

A Mathematical Model of Ionized Gases: Thermodynamic Properties

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§ 1. Introduction

The aim of this note is to give a brief account of Asakura-Corli [1], showing the thermodynamic property of a particular mathematical model of ionized gases. Thermal ionization occurs in a high temperature region behind a single shock wave passing through the gas. By assuming the local state attains the thermal equilibrium, the thermodynamic quantities: temperature, particle density and degree of ionization are computed by the Rankine-Hugoniot condition and the Saha ionization formula for given initial state and the speed of the shock wave. The mathematical model is proposed by Fukuda-Okasaka-Fujimoto [4], and [1] studies in particular the basic properties of the thermodynamic part of the Hugoniot locus of a given state. To the best of our knowledge such a study has never been done previously, in spite of the fact that the system of gas dynamics attracted the interest of several researchers in the last decade, however mostly for ideal gases Smoller [8]; we quote Menikoff-Plohr [6] for the case of real gases.

First, we summarize, in §2, 3, basic geometric properties of general gas dynamics equations. A particular model of monatomic ionized gas is studied in §4: the physical entropy is constructed and it is shown that the characteristic field is not necessarily genuinely nonlinear. We also find that the degree of ionization α (defined later) and the temperature T are appropriate independent thermodynamic variables. The thermodynamic part of the Hugoniot locus is studied in §5: it is the graph of a strictly increasing function $T = T(\alpha)$ and the pressure and the specific volume are monotone function of α . In the last section, we try to present a direct derivation of the Saha ionization formula (see Zeldovich-Raiser [9, III §5]).

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In a simple thermodynamic system, the state is completely specified if the pressure p , the volume V and the temperature T are given. Indeed, these three quantities are related by an *equation of state* and the state of the system is completely determined by any two of them. The state equation of m (kg) of an ideal gas has the form $pV = \frac{R}{M}mT$, where the gas constant is denoted by R and the molar mass of the gas by M (kg). Sometimes it is useful to introduce the density $\rho = \frac{m}{V}$ and specific volume $v = \frac{1}{\rho}$.

The specific internal energy e and the specific entropy S satisfy the first and second law of thermodynamics:

$$(1.1) \quad de = TdS - pdv.$$

The enthalpy H is defined to be $h = e + pv$ and satisfies

$$(1.2) \quad dH = TdS + vdp.$$

When a gas, for example the hydrogen gas H_2 , is heated to a high temperature, at first almost all of its molecules become dissociated: $H_2 \rightleftharpoons 2H$ and it behaves like a monatomic gas. If it is heated more, some of its atoms become ionized: $H \rightleftharpoons H^+ + e^-$, where H^+ is a hydrogen ion and e^- an electron. Thus, at extremely high temperatures, we have a mixture of three different kinds of particles: atoms, ions and electrons, and each of them behaves like a monatomic gas.

Let X denote an atom of monatomic gas and $X \rightleftharpoons X^+ + e^-$ the ionization reaction. At any given (high) temperature T , the ionization process reaches a state of thermal equilibrium analogous to the chemical equilibrium for an ordinary chemical reaction. By denoting the concentration (number per unit volume) of atoms, ions, electrons by n_a, n_i, n_e , respectively, we may assume that the ratio $\frac{n_i n_e}{n_a}$ depends only on the temperature T . An actual formula is derived by Saha [7], i.e.,

$$(1.3) \quad \frac{n_i n_e}{n_a} = \frac{2G_i}{G_a} \frac{(2\pi m_e kT)^{\frac{3}{2}}}{h^3} e^{-\frac{T_i}{T}}.$$

Here, G_i, G_a denote, respectively, the standardized partition functions of the ion, atom, respectively, m_e the atomic mass of the electron and T_i the ionization energy expressed by the temperature; moreover, k is the Boltzmann constant and h the Planck constant. The degree of ionization is defined by $\alpha = \frac{n_i}{n_a + n_i}$ and considered to be a thermodynamic variable.

The motivation for our study was provided by Fukuda-Okasaka-Fujimoto [4]¹. In the Fukuda laboratory, a spectrometric measurement of the ionization relaxation of plasma was done: the plasma was generated either by helium or by a mixture of helium-hydrogen gas, and a single shock wave was experienced. Indeed, in [4] the authors mainly

¹An English translation of [4] is available upon request to F. Asakura.

focused on a two-component gas: they constructed several ionization models in plasma, carried out computation and, as a result, obtained the approximate ionization relaxation time.

In [1], the gas is assumed to be *monatomic*. This choice simplifies the analysis of the system while catching however the main features of ionization; more general cases (non-monatomic or multicomponent gases) can be considered as well but at the price of much heavier computations. The model equation of state is

$$(1.4) \quad p = \frac{R}{M} \rho T (1 + \alpha)$$

and the enthalpy has the form

$$(1.5) \quad H = \frac{5RT}{2M} (1 + \alpha) + \frac{RT_i}{M} \alpha = \frac{RT}{M} \left[\frac{5}{2} + \left(\frac{5}{2} + \frac{T_i}{T} \right) \alpha \right].$$

When the ionization occurs, an extra equation is needed to determine the fraction α of ionized atoms. By assuming that the equilibrium is attained, an equation to add is the Saha ionization equation

$$(1.6) \quad \alpha = \left[1 + \frac{ph^3}{(2\pi m_e)^{\frac{3}{2}} (kT)^{\frac{5}{2}}} \frac{G_a}{2G_i} e^{\frac{T_i}{T}} \right]^{-\frac{1}{2}}.$$

which comes from (1.3) (see Section 6). Thus the temperature, particle density and degree of ionization of the plasma generated by a single shock wave are computed algebraically by the Rankine-Hugoniot conditions and the Saha ionization equation for given initial data and speed of the shock wave.

§ 2. Equations of Gas Dynamics

Eulerian Equations By neglecting the heat loss and friction against the tube wall, the equations of 1-dimensional gas dynamics in Eulerian coordinates are given by

$$(2.1) \quad \begin{cases} \rho_t + (\rho u)_x = 0, \\ (\rho u)_t + (\rho u^2 + p)_x = 0, \\ (\rho \mathcal{E})_t + (\rho u \mathcal{E} + pu)_x = 0, \end{cases}$$

where ρ is the mass density, u the velocity, p the pressure and e the specific internal energy. The (specific) total energy is denoted by $\mathcal{E} = \frac{1}{2}u^2 + e$. The temperature and entropy are denoted by T, S , respectively and the specific volume by $v = \frac{1}{\rho}$. We have thus introduced six thermodynamic variables: ρ, v, p, e, T, S , where e and v are functions of the other variables. The equation of state and the first and second law of thermodynamics (1.1) are constraints which reduce the number of independent variables to

two. The simplest non-isentropic model of gas is the ideal $pv = RT$ and polytropic $e = C_v T + e_0$ (C_v : specific heat at constant volume). Then S is expressed as

$$S = C_v \log p - \left(1 + \frac{R}{C_v}\right) \log \rho + \text{const.}$$

The Lagrangian form of (2.1) is given by

$$(2.2) \quad \begin{cases} v_t - u_\xi = 0, \\ u_t + p_\xi = 0, \\ (e + \frac{1}{2}u^2)_t + (pu)_\xi = 0. \end{cases}$$

It follows from (1.1) and the third equation in (2.2) that

$$e_t + uu_t + (pu)_\xi = TS_t - pv_t + uu_t + (pu)_\xi = TS_t,$$

which shows that the third equation is formally equivalent to $TS_t = 0$.

