Maximum of the Local Entropy Production Becomes Minimal in Stationary Processes

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In this paper we propose a new principle for stationary thermodynamic processes: The maximum of the local entropy production becomes minimal in stationary processes. In order to show the usefulness of the principle, we consider one-dimensional stationary heat transfer in monatomic gases. Here we solve extended moment schemes that follow from the Boltzmann equation. Such schemes require boundary conditions for all moments under consideration, and these are constructed by means of the new principle. Moreover, we show that the minimum principle for the *global* entropy production does not lead to good results in this case. [S0031-9007(98)06306-6]

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It is well known that the laws of Navier-Stokes and Fourier are not able to properly describe processes in gases with large Knudsen numbers. One successful attempt to describe these rarefied gases is Grad's moment method which has inspired the development of the growing field of extended thermodynamics [1–9]. Despite their great differences in the formal structure, all theories of extended thermodynamics have one common feature. In contrast to classical thermodynamics of irreversible processes [10], the state space is not spanned by the fields of density ϱ, velocity v_i, and temperature T alone. Indeed, in the theory of moments and in extended thermodynamics the state space is enlarged by nonequilibrium quantities, e.g., the pressure deviator $p_{\langle ij\rangle}$, the heat flux q_i, and other quantities, the so-called moments, which do not have an intuitive physical interpretation.

Moment methods and extended thermodynamics derive first order partial differential equations in space-time for the variables that span the state space. Thus, one will need a set of initial and boundary conditions in order to formulate and solve a proper initial boundary value problem. Until now there has been no answer to the question of how initial and boundary conditions for the higher moments—those without intuitive interpretation—may be formulated. Initial data does not cause a big problem, since one may often consider processes which start from equilibrium. But boundary conditions for higher moments present a problem. For this reason extended thermodynamics has so far dealt with initial value problems. The only exception is the calculation of shock waves, where thermodynamic equilibrium prevails far before and behind the shock, and therefore the values of the moments are known at this point [7].

Let us consider the one-dimensional stationary heat transfer problem between rigid walls at rest (see Fig. 1). If the mass or, alternatively, the pressure is fixed, we can successfully control only four parameters: the temperatures T_0 and T_L at the walls and the velocities $v_0 = v_L = 0$ of the walls. By the physics of the problem it is impossible to control other quantities. The heat flux must be adjusted so as to keep the temperatures constant. Thus the heat flux is not an independent quantity in the stationary heat transfer experiment.

Mathematics, however, requires additional boundary conditions for the equations of extended thermodynamics. Since we have control of four quantities only, we must conclude that the other moments will adjust themselves. In other words, there must be a physical principle that identifies the boundary values of the moments.

We propose that the boundary conditions of moments have to be chosen so as to make the maximum over all positions of the local entropy production rate $\Sigma(x)$ minimal,

$$\max_{x\in[0,L]} \Sigma(x) \longrightarrow \min\,. \tag{1}$$

In order to explain this statement, we recall that for $\Sigma(x) = 0$ the gas is in equilibrium at every point x. Since we prescribe different temperatures T_0, T_L, the gas will be in nonequilibrium in the heat transfer experiment, and we may calculate the local entropy production rate $\Sigma(x)$. The value of $\Sigma(x)$ is a measure for the local tendency towards equilibrium which grows with $\Sigma(x)$. The significance of our statement (1) is that the gas "wants" to be as close to equilibrium as possible in *every point*. This is guaranteed in an overall manner by our minimax principle.

The local statement (1) is essentially different from the principle of minimum *global* entropy production,

$$\int_V \Sigma(\mathbf{x})dV \longrightarrow \min\,, \tag{2}$$

where V denotes the volume of the body. This principle

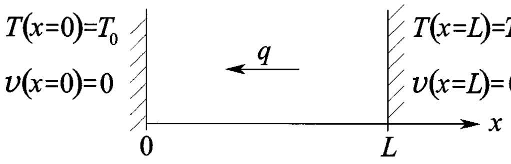

FIG. 1. The stationary heat transfer experiment between rigid walls.

was introduced by Prigogine in the context of linear irreversible thermodynamics [11,12].

