On the consistency of the distribution function in moment method

Yoshinobu OKAMURA*

Abstract

The moment method is reviewed from the point of the consistency of the distribution function and a method to construct the irreversible thermodynamics based on the moment method is discussed. The difficulty to construct it is to find out the distribution function with the consistency on the entropy.

1. Introduction

The distribution function for the i-th component is denoted by $f_i(\mathbf{r},\mathbf{v}_i,t)$. The subscript i of f is necessary, because it refers to the macroscopic variables like the number density of the i-th component when we take the functional hypothesis of the distribution function. Note that the distribution function can be written as $f_i(\{\mathbf{X}_i(\mathbf{r},t)\},\mathbf{v}_i)$, where $\{\mathbf{X}_i(\mathbf{r},t)\}$ represents a set of macroscopic variables. When the macroscopic variables are defined by using the distribution function, we can write out the distribution function in terms of the macroscopic variables and $\mathbf{v}_i$ with the consistency. When a macroscopic variable is defined by

$$\mathbf{X}_i(\mathbf{r},t)=\int \xi_i(\mathbf{v}_i)\, f_i(\{\mathbf{X}_i(\mathbf{r},t)\},\mathbf{v}_i)\, d^3v_i, \tag{1.1}$$

the equation is the identity due to the consistency. The distribution function is always determined through this report such that the equation satisfies the above identity.

In section 2, we introduce the macroscopic variables which in general describe a system. The idea of the consistency is exampled in the case that the number density, barycentric velocity and the energy density are the macroscopic variables. In section 3, the closed coupled differential equations for the macroscopic variables are derived from the kinetic equation. The same idea is applied to the system whose macroscopic variables are the diffusion flux, the stress tensor and the heat flux in addition to those used in section 3, and the distribution function with the "consistency" is derived along the line of Grad's Hermite polynomial expansion[1) in section 4. The method is the generalization for multi-component system of Grad's thirteen moment method[2) for the single-component system. In section 5, The method to construct the irreversible thermodynamics and to obtain the nonlinear transport coefficients with the consistency, is discussed.

2. The macroscopic variables

The macroscopic state of the system at time t is assumed to be specified by the macroscopic variables defined by the one-body distribution function $f_i=f_i(\mathbf{r},\mathbf{v}_i,t)$, where $\mathbf{r}$ and $\mathbf{v}_i$ are the position variable and the velocity variable, respectively. The moments of $\mathbf{v}_i$, some of which correspond to the macroscopic physical quantities such as the average velocity, are introduced. It is convinient to define the number density and the average velocity by

$$n_i=n_i(\mathbf{r},t)=\int f_i\, d^3v_i, \tag{2.1}$$

$$n_i\mathbf{V}_i=n_i(\mathbf{r},t)\,\mathbf{V}_i(\mathbf{r},t)=\int \mathbf{v}_i f_i\, d^3v_i, \tag{2.2}$$

$$\begin{aligned} mn\mathbf{V}=mn(\mathbf{r},t)\,\mathbf{V}(\mathbf{r},t)&=\Sigma_i m_i n_i \mathbf{V}_i \\ &=\Sigma_i \int m_i \mathbf{v}_i f_i\, d^3v_i, \end{aligned} \tag{2.3}$$

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* 宇部工業高等専門学校電気工学科

where

$$n=\Sigma_i n_i, \tag{2.4}$$

$$mn=\Sigma_i m_i n_i. \tag{2.5}$$

We note that $\mathbf{V}_i$ is the average velocity of only component i and $\mathbf{V}$ is the barycentric velocity. Another important physical quantity is the energy density defined by

$$\begin{aligned} n_i \varepsilon_i &= n_i\ (\mathbf{r},t)\ \ \varepsilon_i\ (\mathbf{r},t) \\ &= \int (m_i/2)\ (\mathbf{v}_i-\mathbf{V})^2\ f_i\ d^3v_i. \end{aligned} \tag{2.6}$$

The $n_i \varepsilon_i$ is conventionally written as $(3/2)n_iT$ for monoatomic ideal gas, where the Boltzmann's constant is assumed to be unity.

