

**Dense Gas Theory and Fluctuating Hydrodynamics
Based on Extended Thermodynamics**

拡張された熱力学に基づく
濃密気体理論と流体力学的ゆらぎ理論

by

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Abstract

Non-equilibrium phenomena with evident spatio-temporal changes in physical quantities are notably interdisciplinary and encountered in engineering, physics, chemistry, biology and so on. For example, such phenomena appear in mesoscopic scale fluid flow, shock waves in the field of high-speed hydrodynamics, ultrasonic waves. In particular, in mesoscopic systems, the effects of fluctuations become essentially significant. These phenomena have been studied from the view point of thermodynamics.

For strongly non-equilibrium phenomena, I. Müller, T. Ruggeri and I. S. Liu proposed, developed and applied the extended thermodynamics (ET) theory. ET can be used to describe phenomena beyond the applicable range of well-known theory, that is, thermodynamics of irreversible processes (TIP) proposed by L. Onsager, C. Eckart, J. Meixner and I. Prigogine. For phenomena with fluctuations, the Landau-Lifshitz (LL) theory, a fluctuating hydrodynamics theory based on TIP has shown scope for future study. However, ET and LL have the following problems:

1. ET is presently limited to rarefied monatomic gases.
2. No theory can simultaneously describe fluctuations and strongly non-equilibrium phenomena.

In this thesis, the applicable range of ET is extended to rarefied polyatomic, dense monatomic and dense polyatomic gases. For rarefied polyatomic gases, the validity of this theory is shown by studying the dispersion relation of sound and comparing it with experimental data. The features of the new theory are discussed by paying attention to the process of energy transfer from the molecular translational mode to internal modes. Furthermore a fluctuating hydrodynamics approach based on ET is proposed.

The thesis is organized as follows:

In Chapter 1, the background and the purpose of the present study is discussed. Previous studies regarding non-equilibrium phenomena are briefly introduced by focusing on TIP, kinetic theory and LL. In addition, the recent developed non-equilibrium thermodynamic theory, that is, ET is introduced. In particular, the basic concepts and mathematical structure of ET are discussed.

In Chapter 2, we discuss the ET of dense gases by adopting a system of field equations with a different hierarchical structure than that found in previous works. It is the theory of 14 fields; mass density, velocity, temperature, viscous stress, dynamic pressure and heat flux. As a result, most of the constitutive equations can be explicitly determined by the caloric and thermal equations of state. The proposed theory includes rarefied polyatomic gases, and it is

shown that the rarefied-gas limit is consistent with the kinetic theory of gases. We also use the general theory developed in this chapter to analyze three physically important systems: (1) a gas that can be described with virial equations of state, (2) a hard-sphere system and (3) a van der Waals fluid.

In Chapter 3, we discuss the dispersion relation of sound in rarefied polyatomic gases (hydrogen, deuterium and hydrogen deuteride gases) based on the ET approach for dense gases proposed in Chapter 2. In addition, we compare experimental and theoretical results. The latter were based on the classical Navier-Stokes Fourier (NSF) theory. The applicable frequency-range of the ET approach proved much wider than that of the NSF theory. We also evaluated the bulk viscosity and relaxation times of non-equilibrium processes. The relaxation time related to the dynamic pressure has a possibility to become much larger than the relaxation times related to shear stress and heat flux.

In Chapter 4, using the ET approach for dense gases, we discuss the thermodynamic theory of gases with the energy transfer from the molecular translational mode to the internal modes as an extension of Meixner's theory. We also focus our attention on the simplest case with only one dissipative process due to the dynamic pressure. The derived dispersion relation of sound is compared with that derived with Meixner's theory. The kinetic theoretical basis of the present approach is also discussed.

In Chapter 5, we expand on the fluctuating hydrodynamics based on ET by using a 13-variable theory for a rarefied monatomic gases as an example. After analyzing the relationship between the proposed theory and the LL theory, we discuss the hierarchical structure of the hydrodynamic fluctuations.

In Chapter 6, we summarize all the results, present the conclusions and suggest directions for future investigations.

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Notations

t :	time	t_{ij} :	stress
x_i :	position ($i = 1, 2, 3$)	S_{ij} :	shear stress
c_i :	velocity of a molecule	Π	($= -S_{ii}/3$) : dynamic pressure
V :	volume	q_i :	heat flux
∂V :	surface	μ :	shear viscosity
\mathbf{u} :	independent fields	ν :	bulk viscosity
m :	mass of a molecule	κ :	heat conductivity
k_B :	Boltzmann constant	τ_S :	relaxation time related to shear viscosity
D :	degrees of freedom	τ_{Π} :	relaxation time related to bulk viscosity
h :	specific entropy per unit volume	τ_q :	relaxation time related to heat flux
s :	specific entropy per unit mass	c_v :	specific heat
φ_i	non-convective entropy flux	c_0 :	sound velocity at a equilibrium
Σ :	entropy production	ω :	frequency
ρ :	mass density	k :	complex wave number
T :	temperature	\mathbf{w} :	constant amplitude vector
ε :	specific internal energy per unit mass	v_{ph} :	phase velocity
p :	pressure	α :	attenuation factor
v_i :	velocity of a system		

- A dot on a generic quantity ψ represents the material time derivative:

$$\dot{\psi} \equiv \frac{\partial \psi}{\partial t} + v_i \frac{\partial \psi}{\partial x_i}.$$

- Parentheses around a set of N indices represent the symmetrization with respect to these indices, that is, the sum over all $N!$ permutations of the indices divided by $N!$. For example,

$$a_{(i}b_j) = \frac{1}{2!}(a_i b_j + a_j b_i),$$

$$a_{(i}b_j c_k) = \frac{1}{3!}[a_i(b_j c_k + b_k c_j) + a_j(b_k c_i + b_i c_k) + a_k(b_i c_j + b_j c_i)].$$

- Angular brackets denote the symmetric traceless part with respect to these indices (deviatoric part). For example,

$$a_{\langle ij \rangle} = a_{(ij)} - \frac{1}{3}a_{kk}\delta_{ij}.$$

Chapter 1

Introduction

1.1 Background

1.1.1 What are the theory requirements in modern science and engineering?

The real world is full of complex and different non-equilibrium phenomena, such as the flow of air, the temperature change in the coffee, sound propagation and so on, which tend to approach equilibrium with high probability. Such phenomena attract our genuine curiosity, and draw our attention as they are intimately-connected with our life. Our recognition of nature starts with the recognition of macroscopic materials; we know that such phenomena can be treated well as the time evolution of macroscopic variables, which are a continuum with respect to time and space. In other words, non-equilibrium phenomena can be described by the dynamics of a continuum body without the microscopic details. Thus, the continuum dynamics that include thermodynamics and fluid dynamics were developed. On the other hand, materials are made of molecules, which consist of atoms, and atoms consist of elementary particles. This fact indicates that macroscopic phenomena are caused by the motion of microscopic particles. Thus, statistical mechanics and kinetic theory were developed.

The abovementioned descriptions indicate that we recognize, in nature, a hierarchical structure that depends on scale. Governing equations were proposed for each hierarchical level. For example, in the case of the dynamics of gases, the hierarchical structure and corresponding typical equations are shown in Table 1.1. To understand a macroscopic system, the links among hierarchical levels should be considered.

In modern science and engineering, mesoscopic scale phenomena are noteworthy. As an example, one can consider thermal and hydrodynamic phenomena in the field of micro-fabrication technology, ultrasonic waves, shock waves in high-speed hydrodynamics, chemical reactions within the body and so on. To consider mesoscopic scale phenomena, we need to describe the evident spatio-temporal changes in physical quantities. Moreover, in the spatially mesoscopic

Table 1.1: Hierarchical structure

Hierarchy level	Typical equation
Microscopic scale description	Liouville equation
Mesosopic scale description	Boltzmann equation
Macroscopic scale description	Navier-Stokes Fourier

scale, the effect of “fluctuation”.

In this thesis, we have paid attention to phenomena related to fluids. The Boltzmann equation in Table 1.1 gives good results for gas-related phenomena; however, its applicability range is mainly limited to rarefied gases. To construct a general theory that describes mesoscopic phenomena, with or without fluctuation, a phenomenological approach, *i.e.*, thermodynamical approach is needed. This is our purpose in this thesis. After the formulation of non-equilibrium thermodynamics, the way for statistical mechanical description will be paved as equilibrium thermodynamics guided equilibrium statistical mechanics.

1.1.2 Applications

As already mentioned, the need to understand of the non-equilibrium phenomena is interdisciplinary. Some examples are given below.

Ultrasonic waves: An ultrasonic wave is a high-frequency sound wave in which physical quantities undergo evident changes temporally. Ultrasonic waves are used in non-destructive inspection of construction works, biomedical ultrasound, ultrasonic diagnosis and ultrasonic motor technology. Studies of ultrasonic waves have used ultrasonic wave’s characteristics such as dispersion, absorption, reflection, inflection and interference.

Shock waves: A shock wave is characterized by steep and rapid changes in physical quantities at the shock front. For example, shock waves appear around a spacecraft entering the Earth’s atmosphere. Therefore, to design better and safer spacecrafts, the effect of shock waves must be considered. The structure of a shock wave can be studied by non-equilibrium thermodynamics.

Thermal and hydrodynamic phenomena with fluctuations in fluids at the mesoscopic scale: The rapid development of nanotechnology involves nano-particles and microfabrication method for manufacturing nanodevices such as micro electro mechanical systems(MEMS); hence, more accurate control of fluids in the meso or nano scale is required. In

these technologies, the effect of fluctuations cannot be ignored, especially in flow channels of small width and objects of small size. For example, to control the shape of nanojet ejection or the breakdown of a fluid to droplets, the effect of fluctuations has to be studied [1].

1.2 Brief summary of non-equilibrium physics

In this section, we have summarized some of the most notable achievements in the field of non-equilibrium physics, especially fluid physics. In particular, we concentrated on the historical development of the new non-equilibrium thermodynamics. Therefore, we give a brief summary of non-equilibrium physics from the point of view of (i) continuum dynamics, (ii) kinetic theory and (iii) theory of fluctuations. We do not discuss the topic in detail despite the many good examples from the non-equilibrium statistical mechanics literature.

1.2.1 Continuum dynamics

First, we consider the theory that treats the dynamics of a continuum body, the so-called continuum dynamics. This approach proved extremely fruitful when applied to describe equilibrium and non-equilibrium state of matter. Several particularly important theories were based on this approach.

Equilibrium thermodynamics

We first review the equilibrium thermodynamics, because of its importance in science and engineering. Equilibrium thermodynamics describes the relations between equilibrium states as the name suggests. The definition of equilibrium is that “The system is spatio-temporally uniform at rest.” The system is completely characterized by state variables such as temperature, pressure and density. This theory is systematized based on the law of the conservation of energy (first law of thermodynamics) by Julius Robert von Mayer, James Prescott Joule and Hermann von Helmholtz, and the entropy inequality (second law of thermodynamics) by Rudolf Clausius and William Thomson (Lord Kelvin).

Irreversibility and phenomenological laws

The entropy inequality introduces the concept of irreversibility, which indicates the time evolution of the system, that is, the existence of irreversible processes from a non-equilibrium state to an equilibrium state. Examples of irreversible processes are heat conduction, diffusion, shear flow and electrical conduction. They are caused by the spatio-temporal non-uniformity of a system. Phenomenological relations were proposed and applied to describe the irreversible processes and various non-uniformities of system (Table 1.2).

Table 1.2: The phenomenological relations between irreversible processes and various non-uniformities of system.

Irreversible process	Phenomenological law
Heat conduction	Fourier's law : heat flux \propto temperature gradient
Diffusion	Fick's law : matter flow \propto concentration gradient
Shear flow	Navier-Stokes law : shear stress \propto velocity gradient
Electrical conduction	Ohm's law : electric current \propto electric potential gradient

Field variables and balance equations

To describe the spatio-temporal changes in a system, we introduce field variables that are a function of space x and time t . The changes in field variables are caused by the flux, production and supply from the outside. Therefore, the field variables are governed by the balance equations, which are satisfied by all materials. On the other hand, the materials characteristics are reflected in the constitutive equations. The abovementioned concepts can be summarized as follows: (i) the construction of suitable balance equations for the investigated system and (ii) the derivation of constitutive equations for the investigated materials.

Let us consider the general form of the balance equations for a one-component fluid. The shape, size and location of the system change, because the elements of the surface ∂V of volume V move with velocity $u_i(\mathbf{x}, t)$ ($i = 1, 2, 3$), depend on the position \mathbf{x} and time t . A general quantity Ψ of the system can be expressed by the specific value ψ per mass density ρ as follows:

$$\Psi = \int_V \rho \psi dV. \quad (1.1)$$

By considering the effects of flux, production and supply, the time evolution of Ψ follows the equation of balance:

$$\frac{d}{dt} \int_V \rho \psi dV = - \int_{\partial V} \rho \psi (v_i - u_i) n_i dA - \int_{\partial V} \phi_i n_i dA + \int_v \rho (\pi + \iota) dV. \quad (1.2)$$

The first term on the right-hand side of Eq. (1.2) represents the convective flux through the surface, and the second term represents the non-convective flux through an outer unit normal n_i to ∂V and the third term comprises by the production density $\rho \pi$ and supply density $\rho \iota$. For simplicity, we consider the system at rest. In this case, $u_i = 0$ and V is independent of time. From Eq. (1.2) and by using Gauss's theorem, in a regular point where the smoothness

is guaranteed, we obtain the time evolution equation of ψ in the local form

$$\frac{\partial \rho \psi}{\partial t} + \frac{\partial(\rho \psi v_i + \phi_i)}{\partial x_i} = \rho(\pi + \iota). \quad (1.3)$$

Based on Eq. (1.3), let us consider the balance equations of mass, momentum and energy, i.e. the laws of conservation with no productions. The time evolution of the mass density ρ only depends on the convective flux. The time evolution of the momentum density ρv_i depends on the stress t_{ij} for the non-convective flux and on the external force for the supply. The time evolution of the energy density $\rho \varepsilon$ where ε is the specific internal energy, depends on the heat flux q_i for non-convective flux and on the specific value of absorbed heat radiation Z for supply, where suffixes $i, j = 1, 2, 3$. We summarize ψ, ϕ, π and ι of the conservation laws in Table 1.2.1.

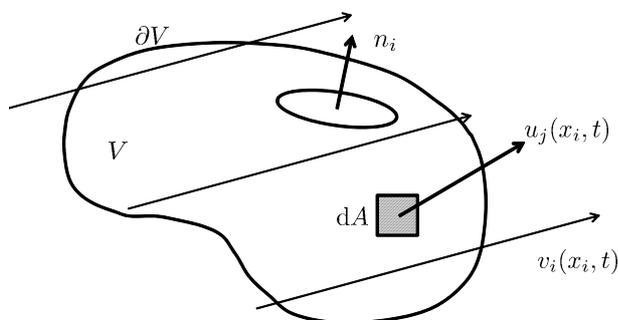


Figure 1.1: The system in the flow.

Table 1.3: The density, non-convective flux, production and supply for conservation laws of mass density, momentum and energy

Ψ	ψ	ϕ	π	ι
Mass	1	0	0	0
Momentum	v_i	$-t_{ij}$	0	f_i
Energy	$\varepsilon + \frac{v^2}{2}$	$-t_{ij}v_j + q_i$	0	$f_i v_i + Z$

Thermodynamics of irreversible process

The thermodynamics of irreversible process (TIP) [2, 24, 88] by Lars Onsager, Carl Henry Eckart, Josef Meixner, Ilya Prigogine to describe non-equilibrium phenomena. Linear TIP theory describes the irreversible processes well and has played a fundamental role in many

engineering and scientific fields, for systems not far from equilibrium. Therefore, a system is characterized by slow variables.

Let us summarize the TIP for a one-component, viscous, heat-conducting fluid, which is characterized by five fields:

$$\begin{aligned} \text{mass density} & \quad \rho(x_i, t), \\ \text{velocity} & \quad v_i(x_i, t), \end{aligned} \tag{1.4}$$

$$\text{temperature} \quad T(x_i, t), \tag{1.5}$$

The time evolution of each field is governed by the law of conservation of mass, momentum and energy. We assume that there is not a body force and supply. In this case, by substituting the elements of Table (1.2.1) with $f_i = 0$ and $\iota=0$ into Eq. (1.3), we obtain

$$\begin{aligned} \rho + \rho \frac{\partial v_j}{\partial x_j} &= 0, \\ \rho \dot{v}_i - \frac{\partial t_{ij}}{\partial x_j} &= 0, \\ \rho \dot{\varepsilon} + \frac{\partial q_j}{\partial x_j} - t_{ij} \frac{\partial v_i}{\partial x_j} &= 0, \end{aligned} \tag{1.6}$$

where the pressure p and the specific internal energy ε depend on ρ and T , and the stress is given by $t_{ij} = -p\delta_{ij} + S_{ij}$ where $\Pi = -S_{ii}/3$ is the dynamic pressure. To obtain the closed field equations, we consider the constitutive equations that relate $\varepsilon, S_{\langle ij \rangle}, \Pi, q_i$ to the independent fields.

At local equilibrium even though the whole system is not in equilibrium, there are elements that are in equilibrium. Based on this assumption, the relation between the specific entropy density $s(\mathbf{x}, t)$ and $\varepsilon(\mathbf{x}, t)$, the so-called Gibbs relation, is

$$\dot{s} = \frac{1}{T} \left(\dot{\varepsilon} - \frac{p}{\rho^2} \dot{\rho} \right), \tag{1.7}$$

where the pressure p is a function of ρ and T . By substituting the laws of conservation in Eq. (1.6) into this relation, we obtain

$$\rho \dot{s} + \frac{\partial}{\partial x_i} \left(\frac{q_i}{T} \right) = -\frac{q_i}{T^2} \frac{\partial T}{\partial x_i} + \frac{1}{T} S_{\langle ij \rangle} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} - \frac{1}{T} \Pi \frac{\partial v_n}{\partial x_n}. \tag{1.8}$$

Equation (1.8) can be interpreted as the balance equation of entropy. Subsequently, the entropy flux and production can be described with the following equations:

$$\begin{aligned} \text{entropy flux:} & \quad \varphi_i = \frac{q_i}{T} \\ \text{entropy production:} & \quad \Sigma = -\frac{q_i}{T^2} \frac{\partial T}{\partial x_i} + \frac{1}{T} S_{\langle ij \rangle} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} - \frac{1}{T} \Pi \frac{\partial v_n}{\partial x_n}. \end{aligned} \tag{1.9}$$

Table 1.4: Thermodynamic fluxes and thermodynamic forces.

Thermodynamic fluxes		Thermodynamic forces	
heat flux	q_i	temperature gradient	$\frac{\partial T}{\partial x_i}$
traceless part of viscous stress	$S_{\langle ij \rangle}$	deviatoric velocity gradient	$\frac{\partial v_{\langle i}}{\partial x_{j \rangle}}$
dynamic pressure	Π	divergence of velocity	$\frac{\partial v_n}{\partial x_n}$

Entropy production is expressed as product of the dissipative flux of the conserved quantities (thermodynamic fluxes) and the gradients of the intensive variables (thermodynamic forces) in Table 1.4.

For the linear constitutive equations, we assume a linear relationship between the thermodynamic fluxes and thermodynamics forces as follows

$$\begin{aligned}
q_i &= -\kappa \frac{\partial T}{\partial x_i}, \\
S_{\langle ij \rangle} &= 2\mu \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \\
\Pi &= -\nu \frac{\partial v_n}{\partial x_n},
\end{aligned} \tag{1.10}$$

where the heat conductivity κ , shear viscosity μ and bulk viscosity ν are positive because of the requirement of the entropy principle in Eq. (1.8). These relations are known as the Navier-Stokes Fourier law, which we mentioned before. When the heat conductivity, shear viscosity and bulk viscosity are given, and the thermal and caloric equations of state $p = \hat{p}(\rho, T)$ and $\varepsilon = \hat{\varepsilon}(\rho, T)$ are adopted, all the coefficients in the basic equations can be determined.

Finally, we summarize the closed field equations of Eq. (1.6) as

$$\begin{aligned}
\dot{\rho} + \rho \frac{\partial v_j}{\partial x_j} &= 0, \\
\rho \dot{v}_i + \frac{\partial}{\partial x_j} [(p + \Pi)\delta_{ij} - S_{\langle ij \rangle}] &= 0, \\
\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \dot{T} + \frac{\partial q_j}{\partial x_j} + \left[\left(p - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T + \Pi \right) \delta_{ij} - S_{\langle ij \rangle} \right] \frac{\partial v_i}{\partial x_j} &= 0.
\end{aligned} \tag{1.11}$$

This set of equations is part of the Navier-Stokes Fourier (NSF) theory which is a well-known theory of viscous heat-conducting fluids in the framework of TIP.

In the present section, we have summarized the case in which the irreversible processes exist independently. However, in general, the irreversible processes appear in a coupled form, such as the Seebeck effect, the Peltier effect and the Soret effect. Such coupled effects are explained by Onsager's reciprocal relations, which are derived from considering the fluctuations.

The problems of TIP

TIP is a successful theory; however, it has two fundamental problems.

The first problem is that the applicable range of TIP is limited by the assumption of local equilibrium. Therefore, TIP cannot describe non-equilibrium phenomena with evident spatio-temporal changes of physical quantities beyond this assumption.

The second problem is that TIP cannot be applied to relativistic phenomena, in principle, because the propagation speed of information becomes infinite. We demonstrate this specifically for a one-component fluid with constant mass density at rest. Then, the time evolution equation of temperature in Eq. (1.11)₃ becomes

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho} \Delta T. \quad (1.12)$$

The solution of this equation is

$$T(\mathbf{x}, t) = \frac{1}{(4\pi \mathcal{D}t)^{3/2}} \int_{-\infty}^{\infty} T(\mathbf{y}, 0) \exp\left(-\frac{(\mathbf{y} - \mathbf{x})^2}{4\mathcal{D}t}\right) d\mathbf{y} \quad (1.13)$$

where $\mathcal{D} = \frac{\kappa}{\rho} / \frac{\partial \varepsilon}{\partial T}$. This implies that the temperature at space \mathbf{x} and time t is influenced by the temperature at all spaces and $t = 0$. This means that the information spreads to space with infinite speed with regard to temperature. From a theoretical point of view, this is the problem of infinite speed of disturbances, which is called the paradox of heat conduction, and it is attributed to the parabolic character of the basic equations that are spatially non-local constitutive equations [3].

Studies beyond TIP

After the establishment of TIP, many studies were proposed to process much stronger non-equilibrium phenomena. These studies may be classified into two types:

1. Far from equilibrium and based on the local equilibrium assumption

In a far-from-equilibrium state, non-linearity becomes increasingly essential and generates diversity. Several approaches were taken based on the foundations of TIP. In this case, the thermodynamic fluxes are no longer linear functions of the thermodynamic forces [4]. Studies based on the theory of stability are necessary because the violation of stability causes a system to transform to a dissipative structure. Then, bifurcation phenomena are observed and the knowledge of dynamical systems is introduced. The Belousov-Zhabotinsky reaction is a well-known example of a dissipative structure.

2. The theory beyond the assumption of local equilibrium

TIP adopts the slow variables as independent variables. To describe the rapid changes in

physical quantities, studies that adopted the fast variables as well as the slow variables were developed. For example, some additive equations, which indicate relaxation of the dissipative variables, are introduced into the laws of conservation in the field of gas dynamics as in Meixner's theory [5, 6, 7]. Although there are many theories such as the extended TIP or extended irreversible thermodynamics, the extended thermodynamics (ET) theory [8, 9], which is based on symmetric hyperbolic system, has been anticipated because of its principled systematic structure and many applications of its.

In particular, we paid attention to the latter approach and subsequently discuss the innovative work of Cattaneo [10]. who wanted to improve the paradox of heat conduction in TIP. He tried to change the character of the basic equations from parabolic to hyperbolic by introducing the time derivative of heat flux. Many theoretical approaches were based on Cattaneo's work, and the results led to the extended thermodynamics theory.