Characteristic Speeds and Vector Fields In the variables (p, u, S) , we have $v_t = v_p p_t$ and Lagrangian equations (2.2) become

$$(2.3) \quad p_t - \frac{1}{v_p} u_\xi = 0, \quad u_t + p_\xi = 0, \quad S_t = 0.$$

In these variables, the *Lagrangian* characteristic speeds are: $-\frac{1}{\sqrt{-v_p}}, 0, \frac{1}{\sqrt{-v_p}}$, with corresponding characteristic vectors

$$(-1, \sqrt{-v_p}, 0)^T, \quad (0, 0, 1)^T, \quad (1, \sqrt{-v_p}, 0)^T.$$

They are called 1, 0 and 2-characteristic vectors, respectively.

Returning to the Eulerian coordinates, we find that system (2.1) is formally equivalent to the system of quasi-linear equations

$$(2.4) \quad \begin{cases} \rho_t + u\rho_x + \rho u_x = 0, \\ u_t + uu_x + \frac{p_x}{\rho} = 0, \\ S_t + uS_x = 0. \end{cases}$$

Suppose that the pressure p is a function of ρ and S . Then we find, by denoting $c = \sqrt{p_\rho}$, that the characteristic roots are: $u - c, \quad u, \quad u + c$, with corresponding characteristic vectors

$$\left(-1, \frac{c}{\rho}, 0\right)^T, \quad (0, 0, 1)^T, \quad \left(1, +\frac{c}{\rho}, 0\right)^T.$$

They are also called 1, 0 and 2-characteristic vectors, respectively. Note that these characteristic vectors are all formed by thermodynamic quantities. The 1, 0 and 2-integral curves are, respectively

$$\begin{aligned} u &= \int \frac{\sqrt{p_\rho(\rho, S_0)}}{\rho} d\rho, \quad S = S_0 : && \text{1-characteristic direction,} \\ &\rho = \rho_0, \quad u = u_0 : && \text{0-characteristic direction,} \\ u &= - \int \frac{\sqrt{p_\rho(\rho, S_0)}}{\rho} d\rho, \quad S = S_0 : && \text{2-characteristic direction.} \end{aligned}$$

In the following discussion, we shall concentrate on the thermodynamic state space, where the integral curves are represented as

$$S = S_0 : \text{1,2-characteristic direction,} \quad \rho = \rho_0 : \text{0-characteristic direction.}$$

§ 3. Rankine-Hugoniot Conditions

Let us consider a shock front with constant speed $x = st$ which separates the left side state (ρ_-, u_-, S_-) from the right side state (ρ_+, u_+, S_+) . The jump of a quantity $\phi = \phi(\rho, u, S)$ across the shock front is denoted by $[\phi]_-^+$. These states, together with the shock front, constitute a weak solution if and only they satisfy the equations

$$\begin{aligned} s[\rho]_-^+ &= -[\rho u]_-^+, \\ s[\rho u]_-^+ &= [\rho u^2 + p]_-^+, \\ s[\rho(e + \tfrac{1}{2}u^2)]_-^+ &= [(\rho(e + \tfrac{1}{2}u^2)u + pu)]_-^+, \end{aligned}$$

which are called Rankine-Hugoniot conditions. By introducing, for convenience, the relative velocity $U = s - u$ and the mass flux $\Sigma = \rho V$, the above conditions are equivalent to

$$(3.1) \quad \rho_- U_- = \rho_+ U_+,$$

$$(3.2) \quad \rho_- U_-^2 + p_- = \rho_+ U_+^2 + p_+,$$

$$(3.3) \quad \Sigma(e_- + \tfrac{1}{2}U_-^2 + p_- v_-) = \Sigma(e_+ + \tfrac{1}{2}U_+^2 + p_+ v_+).$$

Note that $\Sigma_+ = \Sigma_-$ and $u_+ - u_- = -(U_+ - U_-)$. Since $\rho_\pm U_\pm^2 = \frac{\Sigma^2}{\rho_\pm} = \Sigma^2 v_\pm$, we have by (3.1) and (3.2)

$$(3.4) \quad \Sigma^2 = -\frac{p_+ - p_-}{v_+ - v_-},$$

which shows that Σ is the *Lagrangian shock velocity*. Moreover we have

$$(3.5) \quad s = u_+ + \frac{\Sigma}{\rho_+} = u_- + \frac{\Sigma}{\rho_-}.$$

Then, equations (3.1), (3.2) and (3.3) can be written as

$$(3.6) \quad \begin{cases} e_+ - e_- + \frac{1}{2}(p_+ + p_-)(v_+ - v_-) = 0, \\ (U_+ - U_-)^2 = -(p_+ - p_-)(v_+ - v_-). \end{cases}$$

By introducing the enthalpy H , the first equation in (3.6) turns out to be

$$(3.7) \quad H_+ - H_- = \frac{1}{2}(v_+ + v_-)(p_+ - p_-) = 0,$$

which is called the thermodynamic part of the Rankine-Hugoniot conditions. It is clear that the above condition is a relation among the thermodynamic variables.

Variation of Entropy The second law of thermodynamics claims that the entropy increase across the shock from the past to the future. According to this postulate, two states $(\rho_{\pm}, u_{\pm}, S_{\pm})$ are said to be admissible if $S_- < S_+$ for $s < 0$ and $S_+ < S_-$ for $s > 0$. By the first and second law of thermodynamics, we have

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = v.$$

Then we find that

$$\begin{aligned} H_+ - H_- &= T_-(S_+ - S_-) + v_-(p_+ - p_-) \\ &\quad + \frac{1}{2} \left(\frac{\partial v}{\partial p_-}\right)_S (p_+ - p_-)^2 + \frac{1}{6} \left(\frac{\partial^2 v}{\partial p_-^2}\right)_S (p_+ - p_-)^3 \\ &\quad + O(1)(S_+ - S_-)^2 + O(1)(S_+ - S_-)(p_+ - p_-) + O(1)(p_+ - p_-)^4. \end{aligned}$$

Here we used the abbreviation $(\partial v / \partial p_-)_S = (\partial v / \partial p)(p_-, S_-)$. On the other hand, by (3.7) we have

$$\begin{aligned} H_+ - H_- &= \frac{1}{2}(v_+ + v_-)(p_+ - p_-) = v_-(p_+ - p_-) + \frac{1}{2}(v_+ - v_-)(p_+ - p_-) \\ &= v_-(p_+ - p_-) + \frac{1}{2} \left(\frac{\partial v}{\partial p_-}\right)_S (p_+ - p_-)^2 + \frac{1}{4} \left(\frac{\partial^2 v}{\partial p_-^2}\right)_S (p_+ - p_-)^3 \\ &\quad + O(1)(S_+ - S_-)(p_+ - p_-) + O(1)(p_+ - p_-)^4. \end{aligned}$$

Combining the above two expressions and omitting some technical details, we conclude that for a shock wave with small amplitude we have

$$(3.8) \quad T_-(S_+ - S_-) = \frac{1}{12} \left(\frac{\partial^2 v}{\partial p_-^2}\right)_S (p_+ - p_-)^3 + O(1)(p_+ - p_-)^4.$$

Suppose that $v_{pp}(p, S) > 0$. In the case $s < 0$, we have $S_+ > S_-$ if and only if $p_+ > p_-$; in the case $s > 0$, we have instead $S_+ < S_-$ if and only if $p_+ < p_-$.