The application of the principle of global minimum entropy production for the determination of additional boundary conditions leads to solutions where the gas is in equilibrium—with constant temperature T_L—at most points of the interval $[0, L]$ and is not in equilibrium—with steep temperature gradient—only in a small interval $[0, a]$, $a \ll L$ (see the discussion of Figs. 2 and 3 below). This behavior where nonequilibrium would prevail only on the small interval a with a big value of the local entropy production rate is not observed in experiments and is forbidden by our new principle (1).

We emphasize that the new principle—in contrast to the principle of global minimum entropy production—is not restricted to linear theories of thermodynamics. Moreover, we use the principle in order to obtain information about the boundary conditions of the higher moments only. We do not use the principle to determine constitutive equations for the higher moments; this is already done by the constitutive theory of extended thermodynamics or by the moment method before the principle comes into play. Thus the field equations are already known before the principle is applied; the principle merely helps us to *solve* the field equations.

The new principle may be used in all stationary thermodynamic processes of arbitrary dimension. This and the extension to instationary processes will be discussed in future work.

It is well known that problems with large Knudsen numbers require many moments for a successful treatment [2,6]. Here we shall consider nonlinear extended thermodynamics of 14 fields. This requires only *one* additional boundary condition in the heat transfer experiment. A forthcoming paper will deal with extended thermodynamics of many moments which require *more* boundary conditions.

Extended thermodynamics can be based on the kinetic theory of monatomic ideal gases. The set of variables is defined by moments of the distribution function. The equations of transfer for those moments are derived from the Boltzmann equation and the closure problem is solved by maximizing the entropy [2,5,13].

The first 13 variables have an easy physical interpretation. They are the density ϱ, velocity v_i, temperature T, pressure deviator $p_{\langle ij\rangle}$, and heat flux q_i. The angular brackets denote the symmetric traceless part. Here, the linearized equations that follow from the entropy maximizations are equivalent to Grad's 13-moment theory [1,2]. If we add to the first 13 variables the nonequilibrium part Δ of the full trace of the fourth moment, we get a system with 14 moments. We consider a steady state problem in which all variables depend only on one space dimension x. With $\sigma = p_{\langle 11\rangle}$ and $q = q_1$, we have 6 field equations, viz.,

$$\frac{d}{dx}\{\varrho v\} = 0\,, \tag{3}$$

$$\frac{d}{dx}\{\varrho v^2 + \varrho RT + \sigma\} = 0\,, \tag{4}$$

$$\frac{d}{dx}\{\varrho v^3 + 5\varrho RTv + 2\sigma v + 2q\} = 0\,, \tag{5}$$

$$\frac{d}{dx}\left\{\frac{2}{3}\varrho v^3 + \left(\frac{4}{3}\varrho RT + \frac{7}{3}\sigma\right)v + \frac{8}{15}q\right\} = -\alpha\varrho\sigma\,, \tag{6}$$

$$\frac{d}{dx}\left\{\frac{1}{2}\varrho v^4 + \left(4\varrho RT + \frac{5}{2}\sigma\right)v^2 + \left(\frac{16}{5}q\right)v + \frac{5}{2}\varrho R^2T^2 + \frac{7}{2}RT\sigma + \frac{1}{6}\Delta\right\} = -\alpha\varrho\left(\sigma v + \frac{2}{3}q\right), \tag{7}$$

$$\frac{d}{dx}\left\{\varrho v^5 + (14\varrho RT + 8\sigma)v^3 + \left(\frac{84}{5}q\right)v^2 + \left(35\varrho R^2T^2 + 28RT\sigma + \frac{7}{3}\Delta\right)v + 28RTq\right\} = -\alpha\varrho\left(4\sigma v^2 + \frac{16}{3}qv + \frac{2}{3}\Delta\right). \tag{8}$$

R denotes the gas constant and α is a constant that follows by calculation of the collision production for Maxwell molecules. The first three equations are the equations of balance for the conserved quantities mass, momentum, and energy.

We consider the heat transfer problem between two rigid walls at $x = 0$ and $x = L$ with the boundary conditions

$$T(0) = T_0\,, \qquad T(L) = T_L\,, \qquad v(0) = 0\,, \qquad v(L) = 0\,. \tag{9}$$

Note that the system (3)–(8) requires six boundary conditions. Thus, we need two more boundary conditions in addition to the list (9). One may choose any two quantities for the additional boundary conditions. In the following we shall prescribe the pressure p at $x = 0$ and the heat flux q—a choice which tuns out to be most convenient.