Cattaneo equation: Let us return to Eq. (1.12), which is derived from the law of the conservation of energy for a system with constant mass at rest and Fourier's law, Eq. (1.10)₁. The paradox of heat conduction is caused by the fact that Fourier's law does not include a time interval for the propagation of heat. Cattaneo proposed that the duration of heat propagation should be of concern and used the following equation:

$$q_i = -\kappa \left(\frac{\partial T}{\partial x_i} - \tau \left(\frac{\partial \dot{T}}{\partial x_i} \right) \right), \quad (1.14)$$

where τ is the relaxation time. By substituting Eq. (1.14) into the law of the conservation of energy Eq. (1.11)₃ with a constant mass density at rest, the following equation is obtained

$$\dot{T} = \frac{\kappa}{\rho \varepsilon_T} \left(\Delta T - \tau (\Delta \dot{T}) \right).$$

This is still a parabolic equation. To obtain a hyperbolic-type equation, we assume that the operator $\tau \frac{d}{dt}$ is small and consider the following expansion

$$\left(1 - \tau \frac{d}{dt} \right)^{-1} \approx 1 + \tau \frac{d}{dt}.$$

Then, Eq. (1.14) is rewritten as

$$q_i + \tau \dot{q}_i = -\kappa \frac{\partial T}{\partial x_i}. \quad (1.15)$$

This equation is called the Cattaneo equation. From the law of conservation of energy for a system with a constant mass density at rest, we obtain

$$\tau \ddot{T} + \dot{T} = \frac{\kappa}{\rho \varepsilon_T} \Delta T. \quad (1.16)$$

When $\tau > 0$, this equation becomes hyperbolic.

The problem with the Cattaneo equation is its lack of mathematical rigor. Many studies followed Cattaneo's work. I. Müller tried to modify Navier-Stokes Fourier law by adopting a Cattaneo-like equation, and he introduced the time derivatives of stress and heat flux into the constitutive equations by considering that the entropy depends on them. However, this approach has several problems. For example, the material frame indifference is violated, the hyperbolicity of the system is not certain and there are some determined variables in the field equations. Such problems are solved by the extended thermodynamics theory, something that will be discussed below.

1.2.2 Kinetic Theory

Besides the phenomenological approach, the kinetic theoretical approach of molecules plays a crucial role in the field of non-equilibrium physics. This approach considers microscopic details such as the collision of molecules. From a historical view point, this approach originated from the study of Daniel Bernoulli regarding the introduction of equilibrium pressure by considering the change in momentum before or after the collision of molecules to a wall in the early 18th century. After a long while, this idea was reintroduced by John Herapath in the early 19th century. Karl Krönig re-derived the Boyle-Charles law based on kinetic theory. Rudolf Clausius distinguished gas, liquid and solid states based on molecular motion. In addition, he introduced the concept of the mean free path. James Clerk Maxwell introduced the idea of probability distributions and formulated the kinetic theory as we know it today, which became the basis of statistical mechanics theory. Ludwig Eduard Boltzmann deduced the time evolution of the distribution function for rarefied monatomic gases, the so-called Boltzmann equation. Based on the Boltzmann equation, many studies were developed, and the theory is still useful today.

Many studies followed the publication of the Boltzmann equation. Boltzmann derived the collision term based on the physically-feasible assumption, the so-called *Stoßzahlansatz*. To obtain the macroscopic equations based on the Boltzmann equation, Sydney Chapman, David Enskog and David Hilbert proposed the closure method, which derived the constitutive equations, which is consistent with the Navier-Stokes Fourier system. As an extension of the Chapman-Enskog method to constitutive equations with a second- or third-order term, the Burnett equation or super Burnett equation was proposed [11]. On the other hand, Harold Grad also proposed a closure method, which adopted additive moment equations. Moreover, new closure method recently appeared that is based on the maximum entropy principle (MEP) [12, 13] which has usefulness not only in the kinetic theory but also in other fields such as information theory. The details of Grad's and MEP's approach will be discussed below.

Although the kinetic theoretical approach is useful, it is well established only for rarefied monatomic gases. Due to the complexity of the microscopic details, it seems difficult to extend the applicable range of kinetic theoretical approach to rarefied polyatomic, dense monatomic and dense gases. By using a special models, several studies for such gases were appeared. For example, for rarefied polyatomic gases, there appeared some theories [14, 15, 16] based on the so-called Borgnakke-Larsen model [16]. In particular, recently, the theory based on the MEP recently appeared [12, 13]. For dense gases, there are also many studies based on the Enskog equation or the modified Enskog equation, which consider the hard-sphere effect on the Boltzmann equation [17, 18]. For example, moment equations based on the Enskog equation were proposed by Gilberto Medeiros Kremer and E. Rosa [19]. As an extension of the Grad method, the generalized hydrodynamics is proposed by Byung Chan Eu [20]. Moreover, moment equations based on the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchical structure were developed [21, 22].

Hereafter, we recall the Boltzmann equation and the macroscopic equations derived by it to show the usefulness of kinetic theory. Moreover, we introduce the Grad's moment method and the maximum entropy principle as the method of the closure.

Boltzmann equation

Let us consider the rarefied monatomic gases. In the kinetic theoretical approach, the state of the system is characterized by the distribution function on the phase space. In general, the dynamics of N -body system is governed by the Liouville equation which is the equation for N -body distribution function, and the Liouville equation is reduced to the Boltzmann equation for one-body distribution function through the BBGKY-hierarchy structure. The one-body distribution function $f(x_i, c_i, t)$ with the time t , position of the i -th particle x_i and its velocity c_i , is defined through the number of particles in the volume element between x_i and $x_i + dx_i$ with velocities between c_i and $c_i + dc_i$ at t :

$$N = f(x_i, c_i, t)d\mathbf{x}d\mathbf{c}. \quad (1.17)$$

With this the Boltzmann equation without the inertial force is expressed as follows

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} + f_i \frac{\partial f}{\partial c_i} = S, \quad (1.18)$$

where the first, second and third term of left-hand-side are the time variation of f in phase space by time evolution, flux and the effect of external force f_i , respectively. S in right-hand-side is the rate of production and annihilation of the point caused by molecular collisions. Boltzmann put forward the so-called *Stoßzahlansatz*(molecular chaos hypothesis), and estimated as follows:

$$S = \int (f' f^{1'} - f f^1) \sigma g \sin \theta d\theta d\epsilon dc^1, \quad (1.19)$$

where f' , $f^{1'}$, f , f^1 are the distribution function with velocity \mathbf{c}' , $\mathbf{c}^{1'}$, \mathbf{c} , \mathbf{c}^1 , respectively.

Moment equations

The macroscopic quantities are defined as the mean value over a representative elementary volume. In general, the mean value of a function $\psi(\mathbf{x}, \mathbf{c}, t)$ is defined as

$$\bar{\psi}(\mathbf{x}, t) = \frac{1}{\rho} \int m\psi f d\mathbf{c}, \quad (1.20)$$

where ρ is the mass density which defined as the mean value of $\psi = 1$. The time evolution of $\bar{\psi}$ is obtained upon (1.18) by multiplying $m\psi$ and integration over all \mathbf{c} .

$$\begin{aligned} \frac{\partial \rho \bar{\psi}}{\partial t} + \frac{\partial \rho \bar{\psi} c_i}{\partial x_i} - \overline{\rho f_i \frac{\partial \psi}{\partial c_i}} \\ = \rho \left(\frac{\partial \psi}{\partial t} + c_i \frac{\partial \psi}{\partial x_i} \right) + \frac{1}{4} m \int (\psi + \psi^1 - \psi' - \psi^{1'}) (f' f^{1'} - f f^1) \sigma g \sin \theta d\theta d\varepsilon d\mathbf{c} d\mathbf{c}', \end{aligned} \quad (1.21)$$

where the second and third terms on the left-hand-side express flux and the density of supply of $\rho \bar{\psi}$, and the right-hand-side expresses the density of production of $\rho \bar{\psi}$.

Let us express the integration of the case that ψ is given by the moment of c_i as follows:

$$F_{i_1, i_2, \dots, i_N} = \int m c_{i_1} c_{i_2} \cdots c_{i_N} f d\mathbf{c}. \quad (1.22)$$

Then the following physical variables are expressed as follows:

$$\begin{aligned} \text{mass density} & F = \rho, \\ \text{momentum density} & F_i = \rho v_i, \\ \text{momentum flux} & F_{ij} = \int \rho c_i c_j f d\mathbf{c}, \\ \text{flux of momentum flux} & F_{ijk} = \int \rho c_i c_j c_k f d\mathbf{c}. \end{aligned} \quad (1.23)$$

In particular, the trace part of F_{ij} is a value proportional to the energy density. From (1.21) we obtain the time evolution equation of F_{i_1, i_2, \dots, i_N} ,

$$\frac{\partial F_{i_1, i_2, \dots, i_N}}{\partial t} + \frac{\partial F_{i_1, i_2, \dots, i_N, j}}{\partial x_j} - N F_{(i_1, i_2, \dots, i_{N-1}} f_{i_N)} = P_{i_1, i_2, \dots, i_N}, \quad (1.24)$$

where P_{i_1, i_2, \dots, i_N} is the production term expressed by using the right-hand-side term of (1.21).

The balance equation (1.24) indicates that there is a system which the moments satisfy an infinity hierarchy of balance laws. In such system, there is a noticeable feature that the flux in an equation becomes the density in the next equation. As a special case, we express the system truncated the hierarchy at the density with tensor of rank N . When we express the vectors of moments up to tensorial order N as $\mathbf{F}^{(N)}$, $\mathbf{F}_i^{(N)}$ and $\mathbf{P}^{(N)}$, such system is expressed as

$$\frac{\partial \mathbf{F}^{(N)}}{\partial t} + \frac{\partial \mathbf{F}_i^{(N)}}{\partial x_i} = \mathbf{P}^{(N)}, \quad (1.25)$$

where we ignore the external force. By introducing a vector $\Phi^{(N)} = (1, c_{i_1}, c_{i_1}c_{i_2}, \dots, c_{i_1}c_{i_2} \dots c_{i_N})^T$, $\mathbf{F}^{(N)}$, $\mathbf{F}_i^{(N)}$ and $\mathbf{P}^{(N)}$ are expressed as follows:

$$\mathbf{F}^{(N)} = m \int f \Phi^{(N)} d\mathbf{c}, \quad \mathbf{F}_i^{(N)} = m \int f c_i \Phi^{(N)} d\mathbf{c}, \quad \mathbf{P}^{(N)} = m \int S \Phi^{(N)} d\mathbf{c}. \quad (1.26)$$

Here, we have the problem of closure because the last flux and the production terms are not in the list of the densities. To close this system it is necessary to find the constitutive equations. We will see the closure procedures after introducing the several important variables.

We can also define the intrinsic variables of system by introducing the peculiar velocity C_i defined by $C_i = c_i - v_i$. As the moment of C_i , we define the intrinsic variables $\hat{F}_{i_1, i_2, \dots, i_N}$ corresponding to the moments (1.22) as follows:

$$\hat{F}_{i_1, i_2, \dots, i_N} = \int m C_{i_1} C_{i_2} \dots C_{i_N} f d\mathbf{c}. \quad (1.27)$$

It is clear that $\hat{F} = F = \rho$ and $\hat{F}_i = 0$. Moreover the following conventional physical quantities are introduced as follows:

$$\begin{aligned} \text{specific internal energy} & \quad \varepsilon \equiv \frac{\hat{F}_{ii}}{2\rho} = \frac{1}{2\rho} \int m C_i C_i f d\mathbf{c}, \\ \text{stress} & \quad t_{ij} = -p\delta_{ij} + S_{\langle ij \rangle} \equiv -\hat{F}_{ij} = - \int m C_i C_j f d\mathbf{c}, \\ \text{heat flux} & \quad q_i \equiv \frac{\hat{F}_{ppi}}{2} = \frac{1}{2} \int m C_p C_p C_i f d\mathbf{c}. \end{aligned} \quad (1.28)$$

By considering that there is no dynamic pressure $p(\mathbf{x}, t)$ in rarefied monatomic gases, the pressure is defined by the trace part of stress (1.28)₂.

$$p(\mathbf{x}, t) = \frac{1}{3} \int m C^2 f d\mathbf{c} = \frac{2}{3} \rho \varepsilon. \quad (1.29)$$

From the caloric equation of state $\varepsilon = \frac{3}{2} \frac{k_B}{m} T$, we may introduce the temperature T as follows:

$$k_B T = \frac{m}{3\rho} \int m C^2 f d\mathbf{c} \frac{k}{m} T(\mathbf{x}, t). \quad (1.30)$$

From Eqs (1.22) and (1.27), we can realize that there are the relations between two kinds of moments as follows:

$$\begin{aligned} F &= \hat{F} (= \rho), \\ F_i &= \hat{F} v_i (= \rho v_i), \\ F_{ij} &= \hat{F}_{ij} + \rho v_i v_j, \\ F_{ijk} &= \hat{F}_{ijk} + 3\hat{F}_{\langle ij} v_k \rangle + \rho v_i v_j v_k. \end{aligned} \quad (1.31)$$

Balance equation of entropy and local equilibrium

The entropy density is obtained as the mean value of

$$\psi = -\frac{k_B}{m} \left(\ln \left(\frac{f}{y} \right) - 1 \right), \quad (1.32)$$

where the constant $1/y$ is the smallest element in phase space that can accommodate a position and a velocity. The reason why we can interpret such mean value as the entropy principle is clarified when we consider the balance equation of it:

$$\begin{aligned} \frac{\partial \rho \left(-\frac{k_B}{m} \overline{\ln f} \right)}{\partial t} + \frac{\partial}{\partial x_j} \left[\rho \left(-\frac{k_B}{m} \overline{\ln f} \right) v_j + \left(-\frac{k_B}{m} \overline{C_j \ln f} \right) \right] \\ = \frac{k_B}{4} \int \ln \frac{f' f^{1'}}{f f^1} (f' f^{1'} - f f^1) g \sigma \sin \theta d\theta d\epsilon d\mathbf{c}^1 d\mathbf{c}. \end{aligned} \quad (1.33)$$

The production of this balance equation is non-negative. This fact indicates that the balance equation (1.33) can be interpreted as the entropy inequality:

$$\frac{\partial \rho s}{\partial t} + \frac{\partial}{\partial x_j} (\rho s v_j + \varphi_j) = \Sigma \geq 0, \quad (1.34)$$

where s , φ_i and Σ are the specific entropy density, non-convective entropy flux and entropy production. Therefore s , φ_i and Σ are defined as follows

$$\rho s = -k_B \int \ln \left(\frac{f}{y} - 1 \right) f d\mathbf{c}, \quad (1.35)$$

$$\varphi_i = -k_B \int C_i \ln \left(\frac{f}{y} - 1 \right) f d\mathbf{c}, \quad (1.36)$$

$$\Sigma = \frac{k_B}{4} \int \ln \frac{f' f^{1'}}{f f^1} (f' f^{1'} - f f^1) g \sigma \sin \theta d\theta d\epsilon d\mathbf{c}^1 d\mathbf{c}. \quad (1.37)$$

The local equilibrium is defined as the state that entropy production Σ is minimum 0. This result restrict the form of the equilibrium distribution function f_E . By substituting f_E into the moments (1.22), we obtain only ρ , ρv_i and ε at local equilibrium state. This means that f_E can be expressed by these variables, and the explicit expression of it is as follows

$$f_E = \frac{\rho}{m} \sqrt{\left(\frac{m}{2\pi k_B T} \right)^3} e^{-\frac{m}{2k_B T} C^2}. \quad (1.38)$$

This distribution function is called Maxwell distribution.

By using f_E the entropy density s_E is also expressed

$$s_E = \frac{k_B}{m} \left[\frac{3}{2} - \ln \left\{ b \frac{\rho}{m} \sqrt{\left(\frac{m}{2\pi k_B T} \right)^3} \right\} \right]. \quad (1.39)$$

The first derivation of it is

$$ds_E = \frac{k_B}{m} \left(\frac{3}{2} \frac{1}{T} dT - \frac{1}{\rho} d\rho \right).$$

The Gibbs relation which is well-known in the equilibrium thermodynamics is reconstructed.

Closure by Grad's 13 moment method

By introducing the Grad's moment method [23], we consider the closure problem of balance equations (1.25). This method adopts more fields as independent variables than that of NSF theory. Let us consider that the system is characterized by 13 fields F, F_i, F_{ij}, F_{ppi} . The balance equations of these without body force and supply are expressed by Eq. (1.25) as follows:

$$\begin{aligned}
 \frac{\partial F}{\partial t} + \frac{\partial F_i}{\partial x_i} &= 0, \\
 \frac{\partial F_i}{\partial t} + \frac{\partial F_{ij}}{\partial x_j} &= 0, \\
 \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{\langle ij \rangle}, \\
 \frac{\partial F_{ppi}}{\partial t} + \frac{\partial F_{ppik}}{\partial x_k} &= P_{ppi},
 \end{aligned} \tag{1.40}$$

where first two equations and trace part of third equation denote the conservation laws of mass, momentum and energy, respectively. The production terms $P_{\langle ij \rangle}$ and P_{ppi} are estimated when the special model for molecular interaction are assumed. For example, for maxwell molecules we have

$$\begin{aligned}
 P_{\langle ij \rangle} &= -\frac{3}{2}\rho\mathcal{B}(F_{\langle ij \rangle} - \rho v_{\langle i} v_{j \rangle}), \\
 P_{ii} &= -\rho\mathcal{B}(F_{ii} - 3F_{(ii} v_{j)} - \rho v_i v^2),
 \end{aligned} \tag{1.41}$$

where \mathcal{B} is the positive constant which depends on the length of interaction. By substituting (1.28) and (1.31) into (1.40), we can obtain the time evolution equations for $\rho, v_i, \varepsilon, S_{\langle ij \rangle}, q_i$.

$$\begin{aligned}
 \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} &= 0, \\
 \frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho v_i v_j + p \delta_{ij} - S_{\langle ij \rangle}) &= 0, \\
 \frac{\partial (\rho \varepsilon + \frac{\rho}{2} v^2)}{\partial t} + \frac{\partial}{\partial x_j} \left[\left(\rho \varepsilon + \frac{\rho}{2} v^2 \right) v_j + (p \delta_{ij} - S_{\langle ij \rangle}) v_i + q_j \right] &= 0, \\
 \dot{S}_{\langle ij \rangle} + S_{\langle ij \rangle} \frac{\partial v_n}{\partial x_n} - \frac{\partial \hat{F}_{\langle ij \rangle n}}{\partial x_n} - 2p \frac{\partial v_{\langle i}}{\partial x_j} + 2S_{\langle n \langle i} \frac{\partial v_{j \rangle}}{\partial x_n} &= -\frac{3}{2}\mathcal{B}S_{\langle ij \rangle}, \\
 \dot{q}_i + q_i \frac{\partial v_n}{\partial x_n} + \frac{1}{2} \frac{\partial \hat{F}_{in kk}}{\partial x_n} - \frac{1}{\rho} (-p \delta_{ik} + S_{\langle ik \rangle}) \frac{\partial (-p \delta_{kn} + S_{\langle kn \rangle})}{\partial x_n} \\
 + \frac{3p}{2\rho} \frac{\partial (-p \delta_{in} + S_{\langle in \rangle})}{\partial x_n} + q_n \frac{\partial v_i}{\partial x_n} + \hat{F}_{nij} \frac{\partial v_j}{\partial x_n} &= -\rho \mathcal{B} q_i
 \end{aligned} \tag{1.42}$$

The system (1.42) (or Eq. (1.40)) is not closed by $\rho, v_i, \varepsilon, S_{\langle ij \rangle}, q_i$ (or F, F_i, F_{ij}, F_{ppi}). To close the system we assume the following constitutive equations

$$\begin{aligned}
 \hat{F}_{\langle ij \rangle n} &= \hat{F}_{\langle ij \rangle n}(\rho, v_i, T, S_{\langle ij \rangle}, q_i), \\
 \hat{F}_{ij kk} &= \hat{F}_{ij kk}(\rho, v_i, T, S_{\langle ij \rangle}, q_i).
 \end{aligned} \tag{1.43}$$

To obtain the constitutive equations, Grad proposed to expand the distribution function f around f_E , that is, the distribution function at the local equilibrium state, by the Hermit polynomial. Then f is expressed as

$$f = \left(a + a_i \frac{\partial}{\partial c_i} + a_{ij} \frac{\partial^2}{\partial c_i \partial c_j} + a_{ijk} \frac{\partial^3}{\partial c_i \partial c_j \partial c_k} + \dots \right) f_E, \quad (1.44)$$

where a, a_i, a_{ij}, \dots are the function of x_i , and t . By using (1.38), we can rewrite this distribution function as follows

$$f = f_E \left(a - a_i \frac{m}{k_B T} C_i + a_{ij} \left(\frac{m}{k_B T} \right)^2 \left(C_i C_j - \frac{k_B T}{m} \delta_{ij} \right) - a_{ijk} \left(\frac{m}{k_B T} \right)^3 \left(C_i C_j C_k - \frac{k_B T}{m} (\delta_{ij} C_k + \delta_{jk} C_i + \delta_{ki} C_j) \right) + \dots \right). \quad (1.45)$$

By using this distribution function, the average of a function $\psi(\mathbf{x}, \mathbf{c}, t)$ around local equilibrium is obtained as

$$\bar{\psi} = a \bar{\psi}^E - a_i \frac{\partial \psi^E}{\partial c_i} + a_{ij} \frac{\partial^2 \psi^E}{\partial c_i \partial c_j} - a_{ijk} \frac{\partial^3 \psi^E}{\partial c_i \partial c_j \partial c_k} + \dots, \quad (1.46)$$

where the notation E denotes the integration by the Maxwell distribution $\bar{\psi}^E = \frac{m}{\rho} \int \psi f_E d\mathbf{c}$. By putting $\psi = 1, c_i, -\rho C_i C_j, \rho \frac{1}{2} C^2 C_i$ in Eq. (1.46), we obtain the expression of the coefficients a, a_i, a_{ij}, a_{ijk} as the functions of $\rho, v_i, T, S_{\langle ij \rangle}, q_j$ as follows:

$$a = 1, a_i = 0, a_{ii} = 0, a_{ij} = -\frac{1}{2\rho} S_{\langle ij \rangle}, a_{ikk} = -\frac{1}{3\rho} q_i. \quad (1.47)$$

To close the system within 13-moment we ignore $a_{\langle ij \rangle k}$ and the higher order tensors in the expansion of the distribution function. Then we obtain the following distribution function from Eqs. (1.45) and (1.47).

$$f_G = f_E \left(1 - \frac{1}{2\rho} S_{\langle ij \rangle} \left(\frac{m}{k_B T} C_i C_j - \delta_{ij} \right) - \frac{1}{p} \frac{m}{k_B T} q_i C_i \left(1 - \frac{1}{5} \frac{m C^2}{k_B T} \right) \right), \quad (1.48)$$

where f_G is called Grad distribution function. When we exploit the Grad distribution function instead of the original one in (1.22), we can express constitutive quantities (1.43) with 13-moment. Then we obtain

$$\hat{F}_{\langle ij \rangle k} = \frac{2}{5} \left(q_i \delta_{jk} + q_j \delta_{ik} - \frac{2}{3} q_k \delta_{ij} \right), \quad (1.49)$$

$$\hat{F}_{iijk} = 5p \frac{k_B T}{m} \delta_{jk} - \frac{7}{2} S_{\langle pq \rangle} (\delta_{jp} \delta_{kq} + \delta_{jq} \delta_{kp}). \quad (1.50)$$

By using these constitutive equations we obtain the closed field equations.

$$\begin{aligned}
 \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} &= 0, \\
 \frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho v_i v_j + p \delta_{ij} - S_{\langle ij \rangle}) &= 0, \\
 \frac{\partial (\rho \varepsilon + \frac{\rho}{2} v^2)}{\partial t} + \frac{\partial}{\partial x_j} \left[\left(\rho \varepsilon + \frac{\rho}{2} v^2 \right) v_j + (p \delta_{ij} - S_{\langle ij \rangle}) v_i + q_j \right] &= 0, \\
 \dot{S}_{\langle ij \rangle} + S_{\langle ij \rangle} \frac{\partial v_n}{\partial x_n} - \frac{2}{5} \frac{\partial}{\partial x_n} (q_n \delta_{ij} + q_i \delta_{jn} + q_j \delta_{in}) - 2p \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + 2S_{\langle n \langle i} \rangle} \frac{\partial v_{j \rangle}}{\partial x_n} &= -\frac{3}{2} \rho \mathcal{B} S_{\langle ij \rangle}, \quad (1.51) \\
 \dot{q}_i + q_i \frac{\partial v_n}{\partial x_n} + \frac{1}{2} \frac{\partial}{\partial x_n} \left(5p \frac{k_B T}{m} \delta_{in} - \frac{7}{2} S_{\langle pq \rangle} \frac{k_B T}{m} (\delta_{in} \delta_{pq} + \delta_{ip} \delta_{nq} + \delta_{np} \delta_{iq}) \right), \\
 - \frac{1}{\rho} (-p \delta_{ik} + S_{\langle ik \rangle}) \frac{\partial (-p \delta_{kn} + S_{\langle kn \rangle})}{\partial x_n} + \frac{3p}{2\rho} \frac{\partial (-p \delta_{in} + S_{\langle in \rangle})}{\partial x_n} \\
 + q_n \frac{\partial v_i}{\partial x_n} + \frac{2}{5} q_i \frac{\partial v_n}{\partial x_n} + \frac{4}{5} q_n \frac{\partial v_{\langle i}}{\partial x_n} &= -\rho \mathcal{B} q_i.
 \end{aligned}$$

In a similar way, the entropy density s and entropy flux φ_i are also expressed by using the Grad distribution function.

$$s = \frac{k}{m} \ln \frac{T^{3/2}}{\rho} + \zeta - \frac{S_{\langle ij \rangle} S_{\langle ij \rangle}}{4p\rho T} - \frac{q_i q_i}{5p^2 T}, \quad (1.52)$$

$$\varphi_i = \frac{q_i}{T} + \frac{2}{5pT} S_{\langle ij \rangle} q_j. \quad (1.53)$$

Thus we obtain the closed field equations and also the expression of entropy density by adopting the closure by the Grad moment method.