Also, there are a couple of important physical quantities which are intrinsic quantities in nonequilibrium state. The viscous phenomena (momentum transport), the diffusion of matter (mass transport) and the heat conduction (energy transport) are typical nonequilibrium phenomena. When only the number density, the barycentric velocity and the energy density are taken as the macroscopic variables, it is hard to describe the nonequilibrium phenomena. The related macroscopic physical quantities are the diffusion flux, the stress tensor and the heat flux defined by

$$\begin{aligned} \mathbf{J}_i &= m_i n_i\ (\mathbf{V}_i-\mathbf{V}) \\ &= \Sigma_j\ (\delta_{ij}-(m_i n_i/mn))\ \int\ m_j \mathbf{v}_j\ f_j\ d^3v_j, \end{aligned} \tag{2.7}$$

$$\begin{aligned} \mathbf{P}' &= \Sigma_i \mathbf{P}_i' \\ &= \Sigma_i \int\ m_i\ (\mathbf{v}_i-\mathbf{V}_i)\ (\mathbf{v}_i-\mathbf{V}_i)\ f_i\ d^3v_i, \end{aligned} \tag{2.8}$$

$$\begin{aligned} \mathbf{q} &= \Sigma_i \mathbf{q}_i \\ &= \Sigma_i \int\ (m_i/2)\ (\mathbf{v}_i-\mathbf{V}_i)^2\ (\mathbf{v}_i-\mathbf{V}_i)\ f_i\ d^3v_i. \end{aligned} \tag{2.9}$$

The diffusion flux disappears if the summation is taken over all components. Then, the diffusion flux of a particular component is not independent of others. Addition to this, we note that the stress tensor and the heat flux are written as the superposition of each component. It is sometimes convinient to define them in a different way, which specifies the property of the system in a coordinates moving at the speed of the barycentric velocity V. We redefine the stress tensor and the heat flux by

$$\begin{aligned} \mathbf{P} &= \Sigma_i \mathbf{P}_i \\ &= \Sigma_i \int\ m_i\ (\mathbf{v}_i-\mathbf{V})\ (\mathbf{v}_i-\mathbf{V})\ f_i\ d^3v_i, \end{aligned} \tag{2.10}$$

$$\begin{aligned} \mathbf{Q} &= \Sigma_i \mathbf{Q}_i \\ &= \Sigma_i \int\ (m_i/2)\ (\mathbf{v}_i-\mathbf{V})^2\ (\mathbf{v}_i-\mathbf{V})\ f_i\ d^3v_i. \end{aligned} \tag{2.11}$$

The relations between both definitions are as follows;

$$\mathbf{P}_i'=\mathbf{P}_i-(1/m_i n_i)\ \mathbf{J}_i\mathbf{J}_i, \tag{2.12}$$

$$\mathbf{Q}_i=\mathbf{q}_i+\mathbf{h}_i\cdot\mathbf{J}_i, \tag{2.13}$$

where

$$\mathbf{h}_i=(1/m_i n_i)\ [\mathbf{P}_i-\ \{(\mathbf{J}_i\cdot\mathbf{J}_i/m_i n_i)-n_i\varepsilon_i\}\ \mathbf{U}]. \tag{2.14}$$

$\mathbf{U}$ is the unit second rank tensor. Conventionally, $\mathbf{P}_i$ and $\mathbf{q}_i$ are used as the stress tensor and the heat flux respectively, and $\mathbf{h}_i$ is the enthalpy.

