Maximum entropy production far from equilibrium: The example of strong shock waves

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The neglect of either mass, momentum, or energy conservation leaves one degree of freedom in the determination of the steady state behind stationary shock waves, the entropy production rate in the shock front becoming a function of this. In all three cases this function has an absolute maximum that is approached by the entropy production rate of real shock waves for a Mach number Mclose to 6 in the first case and asymptotically approached for $M \rightarrow \infty$ in the last two cases. These results are shown to hold true also when the shock waves are treated relativistically. The example of shock waves demonstrates that some systems far from equilibrium may be characterized by maximum entropy production similarly as certain systems close to equilibrium are characterized by minimum entropy production.

I. INTRODUCTION

The characterization of physical states by extremum properties is not only very useful physically and mathematically, but also especially appealing from the psychological point of view of understanding. Many physical laws can be formulated as extremum principles, and the characterization of thermodynamic equilibrium in closed systems by maximum entropy is one of the most fundamental and fruitful laws of physics. Under certain circumstances, open steady-state systems close to equilibrium can be characterized by extremum principles like minimum entropy production, minimum excess-entropy production, or otherwise (see, e.g., Refs. 1–4).

Stable steady states far from equilibrium are certainly distinguished from their time-dependent neighboring states, but no unique characterization is at hand. It was already noted in other investigations that the entropy production far from equilibrium may be far from minimum.^{5,6} In this paper, the entropy production rate in shock waves is investigated under this point of view, and it is shown that in a sense to be specified later it comes close to maximum if the shock waves represent states far from equilibrium. It should be pointed out that this maximum property of the entropy production rate is meant in a sense similar to the well-known minimum entropy production rate in certain systems close to equilibrium. It should not be confused with a local maximum entropy production principle formulated for systems close to equilibrium.⁴

Heat conduction in a rod is perhaps the most simple example demonstrating why certain systems can be characterized by minimum entropy production close to equilibrium. For the steady-state solution $T = T_0$ $+(T_1 - T_0)(x - x_0)/L$ of the heat conduction equation $\partial_t T = (\kappa/c\rho_0)\partial_{xx}T$ [where T(x) is the rod temperature at position x; $L = x_1 - x_0$, which represents the length of the rod; κ is the heat conductivity; c is the specific heat; ρ_0 is the density; A is the cross section of the rod], the entropy production rate

$$P = \kappa A \int_{x_0}^{x_1} \frac{(\partial_x T)^2}{T^2} dx$$
 (1)

becomes

$$P_{s} = \frac{\kappa A}{L} \frac{(T_{1} - T_{0})^{2}}{T_{0}T_{1}} , \qquad (2)$$

while its minimum is given by

$$\min P = \frac{\kappa A}{L} \ln \frac{T_1}{T_0}$$
(3)

whence

$$p \equiv \frac{P_s}{\min P} = \frac{(T_1/T_0 - 1)(1 - T_0/T_1)}{(\ln T_1/T_0)^2} .$$
 (4)

For large deviations from thermal equilibrium $T \equiv T_0$ (large values of T_1/T_0), P_s becomes appreciably larger than minP, and we even have $p \to \infty$ for $T_1/T_0 \to \infty$. Only for $T_1/T_0 - 1 = \epsilon \ll 1$ we get $p \approx 1 + \epsilon^2/12$, i.e., P and minP coincide up to second order in ϵ , which is the reason why close to equilibrium heat conduction can be characterized by minimum entropy production.

Obviously, (1) poses no upper limit on the entropy production, and from (2) one can conclude that this remains true even if one would impose monotonicity of the temperature profile as a side condition. This shows that the characterization of systems very far from equilibrium by maximum entropy production, which will be demonstrated for strong shock waves in this paper, is not a general property but, like minimum entropy production, is reserved to special systems.

II. FORMULATION OF THE SHOCK-WAVE PROBLEM

In the rest system of a stationary shock-wave mass, momentum and energy must be conserved, yielding the Rankine-Hugoniot equations

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$$p_1 + \rho_1 v_1^2 = p_2 + \rho_2 v_2^2 , \qquad (6)$$

$$\rho_1 v_1 \left[\frac{\gamma}{\gamma - 1} \frac{p_1}{\rho_1} + \frac{v_1^2}{2} \right] = \rho_2 v_2 \left[\frac{\gamma}{\gamma - 1} \frac{p_2}{\rho_2} + \frac{v_2^2}{2} \right]$$
(7)

