

A Model System of Mixed Ionized Gas Dynamics

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Abstract The aim of this paper is to study a one dimensional model system of equations for ionized gas dynamics at high temperature where the gas is a mixture of two kinds of monatomic gas. In addition to the mass density, pressure, temperature and particle velocity, degrees of ionization of both gases are also involved. By assuming that the local thermal equilibrium is attained, Saha's ionization equations are added. Thus the equations are supplemented by the first and second law of thermodynamics, a single equation of state and, in addition, a set of thermodynamic equations.

The equations constitute a strictly hyperbolic system, which guarantees that the initial value problem is well-posed locally in time for sufficiently smooth initial data. However the geometric properties of the system are rather complicated: in particular, we prove the existence of a region where convexity (genuine nonlinearity) fails for forward and backward characteristic fields. Also we study thermodynamic properties of shock waves by a detailed analysis of the Hugoniot locus, which is used in a mathematical study of existence and uniqueness of solutions to the shock tube problem.

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1 Introduction

A shock wave is a propagating discontinuity of density, pressure, temperature and etc., which is supersonic with respect to the gaseous medium ahead of it and subsonic with respect to that behind it. Behind a shock wave, not only

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pressure but also temperature increases abruptly and the gas is heated to high temperatures. Strong shock waves are obtained and replicated by shock tube operations under ordinary circumstances. Hence the shock tube is a convenient and widely used device for obtaining high temperature gases in the laboratory. The shock front and the state behind it in the shock tube are determined by the state ahead of it and the speed of driving gas, which is a mathematical problem called the *shock tube problem* in this paper.

When the gas behind the shock front is heated to a high temperature, almost all molecules become dissociated and finally its atoms become partially ionized: $X \rightleftharpoons X^+ + e^-$. Numerous spectroscopic measurements of atomic parameters and thermodynamic equilibrium of plasma thus generated have been done, for example, in various Helium-Hydrogen mixtures ([9],[10]). The model system of mixed ionized gas dynamics that we discuss in this paper is proposed by Fukuda-Okasaka-Fujimoto in [8]¹ for the purpose of providing a theoretical basis for their observations. The system consists of equations of macroscopic motion for 1-d mixed gas dynamics. Its particular nature is: degree of ionization of each gas is considered to be a thermodynamic variable.

The present paper is a continuation of [1], [2], [3] and our aim is to perform mathematical analysis for the model system and show its basic thermodynamic properties. To the best of our knowledge such a study has never been done previously while the system of gas dynamics attracted the interest of several researchers in the last decade, however mostly for ideal gases [15]; we quote [13] for the case of real gases. For a single monatomic ionized gas, studies have been done in [1], [2], [3].

Basic thermodynamic variables are denoted in this paper by T : temperature, p : pressure, ρ : mass density, $v = 1/\rho$: specific volume, e : specific internal energy and S : specific entropy. The flow velocity is denoted by u and the (specific) total energy by $\mathcal{E} = \frac{1}{2}u^2 + e$. The system of equations of one-dimensional motion for gas dynamics consists of the following three conservation laws: conservation of mass, momentum and energy

$$\begin{cases} \rho_t + (\rho u)_x = 0, \\ (\rho u)_t + (\rho u^2 + p)_x = 0, \\ (\rho \mathcal{E})_t + (\rho \mathcal{E} u + p u)_x = 0, \end{cases} \quad (1)$$

which are supplemented by the first and second law of thermodynamics

$$de = TdS - pdv, \quad (2)$$

a single equation of state and a set of thermodynamic equations. For brevity we will refer to S , e and \mathcal{E} as the entropy, internal and total energy, respectively.

For a partially ionized *single* monatomic gas, let n_a , n_i and n_e denote, respectively, the concentration (number per unit volume) of atoms, ions and

¹ An English translation of [8] is available upon request to F. Asakura.

electrons. The equation of state depends on the *degree of ionization* $\alpha = \frac{n_e}{n_a + n_i}$ having the form

$$p = \frac{R}{M} \rho T (1 + \alpha) \quad (3)$$

where R denotes the *universal gas constant* and M the *molar mass* of the monatomic gas ([8]). This model system is similar to the system of an ideal dissociating diatomic gas studied by Lighthill in [12].

It is found that, at any given high temperature T and volume V , these ionization reactions reach a state of equilibrium which is analogous to the chemical equilibrium for usual chemical reactions whose equilibrium condition is the law of mass action: the ratio $\frac{n_i n_e}{n_a}$ depends only on the temperature T . An actual formula was derived by M. Saha in [14], namely,

$$\frac{n_i n_e}{n_a} = \frac{2G_i}{G_a} \frac{(2\pi m_e k T)^{\frac{3}{2}}}{h^3} e^{-\frac{T_i}{T}}, \quad (4)$$

see also [5],[7],[16],[18]. Here we denote the partition functions of the neutral state and of the 1-ionized state by G_a and G_i , respectively; m_e is the electron mass, k the Boltzmann constant, h the Planck constant and $T_i = \frac{\chi}{k}$ the ionization energy measured by the temperature, where χ is the first ionization potential [16, §5, (4.8)]. On the other hand, Saha's law (4) is written as

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{2G_i}{G_a} \frac{(2\pi m_e)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{ph^3} e^{-\frac{T_i}{T}}, \quad (5)$$

(see [7, (209)], [16, §V.4, (4.9)]), showing that α can be regarded as a thermodynamic variable.

Since the electric intermolecular process of ionization occurs much faster than the fluid-dynamic phenomenon of shock formation, see for instance [18, VII, §11] and [18, VII, §10, Table 7.3], we may assume that a local thermodynamic equilibrium is everywhere attained: that is, Saha's law (5) holds everywhere even in presence of shock waves, which is one of the postulates of the present model system of ionized gas dynamics. Thus the equations (3) and (5) constitute the equation of state and a thermodynamic equation.

Now let us consider one mole mixture of monatomic gases A and B. The ionization reactions are represented as $A \rightleftharpoons A^+ + e^-$, $B \rightleftharpoons B^+ + e^-$. We denote the number of atoms and ions for each gas by N_a^A, N_a^B and N_i^A, N_i^B , respectively. The number of electrons are denoted by N_e . Note that

$$N_a^A + N_i^A + N_a^B + N_i^B = N_0 : \text{Avogadro Number}, \quad N_e = N_i^A + N_i^B.$$

The concentration of atoms, ions and electrons are defined by $n_a^A = \frac{N_a^A}{V}$, $n_a^B = \frac{N_a^B}{V}$, $n_i^A = \frac{N_i^A}{V}$, $n_i^B = \frac{N_i^B}{V}$, $n_e = \frac{N_e}{V}$, respectively.

By denoting G_a^A, G_a^B : the partition functions of the neutral state, G_i^A, G_i^B : same for the 1-ionized state, and χ^A, χ^B : first ionization potentials, the coupled Saha's laws for mixed monatomic gas are presented as the following.

$$\frac{n_i^A n_e}{n_a^A} = \frac{2G_i^A}{G_a^A} \left(\frac{2\pi m_e k T}{h^2} \right)^{\frac{3}{2}} e^{-\frac{\chi^A}{kT}}, \quad \frac{n_i^B n_e}{n_a^B} = \frac{2G_i^B}{G_a^B} \left(\frac{2\pi m_e k T}{h^2} \right)^{\frac{3}{2}} e^{-\frac{\chi^B}{kT}} \quad (6)$$

For A: hydrogen atom A, we have $\chi^A = 13.59844$ eV and for B: helium atom B, $\chi^B = 24.58741$ eV. First ionization temperatures are

$$T_A = \frac{\chi^A}{k} = 1.5780 \times 10^5, \quad T_B = \frac{\chi^B}{k} = 2.8532 \times 10^5.$$

Note that $T_A < T_B < 2T_A$. We have also $\frac{2G_i^A}{G_a^A} = 1$, $\frac{2G_i^B}{G_a^B} = 4$. We will assume that a local thermodynamic equilibrium is everywhere attained: that is the coupled Saha's laws (6) hold everywhere even in presence of shock waves.

The present model system is constructed on the basis of several postulates that we now expose in detail. By denoting the Debye radius [18, III-2-§11] by λ_D , the *plasma parameter*: $A = \frac{4}{3}\pi n_e \lambda_D^3$ is a dimensionless number defined by the number of electrons in a Debye sphere. We recall that the ratio between the potential energy and the kinetic energy is of order $A^{-\frac{2}{3}}$. We first assume that:

- Gas is a mixture of monatomic gases A and B satisfying $T_A < T_B \leq 2T_A$
- All collisions are perfectly elastic (or effects of collisions among the particles can be neglected)
- Gravitational effects, viscosity and thermal conductivities are disregarded
- $A \gg 1$, which means that the interaction potential energies of the charged particles are negligible with respect to the kinetic energies, and electrostatic interactions are relatively rare
- Local thermodynamic equilibrium is everywhere attained

The fourth postulate above is motivated by the high temperatures considered in [8], see [11, §78], [18, (3.77)] for further details.

The *degree of ionization* and *fraction* for each gas is defined by

$$\alpha_A = \frac{n_i^A}{n_a^A + n_i^A}, \quad \alpha_B = \frac{n_i^B}{n_a^B + n_i^B},$$

$$\beta = \frac{N_a^A + N_i^A}{N_0} = \frac{n_a^A + n_i^A}{n_0}, \quad 1 - \beta = \frac{N_a^B + N_i^B}{N_0} = \frac{n_a^B + n_i^B}{n_0}.$$

The density and molar mass of each gas are denoted by ρ_A , ρ_B and M_A , M_B , respectively. The pressure is a sum of partial pressures with respect to atoms, ions and electrons:

$$p = p_a + p_i + p_e = p_a + 2p_i, \quad p_j = kn_j T \quad (j = a, i, e).$$

Then by setting $\alpha = \beta\alpha_A + (1 - \beta)\alpha_B$

$$p = p_a^A + 2p_i^A + p_a^B + 2p_i^B = k(n_a^A + 2n_i^A + n_a^B + 2n_i^B) T$$

$$= k[(n_a^A + n_i^A)(1 + \alpha_A) + (n_a^B + n_i^B)(1 + \alpha_B)] T = kn_0(1 + \alpha) T.$$

By noticing $1 + \frac{n_a^A}{n_i^A} = \frac{1}{\alpha^A}$, $1 + \frac{n_a^B}{n_i^B} = \frac{1}{\alpha^B}$, Saha's laws take the forms

$$\frac{n_i^A n_e}{n_a^A} = \left(\frac{\alpha_A}{1 - \alpha_A} \right) (n_i^A + n_i^B) = \frac{n_0 \alpha_A \alpha}{1 - \alpha_A} = \frac{2G_i^A}{G_a^A} \left(\frac{2\pi m_e k T}{h^2} \right)^{\frac{3}{2}} e^{-\frac{T_A}{T}},$$

$$\frac{n_i^B n_e}{n_a^B} = \left(\frac{\alpha_B}{1 - \alpha_B} \right) (n_i^A + n_i^B) = \frac{n_0 \alpha_B \alpha}{1 - \alpha_B} = \frac{2G_i^B}{G_a^B} \left(\frac{2\pi m_e k T}{h^2} \right)^{\frac{3}{2}} e^{-\frac{T_B}{T}}.$$

Thus we conclude that thermodynamic equations have the forms

$$\begin{aligned} p &= \frac{(1 - \alpha_A)(1 + \alpha)}{\alpha_A \alpha} \frac{2G_i^A}{G_a^A} \frac{(2\pi m_e)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3} e^{-\frac{T_A}{T}} \\ &= \frac{(1 - \alpha_B)(1 + \alpha)}{\alpha_B \alpha} \frac{2G_i^B}{G_a^B} \frac{(2\pi m_e)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3} e^{-\frac{T_B}{T}}. \end{aligned} \quad (7)$$

Also we have a compatibility condition

$$\frac{2G_i^A}{G_a^A} \frac{1 - \alpha_A}{\alpha_A} e^{-\frac{T_A}{T}} = \frac{2G_i^B}{G_a^B} \frac{1 - \alpha_B}{\alpha_B} e^{-\frac{T_B}{T}}. \quad (8)$$

We next assume that:

- Gases are well mixed so that: $\rho = \beta\rho_A + (1 - \beta)\rho_B$;
- Pressure of each gas takes the form

$$p_A = \frac{R\rho_A}{M_A} T(1 + \alpha_A), \quad p_B = \frac{R\rho_B}{M_B} T(1 + \alpha_B)$$

- Specific enthalpies are defined by

$$h_A = \frac{5R}{2M_A} T(1 + \alpha_A) + \frac{RT_A}{M_A} \alpha_A, \quad h_B = \frac{5R}{2M_B} T(1 + \alpha_B) + \frac{RT_B}{M_B} \alpha_B$$

- Macroscopic motion of the gas flow is one-dimensional

We deduce from the above assumptions that the total pressure is

$$p = \beta p_A + (1 - \beta)p_B = \beta \frac{R\rho_A}{M_A} T(1 + \alpha_A) + (1 - \beta) \frac{R\rho_B}{M_B} T(1 + \alpha_B).$$

Thus

$$\frac{p}{\rho} = \frac{\beta \frac{R}{V} T(1 + \alpha_A) + (1 - \beta) \frac{R}{V} T(1 + \alpha_B)}{\beta \frac{M_A}{V} + (1 - \beta) \frac{M_B}{V}} = \frac{RT [1 + \beta\alpha_A + (1 - \beta)\alpha_B]}{\beta M_A + (1 - \beta)M_B}.$$

Denoting $\alpha = \beta\alpha_A + (1 - \beta)\alpha_B$ and $M = \beta M_A + (1 - \beta)M_B$, we obtain

$$p = \frac{R}{M} \rho T(1 + \alpha) \quad (9)$$

which is the equation of state. The total specific enthalpy is

$$h = \frac{\beta M_A h_A + (1 - \beta)M_B h_B}{\beta M_A + (1 - \beta)M_B} = \frac{5RT}{2M} (1 + \alpha) + \frac{R}{M} [\beta T_A \alpha_A + (1 - \beta)T_B \alpha_B] \quad (10)$$

After a short review of basic thermodynamics, we show some basic calculus lemmas in Section 2. The physical entropy functions are constructed in Section 3. We show that system (1) is strictly hyperbolic and compute characteristic fields in Section 4. However, unlike the ideal polytropic case, the forward and backward characteristic fields of the system are not genuinely nonlinear and we study the set where this happens in Section 5. We refer to [6], [15] for more

information on systems of conservation laws. We study in Section 6 the relation between α_A and α_B . A detailed study of the Hugoniot locus of the system is carried out in Section 7. Though Hugoniot loci are monotone in (T, α) -plane in a single monatomic case, they are not always monotone in the present mixed monatomic case: If β is sufficiently small, then they lose monotonicity at some base state. Thus the degree of ionization does not always increase across the shock front, even if the temperature increases. However we prove that the pressure actually increases as the temperature increases. In order to fit the mathematical data to ordinary circumstances, we propose an approximation of Hugoniot locus in Section 8. We apply our results to the shock tube problem in Section 9. Basic results: existence and uniqueness are established, which provides a rigorous mathematical basis to the physical phenomena observed in [8]. Behaviour of isentropes and detailed computations for the proof of uniqueness are shown in appendices.

