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Nonequilibrium Entropy in a Shock

L.G. Margolin

Los Alamos National Laboratory, Los Alamos, NM 87545, USA; len@lanl.gov; Tel.: +1-505-665-1947

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Abstract: In a classic paper, Morduchow and Libby use an analytic solution for the profile of a Navier–Stokes shock to show that the equilibrium thermodynamic entropy has a maximum inside the shock. There is no general nonequilibrium thermodynamic formulation of entropy; the extension of equilibrium theory to nonequililbrium processes is usually made through the assumption of *local thermodynamic equilibrium* (LTE). However, gas kinetic theory provides a perfectly general formulation of a nonequilibrium entropy in terms of the probability distribution function (PDF) solutions of the Boltzmann equation. In this paper I will evaluate the Boltzmann entropy for the PDF that underlies the Navier–Stokes equations and also for the PDF of the Mott–Smith shock solution. I will show that both monotonically increase in the shock. I will propose a new nonequilibrium thermodynamic entropy and show that it is also monotone and closely approximates the Boltzmann entropy.

Keywords: shocks; nonequilibrium thermodynamics; entropy

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1. Introduction

> "The laws of thermodynamics may easily be obtained from the principles of statistical mechanics, of which they are an incomplete expression." (J.W. Gibbs)

> "There are as many formulations of the second law as there have been discussions of it." (Percy Bridgman)

For more than 65 years, a curious result has gone unchallenged in the literature of shock waves. The result, first put forth by Morduchow and Libby [1,2], is that the thermodynamic (equilibrium) entropy has a maximum inside a Navier–Stokes shock profile. I emphasize *equilibrium* entropy because it is the only entropy defined in classical thermodynamics [3].

However, shocks are nonequilibrium processes. It is the purpose of this paper to reconsider the shock profile from the viewpoint of statistical mechanics. There, nonequlibrium entropy is a well defined concept, e.g., as first introduced by Boltzmann in the H-theorem. The two main results of this paper are first, that the Boltzmann entropy has a smooth monotonic profile in the shock and second, that it is possible to define a nonequilibrium thermodynamic entropy that is consistent with the Boltzmann entropy in the shock.

Although the actual calculation of the Boltzmann entropy is straightforward once the underlying statistical distribution of molecular velocities is known, the background and context of the Morduchow–Libby result are interesting and worth retelling. I will begin in Section 2 by describing the important, but not well–known paper of Richard Becker [4]. In 1922, only five years after the Chapman–Enskog expansion provided a kinetic-based derivation of the Navier–Stokes equations from the Boltzmann equation, Becker questioned the applicability of the Navier–Stokes equations to shocks. It would be nearly forty years before experiments would validate Becker's concerns. The 1949 paper of Morduchow and Libby expanded on Becker's solutions and drew attention to the predicted entropy profile. I will summarize those results that are pertinent to the comparisons that are made in later sections.

In Section 3, I will describe the calculation of the Boltzmann entropy for the Navier–Stokes equations. I will evaluate the Boltzmann entropy using the Grad distribution of molecular velocities. The Grad distribution is an alternative derivation that leads to the Navier–Stokes equations in the five-moment approximation. The Boltzmann entropy is not easily calculated analytically, but can be readily evaluated numerically for any particular choice of Mach number and Prandtl number. I will exhibit entropy profiles for two values of the Mach number using the Becker approximation and show that the Boltzmann entropy in each case is monotonically increasing through the shock profile.

It is well known that the Navier–Stokes solutions for shock profiles in gases do not agree with experimental measurements. In Section 4, I will recompute the entropies of Section 3 using the Mott–Smith distribution for molecular velocities. Mott–Smith is not a theory with rigorous derivation, but rather is an ad hoc description that only approximately satisfies the Boltzmann equation. However, it has an advantage over the Navier–Stokes theory, namely that it more accurately describes the experimentally measured profiles of shocks. Similar to the Navier–Stokes theory, the equilibrium entropy of Mott–Smith exhibits a peak inside the shock profile, but the Boltzmann entropy is monotonically increasing.

Under the presumption that the Boltzmann theory is more fundamental than the continuum approximations that can be derived from it, one must then accept that the thermodynamic entropy is a poor approximation to the nonequilibrium kinetic entropy in a shock. In Section 5, I hypothesize that a more accurate thermodynamic entropy, i.e., a nonequilibrium thermodynamic entropy, would result from including the entropy flux in the definition of entropy. To support this hypothesis, I will extend the calculations of Sections 3 and 4 to estimate the entropy flux. Then, I will compare the new nonequlibrium thermodynamic entropy to the Boltzmann entropy. The results of that comparison show that the nonequlibrium thermodynamic entropy does not have a maximum within the shock profile and in fact it closely, if not exactly, matches the Boltzmann entropy.

In Section 6, I will offer some motivational remarks about the future importance of the Mott–Smith theory and the possible importance of nonequilibrium entropy in making this theory more rigorous. I will conclude the paper with a short summary.

It is worth emphasizing that my hypothesis about a nonequilibrium thermodynamic entropy is at this point limited to steady gas shocks, but may prove useful in developing a more general thermodynamic entropy for other nonequilibrium processes. At the very least, I hope this paper will call attention to Becker's insightful paper and the need to explore alternatives to Chapman–Enskog theory.

2. Historical Perspective

Here, I briefly summarize the context and some relevant results of the classic papers of Becker and of Morduchow and Libby.

2.1. *Becker's Approximation*

This story begins with the 1922 paper of Richard Becker [4]. Written only a few years after the Chapman–Enskog perturbation expansion established a relation between the Boltzmann equation and the Navier–Stokes equations, Becker was primarily concerned with questioning the use of Navier–Stokes theory in predicting shock profiles. It is now well established that Navier–Stokes predictions of shock width and shape are not consistent with experimental measurements; This failure is well-known and is discussed in the context of experimental data (among many places) in [3,5,6]. However, Becker's paper is better known today for its derivation of the first (and to my knowledge only) exact Navier–Stokes solution for a shock wave in a perfect gas, e.g., argon, that includes nonzero values for both the viscosity and heat conduction. From this solution, Becker concluded that the width of a Navier–Stokes shock was of the order of the molecular mean free path, from which he inferred that the perturbation parameter (Knudsen number) is not small and that the Chapman—Enskog expansion is not physically valid inside the shock.