Remark. For the Lagrangian equations (2.2), we set $\lambda_{\pm} = \pm \frac{1}{\sqrt{-v_p}}$ and $r_{\pm} = (\pm 1, \sqrt{-v_p}, 0)^T$. Then we have

$$(3.9) \quad r_{\pm} \nabla \lambda_{\pm} = \frac{v_{pp}}{2(-v_p)^{\frac{3}{2}}}$$

and the sign of v_{pp} is equal to that of $r_{\pm} \nabla \lambda_{\pm}$.

Remark. The expression (3.8) was first obtained by H. Bethe in 1942, see [6, (3.44)] and [5, §86]. This formula is notable because it depends neither on the particular equation of state nor on the form of internal structure. In particular, then, it holds for the equation of state (1.4) with (1.5) and (1.6).

§ 4. A Model of Monatomic Ionized Gas

In order to study an ionized gas, we have to add the degree of ionization α to the thermodynamic variables and work with six variables. The state equation is given by (1.4), the enthalpy is defined by (1.5) and the last constraint is the Saha formula in the form (1.6). If we set $\kappa = \frac{h^3}{(2\pi m_e)^{\frac{3}{2}} k^{\frac{5}{2}}} \frac{G_a}{2G_i}$ ($[\kappa] = LM^{-1}T^{\frac{9}{2}}$), we have

$$(4.1) \quad \kappa p = \frac{1 - \alpha^2}{\alpha^2} T^{\frac{5}{2}} e^{-\frac{T_i}{T}},$$

which is useful in the following computations.

Entropy Function Let us construct the physical entropy function. The basic identity is Maxwell's relation

$$(4.2) \quad -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p$$

and we deduce the following result.

Proposition 4.1. *We have*

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

By direct computation, we have

$$\left(\frac{\partial \alpha}{\partial p}\right)_T = -\frac{1}{2p} \alpha(1 - \alpha^2), \quad \left(\frac{\partial \alpha}{\partial T}\right)_p = \frac{1}{2T} \alpha(1 - \alpha^2) \left(\frac{5}{2} + \frac{T_i}{T}\right).$$

and then the basic formula

$$(4.3) \quad -\frac{T}{p} \left(\frac{\partial \alpha}{\partial T}\right)_p = \left(\frac{5}{2} + \frac{T_i}{T}\right) \left(\frac{\partial \alpha}{\partial p}\right)_T.$$

The computation of the entropy is carried out as follows:

$$\begin{aligned} \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_p = -\frac{R}{M} \left[\frac{1}{p}(1+\alpha) + \frac{T}{p} \left(\frac{\partial \alpha}{\partial T}\right)_p \right] \\ &= \frac{R}{M} \left[-\frac{1}{p}(1+\alpha) + \left(\frac{5}{2} + \frac{T_i}{T}\right) \left(\frac{\partial \alpha}{\partial p}\right)_T \right], \\ \left(\frac{\partial S}{\partial T}\right)_p &= \frac{1}{T} \left(\frac{\partial h}{\partial T}\right)_p = \frac{R}{M} \left[\left(\frac{5}{2}\right) \frac{1+\alpha}{T} + \left(\frac{5}{2} + \frac{T_i}{T}\right) \left(\frac{\partial \alpha}{\partial T}\right)_p \right]. \end{aligned}$$

Proposition 4.2. *Let $\eta = \frac{M}{R}S$ be the dimensionless entropy. Then*

$$\eta = -\log p + \log \frac{1+\alpha}{1-\alpha} + \left(\frac{5}{2} + \frac{T_i}{T}\right) \alpha + \frac{5}{2} \log T + \text{Const.}$$

By (4.1) we also have the expression

$$(4.4) \quad \eta = -2 \log \frac{1-\alpha}{\alpha} + \left(\frac{5}{2} + \frac{T_i}{T}\right) (1+\alpha) + \text{Const.},$$

which will be useful later.

Remark. We have also by (4.1),

$$\frac{dp}{p} = -\frac{2d\alpha}{\alpha(1-\alpha^2)} + \left(\frac{5}{2} + \frac{T_i}{T}\right) \frac{dT}{T}.$$

Thus

$$\begin{aligned} Td\eta &= \frac{M}{R} (dh - vdp) \\ &= \frac{5}{2}(1+\alpha)dT + \frac{5}{2}Td\alpha + T_id\alpha - \frac{Mpv}{R} \left[-\frac{2d\alpha}{\alpha(1-\alpha^2)} + \left(\frac{5}{2} + \frac{T_i}{T}\right) \frac{dT}{T} \right] \\ &= \frac{5}{2}(1+\alpha)dT + \left(\frac{5T}{2} + T_i\right)d\alpha + \frac{2Td\alpha}{\alpha(1-\alpha)} - (1+\alpha)\left(\frac{5}{2} + \frac{T_i}{T}\right)dT \\ &= \left[\frac{5T}{2} + T_i + \frac{2T}{\alpha(1-\alpha)} \right] d\alpha - (1+\alpha)\frac{T_i}{T}dT \end{aligned}$$

and then

$$d\eta = \left[\frac{2}{\alpha(1-\alpha)} + \frac{5}{2} + \frac{T_i}{T} \right] d\alpha - (1+\alpha)\frac{T_i}{T^2}dT.$$

Characteristic Vector Fields in pT -Plane We write system (2.3) as

$$U_t + A(U)U_x = 0,$$

where $A(U) = F'(U)$. Let V be a set of new unknowns related to U by $U = U(V)$. We have

$$V_t + B(V)V_x = 0,$$

where $B(V) = (U')^{-1}A(U)U'$ and $U' = U'(V)$ denotes the Jacobian matrix of U . Clearly, if $R(U)$ is a characteristic vector field of $A(U)$, then

$$R(V) = (U'(V))^{-1} R(U(V))$$

is a characteristic field of $B(V)$ and

$$\nabla_u R(U) = \nabla_v R(V).$$

Let us consider p, T as a set of independent variables. The Lagrange equations are formally equivalent to

$$(4.5) \quad \begin{bmatrix} p \\ u \\ T \end{bmatrix}_t + \begin{bmatrix} 0 - \frac{\eta_T}{v_p \eta_T - v_T \eta_p} & 0 \\ 1 & 0 & 0 \\ 0 & \frac{\eta_p}{v_p \eta_T - v_T \eta_p} & 0 \end{bmatrix} \begin{bmatrix} p \\ u \\ T \end{bmatrix}_x = \mathbf{0}$$

and the characteristic roots and vector fields are

$$(4.6) \quad \lambda_{\pm} = \pm \sqrt{-\frac{\eta_T}{v_p \eta_T - v_T \eta_p}}, \quad R_{\pm} = \left(1, \mp \frac{1}{\sqrt{-\frac{\eta_T}{v_p \eta_T - v_T \eta_p}}}, -\frac{\eta_p}{\eta_T} \right)^T,$$

$$(4.7) \quad \lambda_0 = 0, \quad R_0 = (0, 0, 1)^T.$$

After some computations we obtain the following result.