(see, e.g., Ref. 7). Here, indices 1 and 2 denote the steady states in front of and behind the shock wave respectively; ρ is the density; v is the flow velocity; p is the pressure; and $\gamma = c_p / c_v$, which represents the ratio of specific heats. Defining

$$x = \rho_1 / \rho_2, \quad y = p_2 / p_1, \quad z = v_2 / v_1, \quad (8)$$

and employing the Mach number

$$M = v_1 / (\gamma p_1 / \rho_1)^{1/2} , \qquad (9)$$

we can rewrite (5)-(7) as

$$x = z , (10)$$

$$y = 1 + \gamma M^2 \left[1 - \frac{z^2}{x} \right] , \qquad (11)$$

$$y = \frac{1}{z} \left[1 + \frac{\gamma - 1}{2} M^2 \right] - \frac{\gamma - 1}{2} M^2 \frac{z^2}{x} .$$
 (12)

Equations (10)-(12) are solved by

$$x = z = \frac{2 + (\gamma - 1)M^2}{(1 + \gamma)M^2}, \quad y = 1 + \frac{2\gamma}{1 + \gamma}(M^2 - 1) .$$
(13)

The entropy production rate in the shock wave can easily be calculated from the entropy density per mass

$$s = c_v \ln \frac{p \rho^{-\gamma}}{p_1 \rho_1^{-\gamma}} + s_1 \tag{14}$$

 $(s_1$ is the entropy density in state ρ_1, p_1) and the shockwave data. During the time interval Δt , on side 1 where the flow enters the shock wave the mass $M_1 = \rho_1 v_1 F \Delta t$ (F being the cross section of the shock wave) is lost carrying the entropy

$$S_1 = M_1 s_1 = \rho_1 v_1 s_1 F \Delta t . (15)$$

On side 2 where the flow comes out of the shock front, the mass $M_2 = \rho_2 v_2 F \Delta t$ appears carrying the entropy

$$S_2 = M_2 s_2 = \rho_2 v_2 s_2 F \Delta t \quad . \tag{16}$$

From (15) and (16) we get the entropy production rate

$$P = \frac{S_2 - S_1}{\Delta t} = F(\rho_2 v_2 s_2 - \rho_1 v_1 s_1) .$$
 (17)

In the following, we shall consider the normalized entropy production rate

$$P^* = \frac{P}{c_v F \rho_1 v_1} . \tag{18}$$

From (8), (14), (17), and (18) one readily obtains

$$P^* = \left[\frac{z}{x} - 1\right] \frac{s_1}{c_v} + \frac{z}{x} \ln(x^{\gamma} y) .$$
(19)

In real shock waves where (13) holds, the normalized entropy production rate (19) becomes

$$P_{r}^{*}(M) = \ln M^{2} + \ln \frac{1 - \gamma + 2\gamma M^{2}}{(1 + \gamma)M^{2}} + \gamma \ln \frac{2 + (\gamma - 1)M^{2}}{(1 + \gamma)M^{2}} .$$
(20)

For large Mach numbers, we get

$$P_r^*|_{M\to\infty} = \ln M^2 . \tag{21}$$

We shall now omit one of the three conservation laws (5)-(7) or (10)-(12), respectively, first mass, then momentum, and last energy conservation, and denote the corresponding entropy production rate by P_m^* , P_i^* , and P_e^* , respectively. The remaining two conservation laws leave one of the three variables x, y, z, say z, undetermined, and we will therefore have

$$P_m^* = P_m^*(M,z) ,$$

etc. It turns out that $P_m^*(M,z)$, $P_i^*(M,z)$, and $P_e^*(M,z)$ all have an absolute maximum with respect to z for all given values of M. These maximum values will be denoted by

$$\hat{P}_{e}^{*}(M) = \max_{z} P_{e}^{*}(M,z) ,$$

etc., and compared with the entropy production rate (20) in a real shock wave.

III. SHOCK WAVES WITHOUT MASS CONSERVATION

The entropy constant s_1 enters the entropy production rate (19) only when mass is not conserved, $z \neq x$. It appears reasonable in this case to take into account only those entropy changes which are in agreement with the change of state across the shock front. This means that we shall drop the s_1 term also when mass is not conserved. However, we shall still keep the s_1 term for a while in order to show that its presence does not affect the limiting case $M \rightarrow \infty$.