Maximum entropy principle

Instead of the Grad moment method, we introduce the another closure which is based on maximum entropy principle. This method has shown its usefulness not only kinetic theory but also other fields such as information theory.

The maximum entropy principle states that the actual distribution function f is the one which maximizes the entropy under the system characterized by N -fields $\mathbf{F}^{(N)}$ with balance equation (1.26)₁. We consider the case that the entropy density ($h = \rho s$) is expressed by the following general form;

$$h = \int \psi(f) d\mathbf{c}, \quad (1.54)$$

instead of the expression (1.32). This requirement is expressed as the condition that the following function is maximum

$$\mathcal{L}(f, \Lambda^\alpha) = \int \psi(f) d\mathbf{c} + \Lambda^{(N)} \cdot \left(\mathbf{F}^{(N)} - m \int c_\alpha f d\mathbf{c} \right), \quad (1.55)$$

where Λ^α is the Lagrange multipliers and $\mathbf{\Lambda}^{(N)}$ is the vector composed of Λ^α . Therefore first variation of \mathcal{L} with respect to f must be 0, then we obtain

$$\int \left(\frac{d\psi}{df} - m\mathbf{\Lambda}^{(N)} \cdot \mathbf{\Phi}^{(N)} \right) \delta f d\mathbf{c} = 0, \quad (1.56)$$

and this indicates

$$\frac{d\psi}{df} = m\mathbf{\Lambda}^{(N)} \cdot \mathbf{\Phi}^{(N)}. \quad (1.57)$$

Moreover, from this, we conclude that f is a function of

$$\chi = m\mathbf{\Lambda}^{(N)} \cdot \mathbf{\Phi}^{(N)}, \quad (1.58)$$

and $\psi(f)$ has the form

$$\psi(f) = \chi f - \int f d\chi. \quad (1.59)$$

In particular, in the case that the entropy is expressed by (1.32), i.e, $\psi = -k_B f \left(\ln \frac{f}{y} - 1 \right)$, we obtain the distribution function

$$f = y \exp \left(-\frac{1}{k_B} \tilde{\mathbf{\Lambda}} \cdot \mathbf{\Phi} \right), \quad (1.60)$$

where $\tilde{\mathbf{\Lambda}} = \mathbf{\Lambda} - \mathbf{\Lambda}_E$. The distribution function f is expanded in the neighborhood of local equilibrium, then it can be approximated as

$$f = f_E \left(1 - \frac{1}{k_B} \tilde{\mathbf{\Lambda}}^\alpha \psi_\alpha \right), \quad (1.61)$$

where f_E denotes the Maxwell distribution function (1.38). By substituting Eqs.(1.61) into (1.26), we obtain the Lagrange multipliers

$$\mathbf{F}^{(N)} - \mathbf{F}_E^{(N)} = \int f_E(x_i, c_i, t) \left(-\frac{\chi}{k_B} \right) d\mathbf{c}. \quad (1.62)$$

Inserting the Lagrange multipliers which are the solutions of (1.61) and (1.62) into (1.26)_{2,3}, we obtain the constitutive equations by

$$\begin{aligned} \mathbf{F}_i^{(N)} &= m \int c_i \mathbf{\Phi} \left(1 - \frac{m}{k_B} \tilde{\mathbf{\Lambda}} \cdot \mathbf{\Phi} \right) f_E d\mathbf{c}, \\ \mathbf{P}^{(N)} &= m \int \mathbf{\Phi} S \left(\left(1 - \frac{m}{k_B} \tilde{\mathbf{\Lambda}} \cdot \mathbf{\Phi} \right) f_E \right) d\mathbf{c}. \end{aligned} \quad (1.63)$$

Here, we have seen the case of rarefied monatomic gases. Recently this method exploited in the case of rarefied polyatomic gases [13].

1.2.3 Fluctuation

The brief history of fluctuating hydrodynamics

In 1827 the botanist Robert Brown observed the random motion of small pollen grains of the plant suspended in the water, the so-called Brownian motion. This is the starting point of the study of fluctuation. The theoretical study of fluctuation starts from consideration of Brownian motion by Albert Einstein in 1905 and Marian Smoluchowski in 1906. These studies and the experimental study which checked these theories by Jean Baptiste Perrin in 1909 showed the existence of atoms. Moreover, in 1908, Paul Langevin made up a phenomenological governing equation of a Brownian particle.

In the field of non-equilibrium thermodynamics, Onsager derived the reciprocal relation based on the principle of microscopic reversibility and regression hypothesis. As we mentioned before this relation is the fundamental of TIP. Based on TIP, Lev Davidovich Landau and Evgeny Mikhailovich Lifshitz developed fluctuating-hydrodynamic theory for viscous, heat-conducting fluids with Navier-Stokes Fourier laws in 1950's [86, 24, 87]. In order to incorporate thermal fluctuations into hydrodynamics, they introduced additional stochastic flux terms into the constitutive equations for the viscous stress and heat flux by applying the fluctuation-dissipation theorem by Melville Saul Green, Fujio Nakano and Ryogo Kubo [25, 26, 27, 28], which determine the speed of relaxation from the fluctuation of equilibrium state. See also reviews [29, 30, 31].

Nowadays the Landau-Lifshitz (LL) theory attracts much attention, especially, as the basic theory for microflows and nanoflows, which may play an important role, for example, in the fields of nano-technology [32, 33] and molecular biology [34, 35]. Numerical analysis of the fluctuations by using the theory have been made extensively [36, 37, 38, 39, 40, 41, 42]. The fluctuating-hydrodynamic approach can also contribute to the study of fluctuations in nonequilibrium states [31, 43, 44].

Landau-Lifshitz theory

Here we summarize the Landau-Lifshitz(LL) theory [86, 24, 87].

Let us consider the general case, that is, the case that the entropy production Σ is given by

$$\Sigma = -\dot{x}_a X_a, \tag{1.64}$$

where x_a is the variables which characterize the system and X_a is the coefficients corresponding to x_a . We assume the linear constitutive equations

$$\dot{x}_a = C_{ab} X_b, \tag{1.65}$$

where C_{ab} is the phenomenological coefficients.

We introduce the Gaussian white noise f_a into the constitutive equation in such a way that

$$\dot{x}_a = -C_{ab}X_b + f_a. \quad (1.66)$$

The average and the correlations of f_a are given by

$$\begin{aligned} \langle f_a(\mathbf{x}, t) \rangle &= 0, \\ \langle f_a(\mathbf{x}, t) f_b(\mathbf{x}', t') \rangle &= k_B(C_{ab} + C_{ba})\delta(\mathbf{x} - \mathbf{x}')\delta(t - t'), \end{aligned} \quad (1.67)$$

where the brackets $\langle \ \rangle$ in the left-hand side stand for the statistical average at the reference equilibrium state.

Let us return to the NSF theory, and recall (1.9). In this case we have

$$\dot{x}_i = \{S_{ij}, q_i\}, \quad X_i = \left\{ -\frac{1}{T} \frac{\partial v_{(i}}{\partial x_{j)}} , \frac{1}{T^2} \frac{\partial T}{\partial x_i} \right\}. \quad (1.68)$$

The random forces are introduced as follows:

$$S_{\langle ij \rangle} = 2\mu \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + f_{\langle ij \rangle}, \quad \Pi = \nu \frac{\partial v_n}{\partial x_n} + f_{ii}, \quad q_i = -\kappa \frac{\partial T}{\partial x_i} + g_i, \quad (1.69)$$

and

$$\langle f_{ik}(\mathbf{x}, t) f_{lm}(\mathbf{x}', t') \rangle = 2T \left(\mu(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl}) + \left(\nu - \frac{2}{3}\mu \right) \delta_{ik}\delta_{lm} \right) \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'), \quad (1.70)$$

$$\langle g_i(\mathbf{x}, t) g_j(\mathbf{x}', t') \rangle = 2\kappa T^2 \delta_{ij} \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \quad (1.71)$$

We obtained the method how to introduce the random forces into the continuum dynamics and clarified the its properties. However the present procedure is based on TIP. Therefore the present theory cannot be applied to strongly non-equilibrium.

1.3 Extended thermodynamics

In the previous section, we have briefly summarized the non-equilibrium physics, in particular, TIP, kinetic theory based on Boltzmann equation and LL, and made clear the problems of each approaches. To overcome these problems, through the many studies for non-equilibrium thermodynamics theory, there appeared the new theory; extended thermodynamics (ET) [8, 9] from the view point of continuum dynamics by Ingo Müller. ET is a phenomenological field theory capable for description of non-equilibrium phenomena with steep gradients and rapid changes of physical variables. Therefore this theory may be suitable for the out of local equilibrium, while TIP relies essentially on the assumption of local equilibrium. In this respect, the validity range of ET is wider than that of TIP. Moreover, ET can predict finite speeds

of disturbances as its basic system of equations is hyperbolic. On the contrary, TIP predicts infinite speeds of disturbances because of its parabolic character.

In the early stage of ET, a theory for rarefied monatomic gases was developed [8, 45]. For example, the ET theory of rarefied monatomic gases with 13 fields is a theory of 13 independent fields; mass density, momentum density, momentum flux, and energy flux. By the use of the proper constitutive equations compatible with the universal physical principles, a closed system of field equations is obtained. A remarkable point is that the constitutive equations can be explicitly determined from the equilibrium caloric and thermal equations of state. It is shown that the NSF theory comes out as a limiting case of ET through carrying out the Maxwellian iteration [46]. The closed system of field equations is totally consistent with the counterpart system of the moments in the kinetic theory which we have already seen in Chapter 1, Section 2.2.

In the following part we explain the formal structure of ET of rarefied monatomic gases described above, and as a typical case, we will see the 13 fields case.

1.3.1 Independent variables and balance equations

Let us consider a one-component fluid. In the NSF theory the system is characterized by 5 slow variables; the mass density, velocity and temperature. On the other hand, ET adopts fast variables in addition to slow variables as independent fields. Here we consider N independent fields \mathbf{u} case. The closed field equations are based on the balance equations for N densities; $\mathbf{F} = (F, F_{k_1}, \dots, F_{k_1 k_2 \dots k_n}, \dots)$. Corresponding to Eq. (1.3), we symbolize the non-convective fluxes and productions as $\mathbf{I} = (0, I_{ik_1}, \dots, I_{ik_1 k_2 \dots k_n}, \dots)$ and $\mathbf{P} = (0, 0, \dots, P_{k_1 k_2 \dots k_n}, \dots)$, respectively. We can summarize these symbols in Table 1.5 corresponding to Table 1.2.1.

Table 1.5: The density, non-convective flux and production for the balance equations of ET.

Ψ	$\rho\psi$ (density)	ϕ (non-convective flux)	$\rho\pi$ (production)
Mass	$F \equiv \rho$	0	0
Momentum	$F_{k_1} \equiv \rho v_i$	I_{ik_1}	0
Second order tensor	$F_{k_1 k_2}$	$I_{ik_1 k_2}$	$P_{\langle ij \rangle}$
\vdots	\vdots	\vdots	\vdots
N -th order tensor	$F_{k_1 k_2 \dots k_n}$	$I_{ik_1 k_2 \dots k_n}$	$P_{k_1 k_2 \dots k_n}$

When we put the elements of Table 1.5 on (1.3), the balance equation for each densities are obtained as follows:

$$\begin{aligned}
 \frac{\partial F}{\partial t} + \frac{\partial F_i}{\partial x_i} &= 0, \\
 \frac{\partial F_{k_1}}{\partial t} + \frac{\partial F_{ik_1}}{\partial x_i} &= 0, \\
 \frac{\partial F_{k_1 k_2}}{\partial t} + \frac{\partial F_{ik_1 k_2}}{\partial x_i} &= P_{(k_1 k_2)}, \\
 \frac{\partial F_{k_1 k_2 k_3}}{\partial t} + \frac{\partial F_{ik_1 k_2 k_3}}{\partial x_i} &= P_{k_1 k_2 k_3}, \\
 &\vdots \\
 \frac{\partial F_{k_1 k_2 \dots k_n}}{\partial t} + \frac{\partial F_{ik_1 k_2 \dots k_n}}{\partial x_i} &= P_{k_1 k_2 \dots k_n}, \\
 &\vdots,
 \end{aligned} \tag{1.72}$$

where $F_{ik_1 k_2 \dots k_n} = F_{k_1 k_2 \dots k_n} v_i + I_{ik_1 k_2 \dots k_n}$ is the flux of $F_{k_1 k_2 \dots k_n}$. The first two equations and the trace part of the third equation represent the conservation laws of mass, momentum and energy, respectively. It is noticeable that there are the hierarchy structure of the system with the following two features; (i) the tensorial rank of the equations increases one by one starting from the mass balance equation, and (ii) the flux in one equation becomes the density in the next equation. Such hierarchy is dictated by the moment equations (1.25) in the kinetic theory of monatomic gases. Moreover there is no dynamics pressure, and as a consequence $F_{ii} (= \rho v^2 + 3p)$ is, except for a factor 1/2, equal to the energy density, $\rho v^2/2 + \rho \varepsilon$, and therefore $3p = 2\rho \varepsilon$, where v_i , ε and p are the velocity, specific internal energy density and pressure, respectively. Therefore ET with this hierarchy structure is valid only for *rarefied monatomic* gases.

1.3.2 Constitutive theory of ET

For convenience, we write the balance equations (1.72) as the vector form:

$$\frac{\partial \mathbf{F}}{\partial t} + \frac{\partial \mathbf{F}_i}{\partial x_i} = \mathbf{P}, \tag{1.73}$$

where the components of \mathbf{F} is composed of densities and \mathbf{F}_i and \mathbf{P} are the corresponding fluxes and productions.

When the hierarchy of the basic equations are truncated at some hierarchy level, we need, as a closure procedure, constitutive equations for the quantities that are not independent field variables. In ET, we assume that such quantities depend locally on the densities:

$$\mathbf{F} = \mathbf{F}(\mathbf{u}), \quad \mathbf{F}_i = \mathbf{F}_i(\mathbf{u}), \quad \mathbf{P} = \mathbf{P}(\mathbf{u}). \tag{1.74}$$

The constitutive theory of ET can be summarized that the functional forms of constitutive equations are severely restricted by the universal physical principles;

- Entropy principle
- Material frame indifference principle

In particular the entropy principle is composed of the following two requirements:

1. The entropy inequality

This inequality means that

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} = \Sigma \geq 0, \quad (1.75)$$

where h , h_i and Σ are the entropy density entropy flux and entropy production, respectively. We require this inequality to hold for all thermodynamic processes. Here h , h_i and Σ are constitutive quantities

$$h = h(\mathbf{u}), \quad h_i = h_i(\mathbf{u}), \quad \Sigma = \Sigma(\mathbf{u}). \quad (1.76)$$

2. The convexity of entropy density

This requirement can be expressed that

$$\frac{\partial^2 h}{\partial \mathbf{u} \partial \mathbf{u}} \text{ is negative definite.} \quad (1.77)$$

Most of the constitutive equations are fully prescribed by the equilibrium properties of gases [8, 45]. We study the details of each requirement in following subsections.

Entropy inequality The requirement that the entropy inequality hold for all solutions of the balance equations can be expressed by the following in equality with Lagrange multipliers $\mathbf{\Lambda}$:

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} - \mathbf{\Lambda} \cdot \left(\frac{\partial \mathbf{F}}{\partial t} + \frac{\partial \mathbf{F}_i}{\partial x_i} - \mathbf{P} \right) \geq 0. \quad (1.78)$$

By considering the constitutive equations (1.74) and (1.76), Eq. (1.78) are written as follows:

$$\left(\frac{\partial h}{\partial \mathbf{u}} - \mathbf{\Lambda} \cdot \frac{\partial \mathbf{F}}{\partial \mathbf{u}} \right) \frac{\partial \mathbf{u}}{\partial t} + \left(\frac{\partial h_i}{\partial \mathbf{u}} - \mathbf{\Lambda} \cdot \frac{\partial \mathbf{F}_i}{\partial \mathbf{u}} \right) \frac{\partial \mathbf{u}}{\partial x_i} + \mathbf{\Lambda} \cdot \mathbf{P} \geq 0. \quad (1.79)$$

This inequality must be hold for all $\frac{\partial \mathbf{u}}{\partial t}$ and $\frac{\partial \mathbf{u}}{\partial x_i}$, therefore the coefficients of these must be 0. This means that there must be exist the following relation:

$$\frac{\partial h}{\partial \mathbf{u}} = \mathbf{\Lambda} \cdot \frac{\partial \mathbf{F}}{\partial \mathbf{u}}, \quad \frac{\partial h_i}{\partial \mathbf{u}} = \mathbf{\Lambda} \cdot \frac{\partial \mathbf{F}_i}{\partial \mathbf{u}}. \quad (1.80)$$

These relations can be written as

$$dh = \mathbf{\Lambda} \cdot d\mathbf{F}, \quad dh_i = \mathbf{\Lambda} \cdot d\mathbf{F}_i. \quad (1.81)$$

Then, the residual entropy inequality is expressed as follows:

$$\Sigma = \mathbf{\Lambda} \cdot \mathbf{P} \geq 0 \quad (1.82)$$

Without loss of generality we can choose $\mathbf{u} = \mathbf{F}$, and then, Eqs.(1.80) are rewritten as follows:

$$\frac{\partial h}{\partial \mathbf{u}} = \mathbf{\Lambda}. \quad (1.83)$$

This indicates that $\frac{\partial^2 h}{\partial \mathbf{u} \partial \mathbf{u}} = \frac{\partial \mathbf{\Lambda}}{\partial \mathbf{u}}$, therefore $\frac{\partial \mathbf{\Lambda}}{\partial \mathbf{u}}$ is symmetric and negative definite from the requirement convexity of entropy density (1.77). Then we can invert the independent variables from \mathbf{u} to $\mathbf{\Lambda}$ is locally and globally, and we can take $\mathbf{\Lambda}$ as independent variables.

For the simple calculation we introduce the new potentials

$$h' = \mathbf{\Lambda} \cdot \mathbf{F} - h, \quad h'_i = \mathbf{\Lambda} \cdot \mathbf{F}_i - h_i. \quad (1.84)$$

h' is the Legendre transform of h because of the fact that h is a concave function of \mathbf{F} and Eq. (1.83). The relations (1.81) between h and \mathbf{F} or h_i and \mathbf{F}_i are converted to the relations with respect to h' , h'_i and $\mathbf{\Lambda}$.

$$dh' = \mathbf{F} \cdot d\mathbf{\Lambda}, \quad dh'_i = \mathbf{F}_i \cdot d\mathbf{\Lambda}. \quad (1.85)$$

Therefore \mathbf{F} and \mathbf{F}_i are expressed as follows

$$\mathbf{F} = \frac{\partial h'}{\partial \mathbf{\Lambda}}, \quad \mathbf{F}_i = \frac{\partial h'_i}{\partial \mathbf{\Lambda}}. \quad (1.86)$$

From the integrability of h' we can find that

$$\frac{\partial \mathbf{F}}{\partial \mathbf{\Lambda}} \text{ is symmetric.} \quad (1.87)$$

Furthermore, by considering Eq. (1.86), the entropy density and entropy flux are expressed as the function of $\mathbf{\Lambda}$.

$$h = \mathbf{\Lambda} \cdot \frac{\partial h'}{\partial \mathbf{\Lambda}} - h', \quad h_i = \mathbf{\Lambda} \cdot \frac{\partial h'_i}{\partial \mathbf{\Lambda}} - h'_i. \quad (1.88)$$

Convexity of entropy principle By using Eq. (1.86) the balance equations (1.73) can be written with the Lagrange multipliers as

$$\frac{\partial^2 h'}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \cdot \frac{\partial \mathbf{\Lambda}}{\partial t} + \frac{\partial^2 h'_i}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \cdot \frac{\partial \mathbf{\Lambda}}{\partial x_i} = \mathbf{P}. \quad (1.89)$$

This system is symmetric which obtained by choosing the Lagrange multipliers as the independent fields. In this sense, the Lagrange multipliers show their importance, and these are called *main fields* [47].

This system is symmetric hyperbolic when $\frac{\partial^2 h'}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}}$ is definite, and this is satisfied by the requirement of entropy inequality. In other words, the system is symmetric hyperbolic if the following inequality is satisfied

$$\frac{\partial^2 h'}{\partial \mathbf{\Lambda} \partial \mathbf{\Lambda}} \delta \mathbf{\Lambda} \delta \mathbf{\Lambda} = \delta \mathbf{\Lambda} \delta \mathbf{u} = \frac{\partial^2 h}{\partial \mathbf{u} \partial \mathbf{u}} \delta \mathbf{u} \delta \mathbf{u} < 0. \quad (1.90)$$

The symmetric hyperbolic system has good mathematical properties, that is, the well-posedness of Cauchy problems, i.e. the existence, uniqueness and continuous dependence of the solutions on the data.

Main subsystem

We split the main fields (n -vector) $\mathbf{\Lambda}$ into m -vector \mathbf{L} and $(n - m)$ -vector \mathbf{l} . Then the system (1.89) is split into the two systems, that is,

$$\frac{\partial^2 h'(\mathbf{L}, \mathbf{l})}{\partial \mathbf{L} \partial \mathbf{L}} \cdot \frac{\partial \mathbf{L}}{\partial t} + \frac{\partial^2 h'_i(\mathbf{L}, \mathbf{l})}{\partial \mathbf{L} \partial \mathbf{L}} \cdot \frac{\partial \mathbf{L}}{\partial x_i} = \mathbf{R}(\mathbf{L}, \mathbf{l}), \quad (1.91)$$

$$\frac{\partial^2 h'(\mathbf{L}, \mathbf{l})}{\partial \mathbf{l} \partial \mathbf{l}} \cdot \frac{\partial \mathbf{l}}{\partial t} + \frac{\partial^2 h'_i(\mathbf{L}, \mathbf{l})}{\partial \mathbf{l} \partial \mathbf{l}} \cdot \frac{\partial \mathbf{l}}{\partial x_i} = \mathbf{r}(\mathbf{L}, \mathbf{l}), \quad (1.92)$$

where \mathbf{R} and \mathbf{r} are the corresponding productions to \mathbf{L} and \mathbf{l} , respectively. Let us consider the case that $\mathbf{l} = \mathbf{l}^* = \text{const}$ ¹. Then the remaining system is determined by (1.91)₁, that is,

$$\frac{\partial^2 h'(\mathbf{L}, \mathbf{l}^*)}{\partial \mathbf{L} \partial \mathbf{L}} \cdot \frac{\partial \mathbf{L}}{\partial t} + \frac{\partial^2 h'_i(\mathbf{L}, \mathbf{l}^*)}{\partial \mathbf{L} \partial \mathbf{L}} \cdot \frac{\partial \mathbf{L}}{\partial x_i} = \mathbf{R}(\mathbf{L}, \mathbf{l}^*). \quad (1.93)$$

This system is called main subsystem of the system (1.89). The solutions of the main subsystem satisfy a balance equation of subentropy:

$$\frac{\partial \bar{h}}{\partial t} + \frac{\partial \bar{h}_i}{\partial x_i} = \bar{\Sigma}, \quad (1.94)$$

where subentropy $\bar{h}(\mathbf{\Lambda}, \mathbf{l}^*)$, subentropy flux $\bar{h}_i(\mathbf{\Lambda}, \mathbf{l}^*)$ and subentropy production $\bar{\Sigma}(\mathbf{\Lambda}, \mathbf{l}^*)$ are related to the restrictions of the entropy $h(\mathbf{\Lambda}, \mathbf{l}^*)$, entropy flux $h_i(\mathbf{\Lambda}, \mathbf{l}^*)$ and entropy production $\Sigma(\mathbf{\Lambda}, \mathbf{l}^*)$ of the full system through

$$\begin{aligned} \bar{h}(\mathbf{\Lambda}, \mathbf{l}^*) &= h(\mathbf{\Lambda}, \mathbf{l}^*) - \mathbf{l}^* \cdot \left(\frac{\partial h'(\mathbf{\Lambda}, \mathbf{l})}{\partial \mathbf{l}} \right)_{\mathbf{l}=\mathbf{l}^*}, \\ \bar{h}_i(\mathbf{\Lambda}, \mathbf{l}^*) &= h_i(\mathbf{\Lambda}, \mathbf{l}^*) - \mathbf{l}^* \cdot \left(\frac{\partial h'_i(\mathbf{\Lambda}, \mathbf{l})}{\partial \mathbf{l}} \right)_{\mathbf{l}=\mathbf{l}^*}, \\ \bar{\Sigma}(\mathbf{\Lambda}, \mathbf{l}^*) &= \mathbf{L} \cdot \mathbf{P}(\mathbf{\Lambda}, \mathbf{l}^*). \end{aligned} \quad (1.95)$$

¹The constraint for \mathbf{l} is generalized to the case that \mathbf{l} depends on t and x_i in [48].