2 Basic Thermodynamics and Calculus Lemmas

First we adopt p and T as a set of independent thermodynamic state variables. By introducing the enthalpy $h = e + pv$, the first and second law 1-(2) becomes

$$dh = T dS + v dp = T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left[\left(\frac{\partial S}{\partial p} \right)_T + v \right] dp$$

As usual, a subscript as T or p above means that the derivative is computed by holding the subscripted variable fixed. We also introduce the Gibbs function $g = h - TS$, see [7, (111)], and we have

$$dg = v dp - S dT = \left(\frac{\partial g}{\partial p} \right)_T dp + \left(\frac{\partial g}{\partial T} \right)_p dT. \quad (1)$$

Maxwell's Relations: We deduce by (1) the compatibility condition

$$\left(\frac{\partial v}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T, \quad (2)$$

which is one of so-called Maxwell relations. In turn, by (1) and (2) we obtain

$$\left(\frac{\partial h}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + v = -T \left(\frac{\partial v}{\partial T} \right)_p + v, \quad \left(\frac{\partial h}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p.$$

Thus we have the following proposition.

Proposition 1 (p, T : set of independent variables)

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p, \quad \left(\frac{\partial S}{\partial T} \right)_p = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p$$

The specific volume v is expressed by 1-(9) as $v = \frac{RT}{Mp}(1 + \alpha)$ and the enthalpy is 1-(10). The dimensionless entropy η is defined by $\eta = \frac{M}{R}S$. Consequently we have by Proposition 1

Lemma 1

$$\left(\frac{\partial \eta}{\partial p}\right)_T = -\frac{1}{p} \left[1 + \alpha + T \left(\frac{\partial \alpha}{\partial T}\right)_p \right] \quad (3)$$

$$\left(\frac{\partial \eta}{\partial T}\right)_p = \frac{5}{2T}(1 + \alpha) + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial \alpha_A}{\partial T}\right)_p + (1 - \beta) \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial \alpha_B}{\partial T}\right)_p \quad (4)$$

Saha Equations: Setting

$$T_A = \frac{\chi^A}{k}, \quad T_B = \frac{\chi^B}{k}, \quad \mu_A^{-1} = \frac{2G_i^A}{G_a^A} \frac{(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3}, \quad \mu_B^{-1} = \frac{2G_i^B}{G_a^B} \frac{(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3},$$

we have from 1-(7) and 1-(8)

Lemma 2 *Saha's equations take the forms*

$$\left(\frac{1}{\alpha_A} - 1\right) \left(\frac{1}{\alpha} - 1\right) = \frac{\mu_A p e^{\frac{T_A}{T}}}{T^{\frac{5}{2}}}, \quad \left(\frac{1}{\alpha_B} - 1\right) \left(\frac{1}{\alpha} - 1\right) = \frac{\mu_B p e^{\frac{T_B}{T}}}{T^{\frac{5}{2}}} \quad (5)$$

and the compatibility condition

$$\left(\frac{1}{\alpha_A} - 1\right) \frac{e^{-\frac{T_A}{T}}}{\mu_A} = \left(\frac{1}{\alpha_B} - 1\right) \frac{e^{-\frac{T_B}{T}}}{\mu_B}. \quad (6)$$

Computation of $\left(\frac{\partial \alpha_A}{\partial p}\right)_T$, $\left(\frac{\partial \alpha_A}{\partial T}\right)_p$, $\left(\frac{\partial \alpha_B}{\partial p}\right)_T$, $\left(\frac{\partial \alpha_B}{\partial T}\right)_p$: For the sake of brevity, we set

$$q_A = \alpha_A(1 - \alpha_A), \quad q_B = \alpha_B(1 - \alpha_B), \quad q = \beta q_A + (1 - \beta)q_B.$$

Differentiating Saha's equations, we have a system of Pfaff equations

$$\begin{aligned} & \frac{\alpha(1 + \alpha) + \beta q_A}{\alpha_A^2 \alpha^2} d\alpha_A + \frac{(1 - \alpha_A)(1 - \beta)}{\alpha_A \alpha^2} d\alpha_B \\ &= -\frac{\mu_A p e^{\frac{T_A}{T}}}{T^{\frac{5}{2}}} \left[\frac{dp}{p} - \left(\frac{5}{2} + \frac{T_A}{T}\right) \frac{dT}{T} \right], \end{aligned} \quad (7)$$

$$\begin{aligned} & \frac{(1 - \alpha_B)\beta}{\alpha_B \alpha^2} d\alpha_A + \frac{\alpha(1 + \alpha) + (1 - \beta)q_B}{\alpha_B^2 \alpha^2} d\alpha_B \\ &= -\frac{\mu_B p e^{\frac{T_B}{T}}}{T^{\frac{5}{2}}} \left[\frac{dp}{p} - \left(\frac{5}{2} + \frac{T_B}{T}\right) \frac{dT}{T} \right] \end{aligned} \quad (8)$$

which constitutes a system of linear equation of $d\alpha_A$ and $d\alpha_B$. By the inverse function theorem, we obtain

Lemma 3

$$\left(\frac{\partial\alpha_A}{\partial p}\right)_T = -\frac{\alpha(1+\alpha)q_A}{p[\alpha(1+\alpha)+q]}, \quad \left(\frac{\partial\alpha_B}{\partial p}\right)_T = -\frac{\alpha(1+\alpha)q_B}{p[\alpha(1+\alpha)+q]} \quad (9)$$

$$\left(\frac{\partial\alpha_A}{\partial T}\right)_p = \frac{\alpha(1+\alpha)q_A}{T[\alpha(1+\alpha)+q]} \left(\frac{5}{2} + \frac{T_A}{T}\right) + \frac{(1-\beta)q_Aq_B(T_A - T_B)}{T^2[\alpha(1+\alpha)+q]} \quad (10)$$

$$\left(\frac{\partial\alpha_B}{\partial T}\right)_p = \frac{\alpha(1+\alpha)q_B}{T[\alpha(1+\alpha)+q]} \left(\frac{5}{2} + \frac{T_B}{T}\right) + \frac{\beta q_Aq_B(T_B - T_A)}{T^2[\alpha(1+\alpha)+q]} \quad (11)$$

We deduce from this lemma

$$\begin{aligned} \left(\frac{\partial\alpha_A}{\partial T}\right)_p &= -\frac{p}{T} \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial\alpha_A}{\partial p}\right)_T + \frac{(1-\beta)q_Aq_B(T_A - T_B)}{T^2[\alpha(1+\alpha)+q]} \\ \left(\frac{\partial\alpha_B}{\partial T}\right)_p &= -\frac{p}{T} \left(\frac{5}{2} + \frac{T_B}{T}\right) \left(\frac{\partial\alpha_B}{\partial p}\right)_T + \frac{\beta q_Aq_B(T_B - T_A)}{T^2[\alpha(1+\alpha)+q]}. \end{aligned}$$

Thus we obtain useful lemmas:

Lemma 4

$$-\frac{T}{p} \left(\frac{\partial\alpha}{\partial T}\right)_p = \frac{5}{2} \left(\frac{\partial\alpha}{\partial p}\right)_T + \frac{\beta T_A}{T} \left(\frac{\partial\alpha_A}{\partial p}\right)_T + \frac{(1-\beta)T_B}{T} \left(\frac{\partial\alpha_B}{\partial p}\right)_T$$

Lemma 5

$$\left(\frac{\partial\eta}{\partial p}\right)_T = -\frac{1+\alpha}{p} + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial\alpha_A}{\partial p}\right)_T + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \left(\frac{\partial\alpha_B}{\partial p}\right)_T \quad (12)$$

3 Construction of Entropy Function

We will construct the physical entropy function for the present model system. First we prove:

Lemma 6 *The dimensionless entropy $\eta = \frac{M}{R}S$ takes the form*

$$\begin{aligned} \eta(p, T) &= \log \alpha \\ &+ \beta \log \alpha_A + (1-\beta) \log \alpha_B - 2\beta \log(1-\alpha_A) - 2(1-\beta) \log(1-\alpha_B) \\ &+ \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \alpha_A + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \alpha_B + \mathcal{H}(T). \end{aligned} \quad (13)$$

where \mathcal{H} is an arbitrary function of T .

Proof Integrating (12) with respect to p , we have

$$\eta(p, T) = -\int \frac{1+\alpha}{p} dp + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \alpha_A + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \alpha_B.$$

We notice that: if $dT = 0$, then it follows from (7) and Saha's equation (5)

$$-\frac{1+\alpha}{p}dp = \frac{1+\alpha}{q_A}d\alpha_A + \frac{1}{\alpha}d\alpha = \frac{1+\beta\alpha_A}{q_A}d\alpha_A + \frac{(1-\beta)\alpha_B}{q_A}d\alpha_A + \frac{1}{\alpha}d\alpha. \quad (14)$$

It follows from the compatibility condition (6)

$$\log\left(\frac{1}{\alpha_A} - 1\right) - \frac{T_A}{T} - \log\mu_A = \log\left(\frac{1}{\alpha_B} - 1\right) - \frac{T_B}{T} - \log\mu_B.$$

Hence

$$\frac{d\alpha_A}{q_A} - \frac{T_A}{T^2}dT = \frac{d\alpha_B}{q_B} - \frac{T_B}{T^2}dT.$$

If $dT = 0$, then $\frac{d\alpha_A}{q_A} = \frac{d\alpha_B}{q_B}$ and (14) is found to be

$$-\frac{1+\alpha}{p}dp = \frac{1+\beta\alpha_A}{q_A}d\alpha_A + \frac{(1-\beta)\alpha_B}{q_B}d\alpha_B + \frac{1}{\alpha}d\alpha.$$

By integrating the above expression

$$-\int \frac{1+\alpha}{p}dp = \log\alpha_A - (1+\beta)\log(1-\alpha_A) - (1-\beta)\log(1-\alpha_B) + \log\alpha + \mathcal{H}(T)$$

In a similar manner

$$\begin{aligned} -\frac{1+\alpha}{p}dp &= \frac{1+(1-\beta)\alpha_B}{q_B}d\alpha_B + \frac{\beta\alpha_A}{q_B}d\alpha_B + \frac{1}{\alpha}d\alpha \\ &= \frac{1+(1-\beta)\alpha_B}{q_B}d\alpha_B + \frac{\beta\alpha_A}{q_A}d\alpha_A + \frac{1}{\alpha}d\alpha \end{aligned}$$

and hence

$$-\int \frac{1+\alpha}{p}dp = \log\alpha_B - (2-\beta)\log(1-\alpha_B) - \beta\log(1-\alpha_A) + \log\alpha + \mathcal{H}(T).$$

For symmetry, we have (13).

Next we will determine the form of $\mathcal{H}(T)$, and then obtain the entropy function up to constant.

Theorem 1 *The dimensionless entropy function $\eta(p, T)$ takes the form*

$$\begin{aligned} &\log[\beta\alpha_A + (1-\beta)\alpha_B] \\ &+ \beta \left[\log\alpha_A - 2\log(1-\alpha_A) + \frac{T_A}{T} \right] + (1-\beta) \left[\log\alpha_B - 2\log(1-\alpha_B) + \frac{T_B}{T} \right] \\ &+ \beta \left(\frac{5}{2} + \frac{T_A}{T} \right) \alpha_A + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T} \right) \alpha_B + \text{const.} \end{aligned}$$

Proof Differentiating η with respect to T , we have

$$\begin{aligned} \left(\frac{\partial\eta}{\partial T}\right)_p &= \frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_p - \frac{\beta}{\alpha_A} \left(\frac{\partial\alpha_A}{\partial T}\right)_p - \frac{1-\beta}{\alpha_B} \left(\frac{\partial\alpha_B}{\partial T}\right)_p \\ &\quad + \frac{2\beta}{q_A} \left(\frac{\partial\alpha_A}{\partial T}\right)_p + \frac{2(1-\beta)}{q_B} \left(\frac{\partial\alpha_B}{\partial T}\right)_p - \frac{\beta\alpha_A T_A}{T^2} - \frac{(1-\beta)\alpha_B T_B}{T^2} \\ &\quad + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial\alpha_A}{\partial T}\right)_p + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \left(\frac{\partial\alpha_B}{\partial T}\right)_p + \mathcal{H}'(T). \end{aligned}$$

Using the formulas in Lemma 3 and 4 and setting $\Sigma = \alpha(1+\alpha) + q$, we find that

$$\begin{aligned} &\frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_p - \left[\frac{\beta}{\alpha_A} \left(\frac{\partial\alpha_A}{\partial T}\right)_p - \frac{1-\beta}{\alpha_B} \left(\frac{\partial\alpha_B}{\partial T}\right)_p \right] + \frac{2\beta}{q_A} \left(\frac{\partial\alpha_A}{\partial T}\right)_p + \frac{2(1-\beta)}{q_B} \left(\frac{\partial\alpha_B}{\partial T}\right)_p \\ &= \frac{(1+\alpha)\beta(1-\beta)}{\Sigma T} \left[(1-\alpha_A) \left(\frac{5}{2} + \frac{T_A}{T}\right) - (1-\alpha_B) \left(\frac{5}{2} + \frac{T_B}{T}\right) \right] (\alpha_A - \alpha_B) \\ &\quad + \frac{\beta(1-\beta)(1+\alpha)(1-\alpha_A)(1-\alpha_B)(\alpha_A - \alpha_B)(T_A - T_B)}{\Sigma T^2} \\ &\quad + \frac{2\alpha(1+\alpha)}{\Sigma T} \left[\frac{5}{2} + \frac{\beta T_A}{T} + \frac{(1-\beta)T_B}{T} \right] - \frac{2\beta(1-\beta)(1+\alpha)[q_A - q_B](T_A - T_B)}{\Sigma T^2}. \end{aligned}$$

The terms involving neither T_A nor T_B are

$$\frac{5}{2} \left\{ \frac{(1+\alpha)\beta(1-\beta)}{\Sigma T} [(1-\alpha_A) - (1-\alpha_B)] (\alpha_A - \alpha_B) + \frac{2\alpha(1+\alpha)}{\Sigma T} \right\} = \frac{5(1+\alpha)}{2T}$$

and the terms involving T_A and T_B are

$$\frac{\beta T_A}{T^2} + \frac{(1-\beta)T_B}{T^2} + \frac{\beta\alpha_A T_A}{T^2} + \frac{(1-\beta)\alpha_B T_B}{T^2}$$

Consequently, we have

$$\begin{aligned} \left(\frac{\partial\eta}{\partial T}\right)_p &= \frac{5(1+\alpha)}{2T} + \frac{\beta T_A}{T^2} + \frac{(1-\beta)T_B}{T^2} \\ &\quad + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \left(\frac{\partial\alpha_A}{\partial T}\right)_p + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \left(\frac{\partial\alpha_B}{\partial T}\right)_p + \mathcal{H}'(T) \end{aligned}$$

which has to be equal to (4). Hence $\mathcal{H}'(T) = -\frac{\beta T_A}{T^2} - \frac{(1-\beta)T_B}{T^2}$ and we obtain

$$\mathcal{H} = \frac{\beta T_A}{T} + \frac{(1-\beta)T_B}{T}.$$

4 Equations of Ionized Gas Dynamics

For studying thermodynamic properties of the system (1), the Lagrangian equations [15] are convenient

$$\begin{cases} v_t - u_\xi = 0, \\ u_t + p_\xi = 0, \\ (e + \frac{1}{2}u^2)_t + (pu)_\xi = 0 \end{cases} \quad (15)$$

where p : pressure, v : specific volume, e : specific internal energy and u : flow velocity. For C^1 solutions, equation (15)₃ can be written as ² $\eta_t = 0$.