Omitting now the equation of mass conservation (10) with the help of (11) and (12) x and y can be expressed in terms of z,

$$x = \frac{(\gamma+1)M^2}{2(1+\gamma M^2)} \frac{z^3}{z-a}, \quad y = (\gamma-1)M^2(b/z-c), \quad (22)$$

where

$$a = \frac{2 + (\gamma - 1)M^2}{2(1 + \gamma M^2)} ,$$

$$b = \frac{\gamma [2 + (\gamma - 1)M^2]}{(\gamma^2 - 1)M^2} ,$$

$$c = \frac{1 + \gamma M^2}{(\gamma + 1)M^2} .$$
(23)

Note that for positive values of ρ and p, or x and y, respectively, we must have

$$a \le z \le b / c \quad . \tag{24}$$

With (22), (19) becomes

$$P_{m}^{*}(M,z) = \frac{2(1+\gamma M^{2})}{(\gamma+1)M^{2}} \frac{z-a}{z^{2}} \left[\frac{s_{1}}{c_{v}} + \ln f(z) \right] - \frac{s_{1}}{c_{v}} ,$$
(25)

where

$$f(z) = (\gamma - 1)M^2 \left[\frac{(\gamma + 1)M^2}{2(1 + \gamma M^2)} \right]^{\gamma} \left[\frac{z^3}{z - a} \right]^{\gamma} \left[\frac{b}{z} - c \right] .$$
(26)

For a given M, P_m^* has extrema at $\partial P_m^* / \partial z = 0$ or

$$\left|\frac{s_1}{c_v} + \ln f(z)\right| (2a-z) + \left[-2\gamma c z^2 + (3\gamma a c + 2\gamma b - b)z + a b (1-3\gamma)\right] / (b-cz) = 0.$$
⁽²⁷⁾

If $\gamma = \frac{5}{3}$, using (23) one finds after some calculation that z = 2a is a zero of this equation which can be rewritten

$$(2a-z)\left[\frac{s_1}{c_v} + \ln f(z) + \frac{2\gamma cz + \gamma ac - 2\gamma b + b}{b - cz}\right] = 0$$
(28)

in this case. For $M \to \infty$, $\ln f(z) \to \ln M^2$ and the term with $\ln f(z)$ becomes the dominant one in (27), showing that z = 2a is the location of an extremum also for arbitrary γ then. This extremum turns out to be the absolute maximum of P_m^* . Inserting z = 2a and (23) in (25), to the leading order we get

$$\hat{P}_{m}^{*}|_{M\to\infty} = \frac{\gamma^{2}}{\gamma^{2}-1} \ln M^{2} . \qquad (29)$$

This shows that for large M, the dominant contribution to \hat{P}_m^* does not depend on the entropy constant s_1 . From now on, we shall set $s_1 = 0$ and additionally assume $\gamma = \frac{5}{3}$ in order to take advantage of the simpler extremum condition (28).

Figure 1 shows $P_m^*(M,z)$ as function of z for several values of M. For $M \le 6.95 \ldots$, P_m^* has an absolute maximum, a relative maximum, and a relative minimum. Inserting z = 2a and (23) into (25) and (26), one obtains the extremum value

$$P_{m}^{*} = \frac{25}{16} \left[1 - \frac{9}{5} \frac{1 - 1/5M^{2}}{3 + M^{2}} \right] \left[\ln M^{2} + \frac{16}{3} \ln 2 + \frac{10}{3} \ln \left[1 + \frac{3}{M^{2}} \right] - 4 \ln \left[5 + \frac{3}{M^{2}} \right] \right] = \begin{cases} \check{P}_{m}^{*} & \text{for } M \le 6.25 \dots \\ \hat{P}_{m}^{*} & \text{for } M \ge 6.25 \dots \end{cases}$$
(30)

It is found to be a relative minimum up to M = 6.25..., where it coincides with the smaller one of the two relative maxima coming from the right. Above



FIG. 1. Entropy production rate in shock waves without mass conservation. $P_m^*(M,z)$ is shown as function of the normalized quantity $\tilde{z} = (z-a)/(b/c-a)$ for several values of M. The position of the absolute maximum is indicated by dots, that of the smaller relative maximum by dots and dashes, and that of the relative minimum by dashes. $(\gamma = \frac{5}{3})$

M = 6.25..., z = 2a becomes the position of a relative maximum while the relative minimum wanders to the left. Above M = 6.87..., it becomes the absolute maximum, and at M = 6.95..., the relative minimum and maximum to the left of z = 2a merge and disappear, leaving the absolute maximum at z = 2a as the only extremum. $\hat{P}_m^*(M)$, the absolute maximum of $P_m^*(M,z)$, is shown in Fig. 3.

The surprising result of this section is that for M = 5.73... real shock waves actually assume the maximal value of the entropy production rate which can be attained under the neglect of mass conservation (see Fig. 4 which shows P_r^* / \hat{P}_m^* as a function of *M*), i.e., for M = 5.73... the equation of mass conservation can be replaced by the requirement of maximum entropy production. If at all, one would have expected a result like this for very large Mach numbers. However, for $M \rightarrow \infty$ and reasonable values of γ , according to (21) and (29) the entropy production rate lies well below maximum. Only for $\gamma \to \infty$ do the $M \to \infty$ asymptotic values of P_r^* and \hat{P}_m^* approach each other. A possible interpretation of this result is that, with respect to the entropy production associated with mass creation, real shock waves are furthest away from equilibrium or "strongest" at M = 5.73... At all other Mach numbers one could come further away from equilibrium by creating additional mass in the shock wave.