These relations are come from Eq. (1.91) and the definition of \bar{h} and \bar{h}_i :

$$\begin{aligned}\bar{h}(\mathbf{\Lambda}, \mathbf{l}^*) &= -h'(\mathbf{\Lambda}, \mathbf{l}^*) + \mathbf{L} \cdot \frac{\partial h'(\mathbf{\Lambda}, \mathbf{l}^*)}{\partial \mathbf{L}}, \\ \bar{h}_i(\mathbf{\Lambda}, \mathbf{l}^*) &= -h'_i(\mathbf{\Lambda}, \mathbf{l}^*) + \mathbf{L} \cdot \frac{\partial h'_i(\mathbf{\Lambda}, \mathbf{l}^*)}{\partial \mathbf{L}}.\end{aligned}\tag{1.96}$$

These definition of subentropy density, subentropy flux and subentropy production are equivalent to the relation (1.88) and (1.82) for the full system, respectively. The subentropy is convex, therefore the main subsystem is symmetric hyperbolic.

Moreover it has been proved that there are the following relations between characteristic speeds of full system λ and of subsystem $\bar{\lambda}$:

$$\begin{aligned}\lambda_{\max}(\mathbf{\Lambda}, \mathbf{l}^*, \vec{n}) &\geq \bar{\lambda}_{\max}(\mathbf{\Lambda}, \mathbf{l}^*, \vec{n}), \\ \lambda_{\min}(\mathbf{\Lambda}, \mathbf{l}^*, \vec{n}) &\leq \bar{\lambda}_{\min}(\mathbf{\Lambda}, \mathbf{l}^*, \vec{n}),\end{aligned}\tag{1.97}$$

where $\lambda_{\max} = \max_{k=1,2,\dots,n} \lambda^{(k)}$, $\bar{\lambda}_{\max} = \max_{k=1,2,\dots,m} \bar{\lambda}^{(k)}$, $\lambda_{\min} = \min_{k=1,2,\dots,n} \lambda^{(k)}$, $\bar{\lambda}_{\min} = \min_{k=1,2,\dots,m} \bar{\lambda}^{(k)}$ and \vec{n} is a unit normal of front.

Galilean invariance

We require that the constitutive functions do not changed by the change of frame. Such invariance makes clear the velocity independence of constitutive quantities.

In non-relativistic case, there are three types of transformation of frame:

$$\begin{aligned}\text{Rotation transformation:} & \quad x_i^* = O_{ij}x_j, & t^* &= t, \\ \text{Galilean transformation:} & \quad x_i^* = O_{ij}x_j + c_it, & t^* &= t, \\ \text{Euclidean transformation:} & \quad x_i^* = O_{ij}(t)x_j + b_i(t), & t^* &= t.\end{aligned}\tag{1.98}$$

If a quantity which the relation between before and after Galilean or Euclidean transformation of its are given by

$$T_{i_1 i_2 \dots i_A} = O_{i_1 j_1} O_{i_2 j_2} \dots O_{i_A j_A} T_{j_1 j_2 \dots j_A},\tag{1.99}$$

such quantity is called Galilean or objective tensor, respectively. The velocity is transformed according to the rules:

$$\begin{aligned}\text{Rotation transformation:} & \quad v_i^* = O_{ij}v_j, \\ \text{Galilean transformation:} & \quad v_i^* = O_{ij}v_j + c_i, \\ \text{Euclidean transformation:} & \quad v_i^* = O_{ij}(t)v_j + \dot{O}_{ij}(t)v_j + \dot{b}_i(t).\end{aligned}\tag{1.100}$$

Therefore the velocity is not Galilean or objective tensor.

In general the fields \mathbf{u} may be composed by the velocity v_i and remaining $(N - 3)$ vector \mathbf{w} which are assumed to be Galilean tensors. Then we may write

$$\mathbf{F} = \mathbf{F}(\mathbf{v}, \mathbf{w}), \quad \mathbf{F}_i = \mathbf{F}_i(\mathbf{v}, \mathbf{w}), \quad \mathbf{P} = \mathbf{P}(\mathbf{v}, \mathbf{w}), \quad (1.101)$$

$$h = h(\mathbf{v}, \mathbf{w}), \quad h_i = h_i(\mathbf{v}, \mathbf{w}), \quad \Sigma = \Sigma(\mathbf{v}, \mathbf{w}). \quad (1.102)$$

We can split the fluxes \mathbf{F}^i and h_i into convective and non-convective flux

$$\mathbf{F}_i = \mathbf{F}v_i + \mathbf{I}_i, \quad h = hv_i + \varphi_i, \quad (1.103)$$

where \mathbf{I} and φ_i are the non-convective flux and entropy flux, respectively, and the functions of \mathbf{v}, \mathbf{w} .

Let us summarize the result of the requirement of the Galilean invariance for the system (1.73) and the entropy inequality (1.75) (see details in [49]). From the Galilean invariance for entropy inequality (1.75), we can eliminate the velocity dependence from h , φ_i and Σ , therefore

$$h = h(\mathbf{w}), \quad \varphi_i = \varphi_i(\mathbf{w}), \quad \Sigma = \Sigma(\mathbf{w}). \quad (1.104)$$

On the other hand, the Galilean invariance for the system (1.73) shows that there exist the following relations

$$\mathbf{F} = \mathbf{X}(\mathbf{v})\hat{\mathbf{F}}(\mathbf{w}), \quad \mathbf{I}_i = \mathbf{X}(\mathbf{v})\hat{\mathbf{I}}_i(\mathbf{w}), \quad \mathbf{P} = \mathbf{X}(\mathbf{v})\hat{\mathbf{P}}(\mathbf{w}), \quad (1.105)$$

where $\hat{\mathbf{F}}$, $\hat{\mathbf{I}}_i$ and $\hat{\mathbf{P}}$ are the Galilean tensor and called intrinsic variables. $\mathbf{X}(\mathbf{v})$ is a matrix composed of only \mathbf{v} . From the general theory we can proof that $\mathbf{X}(\mathbf{v})$ has the following properties:

$$\mathbf{X}(\mathbf{v}^{(1)} + \mathbf{v}^{(2)}) = \mathbf{X}(\mathbf{v}^{(1)})\mathbf{X}(\mathbf{v}^{(2)}) = \mathbf{X}(\mathbf{v}^{(2)})\mathbf{X}(\mathbf{v}^{(1)}), \quad \mathbf{X}(\mathbf{0}) = \mathbf{1}. \quad (1.106)$$

And these properties imply that the differential of $\mathbf{X}(\mathbf{v})$ are expressed by using constant matrices \mathbf{A}^r as follows:

$$\frac{\partial \mathbf{X}}{\partial v_r}(\mathbf{v}) = \mathbf{A}^r \mathbf{X}(\mathbf{v}) = \mathbf{X}(\mathbf{v})\mathbf{A}^r, \quad (1.107)$$

where

$$\mathbf{A}^r = \frac{\partial \mathbf{X}}{\partial v_r}(\mathbf{0}), \quad \mathbf{A}^r \mathbf{A}^s = \mathbf{A}^s \mathbf{A}^r. \quad (1.108)$$

Then we can conclude that $\mathbf{X}(\mathbf{v})$ is an exponential function of the components v_r with constant matrices \mathbf{A}^r as coefficients:

$$\mathbf{X}(\mathbf{v}) = e^{\mathbf{A}^r v_r} = \mathbf{1} + \mathbf{A}^r v_r + \frac{1}{2} \mathbf{A}^r \mathbf{A}^s v_r v_s + \cdots. \quad (1.109)$$

Therefore, when \mathbf{A}^r are known, we can obtain the explicit form of $\mathbf{X}(\mathbf{v})$.

By using Eq.(1.105), the balance equations (1.73) are written with intrinsic variables as follows:

$$\mathbf{X} \left\{ \frac{d\hat{\mathbf{F}}}{dt} + \hat{\mathbf{F}} \frac{\partial v_i}{\partial x_i} + \frac{\partial \hat{\mathbf{I}}_i}{\partial x_i} + \mathbf{A}^r \left\{ \hat{\mathbf{F}} \frac{dv_r}{dt} + \hat{\mathbf{I}}_i \frac{\partial v_r}{\partial x_i} \right\} - \hat{\mathbf{P}} \right\} = 0. \quad (1.110)$$

The fact that h , φ_i and Σ are the Galilean tensor restrict the entropy principle. With Eqs. (1.81) and (1.105), we obtain

$$dh = \hat{\mathbf{\Lambda}} \cdot d\hat{\mathbf{F}}, \quad d\varphi^i = \hat{\mathbf{\Lambda}} \cdot d\hat{\mathbf{I}}^i, \quad \hat{\mathbf{\Lambda}} \cdot \hat{\mathbf{P}} = \Sigma \geq 0, \quad (1.111)$$

and constraints

$$\hat{\mathbf{\Lambda}} \cdot \mathbf{A}^r \hat{\mathbf{F}} = 0, \quad \hat{\mathbf{\Lambda}} \cdot \mathbf{A}^r \hat{\mathbf{F}}^i = -\hat{h}' \delta_{ir}, \quad (1.112)$$

where $\hat{\mathbf{\Lambda}}$ is the matrices composed of Galilean tensor and defined with $\mathbf{\Lambda}$ as follows

$${}^t \mathbf{\Lambda} = {}^t \hat{\mathbf{\Lambda}} \mathbf{X}^{-1} = {}^t \hat{\mathbf{\Lambda}} \mathbf{X}(-v). \quad (1.113)$$

From Eqs. (1.105) and (1.113), we can find that the potentials h' and φ'_i (:the non-convective part of h'_i defined $h'_i = h'v_i + \varphi'_i$) are also the Galilean invariant, and expressed

$$h' = \hat{\mathbf{\Lambda}} \cdot \hat{\mathbf{F}} - h, \quad \varphi'_i = \hat{\mathbf{\Lambda}} \cdot \hat{\mathbf{I}}^i - \varphi_i. \quad (1.114)$$

Instead of (1.85) we obtain

$$\begin{aligned} dh' &= \hat{\mathbf{F}} \cdot d\hat{\mathbf{\Lambda}}, \quad d\varphi'_i = \hat{\mathbf{I}}^i \cdot d\hat{\mathbf{\Lambda}}, \\ \text{and } \hat{\mathbf{F}} &= \frac{\partial h'}{\partial \hat{\mathbf{\Lambda}}}, \quad \hat{\mathbf{I}}^i = \frac{\partial \varphi'_i}{\partial \hat{\mathbf{\Lambda}}}. \end{aligned} \quad (1.115)$$

By using (1.115)(or (1.111)) and (1.112), we can determine the constitutive equations.

Finally we consider the explicit form of \mathbf{X} . We require that both the system and its subsystem (with respect to \mathbf{F}) are Galilean invariant. Then, we can find that $\mathbf{X}(\mathbf{v})$ is lower triangular matrix. With (1.108), (1.109) this property, the Galilean invariance of balance equations (1.73) determine the elements of \mathbf{A} and \mathbf{X} by taking several steps of rescaling \mathbf{F} , \mathbf{I}_i and \mathbf{P} [49]. Here we show only the result.

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ v_{k_1} & \delta_{k_1}^{h_1} & 0 & 0 & 0 & 0 \\ v_{k_1} v_{k_2} & 2\delta_{(k_1}^{h_1} v_{k_2)} & 0 & 0 & 0 & 0 \\ v_{k_1} v_{k_2} v_{k_3} & 3\delta^{h_1} v_{(k_1} v_{k_2} v_{k_3)} & \delta_{k_1}^{h_1} \delta_{k_2}^{h_2} \delta_{k_3}^{h_3} & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ v_{k_1} v_{k_2} v_{k_3} \cdots v_{k_n} & \binom{n}{1} \delta^{h_1} v_{(k_1} v_{k_2} \cdots v_{k_n)} & \cdots & \delta_{k_1}^{h_1} \delta_{k_2}^{h_2} \cdots \delta_{k_n}^{h_n} & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ v_{k_1} v_{k_2} v_{k_3} \cdots v_{k_N} & \binom{N}{1} \delta^{h_1} v_{(k_1} v_{k_2} \cdots v_{k_N)} & \cdots & \delta_{k_1}^{h_1} \delta_{k_2}^{h_2} \cdots \delta_{k_n}^{h_n} v_{(k_{n+1}} \cdots v_{k_N)} & \cdots & \delta_{k_1}^{h_1} \delta_{k_1}^{h_1} \delta_{k_2}^{h_2} \cdots \delta_{k_N}^{h_N} \end{pmatrix}. \quad (1.116)$$

1.3.3 13 fields case

As a typical example, we show ET of rarefied monatomic gases with 13 independent fields [8, 45] ;

mass density	$F(= \rho),$
momentum density	$F_i,$
momentum flux	$F_{ij},$
energy flux	$F_{ppi}.$

By adopting the balance equations (Section 3.1) and the constitutive theory (Section 3.2), we obtain the closed field equations.

Balance equation

The system of field equations is of balance type such that

$$\begin{aligned}
\frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\
\frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\
\frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{\langle ij \rangle}, \\
\frac{\partial F_{ppi}}{\partial t} + \frac{\partial F_{ppik}}{\partial x_k} &= P_{ppi},
\end{aligned} \tag{1.117}$$

where F_{ijk} and F_{ppik} are the fluxes of F_{ij} and F_{ppi} , respectively, and $P_{\langle ij \rangle}$ and P_{ppi} are the productions with respect to F_{ij} and F_{ppi} , respectively. Here $P_{\langle ij \rangle}$ is a symmetric traceless tensor. The first two equations and the trace part of the third equation represent the conservation laws of mass, momentum and energy, respectively.

In order to close the system (1.117), we need constitutive equations for

$$F_{\langle ij \rangle k}, F_{ppik}, P_{\langle ij \rangle}, P_{ppi}. \tag{1.118}$$

In ET the constitutive quantities $F_{\langle ij \rangle k}, F_{ppik}, P_{\langle ij \rangle}$ and P_{ppi} are assumed to depend on F, F_i, F_{ij}, F_{ppi} locally and instantaneously.

$$\begin{aligned}
F_{\langle ij \rangle k} &= F_{\langle ij \rangle k}(F, F_i, F_{ij}, F_{ppi}), \\
F_{ppik} &= F_{ppik}(F, F_i, F_{ij}, F_{ppi}), \\
P_{\langle ij \rangle} &= P_{\langle ij \rangle}(F, F_i, F_{ij}, F_{ppi}), \\
P_{ppi} &= P_{ppi}(F, F_i, F_{ij}, F_{ppi}).
\end{aligned} \tag{1.119}$$

Entropy inequality

We recall the entropy inequality (1.75)

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} = \Sigma \geq 0.$$

This inequality is held for all thermodynamics processes, and h and h_i are also constitutive quantities.

$$h = h(F, F_i, F_{ij}, F_{ppi}), \quad h_i = h_i(F, F_i, F_{ij}, F_{ppi}). \quad (1.120)$$

The requirement of the entropy inequality can be expressed by introducing the Lagrange multipliers $\mathbf{\Lambda} = {}^T(\Lambda, \Lambda_i, \Lambda_{ij}, \Lambda_{ppi})$ as Eq. (1.78). Following the general theory, we obtain following relationship between the independent variables and Lagrange multipliers. Corresponding to Eq. (1.80), we obtain

$$\frac{\partial h}{\partial F} = \Lambda, \quad \frac{\partial h}{\partial F_i} = \Lambda_i, \quad \frac{\partial h}{\partial \Lambda_{ij}} = F_{ij}, \quad \frac{\partial h}{\partial \Lambda_{ppi}} = F_{ppi}, \quad (1.121)$$

$$\frac{\partial h_i}{\partial F_i} = \Lambda, \quad \frac{\partial h_i}{\partial F_{ik}} = \Lambda_k, \quad \frac{\partial h_i}{\partial F_{lmi}} = \Lambda_{lm}, \quad \frac{\partial h_i}{\partial F_{ppli}} = \Lambda_{ppi}. \quad (1.122)$$

Then the derivatives of the entropy density and flux are expressed as

$$\begin{aligned} dh &= \Lambda dF + \Lambda_i dF_i + \Lambda_{ij} dF_{ij} + \Lambda_{ppi} dF_{ppi}, \\ dh_i &= \Lambda dF_i + \Lambda_p dF_{pi} + \Lambda_{lm} dF_{lmi} + \Lambda_{ppli} dF_{qqli}. \end{aligned} \quad (1.123)$$

The residual inequality is that

$$\Sigma = \Lambda_{\langle ij \rangle} F_{\langle ij \rangle} + \Lambda_{ppi} F_{qqli} \geq 0. \quad (1.124)$$

Galilean invariance

The system (1.117) should be Galilean invariant. By Eqs (1.105) and (1.116), the velocity dependence of the quantities is made clear with the intrinsic tensors $\hat{\mathbf{F}} = {}^T(\rho, 0, m_{ij}, m_{ppi})$, $\hat{\mathbf{I}}^i = {}^T(0, m_{ij}, m_{ijk}, m_{ppik})$ and $\hat{\mathbf{P}} = {}^T(0, 0, P_{\langle ip \rangle}, P_i)$. Then we obtain the relations between original variables and intrinsic variables as follows:

$$\begin{aligned} F_{ij} &= m_{ij} + \rho v_i v_j, \\ F_{ijk} &= m_{ijk} + 3m_{(ij} v_k) + \rho v_i v_j v_k, \\ F_{ppij} &= m_{ppij} + 4m_{(ijp} v_p) + 6m_{(ip} v_p v_j) + \rho v^2 v_i v_j, \\ P_{ppi} &= P_i + 2P_{\langle ip \rangle} v_p, \end{aligned} \quad (1.125)$$

where $m_{ij}, m_{ijk}, m_{ppi}, P_{\langle ij \rangle}$ and P_i are the Galilean tensors. With Eq.(1.125) the balance equations (1.117) can be expressed as

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
 \rho \dot{v}_i + \frac{\partial m_{ij}}{\partial x_j} &= 0, \\
 \dot{m}_{ij} + m_{ij} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ijk}}{\partial x_k} + 2 \frac{\partial v_{(i}}{\partial x_k} m_{j)k} &= P_{\langle ij \rangle}, \\
 \dot{m}_{ppi} + m_{ppi} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ppik}}{\partial x_k} + 2 \frac{\partial v_p}{\partial x_k} m_{pik} + \frac{\partial v_i}{\partial x_k} m_{ppk} + 2m_{pi} \dot{v}_p + m_{pp} \dot{v}_i &= P_i.
 \end{aligned} \tag{1.126}$$

The first, second and trace part of third equations represent the conservation laws of mass, momentum and energy, respectively, $m_{\langle ij \rangle}, m_{ii}, m_{ppi}$ have the following conventional meaning:

$$\begin{aligned}
 \text{stress} & & t_{ij} (= -p\delta_{ij} + S_{\langle ij \rangle}) &= -m_{\langle ij \rangle}, \\
 \text{specific internal energy} & & \varepsilon &= \frac{1}{2\rho} m_{ii}, \\
 \text{heat flux} & & q_i &= \frac{1}{2} m_{ppi},
 \end{aligned} \tag{1.127}$$

where p and $S_{\langle ij \rangle}$ are the pressure and viscous stress, respectively. Therefore m_{ij} is symmetric because we deal with non-polar materials. As we mentioned before we consider the rarefied monatomic gases, therefore the dynamic pressure is 0, and there is the relation $3p = 2\rho\varepsilon$.

From the Galilean invariance of entropy inequality, we can remove the velocity from h and φ_i .

$$h = h(\rho, m_{ij}, m_{ppi}), \quad \varphi_k = \varphi_k(\rho, m_{ij}, m_{ppi}). \tag{1.128}$$

We have a one-by-one correspondence between constitutive equations $F, F_i, F_{ij}, F_{ijk}, F_{ppik}, h, h_i$ and intrinsic variables $\rho, v_i, m_{ij}, m_{ijk}, m_{ppik}, h, \varphi_i$. Therefore the constitutive equations (1.119) and (1.120) for $\psi' = \{m_{\langle ij \rangle k}, m_{iijk}, P_{\langle ij \rangle}, P_i, h, \varphi_i\}$ are rewritten as follows:

$$\psi' = \psi'(\rho, m_{ij}, m_{ppi}). \tag{1.129}$$

We can also make clear the velocity dependence of the Lagrange multipliers $\mathbf{\Lambda}$. By Eq. (1.113) we obtain the relation between $\mathbf{\Lambda} = {}^T(\Lambda, \Lambda_i, \Lambda_{ij}, \Lambda_{ppi})$ and Galilean tensors $\hat{\mathbf{\Lambda}} = {}^T(\lambda, \lambda_i, \lambda_{ij}, \lambda_{ppi})$ as follows:

$$\begin{aligned}
 \lambda &= \Lambda + \Lambda_i v_i + \Lambda_{ij} v_i v_j + \Lambda_{ppi} v^2 v_i, \\
 \lambda_i &= \Lambda_i + 2\Lambda_{ij} v_j + \Lambda_{ppj} (v^2 \delta_{ij} + 2v_i v_j), \\
 \lambda_{ij} &= \Lambda_{ij} + \Lambda_{ppi} 3v_{(i} \delta_{j)}, \\
 \lambda_{ppi} &= \Lambda_{ppi}.
 \end{aligned} \tag{1.130}$$

Then we obtain the derivatives of h and φ_i from (1.111) as follows:

$$dh = \lambda d\rho + \lambda_{ij} dm_{ij} + \lambda_j dm_{ii}, \quad (1.131)$$

$$d\varphi_k = \lambda_i dm_{ik} + \lambda_{ij} dm_{ijk} + \lambda_j dm_{iij}, \quad (1.132)$$

and the constraints (1.112) are expressed as

$$\lambda_i \rho + \lambda_i m_{kk} + 2\lambda_{ppk} m_{ik} = 0, \quad (1.133)$$

$$-(h - \lambda\rho - \lambda_{rs} m_{rs} - \lambda_r m_{llr}) \delta_{ik} + 2\lambda_{ir} m_{rk} + \lambda_{ppi} m_{rrk} + 2\lambda_{ppr} m_{irk} = 0. \quad (1.134)$$

The residual inequality (1.124) is also rewritten as the form without velocity

$$\Sigma = \lambda_{\langle ij \rangle} P_{\langle ij \rangle} + \lambda_{ppi} P_i \geq 0. \quad (1.135)$$

Equilibrium

The equilibrium is defined as the case that the productions $P_{\langle ij \rangle}$ and P_i are 0:

$$P_{\langle ij \rangle}^E = 0, \quad P_i^E = 0,$$

where the symbol E means the value at equilibrium. In the equilibrium the entropy production have minimum value 0, and its necessarily condition is $d\Sigma^E = 0$:

$$d\Sigma^E = \lambda_{\langle ij \rangle}^E dP_{\langle ij \rangle}|_E + \lambda_{ppi}^E dP_i|_E = 0.$$

Therefore we obtain

$$\lambda_{\langle ij \rangle}^E = 0, \quad \lambda_{ppi}^E = 0. \quad (1.136)$$

From this, we may interpret $\lambda_{\langle ij \rangle}$ and λ_{ppi} as the variables which characterize a nonequilibrium state.