Characteristic speeds and vector fields: For the set of state variables (p, u, η) we have $v_t = v_p p_t$ and equation (15) becomes $p_t - \frac{1}{v_p} u_\xi = 0$, $u_t + p_\xi = 0$, $\eta_t = 0$. The *Lagrangian* characteristic speeds are $\lambda_\pm = \pm \frac{1}{\sqrt{-v_p}}$ and $\lambda_0 = 0$, with corresponding characteristic vectors $\mathbf{r}_\pm = \begin{bmatrix} \pm 1 \\ \sqrt{-v_p} \\ 0 \end{bmatrix}$ and $\mathbf{r}_0 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$. We note that characteristic speeds and characteristic vectors are all thermodynamic quantities.

For further computation, we adopt (p, u, T) as a set of state variables. Since $v_t - u_\xi = v_p p_t + v_T T_t - u_\xi = 0$ and $\eta_t = \eta_p p_t + \eta_T T_t = 0$, we can write system (15) in the form

$$\begin{cases} p_t - \frac{\eta_T}{v_p \eta_T - v_T \eta_p} u_\xi = 0, \\ u_t + p_\xi = 0, \\ T_t + \frac{\eta_p}{v_p \eta_T - v_T \eta_p} u_\xi = 0. \end{cases} \quad (16)$$

Characteristic speeds and vector fields are computed as the following.

Lemma 7 *The characteristic speeds and the corresponding characteristic vector fields of system (16) are*

$$\lambda_\pm = \pm \sqrt{-\frac{\eta_T}{v_p \eta_T - v_T \eta_p}}, \quad \lambda_0 = 0, \quad \mathbf{r}_\pm = \begin{bmatrix} \pm 1 \\ \frac{1}{\sqrt{-\frac{\eta_T}{v_p \eta_T - v_T \eta_p}}} \\ \mp \frac{\eta_p}{\eta_T} \end{bmatrix}, \quad \mathbf{r}_0 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

The eigenvalue λ_0 is linearly degenerate; a pair of Riemann invariants for λ_0 is $\{u, p\}$. A Riemann invariant for both λ_\pm is η . The characteristic speeds of system 1-(1) are then $u + \frac{1}{\rho} \lambda_\pm$ and u .

² We notice that equation $\eta_t = 0$ is equivalent to $(\rho S)_t + (\rho u S)_x = 0$ in Eulerian coordinates.

Computation of η_p, η_T, v_p, v_T : For the sake of brevity, let us introduce the quantities: $q = \beta q_A + (1 - \beta)q_B$,

$$\begin{aligned}\Sigma &= \alpha(1 + \alpha) + \beta q_A + (1 - \beta)q_B = \alpha(1 + \alpha) + q \\ \Phi &= \beta q_A \left(\frac{5}{2} + \frac{T_A}{T} \right)^2 + (1 - \beta)q_B \left(\frac{5}{2} + \frac{T_B}{T} \right)^2, \\ \Psi &= \beta q_A \left(\frac{15}{4} + \frac{3T_A}{T} + \frac{T_A^2}{T^2} \right) + (1 - \beta)q_B \left(\frac{15}{4} + \frac{3T_B}{T} + \frac{T_B^2}{T^2} \right), \\ \Omega &= \beta(1 - \beta)q_A q_B \left(\frac{T_A}{T} - \frac{T_B}{T} \right)^2.\end{aligned}$$

Substituting (9), (10), (11) into (4) and (12), we obtain

$$\left(\frac{\partial \eta}{\partial p} \right)_T = -\frac{1 + \alpha}{p} - \frac{\alpha(1 + \alpha) \left[\beta \left(\frac{5}{2} + \frac{T_A}{T} \right) q_A + (1 - \beta) \left(\frac{5}{2} + \frac{T_B}{T} \right) q_B \right]}{p \Sigma} \quad (17)$$

$$\left(\frac{\partial \eta}{\partial T} \right)_p = \frac{5}{2T}(1 + \alpha) + \frac{\alpha(1 + \alpha)\Phi + \Omega}{T \Sigma}. \quad (18)$$

Since $v = \frac{a^2}{p}T(1 + \alpha)$ ($a^2 = \frac{R}{M}$), we have by applying Lemma 3

$$a^{-2} \left(\frac{\partial v}{\partial p} \right)_T = -\frac{T(1 + \alpha)}{p^2} - \frac{T\alpha(1 + \alpha)q}{p^2 \Sigma}, \quad a^{-2} \left(\frac{\partial v}{\partial T} \right)_p = -\left(\frac{\partial \eta}{\partial p} \right)_T.$$

Computation of λ_{\pm} : Let us first compute $\frac{1}{a^2}(v_p \eta_T - v_T \eta_p)$. That is: $\left(\frac{1 + \alpha}{p} \right)^2$ times of

$$\begin{aligned}& - \left(1 + \frac{\alpha q}{\Sigma} \right) \left[\frac{5}{2} + \frac{\alpha \Phi}{\Sigma} + \frac{\Omega}{(1 + \alpha)\Sigma} \right] \\ & + \left\{ 1 + \frac{\alpha \left[\beta q_A \left(\frac{5}{2} + \frac{T_A}{T} \right) + (1 - \beta)q_B \left(\frac{5}{2} + \frac{T_B}{T} \right) \right]}{\Sigma} \right\}^2 = - \left(\frac{3}{2} + \frac{\alpha \Psi + \Omega}{\Sigma} \right).\end{aligned}$$

Thus we have together with (18)

Theorem 2 *The characteristic speeds λ_{\pm} take the forms $\lambda_{\pm} = \pm \lambda$ where*

$$\lambda = \frac{p}{a\sqrt{T}(1 + \alpha)} \sqrt{\frac{\frac{5}{2}(1 + \alpha)\Sigma + \alpha(1 + \alpha)\Phi + \Omega}{\frac{3}{2}\Sigma + \alpha\Psi + \Omega}}. \quad (19)$$

Remark 1 (Isentropes) In (p, u, T) coordinates, an integral curve of a characteristic vector field \mathbf{r} is a solution to the system of equations

$$\frac{d}{ds} \begin{bmatrix} p \\ u \\ T \end{bmatrix} = \mathbf{r}$$

where \mathbf{r} stands for \mathbf{r}_{\pm} or \mathbf{r}_0 . For \mathbf{r}_{\pm} , we have

$$\frac{d\eta}{ds} = \frac{\partial \eta}{\partial p} \frac{dp}{ds} + \frac{\partial \eta}{\partial T} \frac{dT}{ds} = \pm \left(\frac{\partial \eta}{\partial p} - \frac{\partial \eta}{\partial T} \frac{\eta_p}{\eta_T} \right) = 0$$

and for \mathbf{r}_0 , $p = \text{const.}$ and $u = \text{const.}$ Thus, the thermodynamic part of an integral curve is $\eta = \text{const.}$ for 1, 2-characteristic directions and $p = \text{const.}$ for 0-characteristic field. A curve $\eta = \text{const.}$ is called an *isentrope*. Since $\left(\frac{\partial \eta}{\partial \alpha_A}\right)_T > 0$ (see Appendix B), an isentrope is the graph of a differentiable function $\alpha_A = \alpha_A(T)$ defined on $T \in (0, \infty)$.

5 Genuine Nonlinearity (convexity) and Inflection Loci

Now, we investigate the convexity of the forward and backward fields; each characteristic direction having the eigenvalue λ_{\pm} is called *genuinely nonlinear* if $\mathbf{r}_{\pm} \nabla \lambda_{\pm} \neq 0$. We have chosen characteristic vectors \mathbf{r}_{\pm} so that

$$\mathbf{r}_{\pm} \nabla \lambda_{\pm} = \frac{v_{pp}}{2(-v_p)^{\frac{3}{2}}} = \frac{\partial \lambda}{\partial p} - \frac{\eta_p}{\eta_T} \frac{\partial \lambda}{\partial T}. \quad (20)$$

Hence, genuine nonlinearity implies strict convexity (or concavity) of v as a function of p for fixed S . We refer to [13] for more insight about the failure of this condition and we will see in Remark 2 that the entropy increases across the shock front if $\mathbf{r}_{\pm} \nabla \lambda_{\pm} > 0$. It is convenient to consider a differential operator

$$\mathcal{R} = \Sigma \left[\eta_T \left(\frac{\partial}{\partial p} \right)_T - \eta_p \left(\frac{\partial}{\partial T} \right)_p \right]$$

which is proportional to $\mathbf{r}_{\pm} \nabla$.

Computation of $\mathcal{R}\lambda$ is simple but tedious. First we note that Lemma 1, 3 and 5 yield

Lemma 8

$$\begin{aligned} \mathcal{R}\alpha_A &= \frac{(1+\alpha)q_A}{pT} \left\{ \frac{\alpha(1+\alpha)T_A}{T} \right. \\ &\quad \left. + q_B(1-\beta) \left[1 + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \left(\frac{T_A}{T} - \frac{T_B}{T} \right) \right\}, \\ \mathcal{R}\alpha_B &= \frac{(1+\alpha)q_B}{pT} \left\{ \frac{\alpha(1+\alpha)T_B}{T} + q_A\beta \left[1 + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] \left(\frac{T_B}{T} - \frac{T_A}{T} \right) \right\}, \\ \mathcal{R}\alpha &= \frac{\alpha(1+\alpha)}{pT} \left\{ (1+\alpha) \left[\beta q_A \frac{T_A}{T} + (1-\beta)q_B \frac{T_B}{T} \right] - \Omega \right\}. \end{aligned}$$

The above lemma give the forms of $\mathcal{R}q$, $\mathcal{R}\Sigma$, $\mathcal{R}\Psi$ and $\mathcal{R}\Omega$. Employing these formulas, after a long and tedious computation, we finally find that $\mathcal{R} \log \lambda$ is the summation of the following three expressions: for brevity we denote $Q_T = \beta q_A \frac{T_A}{T} + (1-\beta)q_B \frac{T_B}{T}$.

$$(1) \frac{1+\alpha}{pT} \left\{ 2\Sigma + \Omega + \frac{1}{2}\alpha \left[10q + \beta q_A \left(\frac{7T_A}{T} + \frac{2T_A^2}{T^2} \right) + (1-\beta)q_B \left(\frac{7T_B}{T} + \frac{2T_B^2}{T^2} \right) \right] \right\}$$

$$\begin{aligned}
(2) \quad & \frac{1 + \alpha}{2 \left[\frac{5}{2}(1 + \alpha)\Sigma + \alpha(1 + \alpha)\Phi + \Omega \right] pT} \text{ times of} \\
& \alpha \left[\frac{5}{2}\Sigma + \frac{5}{2}(1 + \alpha)(1 + 2\alpha) + (1 + 2\alpha)\Phi \right] [2(1 + \alpha)Q_T - \Omega] \\
& + (1 - 2\alpha_A) \left\{ \alpha(1 + \alpha) \frac{T_A}{T} + (1 - \beta)q_B \left[1 + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \left(\frac{T_A}{T} - \frac{T_B}{T} \right) \right\} \\
& \quad \times \left\{ (1 + \alpha)\beta q_A \left[\frac{5}{2} + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right)^2 \right] + \Omega \right\} \\
& + (1 - 2\alpha_B) \left\{ \alpha(1 + \alpha) \frac{T_B}{T} + 2\beta q_A \left[1 + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] \left(\frac{T_B}{T} - \frac{T_A}{T} \right) \right\} \\
& \quad \times \left\{ (1 + \alpha)(1 - \beta)q_B \left[\frac{5}{2} + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right)^2 \right] + \Omega \right\} \\
& + \frac{5}{2}\alpha(1 + \alpha)^2 \left[\beta(1 - 2\alpha_A)q_A \frac{T_A}{T} + (1 - \beta)(1 - 2\alpha_B)q_B \frac{T_B}{T} \right] \\
& - 2 \left\{ \alpha(1 + \alpha) \left[\beta q_A \left(\frac{5}{2} + \frac{T_A}{T} \right) \frac{T_A}{T} + (1 - \beta)q_B \left(\frac{5}{2} + \frac{T_B}{T} \right) \frac{T_B}{T} \right] + \Omega \right\} \\
& \times \left\{ \alpha(1 + \alpha) + \beta q_A \left[1 + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] + (1 - \beta)q_B \left[1 + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \right\}
\end{aligned}$$

$$\begin{aligned}
(3) \quad & - \frac{1 + \alpha}{2 \left[\frac{3}{2}\Sigma + \alpha\Psi + \Omega \right] pT} \text{ times of } \alpha \left[\frac{3(1+2\alpha)}{2} + \Psi \right] [2(1 + \alpha)Q_T - \Omega] \\
& + (1 - 2\alpha_A) \left\{ \alpha(1 + \alpha) \frac{T_A}{T} + (1 - \beta)q_B \left[1 + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \left(\frac{T_A}{T} - \frac{T_B}{T} \right) \right\} \\
& \quad \times \left\{ \beta q_A \left[\frac{3}{2} + \alpha \left(\frac{15}{4} + \frac{3T_A}{T} + \frac{T_A^2}{T^2} \right) \right] + \Omega \right\} \\
& + (1 - 2\alpha_B) \left\{ \alpha(1 + \alpha) \frac{T_B}{T} + \beta q_A \left[1 + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] \left(\frac{T_B}{T} - \frac{T_A}{T} \right) \right\} \\
& \quad \times \left\{ (1 - \beta)q_B \left[\frac{3}{2} + \alpha \left(\frac{15}{4} + \frac{3T_B}{T} + \frac{T_B^2}{T^2} \right) \right] + \Omega \right\} \\
& + \frac{3}{2}\alpha(1 + \alpha) \left[\beta(1 - 2\alpha_A)q_A \frac{T_A}{T} + (1 - \beta)(1 - 2\alpha_B)q_B \frac{T_B}{T} \right] \\
& - 2 \left\{ \alpha \left[\beta q_A \left(\frac{3}{2} + \frac{T_A}{T} \right) \frac{T_A}{T} + (1 - \beta)q_B \left(\frac{3}{2} + \frac{T_B}{T} \right) \frac{T_B}{T} \right] + \Omega \right\} \\
& \times \left\{ \alpha(1 + \alpha) + \beta q_A \left[1 + \alpha \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] + (1 - \beta)q_B \left[1 + \alpha \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \right\}
\end{aligned}$$

Now, we study the *inflection locus* which is the point set

$$\mathcal{J} = \{(T, \alpha_A); \mathbf{r}_\pm \nabla \lambda_\pm = 0, T > 0, 0 < \alpha_A < 1\}.$$

Since $\mathbf{r}_+ \nabla \lambda_+ = \mathbf{r}_- \nabla \lambda_-$, both cases lead to the same result. Obviously, $\mathbf{r}_\pm \nabla \lambda_\pm > 0$ for sufficiently large T and we observe that \mathcal{J} is located in a finite region. However it is difficult to get a sketch of \mathcal{J} by purely mathematical reasoning and Fig. 1 shows results of numerical computations.

On the other hand, it is possible to extract from the above heavy expressions asymptotics of the inflection locus for $T \rightarrow 0$. Since α_B is negligible compared with α_A , we observe that there are two branches such that

$$\frac{\alpha_A}{T^2} \rightarrow 0 \quad \text{or} \quad \frac{\alpha_A}{T^2} \rightarrow \infty.$$

Following theorem is a generalisation of [1] Proposition 4.2.