IV. SHOCK WAVES WITHOUT MOMENTUM CONSERVATION

Omitting the equation of momentum conservation (11) from (10) and (12) we obtain

$$x = z, \quad y = \frac{1}{z} \left[1 + \frac{\gamma - 1}{2} M^2 \right] - \frac{\gamma - 1}{2} M^2 z ,$$
 (31)

and (19) yields

$$P_i^*(\boldsymbol{M},\boldsymbol{z}) = \ln\left\{\boldsymbol{z}^{\gamma-1}\left[\left(1+\frac{\gamma-1}{2}\boldsymbol{M}^2\right)-\frac{\gamma-1}{2}\boldsymbol{M}^2\boldsymbol{z}^2\right]\right\}.$$
(32)

Figure 2 shows a typical pattern of P_i^* as function of z for fixed M. P_i^* has an absolute maximum at

$$z_{\max} = \left[\frac{2 + (\gamma - 1)M^2}{(\gamma + 1)M^2}\right]^{1/2},$$
(33)

its value being given by

$$\hat{P}_{i}^{*} = \ln M^{2} + \frac{\gamma + 1}{2} \ln \frac{2 + (\gamma - 1)M^{2}}{(\gamma + 1)M^{2}} .$$
(34)

 $\hat{P}_{i}^{*}(M)$ is shown in Fig. 3. Asymptotically, we have

$$\hat{P}_{i}^{*}|_{M^{2}=1+\epsilon} = \frac{\gamma-1}{2(\gamma+1)}\epsilon^{2} + \cdots, \quad \hat{P}_{i}^{*}|_{M\to\infty} = \ln M^{2},$$
(35)

respectively. For small $M^2 - 1 = \epsilon$, from (21) and (35) we get

$$P_r^*/\widehat{P}_i^* = \frac{4\gamma}{3(\gamma+1)}\epsilon$$
,

showing that P_r^* is far away from \hat{P}_i^* , although P_r^* and \hat{P}_i^* tend both towards zero as $M \to 1$. Strong shock waves can, however, be characterized by a maximum of the entropy production rate without momentum conservation since



FIG. 2. Entropy production rate in shock waves without momentum conservation and without energy conservation. $P_i^*(M,z)$ and $P_e^*(M,z)$ are shown as functions of z for M = 4.



FIG. 3. P_r^* , \hat{P}_m^* , \hat{P}_i^* , and \hat{P}_e^* as functions of M.

vation since

$$P_r^* / \hat{P}_i^* \to 1 \quad \text{for } M \to \infty \quad .$$
 (36)

V. SHOCK WAVES WITHOUT ENERGY CONSERVATION

If energy conservation (12) is omitted, (10), (11), and (19) yield

$$x = z, y = 1 + \gamma M^2 (1 - z)$$
 (37)

and

$$P_e^*(M,z) = \ln\{z^{\gamma}[1+\gamma M^2(1-z)]\}.$$
(38)

A typical pattern of P_e^* is shown in Fig. 2, the absolute maximum of P_e^* with a value of

$$\hat{P}_{e}^{*}(M) = \ln M^{2} + (\gamma + 1) \ln \frac{1 + \gamma M^{2}}{(\gamma + 1)M^{2}}$$
(39)

being obtained at

$$z_{\max} = \frac{1 + \gamma M^2}{(\gamma + 1)M^2} .$$
 (40)

 $\hat{P}_{e}^{*}(M)$ is shown in Fig. 3. The asymptotic values of \hat{P}_{e}^{*} for small and large *M* are

$$\hat{P}_{e}^{*}|_{M^{2}=1+\epsilon} = \frac{\gamma}{2(\gamma+1)}\epsilon^{2}, \quad \hat{P}_{e}^{*}|_{M\to\infty} = \ln M^{2}, \quad (41)$$

respectively. Again, P_r^* is far away from \hat{P}_e^* for small $M^2 - 1 = \epsilon$ since

$$P_r^* / \hat{P}_e^* = \frac{4}{3} \frac{\gamma - 1}{\gamma + 1} \epsilon$$

according to (21) and (41). And again, strong shock waves can be characterized by a maximum of the entropy production rate without energy conservation:

$$P_r^* / \hat{P}_e^* \to 1 \quad \text{for} M \to \infty \quad .$$
 (42)

VI. RELATIVISTIC TREATMENT

According to (9), $M \rightarrow \infty$ requires $v_1 \rightarrow \infty$. This indicates the necessity for a relativistic treatment which is carried out in this section. Relativistic shock waves in an ideal gas have first been treated by Taub.8 (Note that Taub uses normalized flow velocities, but the velocity of light is not normalized.) For the reader's convenience, the basic facts about relativistic shock waves needed in this paper are briefly summarized in the Appendix.

