve to distinguish between the various decreasing state functions and pick one out uniquely.

Since the thermodynamic level of description of a gas is less detailed than the kinetic description, it should be capable of derivation from kinetic theory. All macroscopic state variables Φ must therefore be expressible as integrals over velocity space of some functional ϕ of the one-particle distribution function f:

$$\Phi(\boldsymbol{r}, t) = \iiint \phi[\boldsymbol{v}; f(\boldsymbol{r}, \boldsymbol{v}, t)]\, \mathrm{d}^3\boldsymbol{v}. \tag{1}$$

The Boltzmann equation for the evolution of f is

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{a} \cdot \frac{\partial f}{\partial \boldsymbol{v}} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \tag{2}$$

where $\boldsymbol{a}$ is the external force field and the RHS models the effects of interparticle collisions. In the absence of spatial inhomogeneity and external forces it follows that

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \iiint \frac{\partial \phi}{\partial f}\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \mathrm{d}^3\boldsymbol{v}. \tag{3}$$

Many collision models satisfy an 'H theorem': for an appropriate choice of ϕ, expression (3) is negative, and the corresponding state function Φ always decreases during free thermal relaxation. This property is necessary for identification of such

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a state function as entropy, which always evolves monotonically. McKean (1966) conjectured that the condition can be made sufficient by requiring that the state function to be identified as entropy must be completely monotonic during free relaxation:

$$(-\mathrm{d}/\mathrm{d}t)^n \Phi|_{a=0,\partial/\partial r=0} \geqslant 0 \qquad \forall n \geqslant 0. \tag{4}$$

By defining state function densities in real space and integrating them over this space, (4) could be generalised to the spatially inhomogeneous case; however, we restrict ourselves to the simpler, homogeneous situation.

This approach to choosing an entropy function suffers from several disadvantages: condition (4) might not be satisfied for any choice of Φ, or alternatively it might fail to pick out one state function uniquely. Non-uniqueness has been found in a discrete-velocity collision model (Maass 1970). The meaning of (4) is far from being physically transparent for higher values of n. More importantly, it does not seem reasonable that the prescription for identifying the entropy should be limited to the force-free case (even though the entropy itself then remains defined in the presence of forces).

In this letter we show that (4) is untenable as a criterion for choosing entropy; a combination of collision cross-section and initial distribution function can always be chosen such that (4) breaks down at $n = 2$ for *all* monotonically decreasing state functions. Thus not only is (4) violated, but it cannot serve to distinguish one function uniquely. The value $n = 2$ is the lowest possible for which breakdown can occur, since by hypothesis we are only interested in those state functions which obey (4) for $n = 1$, and should our choice violate (4) at $n = 0$ and become negative, arbitrary multiples of the conserved moments of f can be added in to keep it positive.

We choose an initial velocity distribution function consisting of two opposing streams of particles, each with a narrow but finite range of velocities:

$$f(\boldsymbol{v}, t=0) = \tfrac{1}{2}N[\Delta_b^{(3)}(\boldsymbol{v} - \tfrac{1}{2}\boldsymbol{v}_0) + \Delta_b^{(3)}(\boldsymbol{v} + \tfrac{1}{2}\boldsymbol{v}_0)] \tag{5}$$

where the function $\Delta_b^{(3)}(\boldsymbol{\xi})$ is non-negative and has unit integral over its vector argument $\boldsymbol{\xi}$; most of the contribution to this integral is from the region $\xi < b$. In the limit $b \to 0$, the function $\Delta^{(3)}$ therefore becomes the Dirac delta function in three dimensions. It is necessary for our purposes that the width parameter b be chosen much smaller than the stream velocity:

$$b \ll v_0. \tag{6}$$

Suppose now that the differential collision cross-section σ is very small for collision speeds less than b, and also in a region of width $2b$ around v_0 (figure 1); the dependence

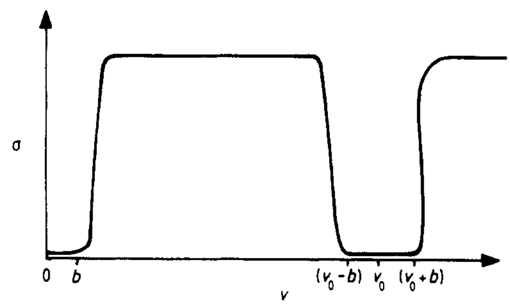

Figure 1. Velocity dependence of the collision cross-section.

of σ on scattering angle is not relevant to the argument. Then all state functions Φ which satisfy an H theorem (and decrease) can only decrease very slowly at first. This is because collisions are only taking place in the regions of velocity space in which the cross-section is small: collisions between particles in the same stream occur in $v < b$, and collisions between particles from each stream occur in the region $(v_0 - b) < v < (v_0 + b)$. Progressively more and more particles will be scattered into those regions in which the cross-section is large; such particles have a greater effect on the evolution than those remaining in the regions where σ is small. Consequently the rate of decrease of the state function will rise. Eventually, as thermal equilibrium is approached, the state function Φ will tail off to a constant value (figure 2). It is apparent that the evolution of Φ includes an inflection. Thus not only is (4) violated (at $n = 2$) but since the argument holds for all decreasing state functions, (4) cannot be used to single any one of them out. We conclude that these criteria are not useful in choosing an entropy function.

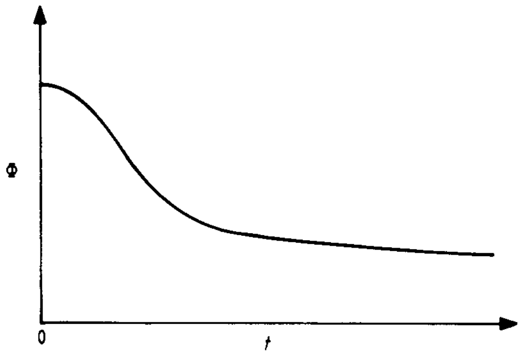

Figure 2. Time evolution of the state function Φ.

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