Becker's solution assumed a particular value of the Prandtl number—the ratio of kinematic viscosity to thermal diffusivity. However, the assumed value of 0.75 is very close to the experimentally measured values for many noble gases [7], which further increases the utility of the assumption. A short note by Thomas [8] in 1944 pointed out that those transport coefficients have a weak temperature dependence that might widen the predicted shock. That note led to the classic paper by Morduchow and Libby [1] in 1949.

2.2. Morduchow and Libby

The main goal of [1] was to investigate the effects of a realistic dependence of viscosity and thermal conductivity on temperature. The effects of that dependence were evaluated by quadrature and indicated that the temperature dependence had only minimal consequences for Becker's estimates of shock width. However, in the process of describing Becker's derivation, Morduchow and Libby evaluated the profile of thermodynamic entropy through the shock and found that entropy had a maximum inside the shock. It is for that surprising result that [1] is mainly remembered today.

Morduchow and Libby wrote a follow-on paper [2] in 1965 and commented that the entropy maximum did not appear to violate the second law of thermodynamics since the entropy behind the shock was larger than the entropy ahead. A more stringent *local* formulation of the second law, the Clausius–Duhem inequality [9], requires that the entropy production must be positive at every point of a stable process. In his 1972 book, Thompson [10] shows that the Navier–Stokes shock profile in any perfect gas satisfies the Clausius–Duhem inequality.

So the equilibrium entropy, extended to nonequilibrium processes through the hypothesis of the local thermodynamic equilibrium (LTE), appears to satisfy the requirements of thermodynamics. However, LTE greatly restricts the scope of nonequilibrium thermodynamics. In Sections 3 and 4, I will demonstrate that the entropy maximum is a feature of the assumption of local thermodynamic equilibrium and that a nonequilibrium entropy is monotonically increasing through the shock.

2.3. Navier–Stokes Solutions

Becker [4] and Morduchow and Libby [1] treat the *full physics* Navier–Stokes equations in one spatial dimension. For completeness, I reproduce them here below with the modification of using the internal energy in place of the temperature. For an ideal gas, the internal energy is simply linearly related to the temperature by the specific heat at constant volume, $\mathcal{E} = c_v T$.

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left[\rho\, u\right] = 0\,, \tag{1}$$

$$\frac{\partial \rho u}{\partial t} + \frac{\partial}{\partial x}\left[\rho\, u^2 + p - \mu\frac{\partial u}{\partial x}\right] = 0\,, \tag{2}$$

$$\frac{\partial}{\partial t}\left[\rho\mathcal{E} + \frac{1}{2}\rho u^2\right] + \frac{\partial}{\partial x}\left[\rho\, u\mathcal{E} + \frac{1}{2}\rho u^3 + pu - \mu\, u\frac{\partial u}{\partial x} - \kappa\frac{\partial \mathcal{E}}{\partial x}\right] = 0\,. \tag{3}$$

The equations are closed with the ideal gas equation of state:

$$p = (\gamma - 1)\rho\mathcal{E}\,. \tag{4}$$

Here, ρ, u, p and $\mathcal{E}$ have their usual meanings of density, velocity, pressure and specific internal energy. Also, the transport coefficient μ is the shear viscosity and $\kappa = k/c_v$ where k is the thermal conductivity.

Both Becker and Morduchow and Libby construct the shock solution in a reference frame in which the shock is at rest. In this frame, each of the partial derivatives with respect to time vanishes and the problem becomes that of three coupled ordinary differential equations. Pertinent to the discussion in Section 5, I note that one could equivalently seek traveling wave solutions where the shock moves into a fluid at rest [11]. In this frame, all the state variables become dependent on the similarity variable $x - vt$. Here, v is the constant shock velocity which is determined from the boundary conditions and conservation. A characteristic length scale, ℓ, can be defined as,

$$\ell \equiv \left(\frac{\mu}{\rho_o v}\right)\left(\frac{2\gamma}{\gamma+1}\right). \tag{5}$$

In all the graphs in Section 3, the nondimensional coordinate is $z = (x - vt)/\ell$. Further, the density and internal energy can be nondimensionalized in terms ρ_o and $\mathcal{E}_o$, which are the properties of the undisturbed fluid ahead of the shock. In these nondimensional units, the Becker solution makes the specific approximation that $\kappa = \gamma\mu$. This relation leads to an analytically tractable ODE in both the steady state and the traveling wave formulations of the problem. In the nondimensional units, the shock speed $v = 1$, the shear viscosity $\mu = 1$ and the conductivity $\kappa = \gamma$. Entropy is only defined up to an additive constant. I will use the entropy scale determined by the Boltzmann definition, Equation (8). Note that the Boltzmann entropy is identical to the equilibrium entropy (up to the additive constant) in the equilibrium regions in front of the shock and far behind the shock; this provides the connection between the various measures of entropy calculated and plotted in this paper. Entropy is nondimensionalized by the specific heat at constant volume.

2.4. Entropy

In this paper, I will calculate and compare several different entropies. Here I will describe a systematic way to differentiate these. There are three types of entropies, which I will distinguish with a superscript: equilibrium entropy S^E, which is calculated with Equation (6) from macroscopic hydrodynamic variables, nonequlibrium entropy S^N, which is calculated using Equation (8) from a statistical mechanics velocity probability distribution function (PDF), and S^M, a modified entropy that I will define in Section 5 to estimate the nonequilibrium entropy using macroscopic variables. In addition, I will use lower case subscripts to identify an entropy that comes from Navier–Stokes theory, S_{ns}, as opposed to an entropy that comes from the Mott–Smith theory, S_{ms}.