From the boundary conditions $(9)_{3,4}$ and the mass balance (3) it follows that the velocity is zero, $v = 0$. Therefore the energy balance (5) requires a constant heat flux, $q = \text{const}$. The balance of the pressure tensor (6) reduces to $\sigma = 0$ and we conclude from the balance of momentum (4) that the pressure $p = \varrho RT$ is a constant, $p = \text{const}$. In order to simplify the equations further, we introduce dimensionless quantities by

$$\hat{x} = \frac{x}{L}\,, \qquad \hat{T} = \frac{T}{T_0}\,, \qquad \hat{\Delta} = \frac{\Delta}{pRT_0}\,,$$

$$\hat{\varrho} = \frac{\varrho RT_0}{p} = \frac{1}{\hat{T}}\,, \qquad \hat{q} = \frac{q}{p\sqrt{RT_0}}\,, \qquad B = \frac{\sqrt{RT_0}^{\,3}}{\alpha L p}\,.$$

B is the Knudsen number for the heat transfer problem. There remains the following simple system of ordinary nonlinear differential equations:

$$\frac{5}{2}\frac{d\hat{T}}{d\hat{x}} + \frac{1}{6}\frac{d\hat{\Delta}}{d\hat{x}} = -\frac{2}{3B}\frac{\hat{q}}{\hat{T}}, \qquad \frac{d\hat{T}}{d\hat{x}} = -\frac{1}{42B}\frac{\hat{\Delta}}{\hat{q}\hat{T}} \tag{10}$$

with the boundary conditions

$$\hat{T}(0) = 1, \qquad \hat{T}(L) = \hat{T}_L\,. \tag{11}$$

Note that the heat flux $\hat{q} = \text{const}$ enters these equations as a parameter while the constant pressure p determines the Knudsen number. The determination of $\hat{q}$ requires an additional boundary condition. The maximization procedure [2,6,13] yields an explicit phase density for nonequilibrium from which we have calculated the dimensionless entropy production as (with $\sigma = 0$)

$$\hat{\Sigma} = \frac{4}{15B}\frac{\hat{q}^2}{\hat{T}^3} + \frac{1}{180B}\frac{\hat{\Delta}^2}{\hat{T}^4}\,. \tag{12}$$

Thus the phase density is quadratic in the nonequilibrium quantities $\hat{q}$ and $\hat{\Delta}$. It is only for small Knudsen numbers, $B \ll 1$, that the equations (10) reduce to Fourier's law for Maxwellian molecules, viz.,

$$\hat{q}_F = -\frac{15}{4}B\hat{T}\frac{d\hat{T}}{d\hat{x}}\,. \tag{13}$$

Because of their nonlinearity, the equations (10) must be solved numerically. We choose

$$\hat{T}(L) = \hat{T}_L = 1.1$$

and consider the case of a dense gas with Knudsen number $B = 0.05$ and the case of a rarefied gas with $B = 1$.

The application of the minimax principle for the local entropy production proceeds as follows: The numerical solution of (10) with a given value of $\hat{q}$ provides $\hat{T} = \hat{T}(\hat{x}, \hat{q})$, $\hat{\Delta} = \hat{\Delta}(\hat{x}, \hat{q})$ and, by (12), the local entropy production $\hat{\Sigma} = \hat{\Sigma}(\hat{x}, \hat{q})$. The maximum of this function is a function of $\hat{q}$ alone, viz., $\hat{\Sigma}_{\max}(\hat{q}) = \max_{x\in[0,1]} \hat{\Sigma}(\hat{x}, \hat{q})$. The minimum of $\hat{\Sigma}_{\max}(\hat{q})$ determines the heat flux $\hat{q}_{\min}$ as the abscissa of the minimum of $\hat{\Sigma}_{\max}(\hat{q})$.

We consider $\hat{q}_{\min}$ to be the correct choice for the heat flux in the description of the heat transfer problem by means of the 14-moment system.

Thus, in order to find the correct minimum $\hat{q}_{\min}$, one must solve the differential equations (10) for various values of $\hat{q}$. This will make the method quite cumbersome in theories with many moments and even more so in two- or three-dimensional problems, where the boundary conditions are functions rather than numbers as in the one-dimensional case. Here, with only one additional boundary condition for $\hat{q}$, the method requires little numerical efforts.