Defining

x = z,

$$x = \rho_1 / \rho_2, \quad y = p_2 / p_1, ,$$

$$z = \left(\frac{v_2}{(1 - v_2^2 / c^2)^{1/2}} \right) / \left(\frac{v_1}{(1 - v_1^2 / c^2)^{1/2}} \right),$$
(43)

and introducing a Mach number

$$M = v_1 / [a_1 (1 - v_1^2 / c^2)^{1/2}], \qquad (44)$$

which becomes infinite for infinitely strong shock waves $(v_1 \rightarrow c)$, the relativistic Rankine-Hugoniot relations (A13)-(A15) can be rewritten as

$$y = \frac{1 + \delta_1 + \gamma_1 M^2 (1 + \delta_1 - z^2 / x)}{1 + \delta_1 + \gamma_1 \delta_2 M^2 z^2} , \qquad (46)$$
$$y = \frac{(\gamma_2 - 1)\gamma_1}{(\gamma_1 - 1)\gamma_2} \left\{ \left[\frac{1 + (Ma_1 / c)^2}{1 + (Ma_1 z / c)^2} \right]^{1/2} + \frac{(\gamma_1 - 1)c^2}{(1 + \delta_1)a_1^2} \left[\left[\frac{1 + (Ma_1 / c)^2}{1 + (Ma_1 z / c)^2} \right]^{1/2} - 1 \right] \right\} , \qquad (47)$$

where

$$\delta_1 = \frac{\gamma_1}{\gamma_1 - 1} \frac{p_1}{\rho_1 c^2}, \quad \delta_2 = \frac{\gamma_2}{\gamma_2 - 1} \frac{p_1}{\rho_1 c^2} , \quad (48)$$

and

$$\gamma_2 = \frac{4 + \zeta [K_1(\zeta) / K_2(\zeta) - 1]}{3 + \zeta [(K_1(\zeta) / K_2(\zeta) - 1]]} , \qquad (49)$$

with

$$\zeta = \frac{\gamma_1 c^2}{a_1^2 x y} \left[1 - \frac{a_1^2}{(\gamma_1 - 1)c^2} \right], \qquad (50)$$

according to (A8), (A12), and (43).

It is not interesting to consider the neglect of particle conservation (45) relativistically since in this case maximum entropy producton is already obtained for M = 5.73..., well in the classical regime. We shall, therefore, make use of (45) to eliminate x. In order to obtain some simplification, we shall furthermore assume that the gas in front of the shock wave is classical, i.e., $\gamma_1 = \frac{5}{3}$, $a_1 \approx (\gamma_1 p_1 / \rho_1)^{1/2} \ll c$, and $\delta_1 \approx (a_1 / c)^2 / (\gamma_1 - 1)$ \ll 1. With this assumption, (46) and (47) can be approximated by

$$y = \frac{3 + 5M^{2}(1-z)}{3 + 5\delta_{2}M^{2}z^{2}},$$

$$y = \frac{5(\gamma_{2}-1)}{2\gamma_{2}} \left\{ \left[\frac{1 + (Ma_{1}/c)^{2}}{1 + (Ma_{1}z/c)^{2}} \right]^{1/2} + \frac{2c^{2}}{3a_{1}^{2}} \left[\left[\frac{1 + (Ma_{1}/c)^{2}}{1 + (Ma_{1}z/c)^{2}} \right]^{1/2} - 1 \right] \right\},$$
(51)

while in (49) we can set

$$\zeta = \frac{5c^2}{3a_1^2 vz} \ . \tag{53}$$

The entropy flux density is given by

$$j_s = snv / (1 - v^2 / c^2)^{1/2}$$
 (54)

Therefore, during the time interval Δt and in the rest system of the shock front, the entropy loss in front and the entropy gain behind are

$$S_{1} = \frac{Fs_{1}n_{1}v_{1}}{(1 - v_{1}^{2}/c^{2})^{1/2}}\Delta t ,$$

$$S_{2} = \frac{Fs_{2}n_{2}v_{2}}{(1 - v_{2}^{2}/c^{2})^{1/2}}\Delta t .$$
(55)