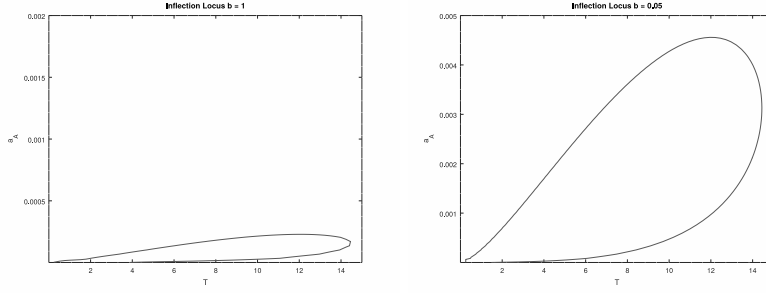


Fig. 1 $T_A = 1576.0, T_B = 2853.2$ left: $\beta = 1$ (monatomic), right: $\beta = 0.05$.

Theorem 3 For $T \rightarrow 0$, the inflection locus has two branches

$$(1) \alpha_A \sim \frac{60}{\beta} \left(\frac{T}{T_A} \right)^3, \quad \alpha_B \sim \frac{60\mu_A}{\beta\mu_B} \left(\frac{T}{T_A} \right)^3 e^{-\frac{T_B-T_A}{T}}$$

$$(2) \alpha_A \sim \frac{1}{\beta} \left(\frac{T}{T_A} \right)^{\frac{3}{2}}, \quad \alpha_B \sim \frac{\mu_A}{\beta\mu_B} \left(\frac{T}{T_A} \right)^{\frac{3}{2}} e^{-\frac{T_B-T_A}{T}}$$

and we conclude that the characteristic directions of λ_{\pm} are not genuinely nonlinear in a neighbourhood of $(T, \alpha_A) = (0, 0)$.

6 Compatibility Condition

The compatibility condition (6) constitutes a thermodynamic state space.

Lemma 9 The compatibility condition takes the form

$$\alpha_B = \frac{\mu_A \alpha_A e^{-\frac{T_B-T_A}{T}}}{\mu_A \alpha_A e^{-\frac{T_B-T_A}{T}} + \mu_B (1 - \alpha_A)}. \quad (21)$$

If $\alpha_A \rightarrow 0$, then $\alpha_B \rightarrow 0$ and we have

$$\alpha_B = \frac{\mu_A}{\mu_B} \alpha_A e^{-\frac{T_B-T_A}{T}} [1 + O(1)\alpha_A]. \quad (22)$$

For A: hydrogen atom and B: helium atom, $\frac{\mu_A}{\mu_B} = 4$.

Incidentally, we find

$$\alpha_B(1 - \alpha_B) = \frac{\mu_A \mu_B \alpha_A (1 - \alpha_A) e^{-\frac{T_B-T_A}{T}}}{\left[\mu_A \alpha_A e^{-\frac{T_B-T_A}{T}} + \mu_B (1 - \alpha_A) \right]^2}$$

and thus derivatives of α_B take the forms

$$\left(\frac{\partial \alpha_B}{\partial T} \right)_{\alpha_A} = \frac{(T_B - T_A) \alpha_B (1 - \alpha_B)}{T^2}, \quad \left(\frac{\partial \alpha_B}{\partial \alpha_A} \right)_T = \frac{\alpha_B (1 - \alpha_B)}{\alpha_A (1 - \alpha_A)}$$

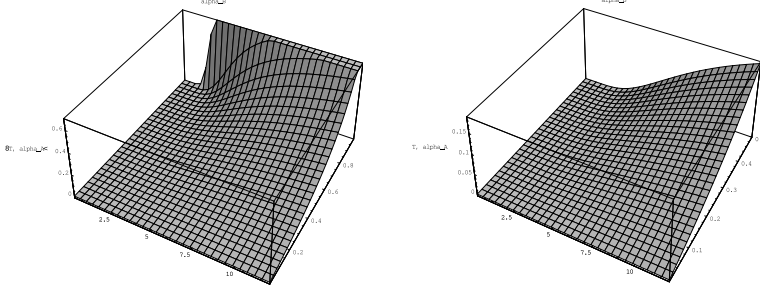


Fig. 2 State space $T_A = 15, T_B = 28$, left: $0 < \alpha_A < 1, 0 < T < 12$, right: $0 < \alpha_A < 0.5, 0 < T < 12$

showing that $\left(\frac{\partial \alpha_B}{\partial T}\right)_{\alpha_A}, \left(\frac{\partial \alpha_B}{\partial \alpha_A}\right)_T > 0$. By setting for brevity

$$q = \beta q_A + (1 - \beta)q_B, \quad Q_{BA} = \frac{(1 - \beta)(T_B - T_A)q_B}{T},$$

derivatives of α take the forms

Lemma 10

$$\left(\frac{\partial \alpha}{\partial T}\right)_{\alpha_A} = \frac{Q_{BA}}{T}, \quad \left(\frac{\partial \alpha}{\partial \alpha_A}\right)_T = \frac{q}{q_A}. \quad (23)$$

In the following sections, we shall adopt T and α_A as a set of independent thermodynamic state variables.

7 Thermodynamic Hugoniot Loci

In the one-dimensional gas dynamics, the Rankine-Hugoniot conditions for a single discontinuity of constant speed s are

$$\begin{cases} s[\rho] = [\rho u], \\ s[\rho u] = [\rho u^2 + p], \\ s[\rho E] = [\rho u E + p u]. \end{cases} \quad (24)$$

Here we denote $[\rho] = \rho_+ - \rho_-$, where ρ_{\pm} denote the right and left limits, respectively, of ρ with respect to x at $x = st$; the same notation is used for the other variables. If $[\rho] = 0$ then $[u] = 0$ by (24)₁ and $[p] = 0$ by (24)₂; in this case, $s = u_{\pm}$: the speed is equal to the flow velocity and the discontinuity is called a *contact discontinuity*. From now on we focus on the discontinuity corresponding to eigenvalues λ_{\pm} and assume $[\rho] \neq 0$. In this case s can be eliminated from the first equation and by substituting it into the other two equations, the conditions (24) are reduced to

$$\begin{cases} (u_+ - u_-)^2 + (p_+ - p_-)(v_+ - v_-) = 0 : \text{kinetic condition}, \\ e_+ - e_- + \frac{1}{2}(p_+ + p_-)(v_+ - v_-) = 0 : \text{thermodynamic condition}. \end{cases} \quad (25)$$

In the following, we consider a single forward shock front; we fix a constant state (p_+, u_+, T_+) and consider $(p, u, T) = (p_-, u_-, T_-)$ as a set of state variables. Under this notation, (25) is a set of equations for *Hugoniot locus* of (p_+, u_+, T_+) . For brevity, we call solutions to (25)₁ and (25)₂, respectively, the *kinetic* and *thermodynamic Hugoniot loci*.

In this section we will give a precise description of thermodynamic Hugoniot loci for the present model system and evaluate, in particular, change of the thermodynamic variables along them; this analysis is fundamental for the study of shock waves (see [2]).

The right thermodynamic state is denoted by (p_+, T_+) and the left state (p_-, T_-) . The thermodynamic Rankine-Hugoniot condition is written as³

$$\begin{aligned} T_- (1 + \alpha^-) \left(4 + \frac{p_+}{p_-} \right) + 2 [\beta T_A \alpha_A^- + (1 - \beta) T_B \alpha_B^-] \\ = T_+ (1 + \alpha^+) \left(4 + \frac{p_-}{p_+} \right) + 2 [\beta T_A \alpha_A^+ + (1 - \beta) T_B \alpha_B^+] \end{aligned}$$

The pressure is expressed as

$$p = \frac{(1 - \alpha_A)(1 + \alpha)}{\mu_A \alpha_A \alpha} T^{\frac{5}{2}} e^{-\frac{T_A}{T}} = \frac{(1 - \alpha_B)(1 + \alpha)}{\mu_B \alpha_B \alpha} T^{\frac{5}{2}} e^{-\frac{T_B}{T}}.$$

and thus

$$\frac{p_-}{p_+} = \frac{(1 - \alpha_A^-)(1 + \alpha^-) \alpha_A^+ \alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+) \alpha_A^- \alpha^-} \left(\frac{T_-}{T_+} \right)^{\frac{5}{2}} e^{-\frac{T_A}{T_-} + \frac{T_A}{T_+}}, \quad \frac{v_-}{v_+} = \frac{p_+ T_- (1 + \alpha^-)}{p_- T_+ (1 + \alpha^+)}. \quad (26)$$

Consequently we have by setting $T = T_-$, $\alpha = \alpha^-$, $\alpha_A = \alpha_A^-$ and $\alpha_B = \alpha_B^-$

$$\begin{aligned} \frac{T}{T_+} \left\{ (1 + \alpha) \left[4 + \frac{(1 - \alpha_A^+)(1 + \alpha^+) \alpha_A \alpha}{(1 - \alpha_A)(1 + \alpha) \alpha_A^+ \alpha^+} \left(\frac{T_+}{T} \right)^{\frac{5}{2}} e^{-\frac{T_A}{T_+} + \frac{T_A}{T}} \right] \right. \\ \left. + 2 \left[\beta \alpha_A \frac{T_A}{T} + (1 - \beta) \alpha_B \frac{T_B}{T} \right] \right\} \\ = (1 + \alpha^+) \left[4 + \frac{(1 - \alpha_A)(1 + \alpha) \alpha_A^+ \alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+) \alpha_A \alpha} \left(\frac{T}{T_+} \right)^{\frac{5}{2}} e^{-\frac{T_A}{T} + \frac{T_A}{T_+}} \right] \\ + 2 \left[\beta \alpha_A^+ \frac{T_A}{T_+} + (1 - \beta) \alpha_B^+ \frac{T_B}{T_+} \right]. \quad (27) \end{aligned}$$

Asymptotics: We have the following asymptotic formulas.

Theorem 4 (Asymptotics) *On the thermodynamic Hugoniot locus (27), if $T \rightarrow 0$, then $\alpha_A, \alpha_B \rightarrow 0$ and by setting*

$$A = \sqrt{\frac{\alpha_A^+ \alpha^+ \{ 4(1 + \alpha^+) + 2 [\beta \alpha_A^+ \frac{T_A}{T_+} + (1 - \beta) \alpha_B^+ \frac{T_B}{T_+}] \} e^{\frac{T_A}{T_+}}}{[\beta + \frac{\mu_A}{\mu_B} (1 - \beta)] (1 - \alpha_A^+) (1 + \alpha^+)}}.$$

³ For the sake of convenience, we adopt the notation α_A^\pm instead of $\alpha_{A\pm}$.

we have

$$\alpha_A \sim A \left(\frac{T}{T_+} \right)^{\frac{3}{4}} e^{-\frac{T_A}{2T}}, \quad \alpha_B \sim \frac{A\mu_A}{\mu_B} \left(\frac{T}{T_+} \right)^{\frac{3}{4}} e^{-\frac{2T_B - T_A}{2T}}. \quad (28)$$

On the other hand, if $T \rightarrow \infty$, then $\alpha_A, \alpha_B \rightarrow 1$ and

$$1 - \alpha_A \sim \frac{4(1 - \alpha_A^+)}{\alpha_A^+ \alpha^+} \left(\frac{T}{T_+} \right)^{-\frac{3}{2}} e^{-\frac{T_A}{T_+}}, \quad 1 - \alpha_B \sim \frac{4\mu_A(1 - \alpha_A^+)}{\mu_B \alpha_A^+ \alpha^+} \left(\frac{T}{T_+} \right)^{-\frac{3}{2}} e^{-\frac{T_A}{T_+}} \quad (29)$$

Proof First we let $T \rightarrow 0$. If $\alpha_A \geq \alpha_0 > 0$, then the first expression of (27) tends to ∞ and the second remains bounded, which is contradiction. Hence $\alpha_A, \alpha_B \rightarrow 0$. By (22), we have $\alpha_B \sim \frac{\mu_A}{\mu_B} \alpha_A e^{-\frac{T_B - T_A}{T}}$ for $\alpha_A, \alpha_B \rightarrow 0$ and hence $\alpha \sim \left[\beta + \frac{\mu_A}{\mu_B} (1 - \beta) \right] \alpha_A$. Suppose that $\alpha_A^2 T^{-\frac{5}{2}} e^{\frac{T_A}{T}} = O(1)$. Then the first expression tends to 0 and the second remains bounded, which is also contradiction.

We set $\alpha_A \sim A \left(\frac{T}{T_+} \right)^\kappa e^{-\frac{T_A}{2T}}$ for some $A > 0$. Then

$$\begin{aligned} & \frac{T}{T_+} \left\{ 4 + \frac{(1 - \alpha_A^+)(1 + \alpha^+) \left[\beta + \frac{\mu_A}{\mu_B} (1 - \beta) \right] A^2 \left(\frac{T}{T_+} \right)^{2\kappa - \frac{5}{2}} e^{-\frac{T_A}{T_+}}}{\alpha_A^+ \alpha^+} \right\} \\ & \sim (1 + \alpha^+) \left\{ 4 + \frac{\alpha_A^+ \alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+) \left[\beta + \frac{\mu_A}{\mu_B} (1 - \beta) \right] A^2 \left(\frac{T}{T_+} \right)^{-2\kappa + \frac{5}{2}} e^{\frac{T_A}{T_+}}} \right\} \\ & + 2 \left[\beta \alpha_A^+ \frac{T_A}{T_+} + (1 - \beta) \alpha_B^+ \frac{T_B}{T_+} \right]. \end{aligned}$$

If $2\kappa - \frac{5}{2} = 0$, then $\kappa = \frac{5}{4}$, which is impossible by the above observation. If $2\kappa - \frac{3}{2} = -2\kappa + \frac{5}{2}$, then $\kappa = 1$ and $2\kappa - \frac{3}{2} = \frac{1}{2} > 0$, which is also contradiction. Thus we conclude that $2\kappa - \frac{3}{2} = 0$ and hence $\kappa = \frac{3}{4}$, which implies $\alpha_A \sim A \left(\frac{T}{T_+} \right)^{\frac{3}{4}} e^{-\frac{T_A}{2T}}$, $\alpha_B \sim \frac{\mu_A}{\mu_B} \alpha_A e^{-\frac{T_B - T_A}{T}} \sim \frac{A\mu_A}{\mu_B} \left(\frac{T}{T_+} \right)^{\frac{3}{4}} e^{-\frac{2T_B - T_A}{2T}}$. Since $-2\kappa + \frac{5}{2} = 1$, A is determined by the equation

$$\begin{aligned} & \frac{(1 - \alpha_A^+)(1 + \alpha^+) \left[\beta + \frac{\mu_A}{\mu_B} (1 - \beta) \right] A^2 e^{-\frac{T_A}{T_+}}}{\alpha_A^+ \alpha^+} \\ & = 4(1 + \alpha^+) + 2 \left[\beta \alpha_A^+ \frac{T_A}{T_+} + (1 - \beta) \alpha_B^+ \frac{T_B}{T_+} \right]. \end{aligned}$$

Next we let $T \rightarrow \infty$. If $\alpha_A \leq 1 - \delta_0$ ($\delta_0 > 0$), then the first expression of (27) goes to 0 and the second ∞ , which is contradiction. Thus $\alpha_A \rightarrow 1$ as $T \rightarrow \infty$ which implies $\alpha_B \rightarrow 1$ and hence $\alpha \rightarrow 1$. Suppose that $(1 - \alpha_A)T^{\frac{5}{2}} = O(1)$.