Proposition 4.3. *We have*

$$(4.8) \quad \lambda_{\pm} = \frac{\pm p}{a\sqrt{T(1+\alpha)}} \sqrt{\frac{\frac{5}{2} + \frac{1}{2}\alpha(1-\alpha)\left(\frac{5}{2} + \frac{T_i}{T}\right)^2}{\frac{3}{2} + \frac{1}{2}\alpha(1-\alpha)\left(\frac{15}{4} + \frac{3T_i}{T} + \frac{T_i^2}{T^2}\right)}}$$

and

$$(4.9) \quad R_{\pm} \nabla = \frac{\partial}{\partial p} + \frac{T \left[1 + \frac{1}{2}\alpha(1-\alpha)\left(\frac{5}{2} + \frac{T_i}{T}\right) \right]}{p \left[\frac{5}{2} + \frac{1}{2}\alpha(1-\alpha)\left(\frac{5}{2} + \frac{T_i}{T}\right)^2 \right]} \frac{\partial}{\partial T}.$$

Genuine Nonlinearity and Inflection Locus By setting $\lambda = \lambda_+ > 0$, we have $R_{\pm} \nabla \lambda_{\pm} = \pm R_{\pm} \nabla \lambda$. Clearly it is easier to compute $R_{\pm} \nabla \log \lambda_{\pm}$ than $R_{\pm} \nabla \lambda_{\pm}$ and it is what we show below.

Proposition 4.4. *We have*

$$\begin{aligned}
 & R_+ \nabla \log \lambda_+ \\
 &= \frac{4}{5p \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{5T^2} \right) \right]} \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{4T^2} \right) \right. \\
 &\quad - \frac{\alpha(1 - \alpha^2)(1 - 2\alpha) \frac{T_i^3}{T^3}}{60 \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{5T^2} \right) \right] \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{3T^2} \right) \right]} \\
 &\quad \left. + \frac{\alpha(1 - \alpha) \frac{T_i^2}{T^2} \left[1 + \frac{1}{2} \alpha(1 - \alpha) \left(\frac{5}{2} + \frac{T_i}{T} \right) \right]^2}{15 \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{5T^2} \right) \right] \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{3T^2} \right) \right]} \right].
 \end{aligned}
 \tag{4.10}$$

The *inflection locus* is the set $\{(\alpha, T); R_+ \nabla \lambda_{\pm} = 0, 0 < \alpha < 1, T > 0\}$, see Figure 1. Obviously, if $\alpha \geq \frac{1}{2}$ then $R_+ \nabla \log \lambda_+ > 0$. On the other hand, for sufficiently small

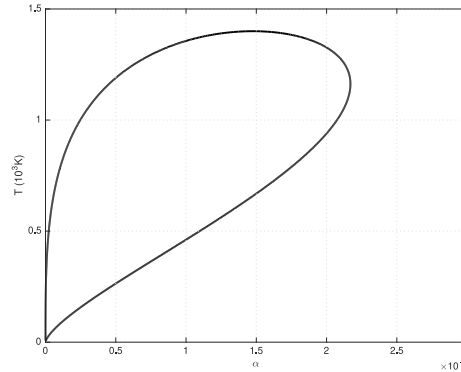


Figure 1. The inflection locus. Here $T_i = 1.5719 \times 10^5 \text{K}$.

$\frac{T}{T_i}$ and $\alpha \sim \frac{T^2}{T_i^2}$, we find $R_+ \nabla \log \lambda_+ < 0$. Thus the characteristic field is not necessarily genuinely nonlinear. We have by asymptotic expansion what follows.

Proposition 4.5. *The inflection locus is an algebraic curve having a singularity at $\alpha = 0, T = 0$. There exist two branches*

$$\alpha \sim 60 \left(\frac{T}{T_i} \right)^3, \quad \left(\frac{T}{T_i} \right)^{\frac{3}{2}}.$$

Since

$$\begin{aligned}
& R_+ \nabla \log \lambda_{\pm} \\
& \geq \frac{4 \left\{ 1 + \alpha(1 - \alpha) \left[\frac{15}{4} + \frac{3T_i}{T} + \left(\frac{1}{4} + \frac{1}{5} + \frac{1}{3} \right) \frac{T_i^2}{T^2} \right] - \frac{\alpha(1-2\alpha)T_i^3}{60T^3} + \frac{\alpha(1-\alpha)T_i^2}{15T^2} \right\}}{5p \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{5T^2} \right) \right]^2 \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{3T^2} \right) \right]} \\
& > \frac{4 \left\{ 1 + \alpha(1 - \alpha) \left[\frac{15}{4} + \frac{3T_i}{T} + \frac{51}{60} \left(\frac{T_i}{T} \right)^2 \right] - \frac{\alpha(1-2\alpha)}{60} \left(\frac{T_i}{T} \right)^3 \right\}}{5p \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{5T^2} \right) \right]^2 \left[1 + \alpha(1 - \alpha) \left(\frac{5}{4} + \frac{T_i}{T} + \frac{T_i^2}{3T^2} \right) \right]},
\end{aligned}$$

we obtain the following result.

Proposition 4.6. *If*

$$(4.11) \quad \alpha(1 - 2\alpha) \left(\frac{T_i}{T} \right)^3 \leq 60 + \alpha(1 - \alpha) \left[225 + 180 \left(\frac{T_i}{T} \right) + 51 \left(\frac{T_i}{T} \right)^2 \right],$$

then each characteristic field is genuinely nonlinear.

We also deduce from this proposition (see also Proposition 4.5) what follows.