Let's split the stress tensor into three parts, the first of which is the local equilibrium pressure p_i. The second is the nonequilibrium pressure Π_i defined by one third of the trace of the stress tensor less p_i and the third is the traceless symmetric part $\mathbf{P}^{\circ}_i$.

$$\mathbf{P}_i=(p_i+\Pi_i)\ \mathbf{U}+\mathbf{P}^{\circ}_i, \tag{2.15}$$

where

$$p_i+\Pi_i=(1/3)\ (\mathbf{P}_i : \mathbf{U}), \tag{2.16}$$

$$p_i=(1/3)\int\ m_i(\mathbf{v}_i-\mathbf{V})^2\ f_i^{(0)}\ d^3v_i=n_iT, \tag{2.17}$$

$$\Pi_i=(1/3)\int\ m_i(\mathbf{v}_i-\mathbf{V})^2\ (f_i-f_i^{(0)})\ d^3v_i, \tag{2.18}$$

and the local equilibrium distribution function is defined by

$$f_i^{(0)}=n_i(m_i/2\pi T)^{(3/2)}\exp\ \{(-m_i/2T)\ (\mathbf{v}_i-\mathbf{V})^2\}. \tag{2.19}$$

We should pay the attention to (2.15) which shows that all diagonal elements of the stress tensor are equal. This holds true only when the system is isotropic, i.e., the distribution function depends on the absolute value of the $(\mathbf{v}_i-\mathbf{V})$. We also note that the antisymmetric part of the stress tensor doesn't exist due to the definition of our stress tensor. We may have the antisymmetric part of the stress tensor in liquid phase but not in gas phase. The substitution of (2.15) into (2.14) gives the precise meaning about the tensor $\mathbf{h}_i$ as follows ;

$$\begin{aligned} \mathbf{h}_i &= (1/m_i n_i)\ (p_i+(3/2)n_iT)\ \mathbf{U} \\ &\quad +(1/m_i n_i)\ [\{\Pi_i-(\mathbf{J}_i\cdot\mathbf{J}_i/m_i n_i)\}\ \mathbf{U}+\mathbf{P}^{\circ}_i]. \end{aligned} \tag{2.20}$$

The first term represents the local equilibrium enthalpy and the second is the nonequilibrium effects of the enthalpy. When we evaluate the diffusion flux, the stress tensor and the heat flux with the local equilibrium distribution function, we obtain

$$\mathbf{J}_i^{(0)} = \int m_i \mathbf{v}_i \, f_i^{(0)} \, d^3v_i - (m_i n_i/mn) \Sigma_j \int m_j \mathbf{v}_j \, f_j^{(0)} \, d^3v_j = 0, \quad (2.21)$$

$$\mathbf{P}_i^{(0)} = \int m_i \, (\mathbf{v}_i - \mathbf{V}) \, (\mathbf{v}_i - \mathbf{V}) \, f_i^{(0)} \, d^3v_i = (2/3) n_i \varepsilon_i \mathbf{U} = p_i \mathbf{U}, \quad (2.22)$$

$$\mathbf{q}_i^{(0)} = \int (m_i/2) \, (\mathbf{v}_i - \mathbf{V})^2 \, (\mathbf{v}_i - \mathbf{V}) \, f_i^{(0)} \, d^3v_i = 0. \quad (2.23)$$

Similarly, the enthalpy is written as

$$\mathbf{h}_i^{(0)} = (1/m_i n_i) \, (p_i + n_i \varepsilon_i) \, \mathbf{U} = (5T/2m_i) \, \mathbf{U}. \quad (2.24)$$

Even if the distribution function does't include the macroscopic variables such as the diffusion flux, the stress tensor and the heat flux, it is possible to evaluate the macroscopic variables in terms of the number density, the barycentric velocity and the energy density. This implies that the distribution function contains the independent macroscopic variables with the consistency.

3. The distribution function with the number density, the barycentric velocity and the energy density as the independent macroscopic variables

The distribution function which includes the number density, the barycentric velocity, the energy density and the mass besides the velocity variable, satisfies the following identities (the requirement of the consistency) ;

$$n_i = \int f_i \, d^3v_i, \quad (3.1)$$

$$n_i \mathbf{V} = n_i \mathbf{V}_i = \int \mathbf{v}_i \, f_i \, d^3v_i, \quad (3.2)$$

$$n_i \varepsilon_i = \int (m_i/2) \, (\mathbf{v}_i - \mathbf{V})^2 \, f_i \, d^3v_i. \quad (3.3)$$