I will use the expression for S^E above equation 13d in [1], rewritten in terms of density ρ and internal energy $\mathcal{E}$,

$$\frac{S^E - S^E_o}{c_v} = \ln\left(\frac{\mathcal{E}}{\mathcal{E}_o}\right) - (\gamma - 1)\ln\left(\frac{\rho}{\rho_o}\right), \tag{6}$$

where c_v is the specific heat at constant volume and S^E_o is the reference entropy of the fluid ahead of the shock. Note that the entropy involves only the jumps in the density and internal energy. Since the Prandtl number in the Becker solution is fixed, the only parameter to study is the Mach number, $\mathcal{M}$, of the shock. Further, as S^N_{ns} and S^N_{ms} will be evaluated numerically, I have chosen two specific values of the Mach number, namely $\mathcal{M} = \sqrt{3}$. and $\mathcal{M} = 3$, as being representative of a weak shock and a stronger shock. Plots of S^E_{ns} for these two cases are shown in Figure 1.

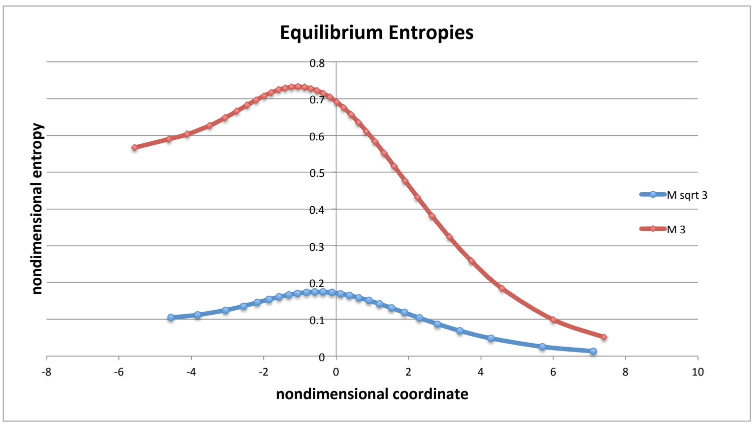

Figure 1. The equilibrium entropies calculated from the Morduchow and Libby solutions of the shock profile for two different Mach numbers, $\mathcal{M} = \sqrt{3}$ and $\mathcal{M} = 3$, are plotted against the traveling wave coordinate in nondimensional units. Both plots show that the entropy has a distinct maximum inside the profile.

3. Grad Nonequilibrium Entropy

In this section, I will derive a nonequilibrium entropy for the Navier–Stokes equations based on gas kinetic theory. The entropy that appears in Equation (6), S^E is the thermodynamic *equilibrium* entropy. The extension to nonequilibrium processes is made through the assumption of local thermodynamic equilibrium [12]. That implies that the macroscopic field quantities, e.g., density, temperature, etc., will depend on the spatial coordinate. However, the gradients of density, energy, etc. do not appear in the equilibrium entropy.

It is unfortunate that, in the sense of thermodynamics, a general nonequilibrium entropy is not defined [13]. However, in the more fundamental descriptions of statistical mechanics and gas kinetic theory, a nonequilibrium entropy can be defined in terms of the velocity probability distribution function. The H-theorem, introduced by Boltzmann in 1872, describes the tendency for the quantity $\mathcal{H}$ to be monotonically decreasing (there are several criticisms of Boltzmann's original proof to the effect that it is not completely rigorous; these are discussed in [14]),

$$\mathcal{H} \equiv \int f \, ln(f) \, d^3v \tag{7}$$

where $f(x_i, v_i, t)$ is any solution of the Boltzmann equation. The nonequilibrium Boltzmann entropy is identified with the negative of this integral,

$$S^N \equiv -\int f \, ln(f) \, d^3v = -\mathcal{H} \, . \tag{8}$$

When the equilibrium Boltzmann–Maxwell distribution,

$$f^{\mathrm{E}}(v) = \rho \left(\frac{1}{2\pi\mathcal{E}} \right)^{3/2} \exp - \frac{(v-u)^2}{2\mathcal{E}} \, , \tag{9}$$

is inserted in Equation (8), one finds that the S^N is identical to the thermodynamic entropy S^E defined in Equation (6), except for additive constants.

Solving the Boltzmann equation for nonequilibrium flows is very difficult, and one is usually constrained to constructing perturbation approximations assuming that the flow is near equilibrium. This is the case for deriving the Navier–Stokes equations. One path from the Boltzmann equation to Navier–Stokes was proposed by Grad [15]. The Grad probability distribution function (PDF), f^{G}, is a perturbation of the equilibrium solution of the Boltzmann equation. The derivation of the 13-moment field equations and its reduction to a five-field theory is described in detail in chapter 4.1 of [16]. Here, I present the Grad PDF with two modifications to ensure the closest comparison with the analysis in [1]. First, I will assume a one-dimensional flow and integrate over the two extraneous dimensions. Second, I will introduce the longitudinal viscosity term, σ.

$$f^{\mathrm{G}}(v) = f^{\mathrm{E}}(v) \left\{ 1 + \frac{1}{2\rho\mathcal{E}^2} \left[\sigma \, (v^2 - \mathcal{E}) + \frac{4}{5} \, qv \left(\frac{v^2}{2\mathcal{E}} - \frac{5}{2} \right) \right] \right\} \, . \tag{10}$$

Here, $\sigma = -\mu \frac{\partial u}{\partial x}$ and $q = -\kappa \frac{\partial \mathcal{E}}{\partial x}$. Note that both the original Grad PDF and my modified version are carefully constructed to ensure that the macroscopic variables of density and average velocity are the equilibrium values. This is an essential feature of the assumption of local thermodynamic equilibrium. The distribution function $f^{\mathrm{G}}(v)$ leads directly to the Navier–Stokes equations as written in Equations (1)–(3). I will define the nonequilibrium entropy for Navier–Stokes derived by inserting Equation (10) into (8):

$$S^N_{ns} \equiv -\int f^{\mathrm{G}} \, ln(f^{\mathrm{G}}) \, dv \, . \tag{11}$$

I have evaluated the integral above numerically using the particular parameters of the Mach $\sqrt{3}$ shock in Figure 2 and of the stronger Mach 3 shock in Figure 2. The issue at hand is not only to compare the equilibrium and nonequilibrium entropies, but more simply to ascertain whether S_{ns}^{N} has a maximum inside the shock profile. The answer to the latter is shown graphically in Figure 2—in contrast to S_{ns}^{E}, *the nonequilibrium entropy* S_{ns}^{G} *is monotonically increasing through the shock profile*. The corresponding result for the Mach 3 shock is shown in Figure 3 and is also seen to be monotonically increasing. Further, as the equilibrium and nonequilibrium entropies must agree in the regions in front of and behind the shock, it is easy to determine the relative scale factors; a direct comparison of the two entropies is shown in Figure 4 for the Mach $\sqrt{3}$ shock and in Figure 5 for the Mach 3 shock.