Theorem 4.7. *If $\alpha \leq 60 \left(\frac{T}{T_i} \right)^3$ or $\frac{T_i}{T} \leq 54.5375$, then each characteristic field is genuinely nonlinear.*

Proof. If the first condition holds, then

$$\alpha(1 - 2\alpha) \left(\frac{T_i}{T} \right)^3 < \alpha \left(\frac{T_i}{T} \right)^3 \leq 60$$

showing that the inequality (4.11) is true. Next, note that

$$\frac{60}{\alpha(1 - 2\alpha)} \geq 480, \quad \frac{1 - \alpha}{1 - 2\alpha} \geq 1 \quad (0 \leq \alpha < \frac{1}{2}).$$

Then (4.11) is true if

$$\left(\frac{T_i}{T} \right)^3 \leq 705 + 180 \left(\frac{T_i}{T} \right) + 51 \left(\frac{T_i}{T} \right)^2.$$

Since $x^3 - 705 - 180x - 51x^2 < 0$ for $0 \leq x \leq 54.5375$, the claim follows. $\square$

§ 5. The Thermodynamic Part of the Rankine-Hugoniot Condition

By using the enthalpy $H = e + pv$ instead of e , the thermodynamic part of the Rankine-Hugoniot conditions turns out to be

$$H_+ - H_- = \frac{1}{2}(p_+ - p_-)(v_+ + v_-).$$

By direct computation, we have

Lemma 5.1. *The thermodynamic part of the Rankine-Hugoniot condition is equivalent to*

$$\frac{T_+}{T_-} = \frac{\left(\frac{8}{3} + \frac{2}{3} \frac{p_+}{p_-}\right) (1 + \alpha_-) + \frac{4}{3} \frac{T_i}{T_-} \alpha_-}{\left(\frac{8}{3} + \frac{2}{3} \frac{p_-}{p_+}\right) (1 + \alpha_+) + \frac{4}{3} \frac{T_i}{T_+} \alpha_+},$$

and the Hugoniot locus of (α_0, T_0) is expressed as

$$\begin{aligned} & T \left[\frac{8}{3} (1 + \alpha) + \frac{2}{3} \left(\frac{p_0}{p} \right) (1 + \alpha) + \frac{4}{3} \frac{T_i}{T} \alpha \right] \\ &= T_0 \left[\frac{8}{3} (1 + \alpha_0) + \frac{2}{3} \left(\frac{p}{p_0} \right) (1 + \alpha_0) + \frac{4}{3} \frac{T_i}{T_0} \alpha_0 \right]. \end{aligned}$$

Note that Rankine-Hugoniot condition is equivalent to the following expression

$$(5.1) \quad \frac{1}{4} \left(\frac{p}{p_0} \right) \frac{T_0 (1 + \alpha_0)}{T (1 + \alpha)} = \frac{1}{4} \left(\frac{p_0}{p} \right) + \frac{T_i (\alpha - \alpha_0)}{2T (1 + \alpha)} - \frac{T_0 (1 + \alpha_0)}{T (1 + \alpha)} + 1.$$

Hugoniot Loci in αT -Plane By virtue of (4.1), we have

$$(5.2) \quad \frac{p}{p_0} = \left(\frac{1 - \alpha^2}{1 - \alpha_0^2} \right) \left(\frac{\alpha_0}{\alpha} \right)^2 \left(\frac{T}{T_0} \right)^{\frac{5}{2}} e^{-\frac{T_i}{T} + \frac{T_i}{T_0}}.$$

Inserting the expression of $\frac{p}{p_0}$ into the equation of the Hugoniot locus, we have

Proposition 5.2. *The thermodynamic part of the Hugoniot locus of (α_0, T_0) is expressed as*

$$(5.3) \quad \begin{aligned} & T \left[\frac{8}{3} (1 + \alpha) + \frac{2}{3} \left(\frac{1 - \alpha_0^2}{1 - \alpha^2} \right) \left(\frac{\alpha}{\alpha_0} \right)^2 \left(\frac{T_0}{T} \right)^{\frac{5}{2}} e^{-\frac{T_i}{T_0} + \frac{T_i}{T}} + \frac{4}{3} \frac{T_i}{T} \alpha \right] \\ &= T_0 \left[\frac{8}{3} (1 + \alpha_0) + \frac{2}{3} \left(\frac{1 - \alpha^2}{1 - \alpha_0^2} \right) \left(\frac{\alpha_0}{\alpha} \right)^2 \left(\frac{T}{T_0} \right)^{\frac{5}{2}} e^{-\frac{T_i}{T} + \frac{T_i}{T_0}} + \frac{4}{3} \frac{T_i}{T_0} \alpha_0 \right]. \end{aligned}$$

Clearly $T \rightarrow 0$ if $\alpha \rightarrow 0$. By asymptotic analysis, we have what follows.

Proposition 5.3. *If $T \rightarrow 0$, then $\alpha \rightarrow 0$ and*

$$\alpha \sim \left[\frac{4(1 + \alpha_0) + \frac{2T_i}{T_0} \alpha_0}{\frac{1 - \alpha_0^2}{\alpha_0^2}} \right]^{\frac{1}{2}} \left(\frac{T}{T_0} \right)^{\frac{3}{4}} e^{-\frac{T_i}{2T} + \frac{T_i}{2T_0}}.$$

If $T \rightarrow \infty$, then $\alpha \rightarrow 1$ and

$$1 - \alpha \sim 4 \left(\frac{1 - \alpha_0}{\alpha_0^2} \right) \left(\frac{T}{T_0} \right)^{-\frac{3}{2}} e^{-\frac{T_i}{T_0}}.$$

This proposition shows that the temperature T is a function of the degree of ionization α and T is a strictly increasing function in neighbourhoods of $\alpha = 0, 1$. The principal aim of this note is to show that T is a strictly increasing function of $0 < \alpha < 1$, which will be used in Asakura-Corli [2].

T as a Function of α The following theorem will be crucial in our study.

Theorem 5.4 (T as a function of α). *In the (α, T) -plane, the thermodynamic part of the Hugoniot locus (5.3) of (α_0, T_0) is the graph of a strictly increasing function $T = T(\alpha)$, for $\alpha \in (0, 1)$. Moreover,*

$$(5.4) \quad \lim_{\alpha \rightarrow 0} T(\alpha) = 0, \quad \lim_{\alpha \rightarrow 1} T(\alpha) = \infty.$$

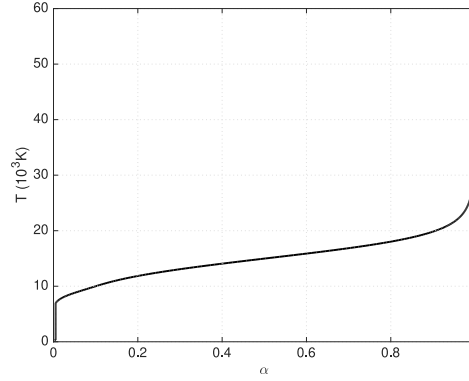


Figure 2. The thermodynamic part of the Hugoniot locus and the function $T = T(\alpha)$, see Theorem 5.4. Here $T_0 = 300\text{K}$, $\alpha_0 = 3.5929 \times 10^{-114}$, $p_0 = 1466.3\text{Pa}$, $T_i = 1.5719 \times 10^5\text{K}$; see [4] for these values.

Proof. We refer to Figure 2 for a graph of the function T . We split the proof into some steps.