Therefore, we might assume the form of the distribution function with the consistency as

$$f_i = n_i (3m_i/4\pi \varepsilon_i)^{(3/2)} \exp\{(-3m_i/4\varepsilon_i) \, (\mathbf{v}_i - \mathbf{V})^2\}. \quad (3.4)$$

Note that (3.4) is the same form of the the local equilibrium distribution function. Strictly speaking, (3.1), (3.2) and (3.3) are the necessary condition of (3.4). Then, there may be other forms of the distribution function satisfying (3.1), (3.2) and (3.3) at the same time. Since the distribution function is obtained with the consistency, it is impossible to determine the number density, barycentric velocity and the energy density as the function of the position and the time.

To do so, we need a kinetic equation for the distribution function such as

$$D_i f_i = \Sigma_j \, C(f_i, f_j), \quad (3.5)$$

where

$$D_i = (\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r}) + (\mathbf{F}_i(\mathbf{r}, \mathbf{v}_i, t)/m_i) \cdot (\partial/\partial \mathbf{v}_i), \quad (3.6)$$

$$C(f_i, f_j) = \int d^3v_j \int d\Omega_{ij} \, g_{ij} \, \sigma_{ij} \, [f'_i f'_j - f_i f_j]. \quad (3.7)$$

Eq. (3.5) is the Boltzmann equation for multi-component dilute gas and the conventional notations are used. gij is the absolute value of the relative velocity $\mathbf{v}_i - \mathbf{v}_j$ and σ_{ij} is the cross-section. We then obtain the coupled differential equations ,i.e., the evolution equations for the macroscopic variables in the following. The streaming operator D_i is rewritten as

$$D_i = (d/dt) + \mathbf{c}_i \cdot (\partial/\partial \mathbf{r}) + (\mathbf{F}_i(\mathbf{r}, \mathbf{v}_i, t)/m_i) \cdot (\partial/\partial \mathbf{v}_i), \quad (3.8)$$

where the substantial derivative and the relative velocity are defind by

$$d/dt = \partial/\partial t + \mathbf{V} \cdot (\partial/\partial \mathbf{r}), \quad (3.9)$$

$$\mathbf{c}_i = \mathbf{v}_i - \mathbf{V}. \quad (3.10)$$

Let $\xi_i^{[n]} \equiv \xi_i^{[n]} (\mathbf{r}, \mathbf{v}_i, t)$ be the microscopic quantities which is the n-th rank tensor and let the integration of $\xi_i^{[n]}$ multiplied by the distribution function be $\Xi_i^{[n]}$.

$$\Xi_i^{[n]} = \int \xi_i^{[n]} \, f_i \, d^3v_i. \quad (3.11)$$

The evolution equation for $\Xi_i^{[n]}$ is in general written as

$$(d/dt)\Xi_i^{[n]} = -\Xi_i^{[n]} (\partial/\partial \mathbf{r}) \cdot \mathbf{V} - (\partial/\partial \mathbf{r}) \cdot \Theta_i^{[n+1]} + B_i^{[n]} + A_i^{[n]} + \Sigma_j \Lambda_{ij}^{[n]}, \quad (3.12)$$

where

$$\Theta_i^{[n+1]} = \int \mathbf{c}_i \, \xi_i^{[n]} \, f_i \, d^3v_i, \quad (3.13)$$

$$B_i^{[n]} = \int (D_i \, \xi_i^{[n]}) \, f_i \, d^3v_i, \quad (3.14)$$

$$A_i^{[n]} = \int \{(\partial/\partial \mathbf{r}) \cdot \mathbf{v}_i + (\partial/\partial \mathbf{v}_i) \cdot (\mathbf{F}_i/m_i)\} \, \xi_i^{[n]} \, f_i \, d^3v_i, \quad (3.15)$$

$$\Lambda_{ij}^{[n]} = \int \xi_i^{[n]} \, C(f_i, f_j) \, d^3v_i. \quad (3.16)$$

The $\Theta_i^{[n+1]}$ represents the flow of the $\Xi_i^{[n]}$. For example, $\mathbf{Q}_i$ is taken as the flow of the energy $n_i \varepsilon_i$ in the case that $\xi_i^{[0]} = (m_i/2)\mathbf{c}_i^2$ and called the heat flux. The $B_i^{[n]}$ can be calculated explicitly. The $A_i^{[n]}$ is zero, since $\mathbf{r}$ and $\mathbf{v}_i$ are independent variables and the force acting on a molecule of the i-th component does not depend on the velocity $\mathbf{v}_i$[3]. As to the Boltzmann collision integral, the following property associated with the H-theorem is well known[4].