By considering $m_{ii} = 2\rho\varepsilon$, the derivation of entropy density at an equilibrium state has the following expression from (1.131)

$$dh^E = \lambda^E d\rho + \frac{2}{3} \lambda_{kk}^E d(\rho\varepsilon). \quad (1.137)$$

At an equilibrium state there is the following relation so-called Gibbs relation:

$$dh^E = -\frac{g}{T} d\rho + \frac{1}{T} d(\rho\varepsilon), \quad (1.138)$$

where $g(= \varepsilon + p/\rho - Ts)$ is the chemical potential and T is the absolute temperature. The comparison between Eq.(1.137) and the Gibbs relation (1.138) gives us the following relations:

$$\lambda^E = -\frac{g}{T}, \quad \lambda_{kk}^E = \frac{3}{2T}. \quad (1.139)$$

In this way ET introduce the temperature through the Lagrange multipliers.

Constitutive equations

By introducing the new potentials h' and φ'_k as (1.84) we adopt $\{\lambda, \lambda_{ij}, \lambda_{ppi}\}$ as independent variable instead of $\{\rho, m_{ij}, m_{ppi}\}$.

$$\begin{aligned} h' &= \lambda\rho + \lambda_{ij}m_{ij} + \lambda_{ppi}m_{qqi} - h \\ \varphi'_k &= \lambda_i m_{ik} + \lambda_{ij}m_{ijk} + \lambda_{ppi}m_{qqik} - \varphi_k \end{aligned} \quad (1.140)$$

Then we obtain

$$\begin{aligned} dh' &= \rho d\lambda + m_{ij}d\lambda_{ij} + m_{qqi}d\lambda_{ppi}, \\ d\varphi'_k &= m_{ik}d\lambda_i + m_{ijk}d\lambda_{ij} + m_{qqik}d\lambda_{ppi}. \end{aligned} \quad (1.141)$$

Let us consider the representation of h' and φ'_k . These are expressed as the expansion near equilibrium, that is, the polynomial in $\lambda_{\langle ij \rangle}$, λ_{ppi} because the new potentials h' and φ'_k are isotropic functions of $\{\lambda, \lambda_{ij}, \lambda_{ppi}\}$. Up to second order near equilibrium state $\{\lambda, \lambda_{ii}\}$, h' and φ'_i are represented as follows

$$\begin{aligned} h' &= h'^E + h_1\lambda_{\langle ij \rangle}\lambda_{\langle ij \rangle} + h_2\lambda_{ppi}\lambda_{qqi} + h_3\lambda_{\langle ij \rangle}\lambda_{\langle ni \rangle}\lambda_{\langle nj \rangle} + h_4\lambda_{\langle ij \rangle}\lambda_{ppi}\lambda_{qqj} + O(3), \\ \varphi'_k &= \beta_1\lambda_{ppk} + \beta_2\lambda_{\langle kj \rangle}\lambda_{ppi} + O(3), \end{aligned} \quad (1.142)$$

where the coefficients $h'^E, h_1, h_2, h_3, h_4, \beta_1, \beta_2$ and β_3 are the function of λ, λ_{ii} . From Eqs.(1.137) and (1.140), we have

$$h'^E = -\frac{pE}{T}.$$

From Eq.(1.142) we obtain

$$\begin{aligned} dh' &= dh'^E + \lambda_{\langle ij \rangle}\lambda_{\langle ij \rangle}dh_1 + \lambda_{ppi}\lambda_{ppi}dh_2 + \lambda_{\langle ij \rangle}\lambda_{\langle ni \rangle}\lambda_{\langle nj \rangle}dh_3 + \lambda_{\langle ij \rangle}\lambda_{ppi}\lambda_{qqj}dh_4 \\ &\quad + (2h_1\lambda_{\langle ij \rangle} + 3h_3\lambda_{\langle ni \rangle}\lambda_{\langle nj \rangle})d\lambda_{\langle ij \rangle} \\ &\quad + (2h_2\lambda_{ppi} + 2h_4\lambda_{\langle ij \rangle}\lambda_{qqj})d\lambda_{ppi} + O(3) \end{aligned} \quad (1.143)$$

$$\begin{aligned} d\varphi'_k &= \lambda_{ppk}d\beta_1 + \lambda_{\langle ki \rangle}\lambda_{ppi}d\beta_2 \\ &\quad + \beta_1d\lambda_{ppk} + \beta_2\lambda_{\langle ki \rangle}d\lambda_{ppi} + \beta_2\lambda_{ppi}d\lambda_{\langle ki \rangle} + O(3). \end{aligned} \quad (1.144)$$

We compare the two expressions of $\frac{\partial h'}{\partial \lambda}, \frac{\partial h'}{\partial \lambda_{ii}}, \frac{\partial h'}{\partial \lambda_{\langle ij \rangle}}$ and $\frac{\partial h'}{\partial \lambda_{ppi}}$ from Eqs.(1.141) and (1.143). Then we obtain

$$\begin{aligned} \rho &= \rho_E + \frac{\partial h_1}{\partial \lambda}\lambda_{\langle ij \rangle}\lambda_{\langle ij \rangle} + \frac{\partial h_2}{\partial \lambda}\lambda_{ppi}\lambda_{ppi} + O(3), \\ m_{ii} &= 2\rho_E\varepsilon_E + 3\frac{\partial h_1}{\partial \lambda_{ii}}\lambda_{\langle ij \rangle}\lambda_{\langle ij \rangle} + 3\frac{\partial h_2}{\partial \lambda_{ii}}\lambda_{ppi}\lambda_{ppi} + O(3), \\ m_{\langle ij \rangle} &= 2h_1\lambda_{\langle ij \rangle} + 3h_2\lambda_{\langle i \rangle\langle n \rangle}\lambda_{\langle nj \rangle} + h_4\lambda_{pp\langle i \rangle}\lambda_{\langle j \rangle} + O(3), \\ m_{ppi} &= 2h_2\lambda_{ppi} + 2h_4\lambda_{\langle ik \rangle}\lambda_{ppk}. \end{aligned} \quad (1.145)$$

Within the linear constitutive equations, we may interpret $\rho = \rho_E$ and $\varepsilon = \varepsilon_E$. Henceforth we ignore the notation E for ρ and ε .

In the same way we compare the two expressions of $\frac{\partial \varphi'_k}{\partial \lambda}$, $\frac{\partial \varphi'_k}{\partial \lambda_{ii}}$, $\frac{\partial \varphi'_k}{\partial \lambda_{(ij)}}$ and $\frac{\partial \varphi'_k}{\partial \lambda_{ppi}}$ from Eqs.(1.141) and (1.144). Then we obtain

$$\begin{aligned}
 \frac{\partial \beta_1}{\partial \lambda} &= -5pT, \\
 \frac{\partial \beta_2}{\partial \lambda} &= -10\frac{p}{\rho}\frac{\partial h_1}{\partial \lambda} - 4h_1T, \\
 \frac{\partial \beta_1}{\partial \lambda_{ll}} &= \frac{2h_2}{3} - \frac{25}{3}\frac{p^2T}{\rho}, \\
 \frac{\partial \beta_2}{\partial \lambda_{ll}} &= \frac{2h_4}{3} + \frac{10p}{\rho}\frac{\partial h_1}{\partial \lambda_{ll}} + \frac{20}{3}h_1\frac{pT}{\rho}, \\
 m_{\langle rs \rangle k} &= \left(\beta_2 - 10h_1\frac{p}{\rho} \right) \lambda_{pp\langle r \delta_s \rangle k} + O(2), \\
 m_{ppik} &= \beta_1 \delta_{ik} + \beta_2 \lambda_{\langle ik \rangle} + O(2).
 \end{aligned} \tag{1.146}$$

Taking into account that $m_{\langle rs \rangle k} = O(2)$, we can obtain the following relation from (1.145)₄ and (1.146)₅.

$$\beta_2 = \frac{4}{5}h_2 + 10\frac{p}{\rho}h_1. \tag{1.147}$$

By substituting (1.140), (1.145) and (1.146) into (1.134), we obtain the following relation

$$h_1 = -pT, \quad h_3 = \frac{4}{3}pT^2, \quad h_4 = -\frac{18}{5}h_2T. \tag{1.148}$$

For convenience, we take $\{\rho, T\}$ as independent variables instead of $\{\lambda, \lambda_{ii}\}$. Then, the relations (1.145) and (1.146) are rewritten in terms of $\{\rho, T\}$. To consider the equations of state, we recall the Gibbs relation. As the integrability condition of Gibbs relation, we have

$$\left(\frac{\partial \varepsilon}{\partial \rho} \right)_T = \frac{1}{\rho^2} \left(p - T \left(\frac{\partial p}{\partial T} \right) \right). \tag{1.149}$$

Furthermore we introduce $z = \rho/T^{3/2}$ instead of ρ . Then we obtain the thermal equation of state from (1.149) as follows

$$p = T^{5/2}F(z), \tag{1.150}$$

which is come out from the integrability condition of Gibbs relation (1.149) and $3p = 2\rho\varepsilon$. This form of pressure can express both the classical and quantum ideal gases. From Eqs. (1.147), (1.148) and first four relation in (1.146), we obtain the explicit form of β_1 and β_2 :

$$\begin{aligned}
 \beta_1 &= 5T^{7/2} \left(\int \frac{FF'}{z} dz + c \right) + C, \\
 \beta_2 &= -14T^{9/2} \left(\int \frac{FF'}{z} dz + c \right),
 \end{aligned} \tag{1.151}$$

where c and C are the integration constants. With these we can calculate the coefficients of h'

$$\begin{aligned}
 h_1 &= -T^{7/2}F(z), \\
 h_2 &= T^{9/2} \left[\frac{25}{2} \frac{F^2}{z} - \frac{35}{2} \left(\int \frac{FF'}{z} dz + c \right) \right], \\
 h_3 &= \frac{4}{3} T^{9/2} F(z), \\
 h_4 &= T^{11/2} \left[-45 \frac{F^2}{z} + 63 \left(\int \frac{FF'}{z} dz + c \right) \right].
 \end{aligned} \tag{1.152}$$

Therefor we determined all coefficients of the representaion of h' and φ'_k by the equilibrium properties, that is, T and z .

The stability of entropy production

Let us consider the representation of production terms $P_{\langle ij \rangle}$ and P_{ppi} in the same manner as the representaion of h' and φ'_k .

$$\begin{aligned}
 P_{\langle ij \rangle} &= \sigma \lambda_{\langle ij \rangle} + O(2), \\
 P_i &= \tau \lambda_{ppi} + O(2),
 \end{aligned} \tag{1.153}$$

where σ and τ are the function of λ and λ_{ll} .

From the entropy inequality (1.135) we obtain

$$\Sigma = \sigma \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + \tau \lambda_{ppi} \lambda_{qqi} + O(3) \geq 0. \tag{1.154}$$

The entropy production must be the minimum 0 in equilibrium, therefore σ and τ must be satisfy the following inequalities

$$\sigma > 0, \quad \tau > 0. \tag{1.155}$$

Linear constitutive equations as function of $\{\rho, T, S_{\langle ij \rangle}, q_i\}$

We obtained the linear constitutive equations (1.146)₃, (1.146)₄ and (1.153) with the relations (1.151) and (1.152) as the function of $\{\rho, T, \lambda_{\langle ij \rangle}, \lambda_{ppi}\}$. By inverting Eqs. (1.145)₃ and (1.145)₄, we can obtain the linear constitutive equations as the function of $\{\rho, v_i, T, S_{\langle ij \rangle}, q_j\}$.

The viscous stress $S_{\langle ij \rangle}$ and heat flux q_i are related to $m_{\langle ij \rangle}$ and m_{ppi} from (1.127)) as $m_{\langle ij \rangle} = -S_{\langle ij \rangle}$ and $m_{ppi} = 2q_i$, therefore (1.145)₃ and (1.145)₄ are expressed within first-order terms with respect to non-equilibrium variables as follows:

$$\begin{aligned}
 S_{\langle ij \rangle} &= -2h_1 \lambda_{\langle ij \rangle} + O(2), \\
 q_j &= h_2 \lambda_{ppi} + O(2).
 \end{aligned} \tag{1.156}$$

Therefore the Lagrange multipliers $\lambda_{\langle ij \rangle}$ and λ_{ppi} are expressed by $S_{\langle ij \rangle}$ and q_i as follows:

$$\begin{aligned}\lambda_{\langle ij \rangle} &= -\frac{1}{2h_1}S_{\langle ij \rangle} + O(2), \\ \lambda_{ppi} &= \frac{1}{h_2}q_j + O(2).\end{aligned}\tag{1.157}$$

Then the constitutive equations are written as

$$\begin{aligned}m_{\langle ij \rangle k} &= \left(\beta_2 - 10\frac{p}{\rho}\right)\frac{1}{h_2}q_{\langle i}\delta_{j \rangle k} + O(2), \\ m_{ppik} &= \beta_1\delta_{ik} - \frac{\beta_2}{2h_1}S_{\langle ik \rangle} + O(2), \\ P_{\langle ij \rangle} &= -\frac{\sigma}{2h_1}S_{\langle ij \rangle} + O(2), \\ P_i &= \frac{\tau}{h_2}q_i + O(2).\end{aligned}\tag{1.158}$$

Entropy density and entropy flux

From (1.140) we obtain the entropy density and entropy flux as the function of $\{\rho, T, m_{\langle ij \rangle}, m_{ppi}\}$.

$$\begin{aligned}h &= \rho \left[\frac{3}{2} \int \left(\frac{F'}{z} - \frac{5}{3} \frac{F}{z^2} \right) dz + \zeta \right] - \frac{m_{\langle ij \rangle} m_{\langle ij \rangle}}{4T^{7/2}F(z)} - \frac{m_{ppi} m_{qqi}}{10T^{7/2}F(z) \left[7\frac{T}{F(z)} \left(\int \frac{FF'}{z} dz + c \right) - 5T\frac{F(z)}{z} \right]}, \\ \varphi_k &= \frac{1}{2T}m_{ppi} - \frac{2}{10} \frac{1}{T^{7/2}F(z)} m_{\langle kj \rangle} m_{ppj}.\end{aligned}\tag{1.159}$$

Convexity near equilibrium

The requirement of convexity of entropy density with respect to $\{\rho, v_i, T, S_{\langle ij \rangle}, q_j\}$ near equilibrium is fulfilled when the following inequalities are satisfied: in equilibrium state

$$F(z) > 0, \quad 7 \left(\int \frac{FF'}{z} dz + c \right) - 5\frac{F^2}{z} > 0,\tag{1.160}$$

$$0 < F' < \frac{5}{3} \frac{F}{z}.\tag{1.161}$$

For classical ideal gases all inequalities are satisfied. For quantum ideal gases all inequalities are also satisfied except for the strongly degenerate Fermi gases and strongly degenerate Bose gases which have the relation $F' = \frac{5}{3} \frac{F}{z}$ and $F' = 0$, respectively.

1.3.4 Field equations

The closed field equations with the equation of state for ideal gases $p = T^{5/2}F(z)$ ($z = \frac{\rho}{T^{3/2}}$) are obtained

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_i}{\partial x_i} &= 0, \\
 \rho \dot{v}_i - \frac{\partial (S_{\langle ij \rangle} - T^{5/2}F(z)\delta_{ij})}{\partial x_j} &= 0, \\
 \rho \frac{3}{2} \left(T \frac{\dot{F}(z)}{z} \right) + \frac{\partial q_j}{\partial x_j} - (S_{\langle ij \rangle} - T^{5/2}F(z)\delta_{ij}) \frac{\partial v_i}{\partial x_j} &= 0, \\
 \rho \left[\left(\frac{\dot{S}_{\langle ik \rangle}}{\rho} \right) + 2 \frac{S_{l\langle i} \partial v_k \rangle}{\rho \partial x_l} \right] - \frac{4}{5} \frac{\partial q_{\langle i}}{\partial x_k} &= -\frac{1}{\tau_S} S_{ik}, \\
 \rho \left[\left(\frac{\dot{q}_i}{\rho} \right) + \frac{q_k}{\rho} \frac{\partial v_i}{\partial x_k} \right] - \frac{1}{2} \frac{\partial}{\partial x_k} \left[\left(7 \frac{T}{F(z)} S_{\langle ij \rangle} - 5T^{7/2}\delta_{ij} \right) \left(\int \frac{FF'}{z} dz + c \right) \right] \\
 + \frac{2}{5} \frac{\partial v_k}{\partial x_k} + \frac{4}{5} q_k \frac{\partial v_i}{\partial x_k} - \frac{(S_{\langle ij \rangle} - T^{5/2}F(z)\delta_{ij})}{\rho} \frac{\partial (S_{\langle jk \rangle} - T^{5/2}F(z)\delta_{jk})}{\partial x_k} \\
 + \frac{3}{2} \frac{T^{5/2}F(z)}{\rho} \frac{\partial (S_{\langle ik \rangle} - T^{5/2}F(z)\delta_{ik})}{\partial x_k} &= -\frac{1}{\tau_q} q_i,
 \end{aligned} \tag{1.162}$$

where the relaxation time τ_S and τ_q are as follows:

$$\begin{aligned}
 \tau_S &= \frac{2T^{7/2}F(z)}{\sigma}, \\
 \tau_q &= \frac{5T^{9/2} \left[7 \left(\int \frac{FF'}{z} dz + c \right) - 5 \frac{F^2}{z} \right]}{\tau}.
 \end{aligned} \tag{1.163}$$

In particular in the case of classical ideal gases, the equation of state has following form

$$p = \rho \frac{k}{m} T, \tag{1.164}$$

therefore, we have

$$F(z) = \frac{k}{m} z. \tag{1.165}$$

By using the equation of state (1.164)(or (1.165)) we obtain the closed field equations for

classical ideal gases.

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_i}{\partial x_i} &= 0, \\
 \rho \dot{v}_i - \frac{\partial(S_{\langle ij \rangle} - p\delta_{ij})}{\partial x_j} &= 0, \\
 \rho \frac{3}{2} \frac{k}{m} \dot{T} + \frac{\partial q_j}{\partial x_j} - (S_{\langle ij \rangle} - p\delta_{ij}) \frac{\partial v_i}{\partial x_j} &= 0, \\
 \dot{S}_{\langle ij \rangle} + 2S_{\langle n(i} \frac{\partial v_j \rangle}{\partial x_n} + S_{\langle ij \rangle} \frac{\partial v_n}{\partial x_n} - \frac{4}{5} \frac{\partial q_{\langle i}}{\partial x_j \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_j \rangle} &= -\frac{1}{\tau_t} S_{\langle ij \rangle}, \\
 \dot{q}_i + q_k \frac{\partial v_i}{\partial x_k} + \frac{7}{5} q_i \frac{\partial v_k}{\partial x_k} + \frac{4}{5} q_k \frac{\partial v_{(i}}{\partial x_k)} - \frac{k}{m} T \frac{\partial S_{\langle ij \rangle}}{\partial x_j} \\
 - \frac{S_{\langle ij \rangle}}{\rho} \frac{\partial S_{\langle jk \rangle}}{\partial x_k} - \frac{7}{2} \frac{k}{m} S_{\langle ij \rangle} \frac{\partial T}{\partial x_j} + \frac{S_{\langle ij \rangle}}{\rho} \frac{\partial p}{\partial x_j} + \frac{5}{2} \frac{k}{m} p \frac{\partial T}{\partial x_i} &= -\frac{1}{\tau_q} q_i.
 \end{aligned} \tag{1.166}$$

In this case the relaxation times are written as

$$\begin{aligned}
 \tau_S &= \frac{2}{\sigma} \frac{k}{m} T^2 \rho, \\
 \tau_q &= \frac{1}{\tau} \left(10 \left(\frac{k}{m} \right)^2 T^3 \rho + 35 T^{9/2} c \right).
 \end{aligned} \tag{1.167}$$

Comparison with kinetic theory

The closed system of field equations is totally consistent with the system of the moments in the kinetic theory as the counterpart. Therefore we may conclude that $c = 0$.

1.3.5 Maxwellian iteration

The NSF theory comes out as a limiting case of ET through carrying out the so-called Maxwellian iteration [46]. In this respect, NSF can be seen as an approximation of ET where the relaxation times of dissipative fluxes (viscous stress and heat flux) are negligible (Navier-Stokes Fourier limit).

We carry out the Maxwellian iteration in the field equations by the following procedures:

1. The 0th iterates; $S_{\langle ij \rangle}^{(0)}$ and $q_i^{(0)}$

The viscous stress and heat flux have it equilibrium values, therefore $S_{\langle ij \rangle}^{(0)} = 0$ and $q_i^{(0)} = 0$.

2. The 1st iterates; $S_{\langle ij \rangle}^{(1)}$ and $q_i^{(1)}$

$S_{\langle ij \rangle}^{(1)}$ and $q_i^{(1)}$ are obtained by substituting the 0th iterates $S_{\langle ij \rangle}^{(0)}$ and $q_i^{(0)}$ into the left-

hand-side of the field equations. Then we obtain

$$\begin{aligned} S_{\langle ij \rangle}^{(1)} &= 2T^{5/2}F(z)\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \\ q_i^{(1)} &= -\frac{5}{4}T^{5/2} \left[5\frac{F^2}{z} - 7 \int \frac{FF'}{z} dz \right] \tau_q \frac{\partial T}{\partial x_i}. \end{aligned} \quad (1.168)$$

On the other hand, we have the laws of Navier-Stokes and Fourier (1.10).

$$S_{\langle ij \rangle} = 2\mu \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \quad q_i = -\kappa \frac{\partial T}{\partial x_i},$$

where μ and κ are the shear viscosity and heat conductivity, respectively. The comparison reveals that

$$\begin{aligned} \mu &= T^{5/2}F(z)\tau_S, \\ \kappa &= -\frac{5}{4}T^{5/2} \left[5\frac{F^2}{z} - 7 \int \frac{FF'}{z} dz \right] \tau_q. \end{aligned} \quad (1.169)$$

In particular, for classical ideal gases, we obtain

$$\begin{aligned} \mu &= \frac{k_B}{m} \rho T \tau_S, \\ \kappa &= \frac{5}{2} \left(\frac{k_B}{m} \right)^2 \rho T \tau_q. \end{aligned} \quad (1.170)$$

We can therefore estimate the values of the relaxation times τ_S and τ_q from the experimental data of the coefficients μ and κ .

The second iterates and higher iterates are obtained in a similar way. $S_{\langle ij \rangle}^{(2)}$ and $q_i^{(2)}$ are obtained which include the second order term with respect to τ_S and τ_q .

$$\begin{aligned} S_{\langle ij \rangle}^{(2)} &= 2p\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} - \rho\tau_S \left[\left(\frac{2p\tau_S}{\rho} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} \right) + \frac{4p\tau_S}{\rho} \frac{\partial v_{\langle i}}{\partial x_{\langle j}} \frac{\partial v_{\rangle k}}{\partial x_l} \right] - \frac{4}{5}\tau_S \frac{\partial \left(\theta\tau_q \frac{\partial T}{\partial x_{\langle i}} \right)}{\partial x_{j \rangle}}, \\ q_i^{(2)} &= -\theta\tau_q \frac{\partial T}{\partial x_i} + \rho\tau_q \left[\left(\frac{\theta\tau_q}{\rho} \frac{\partial T}{\partial x_i} \right) + \frac{\theta\tau_q}{\rho} \frac{\partial T}{\partial x_k} \frac{\partial v_i}{\partial x_k} \right] + \tau_q \frac{\partial \left[7T^{7/2}\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} \int \frac{FF'}{z} dz \right]}{\partial x_j} \\ &\quad + \frac{2}{5}\theta\tau_q^2 \frac{\partial T}{\partial x_i} \frac{\partial v_k}{\partial x_k} + \frac{4}{5}\theta\tau_q^2 \frac{\partial T}{\partial x_k} \frac{\partial v_{\langle i}}{\partial x_k} + 2\frac{p}{\rho}\tau_q\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} \frac{\partial \left(2p\tau_S \frac{\partial v_{\langle j}}{\partial x_k} \right)}{\partial x_k} \\ &\quad - 2\frac{p}{\rho}\tau_q\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} \frac{\partial p}{\partial x_j} - \frac{p}{\rho}\tau_q \frac{\partial \left(2p\tau_S \frac{\partial v_{\langle i}}{\partial x_k} \right)}{\partial x_k} - \frac{3p}{2\rho}\tau_q \frac{\partial \left(2p\tau_S \frac{\partial v_{\langle i}}{\partial x_k} \right)}{\partial x_k}, \end{aligned}$$

where

$$\theta = \frac{5}{4}T^{5/2} \left[5\frac{F^2}{z} - 7 \int \frac{FF'}{z} dz \right] \quad (1.171)$$

For further order iteration, we may estimate that the form include the n -th order term with respect to τ_S and τ_q in n -th order iteration. This means that this iteration scheme is the expansion with respect to the relaxation time.