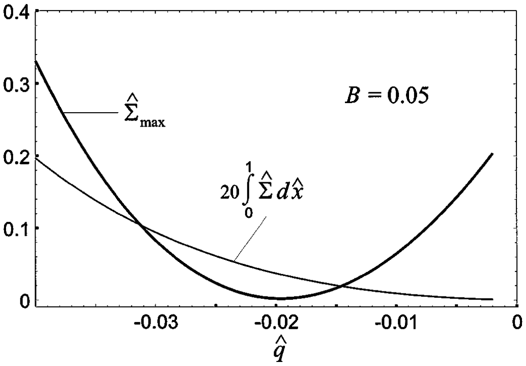

FIG. 2. The local maximum entropy production rate $\hat{\Sigma}_{\max}(\hat{q})$ (bold line) and the global entropy production rate $\int \hat{\Sigma}(\hat{x}, \hat{q})dx$ (thin line) as a function of heat flux $\hat{q}$ for $B = 0.05$.

We start with the discussion of the case with Knudsen number $B = 0.05$. The bold line in Fig. 2 shows $\hat{\Sigma}_{\max}(\hat{q})$ as a function of $\hat{q}$ with only one minimum. The numerical calculation yields $\hat{q}_{\min} = -0.019593$ and this is—due to the small value of B—very close to the solution of (13) which is easily determined as $\hat{q}_F = -0.019688$. The corresponding temperature function $\hat{T}(\hat{x}, \hat{q}_{\min})$ is shown in Fig. 3 by the bold line. The temperature is almost a straight line due to the small temperature difference.

It is instructive to study the space function of the temperature for other values of $\hat{q}$. The thin lines in Fig. 3 represent the temperature function for $\hat{q} = -0.03$, $\hat{q} = -0.01$, and $\hat{q} = -0.002$. If the equations (10) are solved with $\hat{q} = -0.03$, the temperature becomes nonmonotone. Starting at $\hat{x} = 0$ with $\hat{T} = 1$ the temperature decreases first, reaches a minimum, and then increases to $\hat{T} = 1.1$ at the right boundary. This behavior will never be observed, and, of course, it contradicts our new principle.

The case where $\hat{q} = -0.01$ is also interesting. The temperature increases very fast to $\hat{T} \simeq 1.05$ and increases linearly to $\hat{T} = 1.1$, the prescribed temperature at $x = L$. This corresponds to a very small overall entropy production rate $\int \hat{\Sigma}(\hat{x}, \hat{q})dx$. Indeed, the thin line in Fig. 2 shows $\int \hat{\Sigma}(\hat{x}, \hat{q})dx$ as a function of $\hat{q}$ and the overall entropy production becomes smaller, if $\hat{q}$ tends to zero.

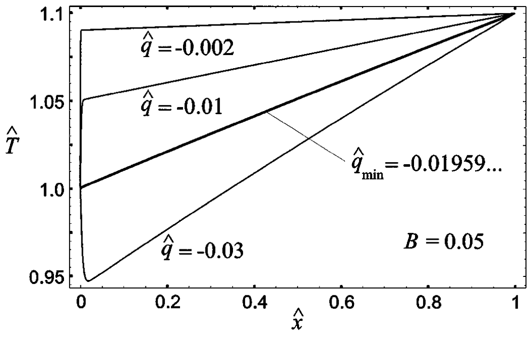

FIG. 3. $\hat{T}(\hat{x}, \hat{q})$ for $\hat{q}_{\min} = -0.019593$ (bold line) and for $\hat{q} = -0.002$, $\hat{q} = -0.01$, and $\hat{q} = -0.03$ (thin lines); $B = 0.05$.

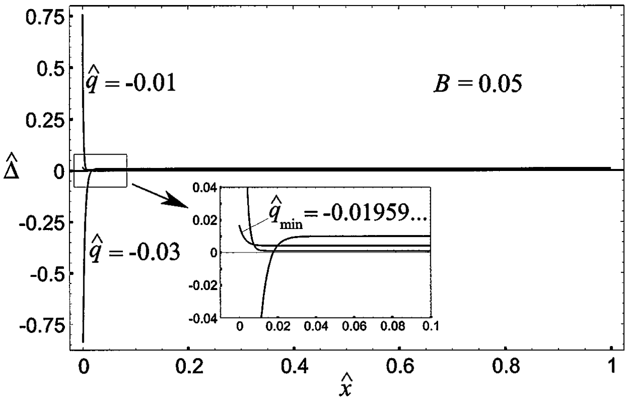

FIG. 4. $\hat{\Delta}(\hat{x},\hat{q})$ for $\hat{q}_{\min} = -0.019593$, $\hat{q} = -0.01$, and $\hat{q} = -0.03$ ($B = 0.05$).