$$\Sigma_l\Sigma_j\Lambda_{lj}^{(n)}=\Sigma_l\Sigma_j\int \xi_l^{(n)}\, C(f_l,f_j)\, d^3\mathbf{v}_l$$
$$=\Sigma_l\Sigma_j\int \left(\xi_l^{(n)}+\xi_j^{(n)}-\xi'^{(n)}_l-\xi'^{(n)}_j\right) C(f_l,f_j)\, d^3v_l. \tag{3.17}$$

If ξ_l is replaced by $(\ln f_l)$, it is easy to see that $\Sigma_l\ \Sigma_j\ \Lambda_{lj} \leqq 0$, where the equality holds only for $f'_l\, f'_j=f_lf_j$.

By using (3.12)-(3.17), we obtain the evolution equations for the number density, the barycentric velocity and the energy density as follows ;

$$(d/dt)n_l=-n_l(\partial/\partial\mathbf{r})\cdot\mathbf{V}, \tag{3.18}$$

$$m_ln_l(d/dt)\mathbf{V}=-(\partial/\partial\mathbf{r})\ \{(2/3)n_l\varepsilon_l\}+\int \mathbf{F}_l\, f_l\, d^3v_l, \tag{3.19}$$

$$n_l(d/dt)\varepsilon_l=-(2/3)n_l\varepsilon_l(\partial/\partial\mathbf{r})\cdot\mathbf{V}+\int \mathbf{c}_l\cdot\mathbf{F}_l\, f_l\, d^3v_l. \tag{3.20}$$

Note that the evolution equations are closed coupled equations with the five unknown macroscopic variables $(n_l, \mathbf{V}, \varepsilon_l)$ as functions of the position and the time. We may solve these equations in principle with the given boundary and initial conditions.

Hence, we review the the idea of the method used. The enough macroscopic variables which describe the system in terms of the molecular expressions are taken and the form of the distribution function is expressed with the consistency. Since the evolution equations obey the kinetic equation describing the system concerned, say, the Boltzmann equation for dilute gas, the coupled differential equations for the evolution of the macroscopic variables are derived with the kinetic equation. By solving them with the boundary and the initial conditions, we obtain the complete information on the system.

4. The distribution function with the diffusion flux, the stress tensor and the heat flux in addition to the previous 3 independent macroscopic variables

If a system can be described by the number density, the barycentric velocity and the energy density only, the local equilibrium distribution function is an example which satisfies the consistency. We extend the case where a system can be represented by the diffusion flux, the stress tensor and the heat flux in addition to those mentioned in section 3. The first problem is to find out the form of the distribution function with the consistency. The form is not unique as discussed before. Therefore, we may impose the conditions to it such that the second law of thermodynamics is satisfied. This point will be discussed in section 5.

Now, let's rewrite the definitions of the macroscopic variables in terms of the relative velocity $\mathbf{c}_l$ as follows ;

$$n_l=\int f_l\, d^3c_l, \tag{4.1}$$

$$n_l(\mathbf{J}_l/m_ln_l)=\int \mathbf{c}_l\, f_l\, d^3c_l, \tag{4.2}$$

$$(2/m_l)n_l\varepsilon_l=\int c_l^2\, f_l\, d^3c_l, \tag{4.3}$$

$$\mathbf{P}_l/m_l=\int \mathbf{c}_l\mathbf{c}_l\, f_l\, d^3c_l, \tag{4.4}$$

$$(2/m_l)(\mathbf{q}_l-h_l\cdot\mathbf{J}_l)=\int \mathbf{c}_lc_l^2\, f_l\, d^3c_l. \tag{4.5}$$