1.3.6 The after the establishment of ET for rarefied monatomic gases

After the establishment of ET for rarefied monatomic gases, this theory has been applied successfully to various nonequilibrium phenomena such as light scattering, sound waves, heat waves (second sound), structure of shock waves [8]. Besides, there appeared many studies of ET for rarefied polyatomic gases [50, 51, 52] and also for dense gases [53, 54, 55, 56, 57]. In contrast to ET for rarefied monatomic gases, in these theories, there exists a fatal difficulty that the constitutive equations cannot be determined in a fully explicit way from the caloric and thermal equations of state. There remain many phenomenological constants in the constitutive equations that are impossible to be evaluated experimentally or theoretically.

On the other hand, from the view point of fluctuating hydrodynamics, the development of ET open new field, that is, the theory which is applicable to the state with evident spatio-temporal changes of physical quantities where LL cannot be applied is much-expected.

1.4 Purpose and organization of this thesis

Up to this point, we have seen the present state of non-equilibrium physics, and these problems. Then our course is decided, that is, the purpose of the present thesis is to construct the following two theories beyond the applicable range of previous works:

1. ET of rarefied polyatomic gases, dense monatomic gases and dense polyatomic gases
2. Fluctuating hydrodynamics based on ET.

Moreover, responding to the construction of these new theories, we should show the validity and features of these. In the present thesis, we show the recent achievement about these studies.

The organization of this thesis can be summarized as follows:

In Chapter 1, the background and purpose of the present study was summarized. The previous studies for non-equilibrium phenomena are briefly summarized by focusing around TIP, kinetic theory and LL. Moreover the recent developed non-equilibrium thermodynamics, i.e., ET was introduced. In particular the basic concepts and mathematical structures of ET were discussed.

In Chapter 2, we study ET of dense gases by adopting the system of field equations with a different hierarchy structure to that adopted in the previous works. It is the theory of 14 fields of mass density, velocity, temperature, viscous stress, dynamic pressure and heat flux. As a result, most of the constitutive equations can be determined explicitly by the caloric and thermal equations of state. This theory includes rarefied polyatomic gases, and it is shown that the rarefied-gas limit of the theory is consistent with the kinetic theory of gases. We also

analyze two physically important systems, that is, a hard-sphere system and a van der Waals fluid, by using the general theory developed in the former part of the present chapter.

In Chapter 3, we study the dispersion relation for sound in rarefied polyatomic gases (hydrogen, deuterium and hydrogen deuteride gases) based on the ET approach proposed in Chapter 2. We compare the relation with those obtained in experiments and by the classical NSF theory. The applicable frequency-range of the ET theory is proved to be much wider than that of the NSF theory. We evaluate the values of the bulk viscosity and the relaxation times involved in nonequilibrium processes. The relaxation time related to the dynamic pressure has a possibility to become much larger than the other relaxation times related to the shear stress and the heat flux.

In Chapter 4, based on ET, we study a thermodynamic theory of gases with the energy transfer from the molecular translational mode to the internal modes as an extension of Meixner's theory. We focus our attention on the simplest case with only one dissipative process due to the dynamic pressure. The dispersion relation for sound derived from the present theory is compared with that from Meixner's theory. The kinetic theoretical basis of the present approach is also discussed.

In Chapter 5, we develop a theory of fluctuating hydrodynamics based on extended thermodynamics through studying the 13-variable theory for a rarefied monatomic gases as a representative case. After analyzing the relationship between the present theory and the LL theory, we discuss the hierarchy structure of the hydrodynamic fluctuations.

In Chapter 6, summary and concluding remarks of this thesis will be shown.

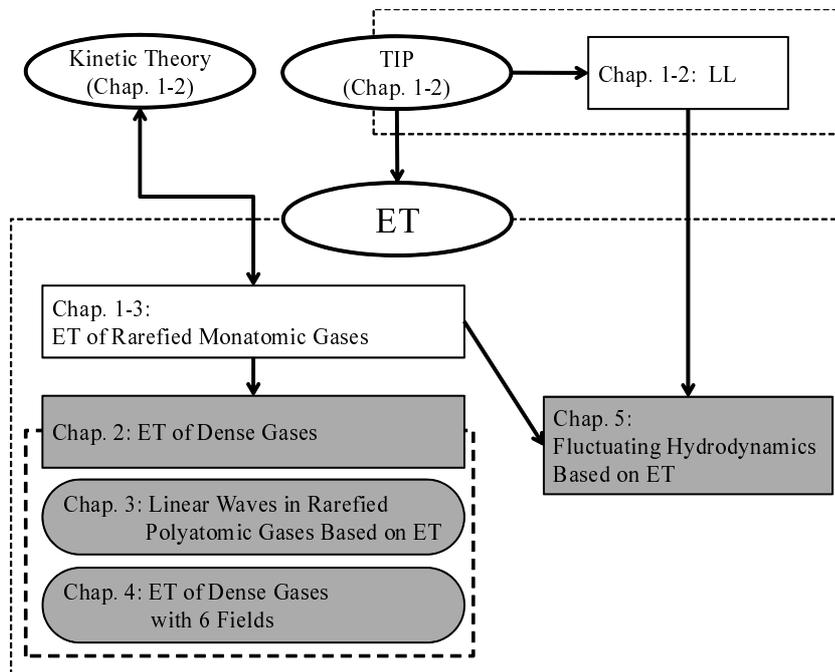


Figure 1.2: Flow chart of this thesis. ET: Extended Thermodynamics, TIP: Thermodynamics of irreversible process, LL: Landau-Lifshitz theory.

Chapter 2

Extended thermodynamics of dense gases

In this chapter the applicable range of extended thermodynamics theory is extended to rarefied polyatomic gases, dense monatomic gases and dense polyatomic gases. The basic ideas of constitutive theory are the same with that shown in Chap 1. The essential difference from the previous theories stems from the hierarchy structure of balance equations. The obtained closed field equations are discussed in the following four cases separately: (i) Rarefied monatomic gases, (ii) rarefied polyatomic gases, (iii) dense monatomic gases, and (iv) dense polyatomic gases. Moreover, the applications for the physically important systems (a hard-sphere system and a van der Waals fluid) are discussed.

2.1 Introduction

Extended thermodynamics (ET) is applicable to highly nonequilibrium phenomena with steep gradients in space and rapid changes in time out of local equilibrium by adopting dissipative fluxes as independent fields and the spatio-temporally local constitutive equations. Such constitutive equations are severely restricted by imposing the universal physical principles; *Entropy principle*, *Causality*, and *Objectivity*. As we have seen in Chap. 1, for rarefied monatomic gases ET is totally consistent with the Grad's procedure in the kinetic theory based on the Boltzmann equation.

The Navier-Stokes Fourier (NSF) theory comes out as a limiting case of ET through carrying out Maxwellian iteration [46] which neglects the relaxation times of dissipative fluxes. However, within its validity range, the classical Navier-Stokes Fourier theory is applicable to any fluids that are not necessarily limited to rarefied gases nor to monatomic gases. Therefore, after the successful establishment of ET for rarefied monatomic gases, there appeared many studies of

ET for rarefied polyatomic gases [50, 51, 52] and also for real gases (or dense gases) [53, 54, 55, 56, 57].

In dense gases, no relationship between the pressure p and the specific internal energy ε exists, and moreover the dynamic pressure Π (trace of the viscous stress) does not vanish. Taking these two facts into account, the previous authors tried to establish ET by postulating a similar hierarchy structure to ET of rarefied monatomic gases (Eq. (1.72)), but with 14 densities including a fourth-rank tensorial density [55, 57]. However, the other feature that a flux in a equation becomes a density in the next equation was abandoned. Because of this generality, the constitutive equations could not be fully determined from the knowledge of the equilibrium properties of gases. Moreover, as we expect, when the Maxwellian iteration procedure is applied, we have to obtain the Navier-Stokes Fourier constitutive equations. The postulation of the fourth-rank tensorial density seems to be not well justified because, as can be seen in the next section, it does not have any straightforward counterpart in the Navier-Stokes Fourier limit.

The objective of the present chapter is to propose an ET theory of dense gases by adopting the system of field equations with a different hierarchy structure to (1.72). We will show that most of the constitutive equations can be determined explicitly by the caloric and thermal equations of state. We will also analyze the theory in the following four cases separately: (i) Rarefied monatomic gases, (ii) rarefied polyatomic gases, (iii) dense monatomic gases, and (iv) dense polyatomic gases. In addition, the two physically important systems, that is, a hard-sphere system and a van der Waals gas, by using the general theory developed in the present chapter.

2.2 Model of dense gases

2.2.1 Heuristic viewpoint

In order to grasp the structure of the basic system appropriate for ET of dense gases, first of all, let us reconsider the structure of the Navier-Stokes Fourier system (Chapter 1, Section 2.1). In addition to the usual conservation laws of mass, momentum, and energy:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k}(\rho v_k) &= 0, \\ \frac{\partial}{\partial t}(\rho v_i) + \frac{\partial}{\partial x_k}(\rho v_i v_k - t_{ik}) &= 0, \\ \frac{\partial}{\partial t} \left(\frac{\rho v^2}{2} + \rho \varepsilon \right) + \frac{\partial}{\partial x_k} \left[\left(\frac{\rho v^2}{2} + \rho \varepsilon \right) v_k - t_{kj} v_j + q_k \right] &= 0, \end{aligned} \tag{2.1}$$

we have the constitutive equations:

$$S_{\langle ij \rangle} = 2\mu \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \quad \Pi = -\nu \frac{\partial v_k}{\partial x_k}, \quad q_i = -\kappa \frac{\partial T}{\partial x_i}, \quad (2.2)$$

where t_{ij} is the stress expressed by

$$t_{ij} = -p\delta_{ij} + S_{ij} = -(p + \Pi)\delta_{ij} + S_{\langle ij \rangle} \quad (2.3)$$

with S_{ij} being the viscous stress and $\Pi (\equiv -S_{ii}/3)$ the dynamic pressure, and q_i is the heat flux. The coefficients μ , ν and κ are the shear viscosity, the bulk viscosity and the heat conductivity, respectively. Here we observe that the equation (2.2) can be rewritten in the form:

$$\begin{aligned} \frac{\partial}{\partial x_k} \left(v_i \delta_{jk} + v_j \delta_{ik} - \frac{2}{3} v_k \delta_{ij} \right) &= \frac{S_{\langle ij \rangle}}{\mu}, \\ \frac{\partial v_k}{\partial x_k} &= -\frac{\Pi}{\nu}, \\ \frac{\partial T}{\partial x_k} &= -\frac{q_k}{\kappa}. \end{aligned} \quad (2.4)$$

The system composed of equations (2.1) and (2.4) can be seen as a system of 14 equations for the 14 unknown variables: ρ , v_i , ε , q_i , $S_{\langle ij \rangle}$ and Π . Its mathematical structure is in the form of balance type, but, in eq. (2.4), we have no term with time derivative. Therefore the system is not hyperbolic but parabolic.

It is, therefore, natural to assume that the mathematical structure of balance laws in ET of dense gases must be of the following type:

$$\begin{aligned} \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\ \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\ \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{ij}, \quad \frac{\partial G_{ii}}{\partial t} + \frac{\partial G_{iik}}{\partial x_k} = 0, \\ \frac{\partial G_{ppi}}{\partial t} + \frac{\partial G_{ppik}}{\partial x_k} &= Q_{ppi}, \end{aligned} \quad (2.5)$$

where F is the mass density, F_i is the momentum density, G_{ii} is the energy density, F_{ij} is the momentum flux, and G_{ppi} is the energy flux. And F_{ijk} and G_{ppik} are the fluxes of F_{ij} and G_{ppi} , respectively, and P_{ij} and Q_{ppi} are the productions with respect to F_{ij} and G_{ppi} , respectively. To justify this structure, we observe that equations (2.1) correspond to (2.5)_{1,2,3} with the condition that F_{ii} is different from G_{ii} because, as mentioned before, no relation exists between the pressure and the internal energy in dense gases. The equation (2.5)₄ can be splitted into the deviatoric and trace parts that have the mathematical structure of (2.4)_{1,2} when the terms with time derivatives are neglected. While equation (2.5)₅ in the steady case have the mathematical structure of the type of the Fourier's law (2.4)₃.

We observe also that the structure of (2.5) is much more restrictive than that adopted in the previous works, and moreover the system does not have the fourth-rank tensor in the set of densities.

To sum up, the hierarchy structure of the system (2.5) is composed of two parallel series: The one is the series starting from the mass and momentum balance equations (F -series) and the other is from the energy balance equation (G -series). In each series, the flux in one equation becomes the density in the next equation. Such a structure is also completely consistent with the structure of the set of balance equations derived from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of many-body distribution functions [22] in statistical mechanics, which is valid not only for rarefied gases but also for dense gases and liquids.

2.2.2 Statement of the model of dense gases

We can now definitely formulate the thermodynamic model for ET of dense gases as follows: The basic system of field equations is of balance type given by (2.5) with 14 independent field variables,

$$\begin{aligned}
 \text{mass density:} & & F & (= \rho), \\
 \text{momentum density:} & & F_i & (= \rho v_i), \\
 \text{energy density:} & & G_{ii}, & \\
 \text{momentum flux:} & & F_{ij}, & \\
 \text{energy flux:} & & G_{ppi}. &
 \end{aligned} \tag{2.6}$$

2.2.3 Galilean invariance

We decompose $F_{i_1 \dots i_n k}$ and $G_{i_1 \dots i_n k}$ into the convective and non-convective parts:

$$\begin{aligned}
 F_{i_1 \dots i_n k} &= F_{i_1 \dots i_n} v_k + H_{i_1 \dots i_n k}, \\
 G_{i_1 \dots i_n k} &= G_{i_1 \dots i_n} v_k + J_{i_1 \dots i_n k}.
 \end{aligned}$$

In particular, the quantities F_{ijk} and G_{ppik} are decomposed as follows: $F_{ijk} = F_{ij} v_k + H_{ijk}$ and $G_{ppik} = G_{ppi} v_k + J_{ppik}$.

As the balance equations (2.5) should be invariant under the Galilean transformation, from the general theory [49], the dependence of the quantities on the velocity can be expressed as

follows:

$$\begin{aligned}
 G_{ii} &= \rho v_i v_i + m_{ii}, \\
 F_{ij} &= \rho v_i v_j + M_{ij}, \\
 G_{ppi} &= \rho v_p v_p v_i + m_{pp} v_i + 2M_{pi} v_p + m_{ppi}, \\
 H_{ijk} &= 2v_{(i} M_{j)k} + M_{ijk}, \\
 J_{ppik} &= 3v_{(p} v_p M_{i)k} + 2v_p M_{pik} + v_i m_{ppk} + m_{ppik}, \\
 Q_{ppi} &= Q_i + 2v_p P_{pi},
 \end{aligned} \tag{2.7}$$

where m_{ii} , M_{ij} , m_{ppi} , M_{ijk} and m_{ppik} do not depend on the velocity, and the productions P_{ij} and Q_i are also independent of the velocity.

With Eq. (2.7), the balance equations (2.5) can be rewritten as

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
 \rho \dot{v}_i + \frac{\partial M_{ij}}{\partial x_j} &= 0, \\
 \dot{m}_{ii} + m_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= 0, \\
 \dot{M}_{ii} + M_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= P_{ii}, \\
 \dot{M}_{(ij)} + M_{(ij)} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{(ij)k}}{\partial x_k} + 2 \frac{\partial v_{(i}}{\partial x_k} M_{j)k} &= P_{(ij)}, \\
 \dot{m}_{ppi} + m_{ppi} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ppik}}{\partial x_k} + 2 \frac{\partial v_p}{\partial x_k} M_{pik} + \frac{\partial v_i}{\partial x_k} m_{ppk} + 2M_{pi} \dot{v}_p + m_{pp} \dot{v}_i &= Q_i.
 \end{aligned} \tag{2.8}$$

As the first three equations represent the conservation laws of mass, momentum and energy, the quantities M_{ij} , m_{ii} and m_{ppi} have the following conventional meanings:

$$\text{stress tensor:} \quad t_{ij} = -M_{ij} (= -(p + \Pi) \delta_{ij} + S_{(ij)}), \tag{2.9}$$

$$\text{specific internal energy:} \quad \varepsilon = \frac{1}{2\rho} m_{ii}, \tag{2.10}$$

$$\text{heat flux:} \quad q_i = \frac{1}{2} m_{ppi}, \tag{2.11}$$

where the pressure p depends only on ρ and m_{ii} . We will see in Section 3.3 that the decomposition in Eq. (2.9) is consistent in the present theory. M_{ij} is symmetric because we deal with non-polar materials. Therefore P_{ij} is symmetric and M_{ijk} is symmetric only with respect to the first two indices.

We may adopt $\{\rho, v_i, m_{ii}, \Pi, M_{(ij)}, m_{ppi}\}$ as a set of independent variables instead of $\{F, F_i, G_{ii}, F_{ii}, F_{(ij)}, G_{ppi}\}$. The balance equation of M_{ii} (Eq.(4.4)₄) is then rewritten as follows:

$$\begin{aligned}
 \dot{\Pi} + \left(\frac{5}{3} p - \rho \frac{\partial p}{\partial \rho} - (m_{rr} + 2p) \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_k}{\partial x_k} + \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{qq}} \right) \Pi \frac{\partial v_k}{\partial x_k} \\
 + 2 \left(\frac{1}{3} - \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_r}{\partial x_k} M_{(rk)} + \frac{1}{3} \frac{\partial M_{rrk}}{\partial x_k} - \frac{\partial p}{\partial m_{qq}} \frac{\partial m_{rrk}}{\partial x_k} = \frac{P_{rr}}{3}.
 \end{aligned} \tag{2.12}$$

2.3 Constitutive equations

We need the constitutive equations in order to set up the closed system of field equations. We assume that the constitutive quantities at one point and time depend on the independent fields at that point and time, i.e., local and instantaneous, therefore we have

$$\Psi = \hat{\Psi}(\rho, m_{ii}, \Pi, M_{(ij)}, m_{ppi}), \quad (2.13)$$

where Ψ is one of the constitutive quantities $\{M_{ijk}, m_{ppik}, P_{ij}, Q_i\}$.

We apply to the present case the constitutive theory established in ET [8] where we impose the following universal physical principles on the constitutive equations:

- *Material frame indifference principle:*

The proper constitutive equations are independent of an observer. The material frame indifference principle together with the requirement of the Galilean invariance of balance laws constitute the so-called objectivity principle (the principle of relativity).

- *Entropy principle:*

All solutions of the system of field equations must satisfy the entropy balance with a non-negative entropy production:

$$\frac{\partial h}{\partial t} + \frac{\partial(hv_k + \varphi_k)}{\partial x_k} = \Sigma \geq 0 \quad \Leftrightarrow \quad \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \varphi_k}{\partial x_k} = \Sigma \geq 0, \quad (2.14)$$

where h is the entropy density, h_k is the entropy flux ($h_k = hv_k + \varphi_k$: φ_k is the non-convective entropy flux), and Σ is the entropy production. Here h and φ_k are constitutive quantities:

$$\begin{aligned} h &= h(\rho, m_{ii}, \Pi, M_{(ij)}, m_{ppi}), \\ \varphi_k &= \varphi_k(\rho, m_{ii}, \Pi, M_{(ij)}, m_{ppi}). \end{aligned} \quad (2.15)$$

- *Causality:*

This requires the concavity of the entropy density and guarantees the hyperbolicity of the system of field equations. This also ensures the well-posedness (local in time) of a Cauchy problem and the finiteness of the propagation speeds of disturbances.

2.3.1 Relations derived from the entropy principle

The entropy principle can be expressed that the following inequality with Lagrange multipliers λ , λ_i , μ_{ll} , λ_{ij} and μ_{lli} must be satisfied for all fields, ρ through m_{ppi} [58]:

$$\begin{aligned}
 & \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \varphi_k}{\partial x_k} - \lambda \left[\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} \right] - \lambda_i \left[\rho \dot{v}_i + \frac{\partial M_{ij}}{\partial x_j} \right] \\
 & - \mu_{ll} \left[\dot{m}_{ii} + m_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} \right] \\
 & - \lambda_{ii} \left[\dot{\Pi} + \left(\frac{5}{3} p - \rho \frac{\partial p}{\partial \rho} - (m_{rr} + 2p) \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_k}{\partial x_k} + \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{qq}} \right) \Pi \frac{\partial v_k}{\partial x_k} \right. \\
 & \left. + 2 \left(\frac{1}{3} - \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_r}{\partial x_k} M_{(rk)} + \frac{1}{3} \frac{\partial M_{rrk}}{\partial x_k} - \frac{\partial p}{\partial m_{qq}} \frac{\partial m_{rrk}}{\partial x_k} - \frac{P_{rr}}{3} \right] \\
 & - \lambda_{(ij)} \left[\dot{M}_{(ij)} + M_{(ij)} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{(ij)k}}{\partial x_k} + 2 \frac{\partial v_{(i}}{\partial x_k} M_{j)k} - P_{(ij)} \right] \\
 & - \mu_{lli} \left[\dot{m}_{ppi} + m_{ppi} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ppik}}{\partial x_k} + 2 \frac{\partial v_p}{\partial x_k} M_{pik} + \frac{\partial v_i}{\partial x_k} m_{ppk} + 2 M_{ip} \dot{v}_p + m_{pp} \dot{v}_i - Q_i \right] \\
 & \geq 0.
 \end{aligned}$$

Using the expressions (4.2.2) and (2.15) and taking into account the fact that the following derivatives,

$$\dot{\rho}, \dot{v}_i, \dot{m}_{ll}, \dot{\Pi}, \dot{M}_{(ij)}, \dot{m}_{ppi}, \frac{\partial \rho}{\partial x_k}, \frac{\partial v_i}{\partial x_k}, \frac{\partial m_{ll}}{\partial x_k}, \frac{\partial \Pi}{\partial x_k}, \frac{\partial M_{(ij)}}{\partial x_k}, \frac{\partial m_{ppi}}{\partial x_k}, \quad (2.16)$$

can have any values, we obtain the relations:

$$dh = \lambda d\rho + \mu_{ll} dm_{ii} + \lambda_{ii} d\Pi + \lambda_{(ij)} dM_{(ij)} + \mu_{lli} dm_{ppi}, \quad (2.17)$$

$$\begin{aligned}
 d\varphi_k &= \lambda_k dp + \lambda_k d\Pi + \lambda_i dM_{(ik)} + \left(\mu_{ll} - \lambda_{ll} \frac{\partial p}{\partial m_{qq}} \right) dm_{iik} \\
 &+ \frac{\lambda_{ll}}{3} dM_{iik} + \lambda_{(ij)} dM_{(ij)k} + \mu_{lli} dm_{ppik},
 \end{aligned} \quad (2.18)$$

and

$$\lambda_i = -\frac{1}{\rho} (\mu_{lli} m_{kk} + 2\mu_{lli} M_{ij}), \quad (2.19)$$

$$\begin{aligned}
 & \left[h - \lambda \rho - \mu_{ll} (m_{ss} + 2p) - 2\mu_{ll} \Pi - \lambda_{ll} \left(\frac{5}{3} p - \rho \frac{\partial p}{\partial \rho} - (m_{ss} + 2p) \frac{\partial p}{\partial m_{rr}} \right) \right. \\
 & \left. - \lambda_{ll} \Pi \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{rr}} \right) - \lambda_{(rs)} M_{(rs)} - \mu_{lli} m_{ssr} \right] \delta_{ik} \\
 & - 2\mu_{ll} M_{(ik)} + 2 \frac{\partial p}{\partial m_{rr}} M_{(ik)} \lambda_{ll} - 2\mu_{lli} M_{(ij)k} - \frac{2}{3} \mu_{lli} M_{ppk} \\
 & - \mu_{lli} m_{ppk} - 2\lambda_{(ir)} M_{(rk)} - \frac{2}{3} \lambda_{ll} M_{(ik)} - 2\lambda_{(ik)} (p + \Pi) = 0.
 \end{aligned} \quad (2.20)$$

The residual inequality is given by

$$\Sigma = \frac{1}{3} \lambda_{ii} P_{jj} + \lambda_{(ij)} P_{(ij)} + \mu_{lli} Q_i \geq 0. \quad (2.21)$$

2.3.2 Equilibrium

Equilibrium is defined as a process in which the productions P_{ii} , $P_{\langle ij \rangle}$ and Q_i vanish. The entropy production Σ becomes minimum and vanishes in equilibrium, and then we obtain the necessary conditions:

$$\lambda_{ii}^E = 0, \quad \lambda_{\langle ij \rangle}^E = 0, \quad \mu_{ll}^E = 0, \quad (2.22)$$

where index E denotes equilibrium. Therefore the Lagrange multipliers λ_{ii} , $\lambda_{\langle ij \rangle}$ and μ_{ll} play a role of characterizing nonequilibrium phenomena, and will be called nonequilibrium variables.