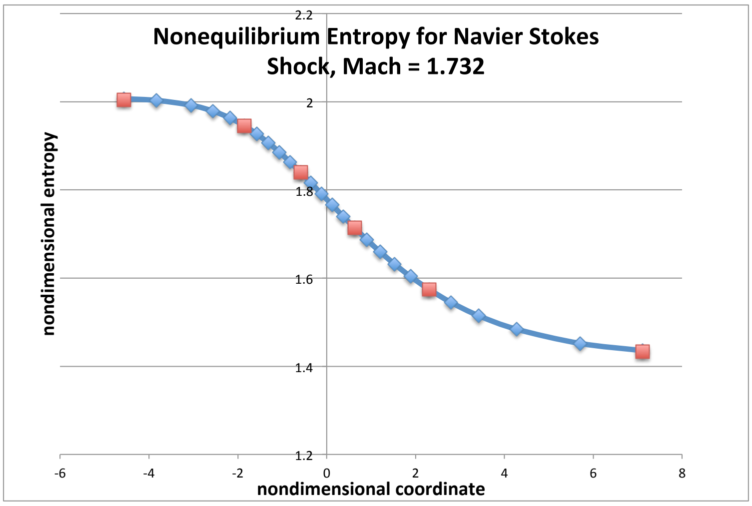

Figure 2. The nonequilibrium entropy calculated from the Grad probability distribution function (PDF) is plotted in the shock profile against coordinate for the case of Mach $\sqrt{3}$ shock in nondimensional units. The plot shows a monotonically increasing profile toward the piston face. Representative points of a separate calculation in which the shear viscosity is removed from the Grad PDF are shown, indicating that the viscosity makes essentially no contribution to the entropy.

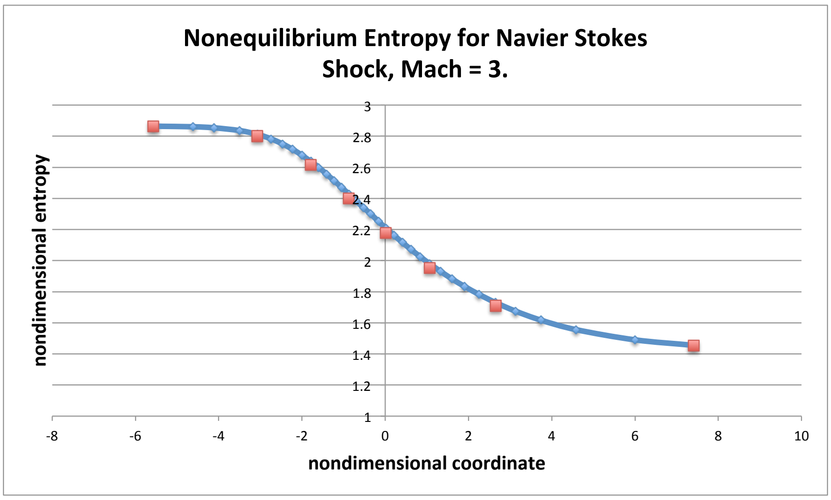

Figure 3. The nonequilibrium entropy calculated from the Grad PDF is plotted in the shock profile against coordinate for the case of Mach 3 shock in nondimensional units. The plot shows a monotonically increasing profile toward the piston face. Representative points of a separate calculation in which the shear viscosity is removed from the Grad PDF are shown, indicating that the viscosity makes essentially no contribution to the entropy.

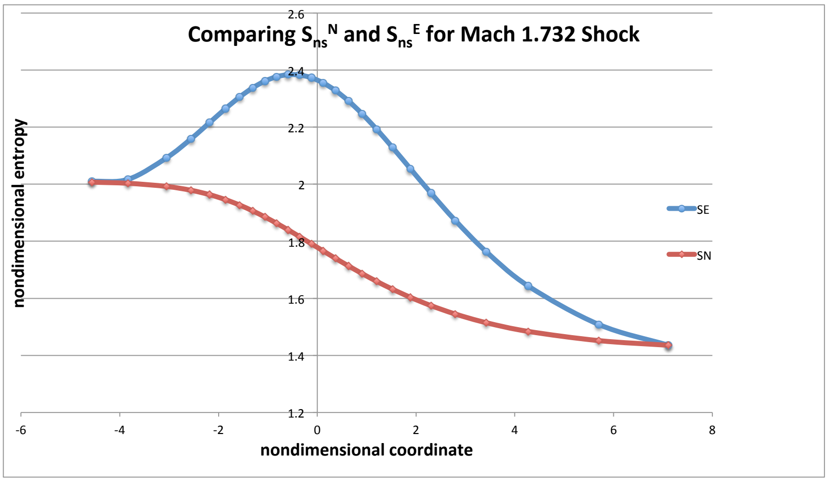

Figure 4. The nonequilibrium entropy S_{ns}^N is compared to the equilibrium entropy S_{ns}^E in nondimensional units for the Mach $\sqrt{3}$ Navier-Stokes shock. The relative additive constants are found by requiring the equilibrium entropies in front and behind the shock to be equal to their nonequilibrium counterparts.