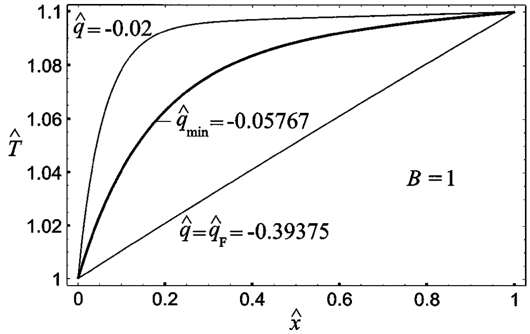

FIG. 5. $\hat{T}(\hat{x},\hat{q})$ for $\hat{q}_{\min}$ (bold line) and for various values of $\hat{q}$ (thin lines); $B = 1$.

Because of numerical instability we could not solve the equations (10) for $|\hat{q}| < 0.002$, but one may extrapolate the thin curve of Fig. 2 to see that the global entropy production becomes minimal at $\hat{q} = 0$. Because of the global principle (2), we should choose this value of $\hat{q}$. Since the temperature is already almost constant for $\hat{q} = -0.002$, we expect to have $\hat{T}(\hat{x}) = 1.1 = \text{const}$ with a jump at $\hat{x} = 0$ in the limit $\hat{q} \to 0$. This is unphysical and we conclude that the application of the criterion (2) is not suitable in this context.

Figure 4 shows those curves of $\hat{\Delta}(\hat{x})$ which correspond to the temperature curves of Fig. 3.

In all cases, $\hat{\Delta}$ has a peak at $\hat{x} = 0$ and is constant in almost all space points. This constant value of $\hat{\Delta}$ decreases if $\hat{q}$ goes to 0. In the case $\hat{q} = 0$—corresponding to minimum global entropy production—we expect that $\hat{\Delta}$ has a large peak value at $\hat{x} = 0$, where the temperature gradient is steep and is zero elsewhere. Since we have $\hat{\Delta} = 0$ in local equilibrium, there is nonequilibrium only in the vicinity of $\hat{x} = 0$ and equilibrium—with $\hat{q} = 0$, $\hat{\Delta} = 0$, and $\hat{\Sigma} = 0$—at all other positions. One might say that the point $\hat{x} = 0$ bears all nonequilibrium of the process. On the other hand, we have a nonvanishing $\hat{\Delta}$ for $\hat{q}_{\min} = -0.019593$—here we have $\hat{\Sigma} \neq 0$ in all points, and one might say that all points share the nonequilibrium.

In the case with $B = 0.05$ the new minimax principle gives a value for $\hat{q}$ very close to the Fourier law. Now, however, we consider a large Knudsen number of $B = 1$. In this case, we expect different results from the Fourier law (13)—which gives $\hat{q}_F = -0.39375$—and the nonlinear 14-field case. We have performed the same procedure as above and found $\hat{q}_{\min} = -0.05767$, which is 6.8 *times* smaller than $\hat{q}_F$. Figure 5 shows $\hat{T}(\hat{x},\hat{q})$ for several values of $\hat{q}$; the curve for $\hat{q}_{\min}$ is drawn as a bold line. Although the temperature difference is small the temperature is not straight in this case. We do not want to overemphasize this result, since 14 moments will not suffice for a proper description of a rarefied gas. Indeed, in rarefied gases we expect coincidence with experimental data only in moment theories with a large number of moments (see [2,6]). A detailed examination of the moment method in stationary heat transfer of rarefied gases is planned for the future.

We have proposed a principle for the selection of boundary values in extended thermodynamics: The maximum of the local entropy production rate becomes minimal in stationary processes. We have exhibited the usefulness of the principle for extended thermodynamics of 14 moments. A paper on stationary heat transfer in extended thermodynamics with more moments is in preparation. We are confident that there are interesting applications for the principle in other fields and look forward to learning about these.

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