From Eq. (2.17) and $m_{ii} = 2\rho\varepsilon$, we have the relation:

$$dh^E = \lambda^E d\rho + 2\mu_{ll}^E d(\rho\varepsilon). \quad (2.23)$$

On the other hand, taking into account that $h^E = \rho s$ where s is the entropy density and that $Tds = d\varepsilon - (p/\rho^2)d\rho$ (the Gibbs equation), we have

$$dh^E = -\frac{g}{T}d\rho + \frac{1}{T}d(\rho\varepsilon), \quad (2.24)$$

where $g (= \varepsilon + p/\rho - Ts)$ is the chemical potential and T the absolute temperature. Now, by comparison, we conclude that

$$\lambda^E = -\frac{g}{T}, \quad \mu_{ll}^E = \frac{1}{2T}. \quad (2.25)$$

We observe that the trace part of Eq. (2.20) in equilibrium becomes an identity.

2.3.3 Derivation of the constitutive equations

In order to transform the independent variables from $\{\rho, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}\}$ to $\{\lambda, \mu_{ll}, \lambda_{ii}, \lambda_{\langle ij \rangle}, \mu_{ll}\}$, we introduce the new potentials h' and φ'_k as follows:

$$h' = \lambda\rho + \mu_{ll}m_{ii} + \lambda_{ii}\Pi + \lambda_{\langle ij \rangle}M_{\langle ij \rangle} + \mu_{ll}m_{ppi} - h, \quad (2.26)$$

$$\varphi'_k = \mu_{ll}m_{iik} + \frac{1}{3}\lambda_{ll}M_{iik} + \lambda_{\langle ij \rangle}M_{\langle ij \rangle k} + \mu_{ll}m_{ppik} - \varphi_k. \quad (2.27)$$

Then we have

$$dh' = \rho d\lambda + m_{ii}d\mu_{ll} + \Pi d\lambda_{ll} + M_{\langle ij \rangle}d\lambda_{\langle ij \rangle} + m_{ppi}d\mu_{ll}, \quad (2.28)$$

$$\begin{aligned} d\varphi'_k = & -\lambda_k(dp + d\Pi) - \lambda_{ik}dM_{\langle ik \rangle} + \frac{\partial p}{\partial m_{jj}}\lambda_{ll}dm_{ppk} \\ & + m_{ppk}d\mu_{ll} + \frac{1}{3}M_{iik}d\lambda_{ll} + M_{\langle ij \rangle k}d\lambda_{\langle ij \rangle} + m_{ppik}d\mu_{ll}. \end{aligned} \quad (2.29)$$

By using the representation theorem that ensures the principle of objectivity, the potentials h' and φ'_k are expanded around an equilibrium state with respect to the nonequilibrium variables $\{\lambda_{kk}, \lambda_{\langle ij \rangle}, \mu_{ll}\}$ as follows:

$$\begin{aligned} h' &= h'^E + h_1 \lambda_{kk} + h_2 \lambda_{kk}^2 + h_3 \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + h_4 \mu_{ppi} \mu_{qqi} + h_5 \lambda_{kk}^3 + h_6 \lambda_{kk} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} \\ &\quad + h_7 \lambda_{\langle ij \rangle} \lambda_{\langle in \rangle} \lambda_{\langle nj \rangle} + h_8 \lambda_{kk} \mu_{ppi} \mu_{qqi} + h_9 \mu_{ppi} \mu_{qqi} \lambda_{\langle ij \rangle} + O(4), \end{aligned} \quad (2.30)$$

$$\varphi'_k = (\beta_1 + \beta_2 \lambda_{ll}) \mu_{ppi} + \beta_3 \lambda_{\langle ki \rangle} \mu_{lli} + O(3), \quad (2.31)$$

where the coefficients h_1, \dots, h_9 and $\beta_1, \beta_2, \beta_3$ are the functions of λ and μ_{ll} . From Eqs. (2.25)-(2.26), we have the relation:

$$h'^E = \lambda^E \rho + \mu_{ll}^E m_{ii} - h^E = -\frac{p^E}{T}. \quad (2.32)$$

From Eqs. (2.30) and (2.31), we obtain

$$\begin{aligned} dh' &= dh'^E + \lambda_{kk} dh_1 + \lambda_{kk}^2 dh_2 + \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} dh_3 + \mu_{ppi} \mu_{qqi} dh_4 + \lambda_{kk}^3 dh_5 \\ &\quad + \lambda_{kk} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} dh_6 + \lambda_{\langle ij \rangle} \lambda_{\langle in \rangle} \lambda_{\langle nj \rangle} dh_7 + \lambda_{kk} \mu_{ppi} \mu_{qqi} dh_8 + \mu_{ppi} \mu_{qqi} \lambda_{\langle ij \rangle} dh_9 \\ &\quad + (h_1 + 2h_2 \lambda_{kk} + 3h_5 \lambda_{kk}^2 + h_6 \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + h_8 \mu_{ppi} \mu_{qqi}) d\lambda_{ll} \\ &\quad + (2h_3 \lambda_{\langle ij \rangle} + 3h_7 \lambda_{\langle n \langle i \rangle} \lambda_{\langle j \rangle n} + 2h_6 \lambda_{kk} \lambda_{\langle ij \rangle} + h_9 \mu_{ppi} \mu_{qqi}) d\lambda_{\langle ij \rangle} \\ &\quad + (2h_4 \mu_{lli} + 2h_8 \lambda_{kk} \mu_{lli} + 2h_9 \lambda_{\langle ij \rangle} \mu_{lli}) d\mu_{ppi} + O(4), \end{aligned} \quad (2.33)$$

$$\begin{aligned} d\varphi'_k &= \mu_{lli} d\beta_1 + \lambda_{ll} \mu_{ppi} d\beta_2 + \lambda_{\langle ki \rangle} \mu_{lli} d\beta_3 + (\beta_1 + \beta_2 \lambda_{ll}) d\mu_{ppi} \\ &\quad + \beta_3 \lambda_{\langle ki \rangle} d\mu_{ppi} + \beta_2 \mu_{ppi} d\lambda_{ll} + \beta_3 \mu_{lli} d\lambda_{\langle ki \rangle} + O(3). \end{aligned} \quad (2.34)$$

Comparing two expressions of $\frac{\partial h'}{\partial \lambda_{ll}}$ derived from Eqs. (2.28) and (2.33) with each other, we obtain

$$\Pi = h_1 + 2h_2 \lambda_{kk} + 3h_5 \lambda_{kk}^2 + h_6 \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + h_8 \mu_{ppi} \mu_{qqi} + O(3). \quad (2.35)$$

As Π vanishes in equilibrium, $h_1 \equiv 0$. In a similar way, we compare two expressions of $\frac{\partial h'}{\partial \lambda}$, $\frac{\partial h'}{\partial \mu_{ll}}$, $\frac{\partial h'}{\partial \lambda_{\langle ij \rangle}}$ and $\frac{\partial h'}{\partial \mu_{li}}$ derived from Eqs. (2.28) and (2.33) with each other, then we obtain

$$\begin{aligned} \rho &= \rho^E + \frac{\partial h_2}{\partial \lambda} \lambda_{kk}^2 + \frac{\partial h_3}{\partial \lambda} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + \frac{\partial h_4}{\partial \lambda} \mu_{ppi} \mu_{qqi} + \frac{\partial h_5}{\partial \lambda} \lambda_{kk}^3 + \frac{\partial h_6}{\partial \lambda} \lambda_{kk} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} \\ &\quad + \frac{\partial h_7}{\partial \lambda} \lambda_{\langle ij \rangle} \lambda_{\langle n \langle i \rangle} \lambda_{\langle j \rangle n} + \frac{\partial h_8}{\partial \lambda} \lambda_{kk} \mu_{ppi} \mu_{qqi} + \frac{\partial h_9}{\partial \lambda} \mu_{ppi} \mu_{qqi} \lambda_{\langle ij \rangle} + O(4), \\ m_{ii} &= m_{ii}^E + \frac{\partial h_2}{\partial \mu_{ll}} \lambda_{kk}^2 + \frac{\partial h_3}{\partial \mu_{ll}} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + \frac{\partial h_4}{\partial \mu_{ll}} \mu_{ppi} \mu_{qqi} + \frac{\partial h_5}{\partial \mu_{ll}} \lambda_{kk}^3 + \frac{\partial h_6}{\partial \mu_{ll}} \lambda_{kk} \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} \\ &\quad + \frac{\partial h_7}{\partial \mu_{ll}} \lambda_{\langle ij \rangle} \lambda_{\langle n \langle i \rangle} \lambda_{\langle j \rangle n} + \frac{\partial h_8}{\partial \mu_{ll}} \lambda_{kk} \mu_{ppi} \mu_{qqi} + \frac{\partial h_9}{\partial \mu_{ll}} \mu_{ppi} \mu_{qqi} \lambda_{\langle ij \rangle} + O(4), \\ M_{\langle ij \rangle} &= 2h_3 \lambda_{\langle ij \rangle} + 3h_7 \lambda_{\langle n \langle i \rangle} \lambda_{\langle j \rangle n} + 2h_6 \lambda_{kk} \lambda_{\langle ij \rangle} + h_9 \mu_{ppi} \mu_{qqi} + O(3), \\ m_{ppi} &= 2h_4 \mu_{lli} + 2h_8 \lambda_{kk} \mu_{lli} + 2h_9 \lambda_{\langle ij \rangle} \mu_{lli} + O(3), \end{aligned} \quad (2.36)$$

where $\rho^E = \rho^E(\lambda, \mu_{ll})$ and $m_{ii}^E = m_{ii}^E(\lambda, \mu_{ll}) = 2\rho^E(\lambda, \mu_{ll})\varepsilon^E(\lambda, \mu_{ll})$. From Eqs. (2.36)_{1,2}, we can represent the pressure p as follows:

$$\begin{aligned}
 p(\rho, m_{ii}) &= p^E(\rho^E, m_{ii}^E) + \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_2}{\partial \lambda} \right)_{\mu_{ll}} + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho} \left(\frac{\partial h_2}{\partial \mu_{ll}} \right)_{\lambda} \right) \lambda_{kk}^2 \\
 &+ \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_3}{\partial \lambda} \right)_{\mu_{ll}} + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho} \left(\frac{\partial h_3}{\partial \mu_{ll}} \right)_{\lambda} \right) \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} \\
 &+ \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_4}{\partial \lambda} \right)_{\mu_{ll}} + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho} \left(\frac{\partial h_4}{\partial \mu_{ll}} \right)_{\lambda} \right) \mu_{ppi} \mu_{qqi} + O(3). \tag{2.37}
 \end{aligned}$$

From equations (2.36)_{1,2} and (2.37), we notice an important point that we have a nonequilibrium density ρ and an equilibrium density ρ^E , and that the difference $\rho - \rho^E$ is in the second order of magnitude with respect to the nonequilibrium variables. This justifies the equality, $\rho = \rho^E$, as far as the linear theory with respect to the nonequilibrium variables is concerned. The same is true for the quantities m_{ii} and p . This point will play a crucial role in the next subsection.

Next we compare two expressions of $\frac{\partial \varphi'_k}{\partial \lambda}$, $\frac{\partial \varphi'_k}{\partial \mu_{ll}}$, $\frac{\partial \varphi'_k}{\partial \lambda_{ll}}$, $\frac{\partial \varphi'_k}{\partial \lambda_{\langle ij \rangle}}$ and $\frac{\partial \varphi'_k}{\partial \mu_{li}}$ derived from Eqs. (2.29) and (2.34) with each other, then we obtain

$$\begin{aligned}
 0 &= \left[\frac{\partial \beta_1}{\partial \lambda} - 2 \frac{\partial p}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{ppi} \\
 &+ \left[\frac{\partial \beta_2}{\partial \lambda} - \frac{4h_2}{\rho} \frac{\partial p}{\partial \lambda} - 2 \frac{\partial p}{\partial m_{ii}} \frac{\partial h_4}{\partial \lambda} - 2 \frac{\partial h_4}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_{ll} \mu_{ppi} \\
 &+ \left[\frac{\partial \beta_3}{\partial \lambda} - 4 \frac{h_3}{\rho} \frac{\partial p}{\partial \lambda} - 2 \frac{\partial h_3}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{ppi} \lambda_{\langle ik \rangle} + O(3), \\
 0 &= \left[\frac{\partial \beta_1}{\partial \mu_{ll}} - 2h_4 - 2 \frac{\partial p}{\partial \mu_{ll}} \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{ppi} \\
 &+ \left[\frac{\partial \beta_2}{\partial \mu_{ll}} - 2h_8 - \frac{4h_2}{\rho} \frac{\partial p}{\partial \mu_{ll}} - 2 \frac{\partial p}{\partial m_{ii}} \frac{\partial h_4}{\partial \mu_{ll}} - 2 \frac{\partial h_4}{\partial \mu_{ll}} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_{ll} \mu_{ppi} \\
 &+ \left[\frac{\partial \beta_3}{\partial \mu_{ll}} - 2h_9 - 4 \frac{h_3}{\rho} \frac{\partial p}{\partial \mu_{ll}} - 2 \frac{\partial h_3}{\partial \mu_{ll}} \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{ppi} \lambda_{\langle ik \rangle} + O(3), \\
 M_{iik} &= 3 \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{ppi} + O(2), \\
 M_{\langle ij \rangle k} &= \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{li} \lambda_{\langle ij \rangle k} + O(2), \\
 m_{ppik} &= \left[\beta_1 + \left\{ \beta_2 - 2h_4 \left(\frac{\partial p}{\partial m_{pp}} \right)_{\rho} \right\} \lambda_{ll} \right] \delta_{ik} + \beta_3 \lambda_{\langle ik \rangle} + O(2). \tag{2.38}
 \end{aligned}$$

We now derive the relations among the coefficients h_2, \dots, h_9 and $\beta_1, \beta_2, \beta_3$. By substitut-

ing Eqs. (2.36), (2.38)_{3,4} and (2.30) into Eq.(2.20), we have

$$\begin{aligned}
 h_2 &= \frac{1}{4\mu_{ll}} \left(-\frac{5}{3}p^E + \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \rho^E + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} m_{rr}^E + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} p^E \right), \\
 h_3 &= -\frac{p^E}{2\mu_{ll}}, \\
 h_5 &= \left(2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} - \frac{7}{6} \right) \frac{h_2}{3\mu_{ll}} - \frac{1}{3} \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \left(\frac{\partial h_2}{\partial \lambda} \right)_{\mu_{ll}} - \frac{1}{3} \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \left(\frac{\partial h_2}{\partial \mu_{ll}} \right)_{\lambda}, \\
 h_6 &= \frac{1}{4\mu_{ll}^2} \left(\frac{7}{3}p^E - \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \rho^E - \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} m_{rr}^E - 4 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} p^E \right), \\
 h_7 &= \frac{p^E}{3\mu_{ll}^2}, \\
 h_8 &= -\frac{1}{3\mu_{ll}} \left[\frac{5}{3}\beta_3 + \beta_2 - \frac{1}{\rho^E} \left(\frac{10}{3}h_3 + 2h_2 \right) (m_{ii}^E + 2p^E) \right] \\
 &\quad - \frac{5}{6\mu_{ll}} h_4 - \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \left(\frac{\partial h_4}{\partial \lambda} \right)_{\mu_{ll}} - \mu_{ll} \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \left(\frac{\partial h_4}{\partial \mu_{ll}} \right)_{\lambda}, \\
 h_9 &= -\frac{1}{\mu_{ll}} \left[\frac{\beta_3}{6} + \beta_2 - \frac{1}{\rho^E} \left(\frac{h_3}{3} + 2h_2 \right) (m_{ii}^E + 2p^E) \right] - \frac{h_4}{\mu_{ll}}.
 \end{aligned} \tag{2.39}$$

From Eqs. (2.38)_{1,2}, we have the relations:

$$\begin{aligned}
 \frac{\partial \beta_1}{\partial \lambda} &= 2 \frac{\partial p^E}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
 \frac{\partial \beta_2}{\partial \lambda} &= \frac{4h_2}{\rho^E} \frac{\partial p^E}{\partial \lambda} + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \frac{\partial h_4}{\partial \lambda} + 2 \frac{\partial h_4}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
 \frac{\partial \beta_3}{\partial \lambda} &= 4 \frac{h_3}{\rho^E} \frac{\partial p^E}{\partial \lambda} + 2 \frac{\partial h_3}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
 \frac{\partial \beta_1}{\partial \mu_{ll}} &= 2h_4 + 2 \frac{\partial p^E}{\partial \mu_{ll}} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
 \frac{\partial \beta_2}{\partial \mu_{ll}} &= 2h_8 + \frac{4h_2}{\rho^E} \frac{\partial p^E}{\partial \mu_{ll}} + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \frac{\partial h_4}{\partial \mu_{ll}} + 2 \frac{\partial h_4}{\partial \mu_{ll}} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
 \frac{\partial \beta_3}{\partial \mu_{ll}} &= 2h_9 + 4 \frac{h_3}{\rho^E} \frac{\partial p^E}{\partial \mu_{ll}} + 2 \frac{\partial h_3}{\partial \mu_{ll}} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right)
 \end{aligned} \tag{2.40}$$

Note that the coefficient h_4 appears only in (2.39)_{6,7} and in (2.40)_{2,4,5}.

2.3.4 Definitions of the temperature and the chemical potential in nonequilibrium

As explained before, from Eqs. (2.36)_{1,2} and (2.37), we notice the following two points: (i) The density ρ and the internal energy m_{ii} at a nonequilibrium state with $(\lambda, \mu_{ll}, \lambda_{kk}, \lambda_{(ij)}, \mu_{li})$ are equal to the equilibrium quantities ρ^E and m_{ii}^E at (λ, μ_{ll}) to within second-order terms.

This means that, as far as the linear constitutive equations are concerned, the values of (λ, μ_{ll}) are exactly those of the associated local equilibrium state [59] with the nonequilibrium state. Therefore we can use the relations (2.25), and can introduce the temperature T and the chemical potential g into the nonequilibrium state through the following relations:

$$\lambda = -\frac{g}{T}, \quad \mu_{ll} = \frac{1}{2T}. \quad (2.41)$$

Hereafter we will use T and g with this understanding. (ii) The pressure p is also equal to the local equilibrium quantity p^E to within second-order terms. Thus we assure the adequateness of the decomposition prescribed in Eq. (2.9).

For convenience, we take $\{\rho, T\}$ as independent variables instead of $\{\lambda, \mu_{ll}\}$. Then the relations (2.39) are rewritten in terms of $\{\rho, T\}$ as follows:

$$\begin{aligned} h_2 &= -\frac{5}{6}Tp + \frac{\rho T}{2} \left(\frac{\partial p}{\partial \rho} \right)_T + \frac{T^2}{2\rho} \frac{\left(\frac{\partial p}{\partial T} \right)_\rho^2}{\left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\ h_3 &= -Tp, \\ h_5 &= \frac{2Th_2}{3} \left(-\frac{7}{6} + \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} \right) + \frac{\rho T}{3} \left(\frac{\partial h_2}{\partial \rho} \right)_T + \frac{T^2}{3} \left(\frac{\partial h_2}{\partial T} \right)_\rho \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\ h_6 &= \frac{7}{3}pT^2 - \rho T^2 \left(\frac{\partial p}{\partial \rho} \right)_T - T^2 \left(p + T \left(\frac{\partial p}{\partial T} \right)_\rho \right) \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\ h_7 &= \frac{4}{3}T^2p, \\ h_8 &= -\frac{2}{3}T\beta_2 - \frac{10}{9}T\beta_3 - \frac{5}{3}Th_4 + \rho T \left(\frac{\partial h_4}{\partial \rho} \right)_T + T^2 \left(\frac{\partial h_4}{\partial T} \right)_\rho \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} \\ &\quad + \frac{8T}{3} \left(\varepsilon + \frac{p}{\rho} \right) \left(h_2 - \frac{5}{3}Tp \right), \\ h_9 &= -2T\beta_2 - \frac{T}{3}\beta_3 - 2Th_4 + 4T \left(\varepsilon + \frac{p}{\rho} \right) \left(2h_2 - \frac{Tp}{3} \right). \end{aligned} \quad (2.42)$$

And the relations (2.40) are rewritten as follows:

$$\begin{aligned}
 \frac{\partial \beta_1}{\partial \rho} &= 2 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial \rho} \right)_T, \\
 \frac{\partial \beta_2}{\partial \rho} &= 4 \frac{h_2}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_T + 4 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial h_2}{\partial \rho} \right)_T + \left(\frac{\partial h_4}{\partial \rho} \right)_T \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\
 \frac{\partial \beta_3}{\partial \rho} &= -4T \left(\varepsilon + 2 \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial \rho} \right)_T, \\
 \frac{\partial \beta_1}{\partial T} &= 2 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial T} \right)_\rho - \frac{h_4}{T^2}, \\
 \frac{\partial \beta_2}{\partial T} &= \frac{2}{3T} \beta_2 + \frac{10}{9T} \beta_3 + \frac{5}{3T} h_4 - \frac{\rho}{T} \left(\frac{\partial h_4}{\partial \rho} \right)_T - h_2 \left[\frac{8}{3T} \left(\varepsilon + \frac{p}{\rho} \right) - \frac{4}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \right] \\
 &\quad + 4 \left(\varepsilon + \frac{p}{\rho} \right) \left[\frac{10}{9} p + \left(\frac{\partial h_2}{\partial T} \right)_\rho \right], \\
 \frac{\partial \beta_3}{\partial T} &= \frac{2}{T} \beta_2 + \frac{1}{3T} \beta_3 + \frac{2}{T} h_4 - 8 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{p}{3} + \frac{h_2}{T} \right) - 4T \left(\varepsilon + 2 \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial T} \right)_\rho.
 \end{aligned} \tag{2.43}$$

We will show in Sections 7 and 8 that, by using the relations (2.42), (2.43) and the equations of state ($\varepsilon = \hat{\varepsilon}(\rho, T)$, $p = \hat{p}(\rho, T)$), we can derive uniquely the explicit expressions of these coefficients except for the integration constants.