1. By (5.3), the thermodynamic part of the Hugoniot locus is the set defined by $F(\alpha, T) = 0$, for

$$(5.5) \quad \begin{aligned} F(\alpha, T) = & T \left[4(1 + \alpha) + \left(\frac{1 - \alpha_0^2}{1 - \alpha} \right) \left(\frac{\alpha}{\alpha_0} \right)^2 \left(\frac{T_0}{T} \right)^{\frac{5}{2}} e^{-\frac{T_i}{T_0} + \frac{T_i}{T}} + \frac{2T_i}{T} \alpha \right] \\ & - T_0 \left[4(1 + \alpha_0) + \left(\frac{1 - \alpha^2}{1 - \alpha_0} \right) \left(\frac{\alpha_0}{\alpha} \right)^2 \left(\frac{T}{T_0} \right)^{\frac{5}{2}} e^{-\frac{T_i}{T} + \frac{T_i}{T_0}} + \frac{2T_i}{T_0} \alpha_0 \right]. \end{aligned}$$

By differentiating (5.5) with respect to T , and then introducing p and p_0 , we com-

pute

$$\begin{aligned}
 F_T(\alpha, T) &= 4(1 + \alpha) - \left(\frac{1 - \alpha_0^2}{1 - \alpha} \right) \left(\frac{\alpha}{\alpha_0} \right)^2 \left(\frac{T_0}{T} \right)^{\frac{5}{2}} \left(\frac{3}{2} + \frac{T_i}{T} \right) e^{-\frac{T_i}{T_0} + \frac{T_i}{T}} \\
 &\quad - \left(\frac{1 - \alpha^2}{1 - \alpha_0} \right) \left(\frac{\alpha_0}{\alpha} \right)^2 \left(\frac{T}{T_0} \right)^{\frac{3}{2}} \left(\frac{5}{2} + \frac{T_i}{T} \right) e^{-\frac{T_i}{T} + \frac{T_i}{T_0}} \\
 (5.6) \quad &= - \left[(1 + \alpha) \frac{p_0}{p} \left(\frac{3}{2} + \frac{T_i}{T} \right) + (1 + \alpha_0) \frac{p T_0}{p_0 T} \left(\frac{5}{2} + \frac{T_i}{T} \right) - 4(1 + \alpha) \right] \\
 &= -4(1 + \alpha) \Phi(\alpha, T),
 \end{aligned}$$

where we defined

$$(5.7) \quad \Phi(\alpha, T) = \frac{1}{4} \left[\frac{p_0}{p} \left(\frac{3}{2} + \frac{T_i}{T} \right) + \frac{p}{p_0} \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} \left(\frac{5}{2} + \frac{T_i}{T} \right) \right] - 1.$$

Obviously, $F_T(\alpha, T) \neq 0$ if and only if $\Phi(\alpha, T) \neq 0$.

2. We consider $0 < \alpha < 1, T > 0$ and $F(\alpha, T) = 0$. We claim that:

$$(5.8) \quad \Phi(\alpha, T) > 0 \quad \text{if} \quad \text{either } 0 < \alpha < \alpha_0, T \leq T_0 \quad \text{or } \alpha \geq \alpha_0.$$

Indeed, the condition $F(\alpha, T) = 0$ is equivalent to (5.1), namely,

$$(5.9) \quad \frac{1}{4} \frac{p}{p_0} \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} = \frac{1}{4} \frac{p_0}{p} + \frac{T_i(\alpha - \alpha_0)}{2T(1 + \alpha)} - \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} + 1.$$

Then, if we denote

$$(5.10) \quad \Delta = 1 - \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} + \frac{T_i(\alpha - \alpha_0)}{2T(1 + \alpha)},$$

we have, for α, T satisfying $F(\alpha, T) = 0$,

$$\Phi(\alpha, T) = \frac{p_0}{p} \left(1 + \frac{T_i}{2T} \right) + \left(\frac{5}{2} + \frac{T_i}{T} \right) \Delta - 1.$$

By (5.9) and (5.10), the quotient $\Pi = \frac{p_0}{p}$ satisfies the equation

$$(5.11) \quad \Pi^2 + 4\Delta\Pi - \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} = 0$$

and then

$$(5.12) \quad \Pi = \sqrt{4\Delta^2 + \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)}} - 2\Delta.$$

As a consequence, we deduce

$$\Phi(\alpha, T) = \left(1 + \frac{T_i}{2T}\right) \sqrt{4\Delta^2 + \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)}} + \frac{\Delta}{2} - 1.$$

If $\Delta > 2$, then $\Phi(\alpha, T) > 0$ for every α and T ; hence, assume $\Delta \leq 2$. If $\Phi(\alpha, T) = 0$, then Δ satisfies the quadratic equation

$$(5.13) \quad \left(\frac{15}{4} + \frac{4T_i}{T} + \frac{T_i^2}{T^2}\right) \Delta^2 + \Delta + \left(1 + \frac{T_i}{2T}\right)^2 \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} - 1 = 0.$$

By (5.10), equation (5.13) can be written as

$$\left(\frac{15}{4} + \frac{4T_i}{T} + \frac{T_i^2}{T^2}\right) \Delta^2 + \frac{T_i}{T} \left[\left(1 + \frac{T_i}{4T}\right) \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} + \frac{\alpha - \alpha_0}{2(1 + \alpha)} \right] = 0.$$

If $\alpha \geq \alpha_0$, then the left-hand side of the above expression is strictly positive, which is a contradiction. If $0 < \alpha < \alpha_0$, we have

$$\left(1 + \frac{T_i}{4T}\right) \frac{T_0(1 + \alpha_0)}{T(1 + \alpha)} + \frac{\alpha - \alpha_0}{2(1 + \alpha)} > \frac{1}{1 + \alpha} \left[\frac{T_0}{T} (1 + \alpha_0) + \frac{\alpha - \alpha_0}{2} \right].$$

If $T \leq T_0$, the above quantity is positive and hence we reach a contradiction again. This proves (5.8).

3. Let us consider again the function F defined in (5.5); clearly $F(\alpha_0, T_0) = 0$ and $F_T(\alpha_0, T_0) \neq 0$ by (5.8). Then it follows from the Implicit Function Theorem that T is a function of α in a neighbourhood of $\alpha = \alpha_0$; moreover, $dT/d\alpha = -F_\alpha(\alpha, T)/F_T(\alpha, T)$. By differentiating (5.5) with respect to α and introducing p and p_0 , we have

$$(5.14) \quad \begin{aligned} F_\alpha(\alpha, T) &= \frac{2T_0\alpha_0^2}{(1 - \alpha_0)} \left(\frac{1}{\alpha^3}\right) \left(\frac{T}{T_0}\right)^{\frac{5}{2}} e^{-\frac{T_i}{T} + \frac{T_i}{T_0}} \\ &\quad - T \left[4 + \frac{(1 - \alpha_0^2)}{\alpha_0^2} \left[\frac{\alpha(2 - \alpha)}{(1 - \alpha)^2} \right] \left(\frac{T_0}{T}\right)^{\frac{5}{2}} e^{-\frac{T_i}{T_0} + \frac{T_i}{T}} + \frac{2T_i}{T} \right] \\ &= \frac{2p}{p_0} \frac{T_0(1 + \alpha_0)}{\alpha(1 - \alpha^2)} + T \left[4 + \frac{(1 + \alpha)(2 - \alpha)}{\alpha(1 - \alpha)} \frac{p_0}{p} + \frac{2T_i}{T} \right]. \end{aligned}$$