We follow the Grad's thirteen moment method to find out the distribution function for multi-component dilute gas, where n_l, $\mathbf{J}_l$, ε_l, $\mathbf{P}_l$ and $\mathbf{q}_l$ are taken as independent macroscopic variables. The independence appears in the fact that we choose the distribution function which automatically satisfies the definition of the macroscopic variables. The distribution function in this method can be expanded in terms of Hermite polynomials.

$$f_l=n_l(3m_l/4\pi\varepsilon_l)^{(3/2)}\exp\ \{(-3m_l/4\varepsilon_l)c_l^2\}$$
$$\times\ [1+\mathbf{a}_{1l}\cdot\mathbf{H}_{1l}+\mathbf{a}_{2l}:\mathbf{H}_{2l}+\mathbf{a}_{3l}\cdot\mathbf{H}_{3l}], \tag{4.6}$$

where

$$\mathbf{H}_{1l}=\sqrt{(3m_l/2\varepsilon_l)}\ \mathbf{c}_l, \tag{4.7}$$

$$\mathbf{H}_{2l}=(3m_l/2\varepsilon_l)\ \mathbf{c}_l\mathbf{c}_l-\mathbf{U}, \tag{4.8}$$

$$\mathbf{H}_{3l}=\sqrt{(3m_l/2\varepsilon_l)}\ \{(3m_l/2\varepsilon_l)c_l^2-5\}\ \mathbf{c}_l. \tag{4.9}$$

If we include the higher order Hermite polynomials, we cannot determine the coefficients without introducing the new macroscopic variables. Therefore, (4.6) is a suitable choice and valid for small $\mathbf{c}_l$. In order to obtain the coefficients a_l's, we carry out the integrals of (4.1)-(4.5) with the distribution function given by (4.6),

which yields

$$n_l\ (\mathbf{J}_l/m_ln_l)=\sqrt{(2\varepsilon_l/3m_l)}\ n_l\mathbf{a}_{1l}, \tag{4.10}$$

$$0=\mathbf{a}_{2l}:\mathbf{U}, \tag{4.11}$$

$$\mathbf{P}_l/m_l=(2\varepsilon_l/3m_l)n_l\mathbf{U}+(4\varepsilon_l/3m_l)\ n_l\mathbf{S}_{2l}, \tag{4.12}$$

$$(2/m_i)(\mathbf{q}_i-h_i\cdot\mathbf{J}_i)=5n_i(2\varepsilon_i/3m_i)^{(3/2)}(\mathbf{a}_{1i}+2\mathbf{a}_{3i}), \tag{4.13}$$

where

$$\mathbf{S}_{2i}=(\mathbf{a}_{2i}+\mathbf{a}_{2i}{}^t)/2. \tag{4.14}$$

It is clear that the transpose of the stress tensor is the same as itself, i.e., $\mathbf{P}_i=\mathbf{P}_i{}^t$. We assume that $\mathbf{a}_{2i}$ is also symmetric. By solving these equations, we obtain

$$\mathbf{a}_{1i}=\sqrt{(3m_i/2\varepsilon_i)}(\mathbf{J}_i/m_in_i), \tag{4.15}$$

$$\mathbf{a}_{2i}=(3/4\varepsilon_in_i)\{\mathbf{P}_i-(2/3)\varepsilon_in_i\mathbf{U}\}, \tag{4.16}$$

$$\mathbf{a}_{3i}=(1/5)(\mathbf{q}_i/m_in_i)(3m_i/2\varepsilon_i)^{(3/2)} -\sqrt{(3m_i/2\varepsilon_i)}\{(1/5)(3m_i/2\varepsilon_i)h_i+\mathbf{U}/2\}\cdot(\mathbf{J}_i/m_in_i). \tag{4.17}$$