Then the first expression is $O(1)T$ and second $O(1)$, which is also contradiction.

We may set $1 - \alpha_A = B \left(\frac{T}{T_+}\right)^{-\kappa}$. Then

$$\begin{aligned} & \frac{2T}{T_+} \left[4 + \frac{(1 - \alpha_A^+)(1 + \alpha^+)}{2B\alpha_A^+\alpha^+} \left(\frac{T}{T_+}\right)^{\kappa - \frac{5}{2}} e^{-\frac{T_A}{T_+}} \right] \\ & \sim 2(1 + \alpha^+) \left[2 + \frac{B\alpha_A^+\alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+)} \left(\frac{T}{T_+}\right)^{-\kappa + \frac{5}{2}} e^{\frac{T_A}{T_+}} \right] \\ & + 2 \left[\beta\alpha_A^+ \frac{T_A}{T_+} + (1 - \beta)\alpha_B^+ \frac{T_B}{T_+} \right]. \end{aligned}$$

If $\kappa - \frac{5}{2} = 0$, then the first expression is $O(1)T$ and second $O(1)$, which is impossible. If $\kappa - \frac{3}{2} = -\kappa + \frac{5}{2}$, then $\kappa = 2$. In this case, the first expression is $O(1)T$ and second $O(1)$, which is also impossible. Thus we find $-\kappa + \frac{5}{2} = 1$ and hence $\kappa = \frac{3}{2}$. We have $4 = \frac{B\alpha_A^+\alpha^+ e^{\frac{T_A}{T_+}}}{1 - \alpha_A^+}$ and thus obtain the asymptotic form of α_A . Formula for α_B is derived from

$$1 - \alpha_B = \frac{\mu_B(1 - \alpha_A)}{\mu_A\alpha_A e^{-\frac{T_B - T_A}{T}} + \mu_B(1 - \alpha_A)}$$

Loss of Monotonicity: For single monatomic gases, Hugoniot loci are graphs of strictly increasing functions in (T, α) plane ([1], [2]). We will show in this subsection that it is not always the case for mixed monatomic gases. Let us denote

$$\Theta^+ = \left(\frac{T_+}{T}\right)^{\frac{5}{2}} e^{-\frac{T_A}{T_+} + \frac{T_A}{T}}, \quad \Theta_+ = \left(\frac{T}{T_+}\right)^{\frac{5}{2}} e^{-\frac{T_A}{T} + \frac{T_A}{T_+}}$$

and

$$K^+ = \frac{(1 - \alpha_A^+)(1 + \alpha^+)\alpha_A\alpha}{(1 - \alpha_A)(1 + \alpha)\alpha_A^+\alpha^+}, \quad K_+ = \frac{(1 - \alpha_A)(1 + \alpha)\alpha_A^+\alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+)\alpha_A\alpha}.$$

Note that $K^+ \rightarrow 0$, $K_+ \rightarrow \infty$ as $\alpha_A \rightarrow 0$ and $K^+ \rightarrow \infty$, $K_+ \rightarrow 0$ as $\alpha_A \rightarrow 1$. Obviously

$$\frac{p_+}{p} = K^+\Theta^+, \quad \frac{p}{p_+} = K_+\Theta_+$$

and

$$\frac{d\Theta^+}{dT} = -\frac{1}{T} \left(\frac{5}{2} + \frac{T_A}{T}\right) \Theta^+, \quad \frac{d\Theta_+}{dT} = \frac{1}{T} \left(\frac{5}{2} + \frac{T_A}{T}\right) \Theta_+. \quad (30)$$

It follows from (23) that

$$\left(\frac{\partial K^+}{\partial \alpha_A}\right)_T = \frac{K^+}{q_A} \left[1 + \frac{q}{\alpha(1 + \alpha)}\right], \quad \left(\frac{\partial K_+}{\partial \alpha_A}\right)_T = -\frac{K_+}{q_A} \left[\frac{1}{q_A} + \frac{q}{\alpha(1 + \alpha)}\right] \quad (31)$$

$$\left(\frac{\partial K^+}{\partial T}\right)_{\alpha_A} = \frac{K^+ Q_{BA}}{\alpha(1 + \alpha)T}, \quad \left(\frac{\partial K_+}{\partial T}\right)_{\alpha_A} = -\frac{K_+ Q_{BA}}{\alpha(1 + \alpha)T^2}. \quad (32)$$

By defining

$$H(T, \alpha_A) = T(1 + \alpha)(4 + K^+\Theta^+) + 2[\beta\alpha_A T_A + (1 - \beta)\alpha_B T_B] \\ - T_+(1 + \alpha^+)(4 + K_+\Theta_+) - 2[\beta\alpha_A^+ T_A + (1 - \beta)\alpha_B^+ T_B], \quad (33)$$

the Rankine-Hugoniot condition (27) is equivalent to $H(T, \alpha_A) = 0$.

Using (23) and (31), we have

$$\left(\frac{\partial H}{\partial \alpha_A}\right)_T = \frac{T(1 + \alpha)}{q_A} \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \frac{p_+}{p} + \frac{T_+(1 + \alpha^+)}{q_A} \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \frac{p}{p_+} \\ + \frac{Tq}{q_A} \left(4 + \frac{p_+}{p}\right) + \frac{2}{q_A} [\beta q_A T_A + (1 - \beta)q_B T_B], \quad (34)$$

showing that $\left(\frac{\partial H}{\partial \alpha_A}\right)_T > 0$. In the same way

$$\left(\frac{\partial H}{\partial T}\right)_{\alpha_A} = 4(1 + \alpha) \left[1 + \frac{Q_{BA}}{1 + \alpha} \left(1 + \frac{T_B}{2T}\right)\right] \\ - (1 + \alpha) \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \frac{p_+}{p} - (1 + \alpha^+) \frac{T_+}{T} \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] \frac{p}{p_+}. \quad (35)$$

Theorem 5 *For every $T > 0$, there is a unique $0 < \alpha_A < 1$ such that $H(T, \alpha_A) = 0$ and the function $\alpha_A = \alpha_A(T)$ is differentiable.*

Proof For every fixed $T > 0$, $H(T, \alpha_A) \rightarrow -\infty$ as $\alpha_A \rightarrow 0$, and $H(T, \alpha_A) \rightarrow \infty$ as $\alpha_A \rightarrow 1$. Thus there is at least one α_A such that $H(T, \alpha_A) = 0$. Since $\left(\frac{\partial H}{\partial \alpha_A}\right)_T > 0$, such α_A is uniquely determined and the correspondence $T \rightarrow \alpha_A$ is differentiable. Thus the theorem follows.

Let us study the sign of $\left(\frac{\partial H}{\partial T}\right)_{\alpha_A}$ at (T_+, α_A^+) .

Theorem 6 *If β is sufficiently close to 0, then*

$$\frac{d\alpha_A}{dT}(T_+) = -\frac{\left(\frac{\partial H}{\partial \alpha_A}\right)_T(T_+, \alpha_A^+)}{\left(\frac{\partial H}{\partial T}\right)_{\alpha_A}(T_+, \alpha_A^+)} < 0,$$

showing that α_A is a decreasing function of T in a neighbourhood of $T = T_+$,

Proof We find by the above expression that $\left(\frac{\partial H}{\partial T}\right)_{\alpha_A} > 0$ if and only if the following $F(T, \alpha_A)$ is negative.

$$F(T, \alpha_A) = \frac{1}{4} \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \frac{p_+}{p} \\ + \frac{T_+(1 + \alpha^+)}{4T(1 + \alpha)} \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] \frac{p}{p_+} - \left[1 + \frac{Q_{BA}}{1 + \alpha} \left(1 + \frac{T_B}{2T}\right)\right]$$

We set $T = T_+$ and $\alpha_A = \alpha_A^+$. Since $\frac{p_+}{p} = \frac{T_+}{T} = \frac{\alpha_+}{\alpha} = 1$, we have

$$\begin{aligned} F(T, \alpha_A) &= 1 + \frac{T_A}{2T} - \frac{(2 + \alpha)Q_{BA}}{4\alpha(1 + \alpha)} - \left[1 + \frac{Q_{BA}}{1 + \alpha} \left(1 + \frac{T_B}{2T} \right) \right] \\ &= \frac{T_A}{2T} - \left[\frac{(1 - \beta)(2 + 5\alpha)q_B}{2\alpha(1 + \alpha)} + \frac{(1 - \beta)T_B q_B}{(1 + \alpha)T} \right] \frac{T_B - T_A}{2T} \end{aligned}$$

Let us consider the case: $\beta = 0$.

$$\begin{aligned} F(T, \alpha_A) &= 1 + \frac{T_A}{2T} - \frac{(2 + \alpha_B)(T_B - T_A)q_B}{4\alpha_B(1 + \alpha_B)T} - \left[1 + \frac{(T_B - T_A)q_B}{(1 + \alpha_B)T} \left(1 + \frac{T_B}{2T} \right) \right] \\ &= \frac{T_A}{2T} \left[1 - \frac{1 - \alpha_B}{1 + \alpha_B} \left(\frac{2 + 5\alpha_B}{2} + \frac{T_B \alpha_B}{T} \right) \frac{T_B - T_A}{T_A} \right]. \end{aligned}$$

Obviously for any $\alpha_B > 0$, there is some $T > 0$ so that the above expression is negative. Recall that α_B is a continuous function of α_A and T , satisfying $\left(\frac{\partial \alpha_B}{\partial \alpha_A} \right)_T > 0$. Moreover $\alpha_B(0, T) = 0$ and $\alpha_B(1, T) = 1$ for any $T > 0$.

Thus we find that: for any $T_+ > 0$ and $0 < \alpha_B^+ < 1$, there is a unique α_A^+ such that $\alpha_B(T_+, \alpha_A^+) = \alpha_B^+$ which implies $F(T_+, \alpha_A^+) < 0$. Since $F(T, \alpha_A)$ is continuous function of β , the theorem follows.

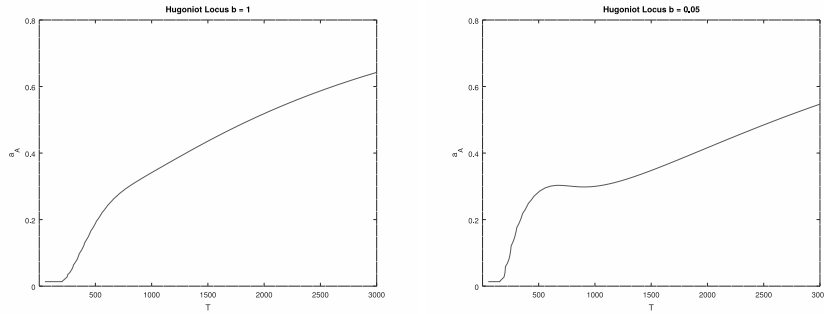


Fig. 3 $T_A = 1576.0, T_B = 2853.2, T = 800, \alpha_A^+ = 0.3$ left: $\beta = 1$ (single monotonic), right: $\beta = 0.05$

Pressure Change: Though the degree of ionization does not always increase across the shock front, even if the temperature increases, we will prove in this subsection:

Theorem 7 *The pressure p strictly increases along the Hugoniot locus as the temperature T increases.*

Proof First we notice that: by setting

$$Q_T = \frac{\beta q_A T_A + (1 - \beta) q_B T_B}{T}, \quad Q_{BA} = \frac{(1 - \beta)(T_B - T_A) q_B}{T}, \quad (36)$$

(34) and (35) together with (26) yield

$$\begin{aligned} \left(\frac{\partial H}{\partial T}\right)_{\alpha_A} &= 4(1 + \alpha) \left[1 + \frac{Q_{BA}}{1 + \alpha} \left(1 + \frac{T_B}{2T}\right)\right] \\ &\quad - \frac{T_+(1 + \alpha^+)}{T} \left\{ \left[\frac{5}{2} + \frac{T_A}{T} + \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] \frac{p}{p_+} + \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \frac{v}{v_+} \right\} \end{aligned} \quad (37)$$

$$\left(\frac{\partial H}{\partial \alpha_A}\right)_T = \frac{4}{q_A} \left(q + \frac{Q_T}{2}\right) + \frac{T_+(1 + \alpha^+)}{q_A} \left\{ \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \frac{p}{p_+} + \left(1 + \frac{q}{\alpha}\right) \frac{v}{v_+} \right\} \quad (38)$$

We now compute $\frac{dp}{dT}$ by differentiating both sides of

$$\log p = \log(1 - \alpha_A) - \log \alpha_A + \log(1 + \alpha) - \log \alpha + \frac{5}{2} \log T - \frac{T_A}{T} + \text{const.}$$

Using (23) and (36), we have

$$\frac{d\alpha}{dT} = \beta \frac{d\alpha_A}{dT} + (1 - \beta) \left(\frac{\partial \alpha_B}{\partial T} + \frac{\partial \alpha_B}{\partial \alpha_A} \frac{d\alpha_A}{dT} \right) = \frac{1}{q_A} \left(q \frac{d\alpha_A}{dT} + \frac{Q_{BA} q_A}{T} \right).$$

Thus we get

$$\begin{aligned} \frac{1}{p} \frac{dp}{dT} &= -\frac{1}{\alpha_A(1 - \alpha_A)} \frac{d\alpha_A}{dT} - \frac{1}{\alpha(1 + \alpha)} \left(\frac{q}{q_A} \frac{d\alpha_A}{dT} + \frac{Q_{BA}}{T} \right) + \frac{1}{T} \left(\frac{5}{2} + \frac{T_A}{T} \right) \\ &= \frac{\left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \left(\frac{\partial H}{\partial T}\right)_{\alpha_A} + \frac{q_A}{T} \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] \left(\frac{\partial H}{\partial \alpha_A}\right)_T}{q_A \left(\frac{\partial H}{\partial \alpha_A}\right)_T}. \end{aligned}$$

Since $\frac{q_A}{T} \left(\frac{\partial H}{\partial \alpha_A}\right)_T > 0$, we examine the numerator, which is computed as

$$\begin{aligned} &\frac{T_+(1 + \alpha^+)}{T} \left\{ \left(1 + \frac{q}{\alpha}\right) \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] - \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \right\} \frac{v}{v_+} \\ &+ 4(1 + \alpha) \left[1 + \frac{Q_{BA}}{1 + \alpha} \left(1 + \frac{T_B}{2T}\right)\right] \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] + 4 \left(q + \frac{Q_T}{2}\right) \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right]. \end{aligned}$$

Note that

$$\begin{aligned} \frac{5}{2} \left(1 + \frac{q}{\alpha}\right) - \frac{3}{2} \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] &= 1 + \frac{1 + \frac{5}{2}\alpha}{\alpha(1 + \alpha)}, \\ \frac{T_A}{T} \left[1 + \frac{q}{\alpha} - 1 - \frac{q}{\alpha(1 + \alpha)}\right] &= \frac{q T_A}{T(1 + \alpha)} \end{aligned}$$

and

$$-\left(1 + \frac{q}{\alpha}\right) \frac{Q_{BA}}{\alpha(1 + \alpha)} + \frac{Q_{BA}}{\alpha} \left[1 + \frac{q}{\alpha(1 + \alpha)}\right] = -\frac{Q_{BA}}{\alpha(1 + \alpha)} + \frac{Q_{BA}}{\alpha} = \frac{Q_{BA}}{1 + \alpha}.$$

Then we find that

$$\begin{aligned} & \left(1 + \frac{q}{\alpha}\right) \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)}\right] - \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \left[1 + \frac{q}{\alpha(1+\alpha)}\right] \\ &= 1 + \frac{1 + \frac{5}{2}\alpha}{\alpha(1+\alpha)} + \frac{qT_A}{T(1+\alpha)} + \frac{Q_{BA}}{1+\alpha} > 0. \end{aligned}$$

Moreover

$$\begin{aligned} & 4Q_{BA} \left(1 + \frac{T_B}{2T}\right) \left[1 + \frac{q}{\alpha(1+\alpha)}\right] - 4 \left(q + \frac{Q_T}{2}\right) \frac{Q_{BA}}{\alpha(1+\alpha)} \\ & > 2Q_{BA} \left[\frac{T_B}{T} - \frac{Q_T}{\alpha(1+\alpha)}\right] > 2Q_{BA} \left[\frac{T_B}{T} - \frac{Q_T}{\alpha}\right] \end{aligned}$$

and noticing

$$\frac{T_B}{T} - \frac{Q_T}{\alpha} = \frac{1}{T} \left[T_B - \frac{\beta q_A T_A + (1-\beta) q_B T_B}{\alpha} \right] > \frac{T_B}{T} \left(1 - \frac{q}{\alpha}\right) \geq 0,$$

we conclude that the numerator is strictly positive and hence the theorem is proved.