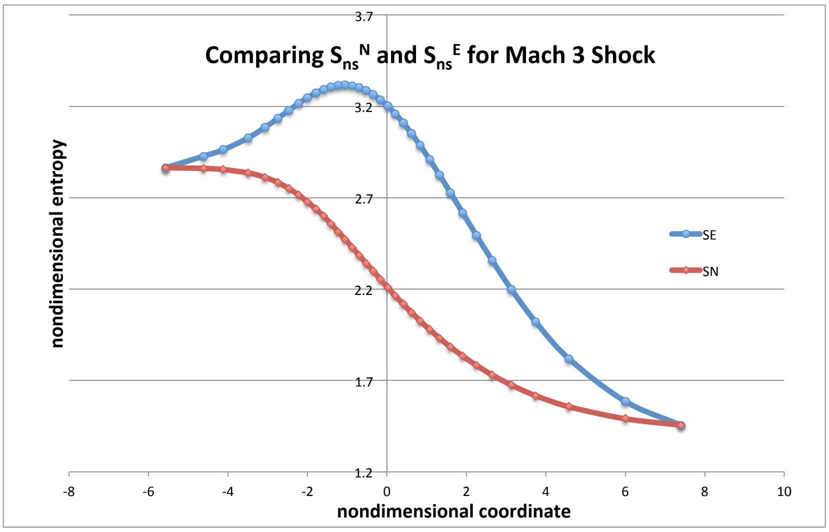

Figure 5. The nonequilibrium entropy S_{ns}^N is compared to the equilibrium entropy S_{ns}^E for the Mach 3 Navier–Stokes shock in nondimensional units.

4. Mott–Smith Nonequilibrium Entropy

As has been noted in the introduction, the Navier–Stokes equations do not accurately predict the experimental shock structure for shocks of even moderate Mach number. In 1951, Mott–Smith proposed an intuitive approximate solution for the Boltzmann equation in which the velocity PDF is taken to be a linear combination of the equilibrium (Maxwell–Boltzmann) far upstream and far downstream [17]. Let the 1-D distribution behind the shock be:

$$f_L(v) = \rho_L \left(\frac{1}{2\mathcal{I}_L}\right)^{1/2} \exp -\left(\frac{(v - v_L)^2}{2\mathcal{I}_L}\right).$$

and that in front of the shock be:

$$f_R(v) = \rho_R \left(\frac{1}{2\mathcal{I}_R}\right)^{1/2} \exp -\left(\frac{(v - v_R)^2}{2\mathcal{I}_R}\right).$$

The form of the Mott–Smith distribution is taken to be:

$$f^M = a_L(x) f_L(v) + a_R(x) f_R(v)$$

Since the mass flux inside a steady shock must be constant, we must have,

$$a_L(x) + a_R(x) = 1.$$

Thus,

$$f^M = a(x) f_L(v) + (1 - a(x)) f_R(v) \tag{12}$$

There is at present no theory to predict a unique form for the mixing function $a(x)$. However, the fact that the complicated structure of a shock can successfully fit with this single degree of freedom suggests that there is some underlying truth to f^M. The form of the approximation further suggests that inside the shock, it is the advective terms that dominate and not the collision integral. This is consistent with the failure of LTE inside the shock. Gombosi suggests the following form for the mixing function,

$$a(x) = \frac{1}{1 + \exp(\alpha\, x)} \tag{13}$$

(equation 8.55 in [18]). I will adopt this form. Rather than choosing a value for α, I will use αx as the dimensionless coordinate in the plots. I will define the nonequilibrium entropy for Mott–Smith derived by inserting Equation (12) into (8):

$$S^N_{ms} \equiv - \int f^M \, ln(f^M) \, dv\,. \tag{14}$$

Also, I will define the equilibrium entropy for Mott–Smith by calculating macroscopic density and internal energy from f^M and using Equation (6).

I have evaluated all the integrals above numerically, again using the particular parameters of the Mach $\sqrt{3}$ shock and of the stronger Mach 3 shock. As was the case for Navier–Stokes, both equilibrium entropies show a maximum inside the shock profile while the corresponding nonequilibrium entropies are monotonically increasing. Specifically, S^N_{ms} and S^E_{ms} are compared for the Mach $\sqrt{3}$ Mott–Smith shock in Figure 6, and for the Mach 3 Mott–Smith shock in Figure 7.

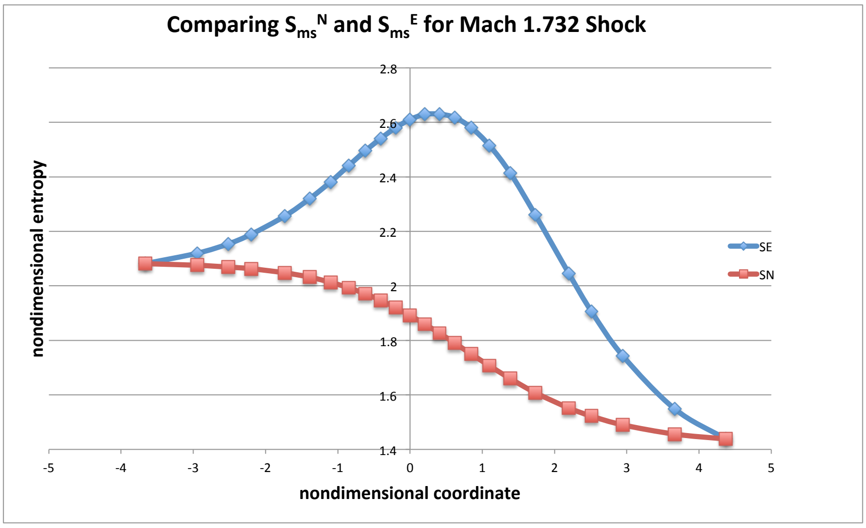

Figure 6. The nonequilibrium entropy S^N_{ms} is compared to the equilibrium entropy S^E_{ms} in nondimensional units for the Mach $\sqrt{3}$ Mott–Smith shock.