From (54) with (A13) we obtain the normalized entropy production rate

$$P^* = \frac{2(1 - v_1^2/c^2)^{1/2}}{3kn_1v_1F} \frac{S_2 - S_1}{\Delta t} = \frac{2}{3k}(s_2 - s_1) , \quad (56)$$

the normalization being chosen such that we obtain just (19) with z = x in the classical limit. With (A19) and (43), and our assumption of a classical state 1 and the corresponding asymptotic expansion

$$K_{2}(\rho_{1}c^{2}/p_{1}) \approx K_{2}(\gamma_{1}c^{2}/a_{1}^{2}) = \left[\frac{\pi a_{1}^{2}}{2\gamma_{1}c^{2}}\right]^{1/2} e^{-\gamma_{1}c^{2}/a_{1}^{2}},$$

from (56) we obtain after some calculation

$$P^{*} = \frac{2}{3} \left[\frac{5(c/a)^{2}}{3yz} + \frac{\gamma_{2}}{\gamma_{2}-1} - \frac{5}{2} + \ln yz^{2} + \ln K_{2} \left[\frac{5c^{2}}{3a_{1}^{2}yz} \right] - \frac{1}{2} \ln \frac{3\pi a_{1}^{2}}{10c^{2}} \right].$$
 (57)

In real shock waves, (51) and (52) must be solved simultaneously yielding y = y(M) and z = z(M). Inserting the results in (57) one obtains the entropy production rate $P_r^*(M)$ for real shock waves. If momentum conservation (51) is neglected, the resolution of (52) with respect to y yields y = y(M,z), and inserting this in (57), one obtains $P_i^*(M,z)$ and $\hat{P}_i^* = \max_z P_i^*(M,z)$. Quite analogously, one obtains $\hat{P}_e^* = \max_z P_e^*(M,z)$. In contrast to the classical case, neither $P_r^*(M)$, $\hat{P}_i^*(M)$, nor $\hat{P}_e^*(M)$ can be determined analytically. They were calculated numerically, and results obtained for a = 0.3 km/sec, $c = 300\,000$ km/sec are shown in Fig. 5. [For the numerical calculation, some equations must be slightly rewritten in order to avoid differences of extremely large numbers. Also, in-

$$\frac{3/M^2 + 5(1-z)}{3/M^2 + 5\delta_2 z^2} = \frac{5}{8z} \left\{ \left[\frac{1/M^2 + (a_1/c)^2}{1/M^2 + (a_1 z/c)^2} \right]^{1/2} + \frac{2c^2}{3a_1^2} \left[\left[\frac{1}{1} \right]^{1/2} + \frac{2c^2}{3a_1^2} \right]^{1/2} + \frac{2c^2}{3a_1^2} \left[\frac{1}{1} \right]^{1/2} + \frac{2c^2}{$$

which is solved by

$$z = \left[\frac{2c}{\sqrt{5}a_1}\right] / M \tag{59}$$

up to terms of order $1/M^2$. The corresponding value of y is

$$y = 5M^2/9$$
 (60)

With (59), (60), and the asymptotic expansion⁹

$$K_2(u) = \frac{2}{u^2} \text{ for } u \to 0 ,$$
 (61)

from (57) we obtain

$$P_r^*(M) \to \frac{4}{3} \ln M \text{ for } M \to \infty$$
 (62)

[Note that $yz \sim M$, $\zeta \sim 1/M$, and with (61) from (49) we get $\gamma_2 \rightarrow \frac{4}{3}$ as assumed.]

Next, we consider the neglect of momentum conservation. From (52) and (57), with $\gamma_2 = \frac{4}{3}$ and $M \to \infty$ we obtain

$$y = \frac{5Mc^2}{12a_1^2 z \left[1 + (Mza_1/c)^2\right]^{1/2}}$$
(63)

and

$$P_{i}^{*}(M,z) = \frac{2}{3} \left[\frac{4a_{1}^{2} [1 + (Mza_{1}/c)^{2}]^{1/2}}{Mc^{2}} + \ln \frac{Mz}{[1 + (Mza_{1}/c)^{2}]^{1/2}} + \ln K_{2} \left[\frac{4[1 + (Mza_{1}/c)^{2}]^{1/2}}{M} \right] + C \right],$$
(64)

where C represents constant terms. Now, transforming from z to the variable

$$w = Mz , \qquad (65)$$

neglecting terms $\sim 1/M$ against terms ~ 1 on the assumption that P_i^* reaches its maximum at some finite w [which is verified by the result (68)], and using the asymp-

stead of $K_i(\zeta)$, the functions $K_i(\zeta)e^{\zeta}$ were evaluated.]

It is still possible, however, to derive analytical results for the extreme relativistic case $M \rightarrow \infty$. The results obtained for classical shock waves imply $T_2 \rightarrow \infty$ and thus $\gamma_2 \rightarrow \frac{4}{3}$ according to the asymptotic evaluation of (49). This will turn out to be consistent with the results obtained for y and z.