Remark 2 It is well known that ([11, §86]): if (p_0, u_0, S_0) and (p_1, u_1, S_1) are connected by a shock front, then

$$S_1 - S_0 = \frac{1}{12T_0} \left(\frac{\partial^2 v}{\partial p_0^2} \right)_S (p_1 - p_0)^3 + O(1)(p_1 - p_0)^4. \quad (39)$$

This formula, first obtained by H. Bethe in [4], is notable, because it depends on neither the particular equation of state nor the form of internal structure. In particular, it is true for present mixed ionized system of equations.

Suppose that $v_{pp}(p, S) > 0$. Then the entropy increases as the pressure increases. It follows from (20) that this condition implies that this characteristic direction is genuinely nonlinear. Consequently, if $|p_1 - p_0|$ is sufficiently small, the Lax condition (see [6], [15]) holds in this case. Thus we can call the above discontinuity a *shock wave* as long as $p_1 > p_0$ and $|p_1 - p_0|$ is sufficiently small.

For discontinuities with arbitrary amplitude

Theorem 8 (Bethe-Weyl) *The thermodynamic Hugoniot locus of the state (v_0, S_0) intersects each isentrope at least once. Moreover, if $p_{vv} > 0$ along an isentrope, then the locus intersects it exactly once; in this case, $|u - \sigma| < c$, if $v_1 < v_0$. while the opposite inequalities hold if $v_1 > v_0$.*

Hence the Lax condition holds even for large $|p_1 - p_0|$ as long as $p_1 > p_0$. Proof is found in [4], [17] and [13, (3.44)]. We may also call this “shock wave”, however the physical entropy does not necessarily increase.

The following theorem in [4] guarantees increase of the physical entropy. Let us introduce the *Grüneisen coefficient* Γ defined by

$$\Gamma = -\frac{v}{T} \frac{\partial^2 e}{\partial S \partial v} = \frac{v}{T} \left(\frac{\partial p}{\partial S} \right)_v = v \left(\frac{\partial p}{\partial e} \right)_v.$$

Theorem 9 (Bethe) *Suppose that $p_{vv} > 0$ and $\Gamma \geq -2$. Then the thermodynamic Hugoniot locus of the state (v_0, S_0) intersects each isentrope exactly once and $S_1 > S_0$ if $v_1 < v_0$, while $S_1 < S_0$ if $v_1 > v_0$.*

In our case, a set of independent thermodynamic variables are α_A and T . The Grüneisen coefficient is expressed as

$$\Gamma = \frac{v \left(\frac{\partial p}{\partial \alpha_A} \frac{\partial v}{\partial T} - \frac{\partial v}{\partial \alpha_A} \frac{\partial p}{\partial T} \right)}{T \left(\frac{\partial S}{\partial \alpha_A} \frac{\partial v}{\partial T} - \frac{\partial v}{\partial \alpha_A} \frac{\partial S}{\partial T} \right)},$$

where $S = \frac{R}{M}\eta$. After simple but tedious computations like in Appendix A, we prove finally $\Gamma > 0$.

8 Approximation of Thermodynamic Hugoniot Loci

Next section, we consider a forward shock front having the right state (p_+, T_+) in ordinary circumstances: the pressure p_+ and the temperature T_+ have proper finite values and α_A^+, α_B^+ are supposed to be 0. However, we find by (26) that $\frac{p}{p_+} \rightarrow 0$ as $\alpha_A^+, \alpha_B^+ \rightarrow 0$, which is contradictory. Notice that

$$p = \frac{(1 - \alpha_A)(1 + \alpha)}{\mu_A \alpha_A \alpha} T^{\frac{5}{2}} e^{-\frac{T_A}{T}}.$$

Then we observe that

$$\alpha_A^+ \alpha^+ = \frac{(1 - \alpha_A^+)(1 + \alpha^+)}{\mu_A p_+} T_+^{\frac{5}{2}} e^{-\frac{T_A}{T_+}} \sim \frac{T_+^{\frac{5}{2}} e^{-\frac{T_A}{T_+}}}{\mu_A p_+}, \quad \text{as } \alpha_A^+, \alpha_B^+ \rightarrow 0.$$

Setting $\hat{L}_+^2 = \frac{T_+^{\frac{5}{2}}}{\mu_A p_+}$, we obtain $\alpha_A^+ \alpha^+ \sim \hat{L}_+^2 e^{-\frac{T_A}{T_+}}$ and an approximate formula

$$\frac{p_+}{p} = \frac{\alpha_A \alpha}{(1 - \alpha_A)(1 + \alpha) \hat{L}_+^2} \cdot \left(\frac{T_+}{T} \right)^{\frac{5}{2}} e^{\frac{T_A}{T}}$$

By letting $\alpha_A^+ \rightarrow 0$, the thermodynamic Rankine-Hugoniot condition takes the form

$$\frac{T}{T_+} (1 + \alpha) \left(4 + \frac{p_+}{p} \right) + \frac{2[\beta T_A \alpha_A + (1 - \beta) T_B \alpha_B]}{T_+} = 4 + \frac{p}{p_+}$$

whose solution is called the *approximate thermodynamic Hugoniot locus* of a laboratory state (p_+, T_+) .

Theorem 10 *Let σ be a positive constant satisfying $\sigma < 60$. If T and T_+ are sufficiently small, so that*

$$\sqrt{\frac{\beta T_+ T_A^{\frac{3}{2}}}{\mu_A p_+}} \left(\frac{T}{T_A} \right)^{-\frac{9}{4}} e^{-\frac{T_A}{2T}} \leq \sigma,$$

then the approximate thermodynamic Hugoniot locus is located in a genuinely nonlinear region for sufficiently small α_A, α_B .

Proof Let us denote $\Pi = \frac{p_+}{p}$. Then the thermodynamic Rankine-Hugoniot condition is found to be a quadratic equation of Π :

$$(1 + \alpha) \frac{T}{T_+} \Pi^2 + 2 \left[2(1 + \alpha) \frac{T}{T_+} + \frac{\beta T_A \alpha_A + (1 - \beta) T_B \alpha_B}{T_+} - 2 \right] \Pi - 1 = 0$$

Let $\Gamma(\Pi)$ denote the left side of the above expression. Clearly $\Gamma(0) = -1 < 0$. Since $T_+ \leq T$,

$$2(1 + \alpha) \frac{T}{T_+} + \frac{\beta T_A \alpha_A + (1 - \beta) T_B \alpha_B}{T_+} - 2 \geq 2 \left(\frac{T}{T_+} - 1 \right) \geq 0,$$

which implies

$$\Gamma \left(\frac{T_+}{T} \right) \geq (1 + \alpha) \frac{T_+}{T} + 4 \left(\frac{T}{T_+} - 1 \right) \frac{T_+}{T} - 1 > 3 \left(1 - \frac{T_+}{T} \right) \geq 0.$$

Thus we conclude that $0 < \Pi = \frac{p_+}{p} < \frac{T_+}{T}$, which is

$$\frac{\mu_A p_+ \alpha_A \alpha}{(1 - \alpha_A)(1 + \alpha) T^{\frac{5}{2}}} e^{\frac{T_A}{T}} < \frac{T_+}{T}.$$

Since we may assume $\alpha_A > \alpha_B$, we find that

$$\begin{aligned} & (1 - \alpha_A)(1 + \alpha) \\ &= 1 + \alpha - \alpha_A - \alpha_A \alpha = 1 - (1 - \beta)(\alpha_A - \alpha_B) - \alpha_A \alpha < 1. \end{aligned}$$

Thus

$$\frac{\beta \mu_A p_+ (\alpha_A)^2}{T^{\frac{5}{2}}} e^{\frac{T_A}{T}} < \frac{\mu_A p_+ \alpha_A \alpha}{T^{\frac{5}{2}}} e^{\frac{T_A}{T}} < \frac{T_+}{T}.$$

and we have

$$0 < \alpha_A < \sqrt{\frac{T_+ T^{\frac{3}{2}}}{\beta \mu_A p_+}} e^{-\frac{T_A}{2T}} = \sqrt{\frac{T_+ T_A^{\frac{3}{2}}}{\beta \mu_A p_+}} \left(\frac{T}{T_A} \right)^{\frac{3}{4}} e^{-\frac{T_A}{2T}}$$

By virtue of Theorem 3, we have the theorem.

9 Shock Tube Problem

The shock tube problem consists in finding the state (α_A^-, T_-) , for given (α_A^+, T_+) and u_{\pm} , satisfying Rankine-Hugoniot conditions

$$\begin{cases} (u_- - u_+)^2 = -(p_- - p_+)(v_- - v_+) : \text{kinetic part,} \\ h_- - h_+ = \frac{1}{2}(v_- + v_+)(p_- - p_+) : \text{thermodynamic part.} \end{cases} \quad (40)$$

The kinetic part takes a form

$$(u_- - u_+)^2 = -p_+ v_+ \left(\frac{p_-}{p_+} - 1 \right) \left(\frac{v_-}{v_+} - 1 \right). \quad (41)$$

Denoting $\alpha_A = \alpha_A^-$, $T = T_-$ and $u_A = u_-$, we define G to be

$$\begin{aligned} G(\alpha_A, T) &= -\frac{(u_A - u_+)^2}{p_+ v_+} - \left(\frac{p}{p_+} - 1\right) \left(\frac{v}{v_+} - 1\right) \\ &= -\frac{M(u_A - u_+)^2}{RT_+(1 + \alpha^+)} + \frac{p}{p_+} + \frac{v}{v_+} - \frac{T(1 + \alpha)}{T_+(1 + \alpha^+)} - 1. \end{aligned}$$

Then the kinetic condition (41) is equivalent to $G(\alpha_A, T) = 0$. Substituting (26) into the above expression, we have actually

$$\begin{aligned} G(\alpha_A, T) &= -\frac{M(u_A - u_+)^2}{RT_+(1 + \alpha^+)} + \frac{(1 - \alpha_A)(1 + \alpha)\alpha_A^+ \alpha^+}{(1 - \alpha_A^+)(1 + \alpha^+)\alpha_A \alpha} \left(\frac{T}{T_+}\right)^{\frac{5}{2}} e^{-\frac{T_A}{T} + \frac{T_A}{T_+}} \\ &\quad + \frac{(1 - \alpha_A^+)\alpha_A \alpha}{(1 - \alpha_A)\alpha_A^+ \alpha^+} \left(\frac{T}{T_+}\right)^{-\frac{3}{2}} e^{-\frac{T_A}{T_+} + \frac{T_A}{T}} - \frac{T(1 + \alpha)}{T_+(1 + \alpha^+)} - 1. \quad (42) \end{aligned}$$

By denoting $\Lambda^+ = \frac{(1 - \alpha_A^+)\alpha_A \alpha}{(1 - \alpha_A)\alpha_A^+ \alpha^+}$, we have $\frac{v}{v_+} = \Lambda^+ \left(\frac{T}{T_+}\right)^{-\frac{3}{2}} e^{-\frac{T_A}{T_+} + \frac{T_A}{T}}$ and

$$\begin{aligned} G(\alpha_A, T) &= K_+ \left(\frac{T}{T_+}\right)^{\frac{5}{2}} e^{-\frac{T_A}{T} + \frac{T_A}{T_+}} + \Lambda^+ \left(\frac{T}{T_+}\right)^{-\frac{3}{2}} e^{-\frac{T_A}{T_+} + \frac{T_A}{T}} \\ &\quad - \frac{T(1 + \alpha)}{T_+(1 + \alpha^+)} - \frac{M(u_A - u_+)^2}{RT_+(1 + \alpha^+)} - 1. \end{aligned}$$

Since

$$\left(\frac{\partial \Lambda^+}{\partial T}\right)_{\alpha_A} = \frac{\Lambda^+ Q_{BA}}{\alpha T}, \quad \left(\frac{\partial \Lambda^+}{\partial \alpha_A}\right)_T = \frac{\Lambda^+}{q_A} \left(1 + \frac{q}{\alpha}\right), \quad (43)$$

we find together with (31) that

$$q_A \left(\frac{\partial G}{\partial \alpha_A}\right)_T = -\left[1 + \frac{q}{\alpha(1 + \alpha)}\right] \left(\frac{p}{p_+}\right) + \left(1 + \frac{q}{\alpha}\right) \left(\frac{v}{v_+}\right) - \frac{Tq}{T_+(1 + \alpha^+)}, \quad (44)$$

$$\begin{aligned} T \frac{\partial G}{\partial T}(\alpha_A, T) &= \frac{p}{p_+} \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1 + \alpha)}\right] - \frac{v}{v_+} \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) \\ &\quad - \frac{T(1 + \alpha)}{T_+(1 + \alpha^+)} - \frac{TQ_{BA}}{T_+(1 + \alpha^+)} \quad (45) \end{aligned}$$

$$= \left(\frac{p}{p_+} - \frac{v}{v_+}\right) \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha}\right) + \left[\frac{p}{p_+} - \frac{T(1 + \alpha)}{T_+(1 + \alpha^+)}\right] \left(1 + \frac{Q_{BA}}{1 + \alpha}\right), \quad (46)$$

where the identity $\frac{1}{\alpha} - \frac{1}{\alpha(1 + \alpha)} = \frac{1}{1 + \alpha}$ is used.

Proposition 2 For every α_A , there are at least two values $T^{(\pm)} = T^{(\pm)}(\alpha_A)$, with $T^{(-)} < T^{(+)}$, such that $G(\alpha_A, T^{(\pm)}) = 0$. Moreover, $p^{(+)} > p_+ > p^{(-)}$.