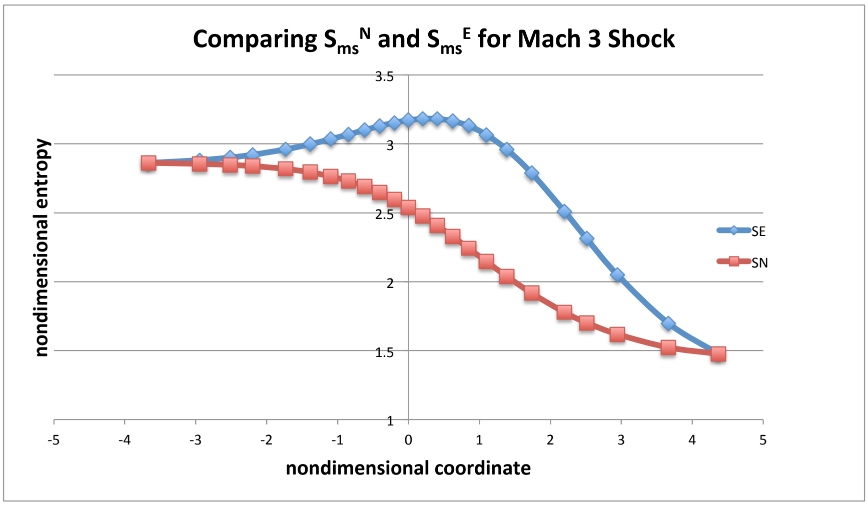

Figure 7. The nonequilibrium entropy S^N_{ms} is compared to the equilibrium entropy S^E_{ms} for the Mach 3 Mott–Smith shock in nondimensionalized units.

5. Conjecture for a Nonequilibrium Thermodynamic Entropy

There is more to learn from the Grad PDF. I next removed the contribution of the σ term (longitudinal viscosity) from f^{G} and recalculated the Boltzmann entropy. Representative points added in Figures 2 and 3 show that there is no discernible contribution to S^N_{ns} from the σ term for either the Mach $\sqrt{3}$ or the Mach 3 shock. Now if in addition, I were to remove the contribution of q term (heat conduction) then what remains is the equilibrium PDF, f^{E}, and the equilibrium entropy S^E_{ns}; thus I conclude that the main difference between S^E_{ns} and S^N_{ns}, is due to the heat flux q in Equation (10).

The importance of the heat flux in the nonequilibrium entropy brings to mind the Clausius–Duhem inequality (CDI). The general form of the CDI in one dimension is [10],

$$\rho\,\frac{DS}{Dt} + \frac{\partial}{\partial x}\left(\frac{q}{T}\right) \geq 0 \quad ; \quad q = -\kappa\frac{\partial \mathcal{E}}{\partial x} \quad ; \quad T = c_v \mathcal{E}\,. \tag{15}$$

To conform to our usage in Equation (3), I will write the heat flux and temperature in terms of the specific internal energy rather than temperature. Now under the traveling wave assumption and assuming Fourier's law, the CDI (i.e., Equation (15)) becomes,

$$-\rho_0 v \frac{\mathrm{d}}{\mathrm{d}y}\left\{S + \frac{\kappa}{\rho_0 v c_v}\frac{\mathrm{d}}{\mathrm{d}y}\left[\ln\left(\frac{\mathcal{E}}{\mathcal{E}_0}\right)\right]\right\} \geq 0. \tag{16}$$

Now the term inside the brackets is a candidate for S^M_{ns}. It is monotonically nondecreasing through the shock (recall that by the choice $y = x - vt$, our shock is moving to the right). Also, it depends on the gradient of the energy as a nonequilibrium entropy should. I will conjecture,

$$S^M_{ns} \equiv S^E_{ns} + \frac{\kappa}{\rho_0 v c_v}\frac{d}{dy}\left[\ln\left(\frac{\mathcal{E}}{\mathcal{E}_o}\right)\right] \tag{17}$$

To test my conjecture, I have calculated S^M_{ns} numerically and compared it to S^N_{ns} in Figures 8 and 9. The agreement is not exact, but is compelling. A revised CDI for the Navier–Stokes equations has the simple form,

$$\frac{dS^M_{ns}}{dy} \geq 0. \tag{18}$$

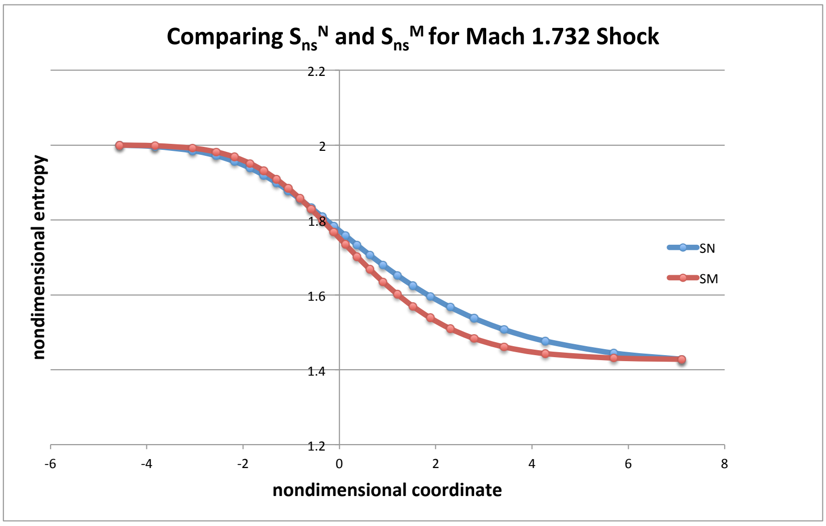

Figure 8. The modified (thermodynamic nonequilibrium) entropy S_{ns}^{M} is compared with the nonequilibrium entropy S_{ns}^{N} for the Mach $\sqrt{3}$ Naver–Stokes shock. Here S_{ns}^{M} is monotonically increasing and closely, but not exactly, estimates S_{ns}^{N}.