Let us first consider real shock waves. With $\gamma_2 = \frac{4}{3}$, the comparison of (51) and (52) yields the equation

$$+\frac{2c^{2}}{3a_{1}^{2}}\left[\left(\frac{1/M^{2}+(a_{1}/c)^{2}}{1/M^{2}+(a_{1}z/c)^{2}}\right)^{1/2}-1\right]\right],$$
(58)

totic expansion (61), we obtain

$$P_i^*(M,w) = \frac{2}{3} \left[2 \ln M + \ln \frac{w}{\left[1 + (wa_1/c)^2\right]^{3/2}} + C \right].$$
(66)

For a given M, the maximum of $P_i^*(M, w)$ is obtained when

$$\frac{\partial P_i^*}{\partial w} = \frac{1}{w} - \frac{3(a_1^2/c^2)w}{1 + (wa_1/c)^2} = 0$$
(67)

or

$$w_{\max} = \frac{c}{\sqrt{2}a_1} . \tag{68}$$

This value was confirmed numerically. Equation (66) shows that, just like $P_r^*(M)$,

$$P_i^*(M) \to \frac{4}{3} \ln M \text{ for } M \to \infty$$
 . (69)

Let us finally consider the neglect of energy conservation. From (51) and (57), and using again the transformation (65), we get



FIG. 4. P_r^* / \hat{P}_m^* , P_r^* / \hat{P}_i^* , and P_r^* / \hat{P}_e^* as functions of M.



FIG. 5. P_r^*/\hat{P}_i^* and P_r^*/\hat{P}_e^* as functions of *M*; the classical results are dotted, the relativistic results ($a_1=0$, 3 km/sec, $c=300\,000$ km/sec) are drawn out.

$$P_e^*(M,u) = \frac{2}{3} \left[2 \ln M + \ln \frac{w^4}{(1 + \frac{5}{3}\delta_2 w^2)^3} + C \right], \quad (70)$$

with maximum again at (68); and according to (66) we have

$$\hat{P}_{e}^{*}(M) \rightarrow \frac{4}{3} \ln M \text{ for } M \rightarrow \infty$$
 . (71)

It follows from (62), (69), and (71) that our classical results (36) and (42) also hold relativistically. The numerical calculations presented in Fig. 5 show that the convergence (69) and (71) is relativistically even better than classically.

VII. SUMMARY

It was found classically and relativistically that in the limit $M \to \infty$, strong shock waves can be characterized by a maximum of the entropy production rate without momentum or energy conservation, just as certain states close to equilibrium are characterized by minimum entropy production. On the other hand, in weak shock waves the entropy production rate is far from maximum. Figures 4 and 5, which show P_r^* / \hat{P}_m^* , P_r^* / \hat{P}_i^* , and P_r^* / \hat{P}_e^* as functions of M, summarize these findings.

However, for the example of heat conduction in a rod, it was shown that no general principle of this kind is valid, and that a maximum of the entropy production rate must not even exist. But even if a maximum exists, one must be careful about the question of what should be considered as being far from equilibrium. Intuitively, one would say that strong shock waves are further away from equilibrium than weak ones. However, the case of omitting mass conservation shows that shock waves with Mach numbers around 6 are further away from equilibrium than very strong shock waves at least in the sense that they approach the maximum of the entropy production rate without mass conservation there. This is perhaps not too surprising if one keeps in mind that a shock wave without mass conservation must be supplemented by a mass production device with its own entropy production rate.

It may be conjectured that the characterization of states far from equilibrium by a maximum of the entropy production rate can be extended also to other classes of systems. The existence of a maximum could be an indication for this possibility. Maximizing the entropy production rate might even be used as a heuristic approach for the determination of steady states far from equilibrium.

APPENDIX

Using summation convention, the relativistic equations for the flow of an ideal gas are

$$\frac{\partial}{\partial X^{\alpha}}(nU^{\alpha}) = 0 \tag{A1}$$

for particle number conservation (*n* is the particle number density per volume in the rest system, U^{α} is the velocity four vector) and

$$\frac{\partial}{\partial X^{\beta}}T^{\alpha\beta}=0, \qquad (A2)$$

with

$$T^{\alpha\beta} = \left[nm + \frac{ne+p}{c^2} \right] U^{\alpha} U^{\beta} - p \eta^{\alpha\beta}$$
(A3)

for momentum and energy conservation (*m* is the particle rest mass, *e* is the internal thermal energy per particle, *p* is the gas pressure in the rest system, $\eta^{\alpha\beta}$ is the metric tensor). For an ideal gas, the following equations of state are valid:¹⁰

$$p = nkT , \qquad (A4)$$

$$e = mc^{2} \left[\frac{K_{1}(mc^{2}/kT)}{K_{2}(mc^{2}/kT)} - 1 \right] + 3kT , \qquad (A5)$$