Thus, by (5.6) and (5.14) we end up with the following expression for $dT/d\alpha$:

$$(5.15) \quad \frac{1}{T} \frac{dT}{d\alpha} = \frac{4 + \frac{2T_i}{T} + \frac{p_0}{p} \frac{(1 + \alpha)(2 - \alpha)}{\alpha(1 - \alpha)} + \frac{2p}{p_0} \frac{T_0(1 + \alpha_0)}{T\alpha(1 - \alpha^2)}}{(1 + \alpha) \frac{p_0}{p} \left(\frac{3}{2} + \frac{T_i}{T}\right) + (1 + \alpha_0) \frac{p}{p_0} \frac{T_0}{T} \left(\frac{5}{2} + \frac{T_i}{T}\right) - 4(1 + \alpha)}.$$

The numerator of the right-hand side in (5.15) is strictly positive for every $0 < \alpha < 1$ and $T > 0$; the denominator is strictly positive in a neighbourhood of $\alpha = \alpha_0$ by (5.8). We conclude that $T(\alpha)$ is a strictly increasing function in this neighbourhood.

4. Let (α_-, α_+) denote the largest (open) interval where the function $T(\alpha)$ is defined. We claim that: $\Phi(\alpha, T(\alpha)) > 0$ for $\alpha \in (\alpha_-, \alpha_+)$.

Indeed, if $\alpha \in (\alpha_0, \alpha_+)$ then the claim follows by (5.8). If $\alpha \in (\alpha_-, \alpha_0)$, clearly $\Phi(\alpha, T(\alpha)) > 0$ in a small neighbourhood of α_0 . Suppose that there is α_1 such that $\alpha_- < \alpha_1 < \alpha_0$ with $\Phi(\alpha_1, T(\alpha_1)) = 0$ and $\Phi(\alpha, T(\alpha)) > 0$ for $\alpha \in (\alpha_1, \alpha_0)$. Since $T(\alpha)$ is increasing in (α_1, α) by (5.15), we have $T_1 := T(\alpha_1) < T_0$ and $F(\alpha_1, T_1) = 0$. Then (5.8) yields $\Phi(\alpha_1, T_1) > 0$, which is a contradiction.

5. Next, we claim that: $\alpha_- = 0$ and $\alpha_+ = 1$.

Note that, since $T = T(\alpha)$ is strictly increasing in (α_-, α_+) , then both limits $T_{\pm} = \lim_{\alpha \rightarrow \alpha_{\pm}} T(\alpha)$ exist. Assume by contradiction $\alpha_+ < 1$. If $T_+ < \infty$, then $F(\alpha_+, T_+) = 0$ by continuity and, since $\alpha_+ > \alpha_0$, we have $F_T(\alpha_+, T_+) \neq 0$ by (5.8). But then the function $T(\alpha)$ can be extended beyond α_+ , which is a contradiction. If $T_+ = \infty$, we find by (5.5) that $F(\alpha, T(\alpha)) \rightarrow -\infty$ as $\alpha \rightarrow \alpha_+$ which is impossible. We conclude that $\alpha_+ = 1$; by the same argument, we have $\alpha_- = 0$.

6. At last, let us denote $T_{\infty} = \lim_{\alpha \rightarrow 1} T(\alpha)$. If $T_{\infty} < \infty$, by (5.5) we find $F(\alpha, T(\alpha)) \rightarrow \infty$ as $\alpha \rightarrow 1$ which is impossible; then $\lim_{\alpha \rightarrow 1} T(\alpha) = \infty$. In the same way we conclude $\lim_{\alpha \rightarrow 0} T(\alpha) = 0$.

The theorem is completely proved. □

We can prove in a similar way that p increases and v decreases as α increases.

Proposition 5.5 (p and v as functions of α). *Let $T = T(\alpha)$ be the function introduced in Theorem 5.4. Then*

$$\frac{d}{d\alpha} p(\alpha, T(\alpha)) > 0 \quad \text{and} \quad \frac{d}{d\alpha} v(\alpha, T(\alpha)) < 0 \quad \text{for } \alpha \geq \alpha_0.$$

§ 6. Saha Ionization Formula

Maxwell-Boltzmann Statistics of an N Particle System ([9, III]) Let us consider a thermodynamic system consisting of N identical particles in a finite volume in equilibrium at the temperature T . Possible states of each particle are denoted by $j = 1, 2, \dots$. Let n_j, ϵ_j be the number and the energy, respectively, of a single particle at the j th state. The Maxwell-Boltzmann Statistics is based on the following postulations.

- The particles are distinguishable and any number of particles are allowed to be in any single state.
- A set of numbers $(n_1, n_2, \dots)$, with $\sum_j n_j = N$, determines the state of the system.
- The probability of j th state of a single particle having energy ϵ_j , is proportional to $e^{-\frac{\epsilon_j}{kT}}$, where k is the Boltzmann constant.

Let g_j denote the statistical weight of the j th state: the number of individual states that are identical with the j th state. The partition function of this single particle is defined by

$$Z_{\text{single}}(T) = \sum_j g_j e^{-\frac{\epsilon_j}{kT}}.$$

Number of ways to make partitions $(n_1, n_2, \dots)$, $\sum_j n_j = N$ is $\frac{N!}{n_1!n_2!\dots}$ and the number of the states having the partition $n_1 + n_2 + \dots = N$ is

$$g_{(n_1, n_2, \dots)} = \frac{N!}{n_1!n_2!\dots} g_1^{n_1} g_2^{n_2} \dots$$

Thus the partition function of the full system is

$$\begin{aligned} Z(T) &= \sum_{n_1+n_2+\dots=N} \frac{N!}{n_1!n_2!\dots} g_1^{n_1} g_2^{n_2} \dots e^{-\frac{1}{kT}(n_1\epsilon_1+n_2\epsilon_2+\dots)} \\ &= \left(\sum_n g_n e^{-\frac{\epsilon_n}{kT}} \right)^N = Z_{\text{single}}^N. \end{aligned}$$

The Boltzmann thermodynamic system consisting of several kinds of particles A, B, ... is considered in the same way. Let $N_A, N_B, \dots$ be the numbers of particles of A, B, ..., respectively, so that $N_A + N_B + \dots = N$ and $\epsilon_1^A, \epsilon_2^A, \dots, \epsilon_1^B, \epsilon_2^B, \dots$, are the possible energies of the particles A, B, ..., respectively.

- Each kind of particles A, B, ... constitutes the Boltzmann thermodynamic system consisting of $N_A, N_B, \dots$ particles, respectively.
- A set of numbers $(n_1^A, n_2^A, \dots, n_1^B, n_2^B, \dots, \dots)$, $n_1^A + n_2^A + \dots = N_A, n_1^B + n_2^B + \dots = N_B, \dots$ determines the state of the system.

Let $Z_A, Z_B, \dots$ denote the partition functions of each single particle A, B, ..., respectively. The partition function of the full system is computed as $Z_A^{N_A} \cdot Z_B^{N_B} \dots$. However, in order to avoid the Gibbs paradox, we adopt the partition function

$$Z(T) = \frac{Z_A^{N_A}}{N_A!} \cdot \frac{Z_B^{N_B}}{N_B!} \dots,$$

assuming that, each set of single kind particles, it is impossible to distinguish them.