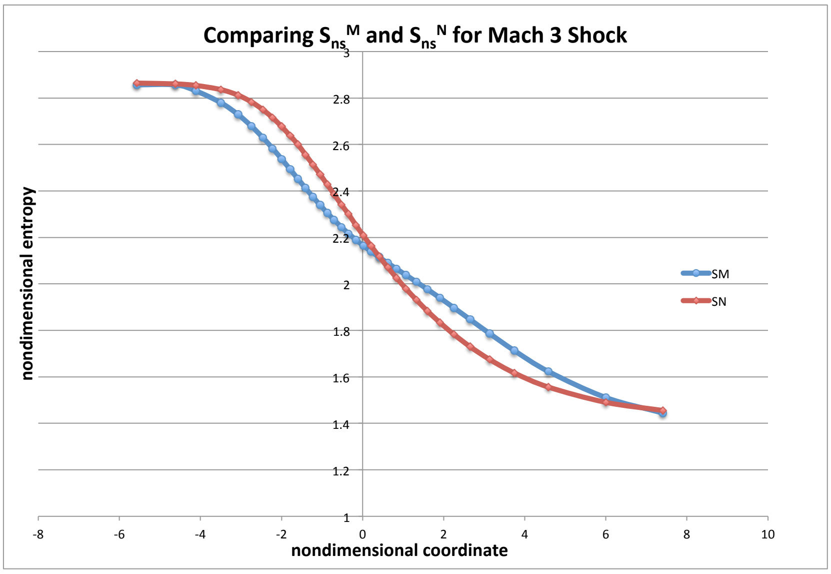

Figure 9. The modified (thermodynamic nonequilibrium) entropy S_{ns}^{M} is compared with nonequilibrium entropy S_{ns}^{N} for the Mach 3 Navier–Stokes shock. Here S_{ns}^{M} is monotonically increasing.

The situation is a little more complicated for the Mott–Smith theory. The Mott–Smith shock is still self–similar, but Fourier's law cannot be assumed. The effective conductivity, i.e., the ratio of numerically calculated heat flux q over the energy gradient $\frac{d\mathcal{E}}{d(\alpha x)}$ for both the Mach $\sqrt{3}$ and the Mach 3 shocks are plotted in Figure 10. Surprisingly, in both cases, the effective conductivity decreases with increasing energy. The plots show an almost linear relation which, however, depends in part on the assumed form of the mixing function $a(x)$ in Equation (13).

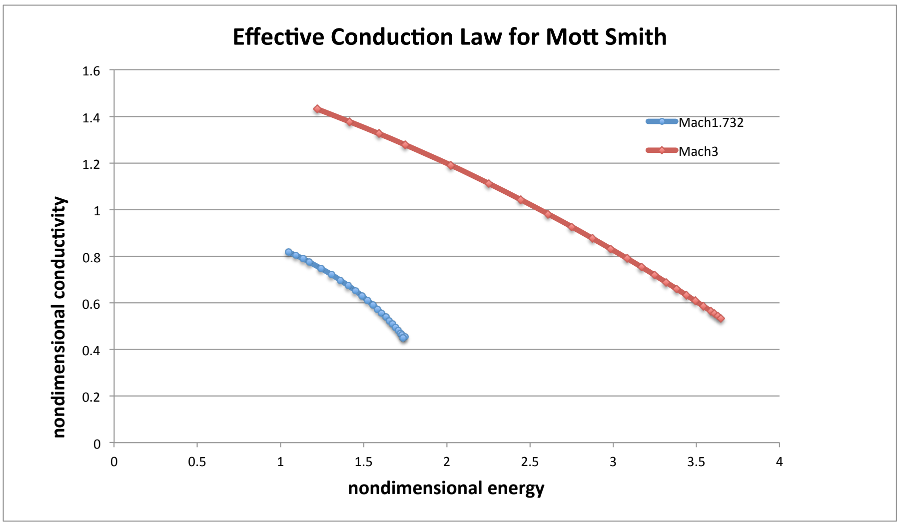

Figure 10. The effective conductivity, i.e., the ratio of heat flux q to energy gradient $\frac{dE}{dx}$, for the Mott–Smith theory is plotted for the Mach $\sqrt{3}$ and the Mach 3 shocks. In both cases, the effective conductivity decreases for increasing energy (temperature).

When the numerically calculated heat flux is added to the equilibrium entropy S^E_{ms} to form the modified entropy S^M_{ms}, the agreement with S^N_{ms} is excellent for both the Mach $\sqrt{3}$ shock in Figure 11 and the Mach 3 shock in Figure 12.

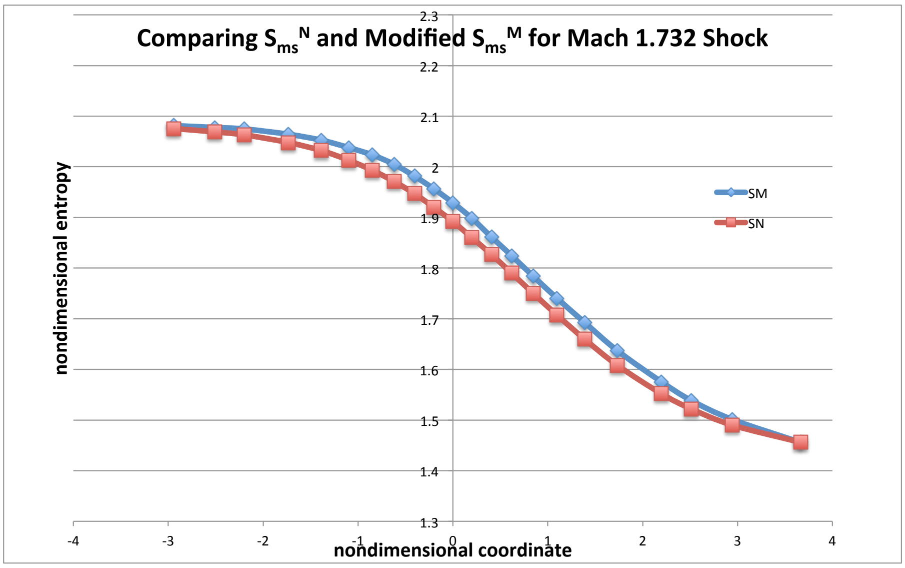

Figure 11. The modified (thermodynamic nonequilibrium) entropy S^M_{ns} is compared with nonequilibrium entropy S^N_{ns} for the Mach $\sqrt{3}$ Mott–Smith shock. Here S^M_{ms} is monotonically increasing and estimates S^N_{ms} quite closely.