 K_1 and K_2 being modified Bessel functions, T is the gas temperature, k is the Boltzmann constant, c is the velocity of light. Setting

$$ne = \frac{p}{\gamma - 1} , \qquad (A6)$$

and introducing the rest mass density

$$\rho = nm$$
 (A7)

(which does not include the mass contribution ne/c^2 of the internal energy), (A4) and (A5) imply

$$\gamma = \frac{4 + (\rho c^2 / p) [K_1(\rho c^2 / p) / K_2(\rho c^2 / p) - 1]}{3 + (\rho c^2 / p) [(K_1(\rho c^2 / p) / K_2(\rho c^2 / p) - 1]]} .$$
(A8)

In the classical limit $T \rightarrow 0$ one gets $\gamma = \frac{5}{3}$, and in the extreme relativistic limit $T \rightarrow \infty$ one obtains $\gamma = \frac{4}{3}$.

In a one-dimensional time-dependent flow, Eqs. (A1)-(A3), (A6), and (A7) yield

$$\frac{1}{c}\partial_{t}\frac{c\rho}{(1-v^{2}/c^{2})^{1/2}} + \partial_{x}\frac{\rho v}{(1-v^{2}/c^{2})^{1/2}} = 0, \quad (A9)$$

$$\frac{1}{c}\partial_{t}\left[\left[\rho + \frac{\gamma}{\gamma-1}\frac{p}{c^{2}}\right]\frac{cv}{1-v^{2}/c^{2}}\right]$$

$$+ \partial_{x}\left[\left[\rho + \frac{\gamma}{\gamma-1}\frac{p}{c^{2}}\right]\frac{v^{2}}{1-v^{2}/c^{2}} + p\right] = 0, \quad (A10)$$

$$\frac{1}{c}\partial_{t}\left[\left[\rho + \frac{\gamma}{\gamma-1}\frac{p}{c^{2}}\right]\frac{c^{2}}{1-v^{2}/c^{2}}\right]$$

$$+ \partial_{x}\left[\left[\rho + \frac{\gamma}{\gamma-1}\frac{p}{c^{2}}\right]\frac{cv}{1-v^{2}/c^{2}}\right] = 0 \quad (A11)$$

for particle, momentum, and energy conservation, respectively. Linearizing (A9)-(A11) around a uniform state and neglecting the ρ , p dependence of γ (in view of its extreme weakness) yields the sound velocity

$$a = \left[\frac{\gamma p / \rho}{1 + \gamma / (\gamma - 1)p / \rho c^2}\right]^{1/2}.$$
 (A12)

The relativistic Rankine-Hugoniot equations for shock waves

$$\rho_1 v_1 / (1 - v_1^2 / c^2)^{1/2} = \rho_2 v_2 / (1 - v_2^2 / c^2)^{1/2}$$
, (A13)

$$\left[\rho_1 + \frac{\gamma_1}{\gamma_1 - 1} \frac{p_1}{c^2} \right] v_1^2 / (1 - v_1^2 / c^2) + p_1 \\
= \left[\rho_2 + \frac{\gamma_2}{\gamma_2 - 1} \frac{p_2}{c^2} \right] v_2^2 / (1 - v_2^2 / c^2) + p_2 , \quad (A14)$$

$$\left| \rho_1 + \frac{\gamma_1}{\gamma_1 - 1} \frac{p_1}{c^2} \right| v_1 / (1 - v_1^2 / c^2)$$
$$= \left| \rho_2 + \frac{\gamma_2}{\gamma_2 - 1} \frac{p_2}{c^2} \right| v_2 / (1 - v_2^2 / c^2) \quad (A15)$$

are obtained from (A9)–(A11) with $\partial_t \equiv 0$ and integration over x.

If s denotes the entropy per particle in the rest system of the gas, the Gibbs-Duhem relation is¹⁰

$$s = \frac{1}{T} [(e + mc^2) - \mu + kT], \qquad (A16)$$

the chemical potential μ being given by¹⁰

$$\mu = kT \ln \frac{\alpha \rho^2}{pK_2(\rho c^2/p)}, \quad \alpha = \frac{(2\pi\hbar)^3}{4\pi m^4 c}$$
(A17)

 $(\hbar = h/2\pi, h \text{ is the Planck constant})$. The combination of (A4), (A6), (A7), and (A16) and (A17) yields

$$s = k \left[\frac{\rho c^2}{p} + \frac{\gamma}{\gamma - 1} - \ln \alpha + \ln p \rho^{-2} + \ln K_2 (\rho c^2 / p) \right].$$
(A18)

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