The free energy of a thermodynamic system is defined by $F = -kT \log Z$. Thus replacing $N!$ with $N^N e^{-N}$ by the Stirling formula, we have

$$F = -kT \left[N_A \log \frac{eZ_A}{N_A} + N_B \log \frac{eZ_B}{N_B} + \dots \right].$$

Classical Limit Now let us consider a single particle contained in a cube of edge length L (volume: $V = L^3$), and having the mass m and the momentum $\mathbf{p}$. The wavelength is denoted by λ and the Planck constant h . De Broglie relation says $|\mathbf{p}| = \frac{h}{\lambda}$. Let $\lambda_x, \lambda_y, \lambda_z$ denote the projections of the 3-dimensional wavelength with respect to the x, y, z axes, respectively. We have

$$\lambda_x = \frac{L}{l_x}, \quad \lambda_y = \frac{L}{l_y}, \quad \lambda_z = \frac{L}{l_z} \quad \text{and} \quad \left(\frac{\lambda}{\lambda_x} \right)^2 + \left(\frac{\lambda}{\lambda_y} \right)^2 + \left(\frac{\lambda}{\lambda_z} \right)^2 = 1.$$

Hence we have

$$\frac{1}{\lambda} = \sqrt{\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2}} = \frac{\sqrt{l_x^2 + l_y^2 + l_z^2}}{L}, \quad l_x, l_y, l_z = 0, \pm 1, \pm 2, \dots$$

Thus the kinetic energy is $\epsilon = \frac{|\mathbf{p}|^2}{2m} = \frac{h^2}{2m\lambda^2}$ and that of the (l_x, l_y, l_z) state is $\epsilon_n = \frac{h^2(l_x^2 + l_y^2 + l_z^2)}{2mL^2}$. The partition function is

$$Z_{\text{single}}(T, V) = \sum_{l_x, l_y, l_z \in \mathbb{Z}} e^{-\frac{h^2(l_x^2 + l_y^2 + l_z^2)}{2mkTL^2}}.$$

We have

$$\begin{aligned} \lim_{L \rightarrow \infty} \frac{Z_{\text{single}}}{L^3} &= \lim_{L \rightarrow \infty} \frac{1}{L^3} \sum_{l_x, l_y, l_z \in \mathbb{Z}} e^{-\frac{h^2}{2mkT} \left[\left(\frac{l_x}{L} \right)^2 + \left(\frac{l_y}{L} \right)^2 + \left(\frac{l_z}{L} \right)^2 \right]} \\ &= \iiint_{\mathbb{R}^3} e^{-\frac{h^2(x^2 + y^2 + z^2)}{2mkT}} dx dy dz \\ &= \left(\int_{-\infty}^{\infty} e^{-\frac{h^2 x^2}{2mkT}} dx \right)^3 = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}. \end{aligned}$$

Thus for sufficiently large L , we may assume

$$Z_{\text{single}}(T, V) = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} L^3.$$

For N particles contained in a cube of edge length L , we have similarly

$$Z(T, V) = Z_{\text{single}}(T, V)^N = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}N} L^{3N}.$$

Thermal Ionization The ionization process is described as $X \rightleftharpoons X^+ + e^-$ in a manner analogous to the chemical reaction, and reaches a state of thermal equilibrium, at constant T and V , as an ordinary chemical reaction whose equilibrium condition is the law of mass action $\delta F = 0$. Let us denote the number of atoms, ions and electrons, respectively, by N_a, N_i and N_e and suppose that these particles obey the Maxwell-Boltzmann Statistics. Then the free energy is

$$F = -kT \left[N_a \log \frac{eZ_a}{N_a} + N_i \log \frac{eZ_i}{N_i} + N_e \log \frac{eZ_e}{N_e} \right].$$

Thus under the condition $\delta N_i = \delta N_e = -\delta N_a$, we have

$$\begin{aligned} \delta F &= -kT \left[\log \frac{Z_a}{N_a} - \log \frac{Z_i}{N_i} - \log \frac{Z_e}{N_e} \right] \delta N_a \\ &= -kT \delta N_a \log \frac{N_i N_e Z_a}{N_a Z_i Z_e}. \end{aligned}$$

Thus we have obtained by the law of mass action the equilibrium condition

$$(6.1) \quad \frac{N_i N_e}{N_a} = \frac{Z_i Z_e}{Z_a}.$$

Since a free electron has two possible spins, the partition function of a single free electron is the product of the partition function of a single particle having mass m_e and statistical weight 2:

$$Z_e = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} L^3.$$

Let $\epsilon_j^a, \epsilon_j^i$ denote, respectively, the energies of the j th state ($j = 1, 2, \dots$) of the atom and ion. The differences $\epsilon_j^a - \epsilon_1^a, \epsilon_j^i - \epsilon_1^i$ are called the excitation energies of the atom and ion, respectively, in the j th state, and $\chi = \epsilon_1^i - \epsilon_1^a$ the ionization potential. By introducing the standardized partition functions

$$G_a = \sum_j g_j^a e^{-\frac{\epsilon_j^a - \epsilon_1^a}{kT}}, \quad G_i = \sum_j g_j^i e^{-\frac{\epsilon_j^i - \epsilon_1^i}{kT}}$$

we have

$$\frac{Z_i}{Z_a} = \frac{e^{-\frac{\epsilon_1^i}{kT}} G_i}{e^{-\frac{\epsilon_1^a}{kT}} G_a} = \frac{G_i}{G_a} e^{-\frac{\chi}{kT}}.$$

Thus by denoting the concentration of atoms, ions and electrons, respectively, by $n_a = \frac{N_a}{L^3}, n_i = \frac{N_i}{L^3}, n_e = \frac{N_e}{L^3}$, we have obtained the Saha formula

$$\frac{n_i n_e}{n_a} = \frac{2G_i}{G_a} \left(\frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} e^{-\frac{\chi}{kT}}.$$

For the hydrogen atom, we have $\chi = 13.598$ eV and the ionization potential expressed by the temperature is $T_i = \frac{\chi}{k} = 1.5719 \times 10^5$ K.

Degree of Ionization By assuming that $n_i = n_e$, we will deduce (1.6). We note that the pressure is a sum of partial pressures with respect to atoms, ions and electrons: $p = p_a + p_i + p_e$, $p_j = kn_jT$ ($j = a, i, e$). Then

$$p = p_a + 2p_i = kn_i \left(2 + \frac{n_a}{n_i} \right) T \quad \text{and} \quad 1 + \frac{n_a}{n_i} = \frac{1}{\alpha}.$$

We have

$$\frac{2G_i}{G_a} \frac{(2\pi m_e kT)^{\frac{3}{2}}}{h^3} e^{-\frac{T_i}{T}} = \frac{n_i^2}{n_a} = \frac{\alpha^2 p}{(1 - \alpha^2)kT}$$

which is equivalent to (1.6).

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