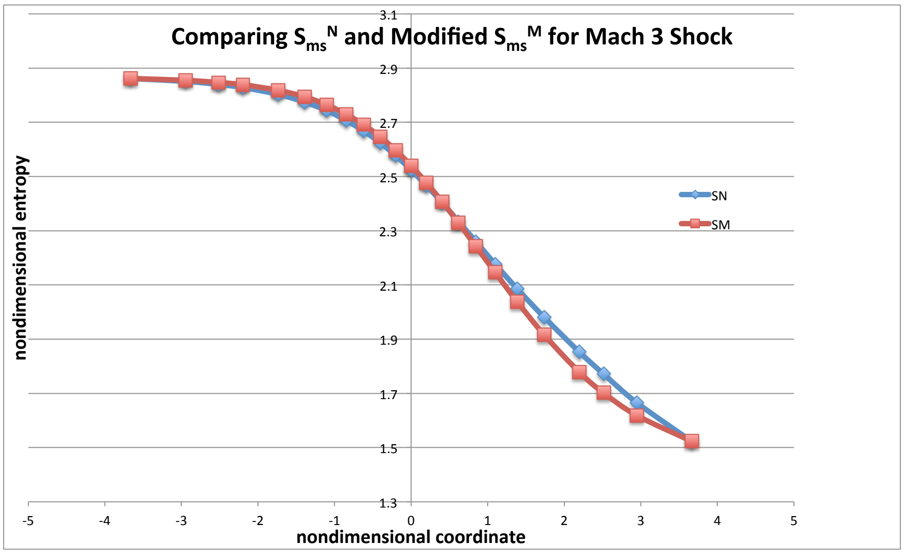

Figure 12. The modified (thermodynamic nonequilibrium) entropy S_{ms}^M is compared with nonequilibrium entropy S_{ms}^N for the Mach 3 Mott–Smith shock. Here S_{ms}^M is monotonically increasing and estimates S_{ms}^N quite closely.

6. Shock Structure and Numerical Simulation

"The purpose of computing is insight, not numbers." (Cecil Hastings)

"There's no sense in being precise when you don't even know what you're talking about." (John von Neumann)

I have included the evaluation of Mott–Smith entropies in Section 4 because I believe this currently ad hoc theory will play an important role in a macroscopic theory of shock structure. There has been a small, but continuing interest in the Mott–Smith model [17] since its publication in 1951. However, I anticipate a resurgence of interest in the near future. The reason is the rapidly growing power of computers. Flows with shocks have been of interest since the origins of computational fluid dynamics (CFD). Early computers could not resolve shock structure for lack of speed and memory, and CFD pioneer John von Neumann introduced the concept of artificial viscosity [19] and regularized Euler equations to overcome those limitations. Now, 67 years later, we are just beginning to resolve shock structure in two spatial dimensions for problems posed to gain insight into processes of practical interest [20].

However, Navier–Stokes theory has proven inadequate to predict experimentally measured structure in all but the very weakest shocks. This failure is well-known and is illustrated (among many places) in Figure 3 of [5] and Figure 10 of [6], where the Navier–Stokes predicted shock width is seen to be about half the measured shock width (note that it is inverse shock width that is plotted in that figure). The United States Department of Energy project to develop the exascale computer [21] is scheduled to complete in about 2024. Seven years seems a short time in which to develop a more rigorous alternative to Navier–Stokes.

Some effort in that direction has gone into studying higher moments of Chapman–Enskog theory [22] and Grad theory [23]. Those studies would seem to ignore the basic message of Becker [4] that the Knudsen number as an expansion parameter is not small in the shock, and Chapman–Enskog theory and associated moment methods are not convergent in shocks. The attraction of the Mott-Smith theory is that it is not a perturbation of the equilibrium solution; its form indicates that it represents a regime in which it is the advective terms, not the collision integral, that is dominant. Even so, it has been demonstrated that the Mott–Smith PDF is indeed an approximate solution of the Boltzmann equation [24].

The present question in Mott–Smith theory is how to derive the mixing function, which I termed $a(x)$ in Equation (12). That form, proposed by Gombosi [18], is based on the collision integral. However, other authors [25,26] have proposed using the entropy balance as a means to determine the mixing function. Perhaps a more modern approach based on maximum entropy production principles [27] can be applied to the modified entropy S_{ms}^{M} defined in Section 5.

7. Summary

I had two goals in mind when beginnning to write this paper. First, I wanted to understand the distribution of entropy in a shock profile and in particular, to understand the significance of the curious result of Morduchow and Libby that predicts an entropy maximum inside the shock profile. Second, I wanted to draw attention to (an anticipated) reborn interest in creating a hydrodynamic theory that accurately describes the distribution of all state variables in a shock profile and to call attention to the Mott–Smith theory as a potential framework.

With respect to the first goal, I followed Gibb's quote in the introduction and looked toward the more fundamental description of statistical mechanics. In Section 3, I used the Grad PDF that underlies one derivation of the Navier–Stokes equations to evaluate (numerically) the Boltzmann entropy. For two particular cases, the Mach $\sqrt{3}$ and the Mach 3 shocks, the entropy profile monotonically increases through the shock. As to the Morduchow and Libby result, my final conclusion is that the thermodynamic equilibrium entropy provides only a poor estimate of the nonequilibrium entropy. Further, I showed how redefining the equilibrium entropy to include the entropy flux provides a close estimate of the nonequilibrium entropy; that estimate also monotonically increases through the profile and by construction satisfies the Clausius Duhem inequality.

As regards the second goal, I have demonstrated that the Mott–Smith theory also contains a monotonically increasing nonequlibrium entropy and that a nonequilibrium thermodynamic entropy can be defined that closely estimates that nonequilibrium entropy. More generally, I have tried to motivate a renewed interest in developing a macroscopic hydrodynamic theory that can accurately describe shocks and other highly nonequilibrium processes.

> "The future belongs to those who can manipulate entropy; those who understand but energy will be only accountants." (Frederic Keffer)

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