Therefore, the distribution function is denoted by

$$\begin{aligned} f_i=&n_i(3m_i/4\pi\varepsilon_i)^{(3/2)}\exp\{(-3m_i/4\varepsilon_i)c_i^2\} \\ &\times[1+(3m_i/2\varepsilon_i)(\mathbf{J}_i/m_in_i)\cdot\mathbf{c}_i \\ &+(3/4\varepsilon_in_i)\{\mathbf{P}_i-(2/3)\varepsilon_in_i\mathbf{U}\}:\{(3m_i/2\varepsilon_i)\mathbf{c}_i\mathbf{c}_i-\mathbf{U}\} \\ &+(3m_i/2\varepsilon_i)\{(3m_i/2\varepsilon_i)c_i^2-5\}\mathbf{c}_i\cdot[(1/5)(3m_i/2\varepsilon_i) \\ &\times(\mathbf{q}_i/m_in_i)-\{(1/5)(3m_i/2\varepsilon_i)h_i+\mathbf{U}/2\}\cdot(\mathbf{J}_i/m_in_i)], \end{aligned} \tag{4.18}$$

with the conditions $\mathbf{P}_i:\mathbf{U}=2\varepsilon_in_i$ and $\Sigma_i\mathbf{J}_i=0$. The enthalpy h_i is represented by other macroscopic variables and the the nonequilibrium contribution is taken into account. This is the same distribution function as Moreau used on studying a chemical reaction, although he didn't write it explicitly[5].

The advantage of (4.18) is the following. It satisfies the consistency and enables us to observe how the macroscopic physical quantities are included in the distribution function and to see new macroscopic physical quantities, say, the entropy density in terms of the given macroscopic variables by the direct integration over the velocity space. The change of the macroscopic variables can be described by the closed coupled differential equations in a similar manner.

5. Discussion on the distribution function with the entropy as a macroscopic variable

In moment method, we assume the form of the distribution. Grad expanded it in terms of Hermite polynomials and took the thirteen moment approximation for the distribution function. His method is mathematically rigorous and thus it is easy to see the extent of the approximation. We take the method from another point of view related to the entropy. The distribution function is written as

$$f_i=f_i(n_i,\varepsilon_i,\mathbf{J}_i,\mathbf{P}_i,\mathbf{q}_i;\mathbf{c}_i). \tag{5.1}$$

We note that the distribution function depends on the velocity variable and the integral over velocity space gives the macroscopic variable. If n_i, ε_i, $\mathbf{J}_i$, $\mathbf{P}_i$ and $\mathbf{q}_i$ are independent variables for the i-th component, (4.1)-(4.5) denote the identities due to the consistency as discussed in section 4. Inversely speaking, if these relations don't hold true with the consistency, they are not independent. Since the entropy is left out in (4.1)-(4.5), we define it by the Boltzmann's H with negative sign. Then, the H-function is denoted by

$$H=\Sigma_iH_i, \tag{5.2}$$

$$H_i=H_i(n_i,\varepsilon_i,\mathbf{J}_i,\mathbf{P}_i,\mathbf{q}_i)=\int(\ln f_i-1)f_i\,d^3c_i. \tag{5.3}$$

The integral shows that H is not the independent macroscopic variable, but depends on others. In the thirteen moment method, the entropy is only taken as a new macroscopic variable and no consideration about the entropy is paid in the distribution function. It seems to be why Grad's method gives rise to the entropy balance equation inconsistent with Gibbs relation. As has been discussed by Eu[6], it is essential not to leave out the entropy in the solution method of the Boltzmann equation in order to construct the irreversible thermodynamics without the restriction of near equilibrium.

In order to construct the irreversible thermodynamics based on the Boltzmann equation by moment method, we first choose the adequate independent macroscopic variables with the entropy. To find out the form of the distribution function with the consistency on those macroscopic variables is necessary. The evolution equations for the macroscopic variables leads to the modified form of the Gibbs relation and the nonlinear transport coefficients are obtained from the coupled differential equations. The difficulty to construct the irreversible thermodynamics along this line is mainly to find out the distribution function with the consistency on the entropy.

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