Proof By virtue of the assumption: $T_A < T_B \leq 2T_A$, we find that

$$\frac{T_A}{T} - \frac{Q_{BA}}{\alpha} = \frac{T_A}{T} - \frac{(1-\beta)(T_B - T_A)q_B}{\alpha T} \geq \frac{2T_A}{T} - \frac{T_B}{T} \geq 0. \quad (47)$$

Hence

$$\left[\frac{\partial}{\partial T} \left(\frac{p}{p_+} \right) \right]_{\alpha_A} = \frac{p}{p_+ T} \left[\frac{5}{2} + \frac{T_A}{T} - \frac{(1-\beta)(T_B - T_A)q_B}{\alpha(1+\alpha)T} \right] \geq \frac{5p}{2p_+ T}$$

which shows that the function $T \mapsto \frac{p}{p_+}$ is strictly increasing and valued in $[0, \infty)$. Then, for every $\alpha_A > 0$ there exists a unique $T_* = T_*(\alpha_A)$ ($T_*(\alpha^+) = T_+$) such that, by (26),

$$\frac{p_*}{p_+} = \frac{(1-\alpha_A)(1+\alpha)\alpha_A^+ \alpha^+}{(1-\alpha_A^+)(1+\alpha^+)\alpha_A \alpha} \left(\frac{T_*}{T_+} \right)^{\frac{5}{2}} e^{-\frac{T_A}{T_*} + \frac{T_A}{T_+}} = 1,$$

for $p_* = p(\alpha_A, T_*(\alpha_A))$. Thus $G(\alpha_A, T_*(\alpha_A)) = -\frac{(u-u_0)^2}{a^2 T_0(1+\alpha_0)} < 0$.

For every fixed α_A we have that $G(\alpha_A, T) \rightarrow \infty$ for both $T \rightarrow 0$ and $T \rightarrow \infty$. We conclude that there are at least two values $T^{(\pm)} = T^{(\pm)}(\alpha_A)$, with $T_- < T_* < T_+$, such that $G(\alpha_A, T^{(\pm)}) = 0$. Note that $\frac{p^{(+)}}{p_+} > \frac{p_*}{p_+} = 1$ and $\frac{p^{(-)}}{p_+} < \frac{p_*}{p_+} = 1$.

We call the set of $(\alpha_A, T^{(+)})$ the *compressive part* of $G(\alpha_A, T) = 0$ and the set of $(\alpha_A, T^{(-)})$ its *expansive part*.

Asymptotics and Monotonicity: First we shall show the asymptotic behavior of the set $G(\alpha_A, T^{(\pm)}) = 0$ for α_A close to 1.

Proposition 3 *Suppose that $0 < \alpha_A^+ < 1$. Then we have*

$$1 - \alpha_A \sim \frac{1 - \alpha_A^+}{\alpha_A^+ \alpha^+} e^{-\frac{T_A}{T_+}} \left(\frac{T}{T_+} \right)^{-\frac{3}{2}} \quad \text{for } T \rightarrow \infty \quad (48)$$

for the compressive part and

$$1 - \alpha_A \sim \frac{(1 - \alpha_A^+)(1 + \alpha^+)}{2\alpha_A^+ \alpha^+} e^{-\frac{T_A}{T_+}} \left(\frac{T}{T_+} \right)^{-\frac{5}{2}} \quad \text{for } T \rightarrow \infty \quad (49)$$

for the expansive part. Hence, for α_A close to 1, both parts of $G(\alpha_A, T) = 0$ constitute strictly increasing curves in (T, α_A) plane.

Proof It is easy to see from (42) and compatibility condition that: if $\alpha_A \rightarrow 1$ on $G(\alpha_A, T) = 0$, then $\alpha_B \rightarrow 1$ and $T \rightarrow \infty$. We set $1 - \alpha_A \sim K \left(\frac{T}{T_+} \right)^{-\mu}$ with $\mu > 0$. By (42)

$$\begin{aligned} & \frac{2\alpha_A^+ \alpha^+ K}{(1 - \alpha_A^+)(1 + \alpha^+)} \left(\frac{T}{T_+} \right)^{\frac{5}{2} - \mu} e^{\frac{T_A}{T_+}} + \frac{1 - \alpha_A^+}{\alpha_A^+ \alpha^+ K} \left(\frac{T_0}{T} \right)^{\frac{3}{2} - \mu} e^{-\frac{T_A}{T_+}} \\ & \sim \frac{2T}{T_+(1 + \alpha^+)} + 1 + \frac{M(u_A - u_+)^2}{RT_+(1 + \alpha^+)}. \end{aligned}$$

If $T^{\frac{5}{2}-\mu}$ and $T^{\mu-\frac{3}{2}}$ are equally large as $T \rightarrow \infty$, we have $\mu = 2$. Then both terms are $O(1)T^{\frac{1}{2}}$, which is a contradiction. In the case $\frac{5}{2} - \mu = 1$, we have $\mu = \frac{3}{2}$ and $K = \frac{1-\alpha_A^+}{\alpha_A^+\alpha^+} e^{-\frac{T_A}{T^+}}$, which is the compressive part, and obtain (48).

Otherwise, if $\mu - \frac{3}{2} = 1$, we have $\mu = \frac{5}{2}$ and $K = \frac{(1-\alpha_A^+)(1+\alpha^+)}{2\alpha_A^+\alpha^+} e^{-\frac{T_A}{T^+}}$, which is the expansive part. In both cases monotonicity with respect to α_A close to 1 is obvious.

Smoothness of the Compressive Part:

Theorem 11 *For any fixed (α_A^+, T_+) , the compressive part of $G(\alpha_A, T) = 0$, constitutes a single differentiable curve.*

Proof Since $G(\alpha_A, T) = 0$ is written as $\frac{p}{p_+} - \frac{T(1+\alpha)}{T_+(1+\alpha^+)} = 1 - \frac{v}{v_+} + \frac{M(u_A - u_+)^2}{RT_+(1+\alpha^+)}$ then it follows from (46) and (47) that

$$\begin{aligned} T \frac{\partial G}{\partial T}(\alpha_A, T) &= \left(\frac{p}{p_+} - \frac{v}{v_+} \right) \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha} \right) \\ &\quad + \left(1 + \frac{Q_{BA}}{1+\alpha} \right) \left[\left(1 - \frac{v}{v_+} \right) + \frac{M(u_A - u_+)^2}{RT_+(1+\alpha^+)} \right] > 0 \end{aligned} \quad (50)$$

on the compressive part $p > p_+$, $v < v_+$. Thus we have proved that: in a neighbourhood of every state $(\alpha_A, T^{(+)})$, the compressive part of $G(\alpha_A, T) = 0$ is a graph of a differentiable function of α_A . Consequently, the compressive part constitutes a differentiable curve.

Solution to the Shock Tube Problem:

Theorem 12 (Intersection with Hugoniot loci) *Fix (T_+, α_A^+) and $u_+ \neq u_A$. Then, in the region $\alpha_A^+ < \alpha_A < 1$, there is at least one intersection point of the compressive part of $G(\alpha_A, T) = 0$ and the thermodynamic Hugoniot locus (25) of (T_+, α_A^+) .*

Proof Let $\alpha_A = \alpha_A(T)$ denote thermodynamic Hugoniot locus of (T_+, α_A^+) in (α_A, T) -plane. Clearly, $G(\alpha_A^+, T_+) = -\frac{M(u_A - u_+)^2}{RT_+(1+\alpha^+)} < 0$ by (42), while $\alpha_A^+ = \alpha_A(T_+)$. Through the proof of Proposition 2, we have found that the graph of $T = T^{(+)}(\alpha_A)$ is located above the thermodynamic part the Hugoniot locus of (T_+, α_A^+) near $\alpha_A = \alpha_A^+$.

On the other hand, by (29) the Hugoniot locus of (α_B, T_B) takes an asymptotic form $1 - \alpha_A \sim \frac{4(1-\alpha^+)}{\alpha_A^+\alpha^+} \left(\frac{T}{T_+} \right)^{-\frac{3}{2}} e^{-\frac{T_A}{T^+}}$ and by (48) $T_+(\alpha)$ has $1 - \alpha_A \sim \frac{1-\alpha_A^+}{\alpha_A^+\alpha^+} e^{-\frac{T_A}{T^+}} \left(\frac{T}{T_+} \right)^{-\frac{3}{2}}$. as $\alpha_A \rightarrow 1$. Thus we conclude that the graph of $T = T^{(+)}(\alpha_A)$ is located under the Hugoniot locus as $\alpha_A \rightarrow 1$, which proves the assertion.

Uniqueness of the Solution: The aim of this subsection is to prove that the solution obtained in Theorem 12 is unique.

Theorem 13 (Uniqueness of the intersection point) *Fix (α_A^+, T_+) and $u_+ \neq u_A$. Then, in the region $\alpha_A^+ < \alpha_A < 1$ the intersection point of the compressive part of $G(\alpha_A, T) = 0$ and the thermodynamic Hugoniot locus (25) of (T_+, α_A^+) is unique.*

Proof Since the thermodynamic Hugoniot locus is the graph of $\alpha_A = \alpha_A(T)$, the solution is a zero of $G(\alpha_A(T), T)$ (denoted by $T = T_*$) and proof will be completed by showing

$$\frac{dG}{dT}(\alpha_A(T_*), T_*) = \frac{\left[\left(\frac{\partial G}{\partial T} \right)_A \left(\frac{\partial H}{\partial \alpha_A} \right)_T - \left(\frac{\partial G}{\partial \alpha_A} \right)_T \left(\frac{\partial H}{\partial T} \right)_A \right]_{(\alpha_A(T_*), T_*)}}{\left(\frac{\partial H}{\partial \alpha_A} \right)_T (\alpha_A(T_*), T_*)} > 0.$$

Recall that $\left(\frac{\partial H}{\partial \alpha_A} \right)_T > 0$. By substituting the expressions (37), (38), (44), (45)

into the above, the numerator is written as $\frac{T_+(1+\alpha^+)}{qAT(1+\alpha)}$ times of

$$\left| \begin{aligned} & \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right] \frac{p}{p_+} - \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha} \right) \frac{v}{v_+} - \frac{T(1+\alpha)}{T_+(1+\alpha^+)} - \frac{TQ_{BA}}{T_+(1+\alpha^+)} \\ & - (1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \frac{p}{p_+} + (1+\alpha) \left(1 + \frac{q}{\alpha} \right) \frac{v}{v_+} - \frac{qT(1+\alpha)}{T_+(1+\alpha^+)} \\ & - \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right] \frac{p}{p_+} - \left(\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha} \right) \frac{v}{v_+} + \frac{4T(1+\alpha)}{T_+(1+\alpha^+)} \left[1 + \frac{Q_{BA}}{1+\alpha} \left(1 + \frac{T_B}{2T} \right) \right] \\ & (1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \frac{p}{p_+} + (1+\alpha) \left(1 + \frac{q}{\alpha} \right) \frac{v}{v_+} + \frac{4T(1+\alpha)}{T_+(1+\alpha^+)} \left(q + \frac{QT}{2} \right) \end{aligned} \right|.$$

As shown in section A, its final form will be

$$\begin{aligned} & 3(1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1+\alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\ & + 8 \left\{ q \left[\left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) - \frac{T_A}{4T} \right] + \left[\frac{q(T_B - T_A)}{T} - Q_{BA} \right] \frac{Q_{BA}}{\alpha(1+\alpha)} \right. \\ & \left. + \left(\frac{15}{4} + \frac{T_A + T_B}{T} \right) Q_{BA} \right\} \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} - 1 \right] \\ & + 6(1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1+\alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\ & + 2 \left\{ q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + \left[\frac{q(T_B - T_A)}{T} - Q_{BA} \right] \frac{Q_{BA}}{\alpha(1+\alpha)} \right. \\ & \left. + \left(4 + \frac{T_A + T_B}{T} \right) Q_{BA} \right\} \frac{[\beta T_A(\alpha_A - \alpha_A^+) + (1-\beta)T_B(\alpha_B - \alpha_B^+)]}{T_+(1+\alpha^+)} \\ & + 2 \left(\frac{v}{v_+} \right) \left[\frac{q(T_B - T_A)}{T} - Q_{BA} \right] \left(\frac{p}{p_+} - 1 \right) \frac{Q_{BA}}{1+\alpha}. \end{aligned} \quad (51)$$

Notice that

$$\frac{q(T_B - T_A)}{T} - Q_{BA} = \frac{\beta(T_B - T_A)q_A}{T} > 0, \quad (52)$$

which shows that the expression (51) is positive and the theorem follows.

10 Conclusions and Discussions

In this paper, we have studied a model system for macroscopic motion of an ionized gas which is a mixture of two monatomic gas A and B; the mixture ratio is $\beta : 1 - \beta$. This model system is proposed by [8] and consists of three conservation laws in one space dimension together with the first and second law of thermodynamics which are supplemented by an equation of state and two more thermodynamic equations called Saha's laws. We have assumed that the interaction potential energies and effects of collisions between charged particles are negligible and the local thermodynamic equilibrium is attained. We further assume that T_B : the first ionization temperature of the gas B is higher than T_A : that of the gas A and $2T_A \geq T_B$. Note that A: hydrogen and B: helium satisfy these assumptions.

The physical entropy functions are constructed and it is remarkable that they are expressed in terms of elementary functions. Saha's two equations bring about a compatibility condition involving α_A, α_B and T . It is shown that α_B is a differentiable function of α_A and T whose graph constitutes the thermodynamic state space. We propose that (T, α_A) is a suitable pair of independent thermodynamic state variables.

The system of conservation laws is shown to constitute a strictly hyperbolic system, which implies that the initial-value problem is well-posed locally in time for sufficiently smooth initial data. Characteristic fields are computed and geometric properties are studied: unlike the polytropic (non-ionized) case, the convexity (genuine nonlinearity) of the forward and backward characteristic fields of the system is lost and the set where this happens is determined in a neighbourhood of $T = \alpha_A = 0$. Whole set is located in a finite region in (T, α_A) plane but it is difficult to get its full picture by purely mathematical reasoning; only pictures by numerical computation are presented.

A detailed study of the thermodynamic Hugoniot locus is performed. For every $T > 0$, there is a unique $0 < \alpha_A < 1$ satisfying the thermodynamic Rankine-Hugoniot condition and α_A is a smooth function of T . Hence the Hugoniot locus is a smooth graph in the (T, α_A) plane. While the thermodynamic Hugoniot locus is monotone in (T, α) plane in a single monatomic case, for the mixed monatomic case it is shown that: if β is sufficiently small, then it loses monotonicity at some base state. Thus the degree of ionization does not always increase across the shock front, even if the temperature increases. However the pressure is actually proved to increase as the temperature increases which ensures that $T > T_+$ is the admissible branch.

In order to fit the mathematical data to ordinary circumstances, an approximation of thermodynamic Hugoniot loci is proposed and proved that, for small T , it is limited in a "classical" region where the forward and backward characteristic fields are convex (genuinely nonlinear) and the physical entropy increases along the admissible branch. We expect that actual experiments are usually performed in such a classical region.

These results are applied to the mathematical analysis of the shock tube problem: existence and uniqueness of the solution are established, which pro-

vides a rigorous mathematical basis to the physical phenomena observed and reported in [8], [9], [10].

A Computation of (51)

Substitution of (37), (38), (44), (45) into $q_A \left[\left(\frac{\partial G}{\partial T} \right)_{\alpha_A} \left(\frac{\partial H}{\partial \alpha_A} \right)_T - \left(\frac{\partial G}{\partial \alpha_A} \right)_T \left(\frac{\partial H}{\partial T} \right)_{\alpha_A} \right]$ gives

$$\begin{aligned}
& \left| - \left(3 + \frac{2T_A}{T} - \frac{2Q_{BA}}{\alpha} \right) - \left[5 + \frac{2T_A}{T} - \frac{2Q_{BA}}{\alpha(1+\alpha)} \right] \right| \\
& \quad \left(1 + \alpha \right) \left(1 + \frac{q}{\alpha} \right) \quad \left(1 + \alpha \right) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left| \right. \\
& \quad + \frac{p}{p_+} \left| \frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \quad 3 + \frac{3Q_{BA}}{1+\alpha} + \frac{2T_B Q_{BA}}{T(1+\alpha)} \right| \\
& \quad \quad \quad \left. - (1 + \alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \quad (3q + 2Q_T) \right| \\
& \quad - \frac{v}{v_+} \left| \frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha} \quad 5 + \frac{5Q_{BA}}{1+\alpha} + \frac{2T_B Q_{BA}}{T(1+\alpha)} \right| \\
& \quad \quad \quad \left. - (1 + \alpha) \left(1 + \frac{q}{\alpha} \right) \quad (5q + 2Q_T) \right| \\
& \quad - \frac{T(1+\alpha)}{T_+(1+\alpha^+)} \left| 1 + \frac{Q_{BA}}{1+\alpha} \quad 4 \left[1 + \frac{Q_{BA}}{1+\alpha} \left(1 + \frac{T_B}{2T} \right) \right] \right| \\
& \quad \quad \quad \left. q \quad 4 \left(q + \frac{Q_T}{2} \right) \right| \\
& = -(1 + \alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(3 + \frac{2T_A}{T} - \frac{2Q_{BA}}{\alpha} \right) + (1 + \alpha) \left(1 + \frac{q}{\alpha} \right) \left[5 + \frac{2T_A}{T} - \frac{2Q_{BA}}{\alpha(1+\alpha)} \right] \\
& \quad + 2 \left(\frac{p}{p_+} \right) \left(\frac{3}{2} q + Q_T \right) \left[\frac{5}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right] \\
& \quad + (1 + \alpha) \left(\frac{p}{p_+} \right) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left[3 + 2 \left(\frac{3}{2} + \frac{T_B}{T} \right) \frac{Q_{BA}}{1+\alpha} \right] \\
& \quad - 2 \left(\frac{v}{v_+} \right) \left(\frac{5}{2} q + Q_T \right) \left[\frac{3}{2} + \frac{T_A}{T} - \frac{Q_{BA}}{\alpha} \right] \\
& \quad - (1 + \alpha) \left(\frac{v}{v_+} \right) \left(1 + \frac{q}{\alpha} \right) \left[5 + 2 \left(\frac{5}{2} + \frac{T_B}{T} \right) \frac{Q_{BA}}{1+\alpha} \right] \\
& \quad \quad \quad - \frac{T(1+\alpha)}{T_+(1+\alpha^+)} \left[2Q_T \left(1 + \frac{Q_{BA}}{1+\alpha} \right) - \frac{2qT_B Q_{BA}}{T(1+\alpha)} \right].
\end{aligned}$$

Notice that

$$qQ_T - \frac{qT_A}{T} = \frac{\beta q_A T_A + (1 - \beta) q_B T_B}{T} - \frac{T_A}{T} = \frac{(1 - \beta) q_B (T_B - T_A)}{T} = Q_{BA}.$$

Hence we have $qQ_T = \frac{qT_A}{T} + Q_{BA}$. By this formula, the above expression is found to be

$$\begin{aligned}
& 3(1 + \alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1 + \alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\
& + 2 \left[q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + q \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{\alpha} + \left(4 + \frac{T_A + T_B}{T} - \frac{Q_{BA}}{\alpha} \right) Q_{BA} \right] \left(\frac{p}{p_+} - \frac{v}{v_+} \right) \\
& \quad - 2q \left(\frac{p}{p_+} \right) \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{1+\alpha} + 2 \left(\frac{p}{p_+} \right) \frac{Q_{BA}^2}{1+\alpha} \\
& \quad - 2q \left(\frac{T_A}{T} + \frac{Q_{BA}}{q} \right) \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} \left(1 + \frac{Q_{BA}}{1+\alpha} \right) - 1 \right] + \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} \right] \frac{2qT_B Q_{BA}}{T(1+\alpha)} \\
& = 3(1 + \alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1 + \alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\
& + 2 \left[q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + q \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{\alpha(1+\alpha)} + \left(4 + \frac{T_A + T_B}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right) Q_{BA} \right] \left(\frac{p}{p_+} - \frac{v}{v_+} \right) \\
& \quad - 2q \left(\frac{v}{v_+} \right) \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{1+\alpha} + 2 \left(\frac{v}{v_+} \right) \frac{Q_{BA}^2}{1+\alpha} \\
& - 2q \left(\frac{T_A}{T} + \frac{Q_{BA}}{q} \right) \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} - 1 \right] - \frac{2T(1+\alpha)}{T_+(1+\alpha^+)} \frac{Q_{BA}^2}{1+\alpha} + \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} \right] \frac{2q(T_B - T_A) Q_{BA}}{T(1+\alpha)}.
\end{aligned}$$

Note that $\frac{pv}{p_+v_+} = \frac{T(1+\alpha)}{T_+(1+\alpha^+)}$. Then

$$2q \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} \right] \frac{T_B - T_A}{T} \frac{Q_{BA}}{1+\alpha} - 2q \left(\frac{v}{v_+} \right) \frac{T_B - T_A}{T} \frac{Q_{BA}}{1+\alpha} = 2q \left(\frac{v}{v_+} \right) \frac{(T_B - T_A) Q_{BA}}{T(1+\alpha)} \left(\frac{p}{p_+} - 1 \right) \geq 0, \\ - \frac{2T(1+\alpha)}{T_+(1+\alpha^+)} \frac{Q_{BA}^2}{1+\alpha} + 2 \left(\frac{v}{v_+} \right) \frac{Q_{BA}^2}{1+\alpha} = -2 \left(\frac{v}{v_+} \right) \left(\frac{p}{p_+} - 1 \right) \frac{Q_{BA}^2}{1+\alpha},$$

and we conclude that the above expression is equal to

$$3(1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1+\alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\ + 2 \left[q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + q \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{\alpha(1+\alpha)} + \left(4 + \frac{T_A + T_B}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right) Q_{BA} \right] \left(\frac{p}{p_+} - \frac{v}{v_+} \right) \\ - 2q \left(\frac{T_A}{T} + \frac{Q_{BA}}{q} \right) \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} - 1 \right] + 2 \left(\frac{v}{v_+} \right) \left[\frac{q(T_B - T_A)}{T} - Q_{BA} \right] \left(\frac{p}{p_+} - 1 \right) \frac{Q_{BA}}{1+\alpha}.$$

Recall that the thermodynamic Rankine-Hugoniot condition is equivalent to

$$\frac{p}{p_+} - \frac{v}{v_+} = \frac{4T(1+\alpha)}{T_+(1+\alpha^+)} - 4 + \frac{2 \left[\beta T_A (\alpha_A - \alpha_A^+) + (1-\beta) T_B (\alpha_B - \alpha_B^+) \right]}{T_+(1+\alpha^+)}.$$

Thus $q_A \left[\left(\frac{\partial G}{\partial T} \right)_{\alpha_A} \left(\frac{\partial H}{\partial \alpha_A} \right)_T - \left(\frac{\partial G}{\partial \alpha_A} \right)_T \left(\frac{\partial H}{\partial T} \right)_{\alpha_A} \right]$ is:

$$3(1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1+\alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\ + 8 \left[q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + q \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{\alpha(1+\alpha)} \right. \\ \left. + \left(4 + \frac{T_A + T_B}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right) Q_{BA} - \frac{1}{4} \left(\frac{qT_A}{T} + Q_{BA} \right) \right] \left[\frac{T(1+\alpha)}{T_+(1+\alpha^+)} - 1 \right] \\ + 6(1+\alpha) \left[1 + \frac{q}{\alpha(1+\alpha)} \right] \left(\frac{p}{p_+} - 1 \right) + 5(1+\alpha) \left(1 + \frac{q}{\alpha} \right) \left(1 - \frac{v}{v_+} \right) \\ + 2 \left[q \left(\frac{3}{2} + \frac{T_A}{T} \right) \left(\frac{5}{2} + \frac{T_A}{T} \right) + q \left(\frac{T_B - T_A}{T} \right) \frac{Q_{BA}}{\alpha(1+\alpha)} \right. \\ \left. + \left(4 + \frac{T_A + T_B}{T} - \frac{Q_{BA}}{\alpha(1+\alpha)} \right) Q_{BA} \right] \frac{\left[\beta T_A (\alpha_A - \alpha_A^+) + (1-\beta) T_B (\alpha_B - \alpha_B^+) \right]}{T_+(1+\alpha^+)} \\ + 2 \left(\frac{v}{v_+} \right) \left[\frac{q(T_B - T_A)}{T} - Q_{BA} \right] \left(\frac{p}{p_+} - 1 \right) \frac{Q_{BA}}{1+\alpha}$$

which implies (51).

B Isentropes

In (p, u, T) coordinates, we have observed by Remark 1 that: the thermodynamic part of an integral curve is $\eta = \text{const.}$ for 1, 2-characteristic directions and $p = \text{const.}$ for 0-characteristic field. A curve $\eta = \text{const.}$ in (T, α_A) plane is called an *isentrope*.

Theorem 14 *An isentrope $\eta = \eta_0$ is the graph of a differentiable function $\alpha_A = \alpha_A(T)$ defined on $T \in (0, \infty)$.*

Proof Derivative of η with respect to α_A takes a form

$$\left(\frac{\partial \eta}{\partial \alpha_A} \right)_T = \beta \left[\frac{1}{\beta \alpha_A + (1-\beta) \alpha_B} + \frac{1 + \alpha_A}{q_A} + \left(\frac{5}{2} + \frac{T_A}{T} \right) \right] \\ + (1-\beta) \left[\frac{1}{\beta \alpha_A + (1-\beta) \alpha_B} + \frac{1 + \alpha_B}{q_B} + \left(\frac{5}{2} + \frac{T_B}{T} \right) \right] \left(\frac{\partial \alpha_B}{\partial \alpha_A} \right)_T. \quad (53)$$

By (23) we find $\left(\frac{\partial \eta}{\partial \alpha_A}\right)_T > 0$. We have also

$$\left(\frac{\partial \eta}{\partial T}\right)_{\alpha_A} = -\frac{T_A}{T^2}(1+\alpha) + (1-\beta) \left[\frac{1}{\alpha} + \left(\frac{5}{2} + \frac{T_B}{T}\right) \right] \frac{(T_B - T_A)q_B}{T^2}.$$

First we shall prove that α_A is a function of T defined on $(0, \infty)$. Let us fix any T in $(0, \infty)$. It follows from (22) $\alpha_B \sim \frac{\mu_A}{\mu_B} \alpha_A e^{-\frac{T_B - T_A}{T}}$ as $\alpha_A \rightarrow 0$. Hence

$$\log \alpha_B \sim \log \alpha_A + O(1), \quad \log [\beta \alpha_A + (1-\beta)\alpha_B] \sim \log \alpha_A + O(1).$$

Thus we find $\eta(\alpha_A, \alpha_B, T) \sim 2 \log \alpha_A + O(1) \rightarrow -\infty$ for $\alpha_A \rightarrow 0$.

On the other hand, when $\alpha_A \rightarrow 1$, obviously $\alpha_B \rightarrow 1$ and

$$\eta(\alpha_A, \alpha_B, T) \sim -2\beta \log(1-\alpha_A) - 2(1-\beta) \log(1-\alpha_B) + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \rightarrow \infty.$$

Consequently, since $\left(\frac{\partial \eta}{\partial \alpha_A}\right)_T > 0$, we conclude that there is a unique single root $\alpha_A(T)$ such that

$$\eta(\alpha_A(T), \alpha_B(T), T) = \eta_0 \quad \text{and} \quad 0 < \alpha_A(T) < 1.$$

Next we consider the behaviour as $T \rightarrow 0$.

Proposition 4 *If $T \rightarrow 0$, then $\alpha_A \rightarrow 0$ and $\alpha_A \sim \frac{1}{\sqrt{\beta}} \left(\frac{\mu_A}{\mu_B}\right)^{-\frac{1}{2}(1-\beta)} e^{-\frac{T_A}{2T} + \frac{\eta_0}{2}}$.*

Proof If $\alpha_A \geq c > 0$ or $\alpha_B \geq c > 0$, then $\eta \rightarrow \infty$ which is contradiction. Hence $\alpha_A, \alpha_B < c$. By compatibility condition, we have

$$\frac{1 - \alpha_B}{\alpha_B} = \frac{\mu_B(1 - \alpha_A)}{\mu_A \alpha_A} e^{\frac{1}{T}(T_B - T_A)}.$$

If $\alpha_A \leq c < 1$, then by setting $T \rightarrow 0$ in the above equation, we have $\alpha_B \rightarrow 0$. Suppose that $\alpha_A \geq c' (c > c' > 0)$. Since $\log \alpha_B = \log(1 - \alpha_B) - \log \frac{1 - \alpha_A}{\alpha_A} - \frac{1}{T}(T_B - T_A) + O(1)$, we have by substituting the above into the expression of the entropy

$$\begin{aligned} \eta &= \log [\beta \alpha_A + (1-\beta)\alpha_B] + \log \alpha_A - (1+\beta) \log(1 - \alpha_A) - (1-\beta) \log(1 - \alpha_B) \\ &\quad + \frac{T_A}{T} + \beta \left(\frac{5}{2} + \frac{T_A}{T}\right) \alpha_A + (1-\beta) \left(\frac{5}{2} + \frac{T_B}{T}\right) \alpha_B + O(1). \end{aligned}$$

Clearly $\log(1 - \alpha_A) < 0$, $\log(1 - \alpha_B) < 0$, and $\log [\beta \alpha_A + (1-\beta)\alpha_B] \geq -c$ for some $c > 0$. Thus we find $\eta \rightarrow \infty$ as $T \rightarrow 0$, which is also contradictory. Thus $\alpha_A \rightarrow 0$ and the first part of proposition is proved.

It follows from (22) $\log \alpha_B \sim \log \frac{\mu_A}{\mu_B} + \log \alpha_A - \frac{T_B - T_A}{T}$ as $\alpha_A \rightarrow 0$ and

$$\begin{aligned} \eta &\sim \log \beta + \log \alpha_A + \beta \left(\log \alpha_A + \frac{T_A}{T} \right) + (1-\beta) \left(\log \frac{\mu_A}{\mu_B} + \log \alpha_A - \frac{T_B - T_A}{T} + \frac{T_B}{T} \right) \\ &\sim \log \beta + (1-\beta) \log \frac{\mu_A}{\mu_B} + 2 \log \alpha_A + \frac{T_A}{T} \sim \eta_0. \end{aligned}$$

Thus $\alpha_A \sim C e^{-\frac{T_A}{T}}$ with a certain constant C satisfying $\log C + \log \beta + (1-\beta) \log \frac{\mu_A}{\mu_B} = \eta_0$ and we obtain the asymptotic formula.

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