2.3.5 Linear constitutive equations

From Eqs. (2.36) and (2.38)_{3,4,5}, the linear constitutive equations are summarized as follows:

$$\begin{aligned}
 \Pi &= 2h_2 \lambda_{kk}, \\
 M_{\langle ij \rangle} &= 2h_3 \lambda_{\langle ij \rangle}, \\
 m_{ppi} &= 2h_4 \mu_{li}, \\
 M_{iik} &= 3 \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{lk}, \\
 M_{\langle ij \rangle k} &= \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right] \mu_{li \langle i} \delta_{j \rangle k}, \\
 m_{ppik} &= \left[\beta_1 + \left\{ \beta_2 - h_4 \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} \right\} \lambda_{ll} \right] \delta_{ik} + \beta_3 \lambda_{\langle ik \rangle}.
 \end{aligned} \tag{2.44}$$

It is usually more convenient to take $\{\rho, T, S_{\langle ij \rangle}, \Pi, q_i\}$ as independent variables instead of $\{\rho, T, \lambda_{\langle ij \rangle}, \lambda_{ll}, \mu_{li}\}$. From Eqs. (2.44)_{1,2,3}, (2.9) and (2.10), the Lagrange multipliers are expressed by

$$\lambda_{kk} = \frac{1}{2h_2} \Pi, \quad \lambda_{\langle ij \rangle} = -\frac{1}{2h_3} S_{\langle ij \rangle}, \quad \mu_{li} = \frac{1}{h_4} q_i. \tag{2.45}$$

Then we may express the linear constitutive equations as follows:

$$\begin{aligned}
 M_{ik} &= 3Lq_k, \\
 M_{\langle ij \rangle k} &= Kq_{\langle i \delta_j \rangle k}, \\
 m_{ppik} &= \left[\beta_1 + \left\{ \frac{h_4}{2h_2} \left(L - \frac{(\frac{\partial p}{\partial T})\rho}{\rho(\frac{\partial \varepsilon}{\partial T})\rho} \right) + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right\} \Pi \right] \delta_{ik} - \left(\frac{h_4}{2h_3} K + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right) S_{\langle ik \rangle},
 \end{aligned} \tag{2.46}$$

where the coefficients h_2, h_3, h_4 and $\beta_1, \beta_2, \beta_3$ are the functions of ρ and T . And instead of β_2 and β_3 , we introduce the coefficients L and K that are the functions of ρ and T defined by

$$L = \frac{1}{h_4} \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right], \quad K = \frac{1}{h_4} \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right]. \tag{2.47}$$

2.3.6 Entropy density and entropy flux

With Eqs. (2.26), (2.27), (2.30), (2.31) and the constitutive equations (4.5), the entropy density and the entropy flux are expressed as

$$h = h^E + \frac{1}{4h_2} \Pi^2 + \frac{1}{4h_3} S_{\langle ij \rangle} S_{\langle ij \rangle} + \frac{1}{h_4} q_i q_i, \tag{2.48}$$

$$\varphi_k = \frac{1}{T} q_k + \frac{1}{2h_2} \left(L - \frac{(\frac{\partial p}{\partial T})\rho}{\rho(\frac{\partial \varepsilon}{\partial T})\rho} \right) \Pi q_k - \frac{K}{2h_3} q_i S_{\langle ik \rangle}. \tag{2.49}$$

2.3.7 Productions

The productions are also expanded with respect to the nonequilibrium variables $\{\lambda_{kk}, \lambda_{\langle ij \rangle}, \mu_{li}\}$ around an equilibrium state. In the linear approximation, we have

$$P_{\langle ij \rangle} = \sigma \lambda_{\langle ij \rangle}, \quad P_{ii} = 3\zeta \lambda_{kk}, \quad Q_i = \tau \mu_{li}. \tag{2.50}$$

Then we obtain

$$\Sigma = \sigma \lambda_{\langle ij \rangle} \lambda_{\langle ij \rangle} + \zeta \lambda_{kk}^2 + \tau \mu_{li} \mu_{li} \geq 0. \tag{2.51}$$

There are three conditions for the coefficients:

$$\sigma > 0, \quad \zeta > 0, \quad \tau > 0. \tag{2.52}$$

The constitutive equations (2.50) may also be expressed as

$$P_{\langle ij \rangle} = -\frac{\sigma}{2h_3} S_{\langle ij \rangle}, \quad P_{ii} = \frac{3\zeta}{2h_2} \Pi, \quad Q_i = \frac{\tau}{h_4} q_i. \tag{2.53}$$

2.4 Concavity of the entropy density and causality

The system (2.5) must be symmetric hyperbolic so as to ensure the causality. Near equilibrium this requirement corresponds to the condition of the concavity of the entropy density [8, 60].¹

As the second derivative of the entropy density h near equilibrium is given by

$$d^2h = d^2h^E + \frac{1}{4h_2}(d\Pi)^2 + \frac{1}{4h_3}dS_{\langle ij \rangle}dS_{\langle ij \rangle} + \frac{1}{h_4}dq_idq_i, \quad (2.54)$$

the condition is satisfied when h^E is a concave function with respect to $\{\rho, m_{ii}\}$ and the following inequalities are fulfilled:

$$h_2 < 0, \quad h_3 < 0, \quad h_4 < 0. \quad (2.55)$$

Using the well-known results of thermodynamic stability in equilibrium thermodynamics and the relations (2.42)_{2,3} and (2.43)₄, the concavity condition is expressed as follows:

$$\begin{aligned} p > 0, \quad \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho}\right)_T > 0, \\ -\frac{5}{6}Tp + \frac{\rho T}{2} \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{T^2}{2\rho} \left(\frac{\partial p}{\partial T}\right)_\rho^2 < 0, \\ 2T^2 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho - T^2 \left(\frac{\partial \beta_1}{\partial T}\right)_\rho < 0. \end{aligned} \quad (2.56)$$

¹The entropy density used in the mathematical community has usually opposite sign to the present entropy density. As a consequence, they speak about convexity instead of concavity.

2.5 Field equations

The closed system of field equations is obtained by substituting the equations (4.5) into the system (4.4):

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
 \rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} - \frac{\partial S_{\langle ij \rangle}}{\partial x_j} &= 0, \\
 \rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \dot{T} + \left[p + \Pi - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \frac{\partial v_k}{\partial x_k} - \frac{\partial v_i}{\partial x_k} S_{\langle ik \rangle} + \frac{\partial q_k}{\partial x_k} &= 0, \\
 \dot{S}_{\langle ij \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_j \rangle} + S_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_j \rangle} + 2 \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle j \rangle k} & \\
 + C_{S1} \frac{\partial \rho}{\partial x_k} q_{\langle i} \delta_{j \rangle k} + C_{S2} \frac{\partial T}{\partial x_k} q_{\langle i} \delta_{j \rangle k} + C_{S3} \frac{\partial q_{\langle i}}{\partial x_j \rangle} &= -\frac{1}{\tau_S} S_{\langle ij \rangle}, \tag{2.57}
 \end{aligned}$$

$$\begin{aligned}
 \dot{\Pi} + (C_{\Pi 1} + C_{\Pi 2} \Pi) \frac{\partial v_k}{\partial x_k} + C_{\Pi 3} \frac{\partial v_{\langle i}}{\partial x_k \rangle} S_{\langle ik \rangle} + C_{\Pi 4} q_k \frac{\partial \rho}{\partial x_k} + C_{\Pi 5} q_k \frac{\partial T}{\partial x_k} + C_{\Pi 6} \frac{\partial q_k}{\partial x_k} &= -\frac{1}{\tau_\Pi} \Pi, \\
 \dot{q}_i + C_{q1} q_i \frac{\partial v_k}{\partial x_k} + C_{q2} q_k \frac{\partial v_k}{\partial x_i} + C_{q3} q_k \frac{\partial v_i}{\partial x_k} + C_{q4} \frac{\partial T}{\partial x_i} + C_{q5} \frac{\partial \Pi}{\partial x_i} + C_{q6} \frac{\partial S_{\langle ik \rangle}}{\partial x_k} & \\
 + \Pi \left(C_{q7} \frac{\partial \rho}{\partial x_i} + C_{q8} \frac{\partial T}{\partial x_i} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_i} + \frac{1}{\rho} \frac{\partial S_{\langle ik \rangle}}{\partial x_k} \right) & \\
 - S_{\langle ik \rangle} \left(C_{q9} \frac{\partial \rho}{\partial x_k} + C_{q10} \frac{\partial T}{\partial x_k} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_k} + \frac{1}{\rho} \frac{\partial S_{\langle jk \rangle}}{\partial x_j} \right) &= -\frac{1}{\tau_q} q_i, \tag{2.58}
 \end{aligned}$$

where the coefficients C_{Sa} ($a = 1, 2, 3$), $C_{\Pi b}$ ($b = 1, \dots, 6$) and C_{qc} ($c = 1, \dots, 10$), and the relaxation times τ_S, τ_q, τ_Π are the functions of ρ and T . With h_2, h_3, h_4, L and K , these are expressed as follows:

$$\begin{aligned}
 C_{S1} &= -\left(\frac{\partial K}{\partial \rho} \right)_T, \quad C_{S2} = -\left(\frac{\partial K}{\partial T} \right)_\rho, \quad C_{S3} = -K, \\
 C_{\Pi 1} &= -\frac{2h_2}{T}, \quad C_{\Pi 2} = \frac{5}{3} - \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1}, \quad C_{\Pi 3} = -\frac{2}{3} + \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1}, \\
 C_{\Pi 4} &= \frac{5}{6} \left(\frac{\partial K}{\partial \rho} \right)_T, \quad C_{\Pi 5} = \left(\frac{\partial L}{\partial T} \right)_\rho, \quad C_{\Pi 6} = L - \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1}, \\
 C_{q1} &= 1 + \frac{K}{2}, \quad C_{q2} = \frac{K}{2}, \quad C_{q3} = 1 + L - \frac{K}{3}, \quad C_{q4} = -\frac{h_4}{2T^2}, \\
 C_{q5} &= \frac{h_4}{4h_2} \left(L - \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1} \right), \quad C_{q6} = -\frac{h_4}{4h_3} K, \\
 C_{q7} &= \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T - \frac{p}{\rho^2} + \left(\frac{\partial C_{q5}}{\partial \rho} \right)_T, \quad C_{q8} = \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho + \left(\frac{\partial C_{q5}}{\partial T} \right)_\rho, \\
 C_{q9} &= \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T - \frac{p}{\rho^2} - \left(\frac{\partial C_{q6}}{\partial \rho} \right)_T, \quad C_{q10} = \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho - \left(\frac{\partial C_{q6}}{\partial T} \right)_\rho, \tag{2.59}
 \end{aligned}$$

and

$$\tau_S = -\frac{2h_3}{\sigma}, \quad \tau_\Pi = -\frac{2h_2}{\zeta}, \quad \tau_q = -\frac{2h_4}{\tau}. \quad (2.60)$$

2.6 Relationship between ET and Navier-Stokes-Fourier theory

We carry out the Maxwellian iteration [8, 46] in the system (2.57): The first iterates $\Pi^{(1)}$, $S_{\langle ij \rangle}^{(1)}$ and $q_i^{(1)}$ are obtained by the substitution of the 0th iterates $S_{\langle ij \rangle}^{(0)} = 0$, $\Pi^{(0)} = 0$ and $q_i^{(0)} = 0$ into the left hand side of (2.57)_{4,5,6}. Then we obtain

$$S_{\langle ij \rangle}^{(1)} = 2p\tau_S \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \quad \Pi^{(1)} = \frac{2h_2}{T} \tau_\Pi \frac{\partial v_k}{\partial x_k}, \quad q_i^{(1)} = \frac{h_4}{2T^2} \tau_q \frac{\partial T}{\partial x_i}. \quad (2.61)$$

On the other hand, we have the laws of Navier-Stokes and Fourier expressed by (2.2). The comparison reveals that

$$\mu = p\tau_S, \quad \nu = -\frac{2h_2}{T} \tau_\Pi, \quad \kappa = -\frac{h_4}{2T^2} \tau_q. \quad (2.62)$$

We can therefore estimate the values of the relaxation times τ_S , τ_q and τ_Π from the experimental data of the coefficients μ , ν and κ .

The second iterates are obtained by substituting the first iterates into the left hand side of (2.57)_{4,5,6}, and higher iterates are obtained in a similar way.

In conclusion, the system can be certainly closed by the universal principles except for some nonessential constants, provided that we know the thermal and caloric equations of state and the viscosity and heat conductivity coefficients. This surprising result, which could not be achieved in previous works on this subject, shows clearly the power of our hierarchy assumption.

2.7 Characteristic Features of the Theory

As shown above, the thermal and caloric equations of state play a crucial role in the ET theory of dense gases. In general, the equations of state can be expressed as

$$p = p_{ideal}(\rho, T) + p_\phi(\rho, T), \quad \varepsilon = \varepsilon_{ideal}(T) + \varepsilon_\phi(\rho, T), \quad (2.63)$$

where p_{ideal} and ε_{ideal} are, respectively, the pressure and the specific internal energy in a rarefied gas limit. In a dense gas, as the average distance between the constituent molecules is finite, the interaction between the molecules also contributes to both the pressure and the specific internal energy, which are denoted by p_ϕ and ε_ϕ . Furthermore, ε_{ideal} can be divided into two parts:

$$\varepsilon_{ideal} = \varepsilon_{trans}(T) + \varepsilon_{int}(T),$$

where ε_{trans} and ε_{int} are the specific internal energies due to, respectively, the molecular translational modes and the internal modes of a molecule such as rotational and vibrational modes. Between p and ε , there is a relation which comes from the integrability condition of Gibbs equation (1.149);

$$\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T = \frac{1}{\rho^2} \left(p - T \left(\frac{\partial p}{\partial T} \right)_\rho \right).$$

Between p_{ideal} and ε_{ideal} , there is a following relation:

$$3p_{ideal} = 2\rho\varepsilon_{trans}. \quad (2.64)$$

Owing to the general character of the equations of state mentioned above, we have the following four disjoint CASEs 1-4:

CASE 1 Rarefied monatomic gases ($p_\phi = 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi = 0$),

CASE 2 Rarefied polyatomic gases ($p_\phi = 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi = 0$),

CASE 3 Dense monatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi \neq 0$),

CASE 4 Dense polyatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi \neq 0$).

Any gas belongs to one of the cases. See also Fig.2.1.

An advantage of this classification is that the effect of the internal modes of a molecule on nonequilibrium phenomena in a gas can be analyzed clearly by comparing the results of CASE 1 and CASE 2 (or of CASE 3 and CASE 4). In a similar way, the effect of the inter-molecular potential, for example, can be analyzed by comparing the results of CASE 1 and CASE 3 (or of CASE 2 and CASE 4). CASE 1 has already been fully developed [8], while CASEs 2-4 are those to be explored by the present ET theory of dense gases.

In this section, we discuss the characteristic features of the present theory in CASEs 1-4 separately.

2.7.1 CASE 1: Rarefied monatomic gases

The equations of state are given by

$$p = p_{ideal}(\rho, T), \quad \varepsilon = \varepsilon_{trans}(T), \quad (2.65)$$

and there is a relationship between p and ε :

$$3p = 2\rho\varepsilon.$$

For classical gases, in particular, we have

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T,$$

	$p_\phi = 0, \varepsilon_\phi = 0$	$p_\phi \neq 0, \varepsilon_\phi \neq 0$
$\varepsilon_{int} = 0$	Rarefied monatomic (CASE 1)	Dense monatomic (CASE 3)
$\varepsilon_{int} \neq 0$	Rarefied polyatomic (CASE 2)	Dense polyatomic (CASE 4)

Figure 2.1: Any gas belongs to one of the CASEs 1-4. The darker part is an unexplored territory and is expected to be studied by the present ET theory of dense gases.

where k_B and m are, respectively, the Boltzmann constant and the mass of a molecule. We may utilize these equations of state to obtain the system of field equations in CASE 1.

Let us discuss a subtle point in the system thus obtained. Eq. (2.57)₅ is now reduced to $\Pi = 0$ as is expected for rarefied monatomic gases, and it plays no more role. The theory, therefore, becomes singular because of the change of the system itself, that is, the change from 14 equations to 13 equations. Furthermore, as G_{ii} is congruent with F_{ii} in this case, the G -series merges with F -series. As a result we have the following system of field equations:

$$\begin{aligned}
 \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\
 \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\
 \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{\langle ij \rangle}, \\
 \frac{\partial F_{ppi}}{\partial t} + \frac{\partial F_{ppik}}{\partial x_k} &= P_{ppi},
 \end{aligned} \tag{2.66}$$

where F_{ppik} and P_{ppi} are the flux and production of F_{ppi} , respectively. This is exactly the same as that of ET of rarefied monatomic gases (Chapter 1, Section 3, Eq. (1.117)). In conclusion, the system of field equations (2.57) for dense gases contains the system of 13 field equations for rarefied monatomic gases as a special case in a singular way.

2.7.2 CASE 2: Rarefied polyatomic gases

The equations of state, when the temperature is not extremely low, are expressed as

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T + \varepsilon_{int}(T). \tag{2.67}$$

It may be useful to introduce the specific heat $c_v = d\varepsilon/dT$, which, in general, depends on the temperature. Then we obtain the system of field equations for non-polytropic gases.

In this case the coefficients $h_2, h_3, h_4, \beta_1, L$ and K are easily obtained from the relations (2.42) and (2.43): as follows

$$\begin{aligned} h_2 &= \left(\frac{1}{2c_v^*} - \frac{1}{3} \right), \quad h_3 = -\frac{k_B}{m} \rho T^2, \quad h_4 = -2 \left(\frac{k_B}{m} \right)^2 T^3 \rho (1 + c_v^*), \\ \beta_1 &= 2 \left(\varepsilon + \frac{k_B T}{m} \right) \frac{k_B}{m} T \rho, \quad K = \frac{2}{1 + c_v^*}, \quad L = \frac{5}{3} \frac{1}{1 + c_v^*}, \end{aligned} \quad (2.68)$$

where $c_v^* = \frac{c_v}{k_B/m}$ is the dimensionless specific heat. We assume that the integration constants in $\beta_1, \beta_2, \beta_3$ vanish. This assumption is reasonable because of the fact that our results below are consistent with those of the kinetic theory [15, 13].

The linear constitutive equations are given by

$$\begin{aligned} M_{iik} &= \frac{5}{c_v^* + 1} q_k, \\ M_{\langle ij \rangle k} &= \frac{2}{c_v^* + 1} q_{\langle i} \delta_{j \rangle k}, \\ m_{ppik} &= 2 \frac{k_B}{m} T [(c_v^* + 1)p + (c_v^* + 2)\Pi] \delta_{ik} - 2 \frac{k_B}{m} T (c_v^* + 2) S_{\langle ik \rangle}, \\ P_{ii} &= -\frac{9c_v^* \zeta}{(2c_v^* - 3) \frac{k_B}{m} \rho T^2} \Pi, \\ P_{\langle ij \rangle} &= \frac{\sigma}{2 \frac{k_B}{m} \rho T^2} S_{\langle ij \rangle}, \\ Q_i &= -\frac{\tau}{2(c_v^* + 1) \left(\frac{k_B}{m} \right)^2 \rho T^3} q_i. \end{aligned} \quad (2.69)$$

The coefficients of field equations are expressed as

$$\begin{aligned} C_{S1} &= 0, \quad C_{S2} = \frac{2c_v^{*'}}{(1 + c_v^*)^2}, \quad C_{S3} = -\frac{2}{1 + c_v^*}, \\ C_{\Pi 1} &= \left(\frac{2}{3} - \frac{1}{c_v^*} \right) \frac{k_B}{m} \rho T, \quad C_{\Pi 2} = \frac{5}{3} - \frac{1}{c_v^*}, \quad C_{\Pi 3} = \frac{1}{c_v^*} - \frac{2}{3}, \\ C_{\Pi 4} &= 0, \quad C_{\Pi 5} = -\frac{5}{3} \frac{c_v^{*'}}{(1 + c_v^*)^2}, \quad C_{\Pi 6} = \frac{2c_v^* - 3}{3c_v^*(1 + c_v^*)}, \\ C_{q1} &= \frac{2 + c_v^*}{1 + c_v^*}, \quad C_{q2} = \frac{1}{1 + c_v^*}, \quad C_{q3} = \frac{2 + c_v^*}{1 + c_v^*}, \quad C_{q4} = \left(\frac{k_B}{m} \right)^2 T \rho (1 + c_v^*), \\ C_{q5} &= \frac{k_B}{m} T, \quad C_{q6} = -\frac{k_B}{m} T, \quad C_{q7} = -\frac{k_B T}{m \rho}, \quad C_{q8} = \frac{k_B}{m} (1 + c_v^*), \\ C_{q9} &= -\frac{k_B a T}{m \rho}, \quad C_{q10} = \frac{k_B}{m} (1 + c_v^*). \end{aligned} \quad (2.70)$$

The relaxation times τ_S , τ_q and τ_Π are given by

$$\tau_S = \frac{2pT}{\sigma}, \quad \tau_\Pi = \frac{(2c_v^* - 3)pT}{3c_v^* \zeta}, \quad \tau_q = \frac{4(c_v^* + 1) \left(\frac{k_B}{m}\right)^2 \rho T^3}{\tau}. \quad (2.71)$$

These are related to the shear and bulk viscosities and the heat conductivity:

$$\mu = p\tau_S, \quad \nu = \frac{2c_v^* - 3}{3c_v^*} p\tau_\Pi, \quad \kappa = (c_v^* + 1) \frac{p^2}{\rho T} \tau_q. \quad (2.72)$$

The entropy density and the entropy flux are expressed as

$$h = h^E - \frac{3c_v^*}{2(2c_v^* - 3) \frac{k_B}{m} \rho T^2} \Pi^2 - \frac{1}{4 \frac{k_B}{m} \rho T^2} S_{\langle ij \rangle} S_{\langle ij \rangle} - \frac{1}{2(c_v^* + 1) \left(\frac{k_B}{m}\right)^2 \rho T^3} q_i q_i + O(3), \quad (2.73)$$

$$\varphi_k = \frac{1}{T} q_k - \frac{2c_v^{*2} + 6c_v^* - 6}{(2c_v^* - 3)(c_v^* + 1) \frac{k_B}{m} \rho T^2} \Pi q_k + \frac{1}{(c_v^* + 1) \frac{k_B}{m} \rho T^2} q_i S_{\langle ik \rangle} + O(3). \quad (2.74)$$

The requirement of the concavity of the entropy density are expressed as

$$p > 0, \quad \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho}\right)_T > 0, \quad (2.75)$$

$$\frac{2c_v^* - 3}{c_v^*} \frac{k_B}{m} \rho T^2 > 0, \quad 2(c_v^* + 1) \left(\frac{k_B}{m}\right)^2 \rho T^3 > 0.$$

It is easy to see that all inequalities are identically satisfied for classical polyatomic gases with $c_v^* > 3/2$.

It can be proved that the system of field equations in CASE 2 is fully consistent with the system derived from a kinetic model for diatomic gases [15] and from the kinetic theory with the maximum entropy principle [14, 61, 48, 12] for polyatomic gases [13]. This consistency is, of course, vitally important for the validity test of the theory of dense gases itself as a necessary condition. The detailed study of such an interrelationship between ET and the kinetic theory must be a promising new direction in the future research.

We remark the case that $c_v^* = 3/2$. In this case, we notice a subtle point in these expression and also Eq. (2.69)₄ for the case of rarefied monatomic gases where $c_v^* = 3/2$. This subtle point comes from the fact that $h_2 = 0$ when $c_v^* = 3/2$. Therefore, as we mentioned in the previous subsection, we need to treat this case as CASE 1.

2.7.3 CASE 3: Dense monatomic gases

The CASE 3 has been little explored by ET up to now, but is the case that is highly expected to be studied by the present ET theory. Such a study must be challenging not only theoretically but also practically.

The equations of state are expressed as

$$p = \frac{k_B}{m} \rho T + p_\phi(\rho, T), \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T + \varepsilon_\phi(\rho, T). \quad (2.76)$$

The explicit forms of p_ϕ and ε_ϕ may be given in the virial expansion form. Up to the first correction with respect to ρ , with the help of the integrability condition of Gibbs equation (1.149), we have the following expression:

$$p_\phi = \frac{k_B}{m} T B_2(T) \rho^2 + O(\rho^3), \quad \varepsilon_\phi = -\frac{k_B}{m} T^2 B_2'(T) \rho + O(\rho^2), \quad (2.77)$$

where the second virial coefficient B_2 is the function of the temperature T , and a prime means a derivative with respect to T .

Using the equations of state (2.76) and (2.77), we can obtain the explicit expressions of the coefficients in the constitutive equations in the following way: We obtain $h_2, h_3, h_5, \dots, h_8$ except for h_4 from (2.42). Integrating (2.43)₁ with respect to ρ , we obtain β_1 as follows:

$$\begin{aligned} \beta_1 &= \int_{\rho_0}^{\rho} 2 \left(\varepsilon(\bar{\rho}, T) + \frac{p(\bar{\rho}, T)}{\bar{\rho}} \right) \left(\frac{\partial p(\bar{\rho}, T)}{\partial \bar{\rho}} \right)_T d\bar{\rho} + C_1(\rho_0, T, T_0), \\ &= 5 \left(\frac{k_B}{m} \right)^2 T^2 \rho + \left(\frac{k_B}{m} \right)^2 (6B_2 - TB_2') T^2 \rho^2 + O(\rho^3) + C_2(\rho_0, T, T_0), \end{aligned}$$

where $C_{1,2}(\rho_0, T, T_0)$ are integration functions, and ρ_0 and T_0 are, respectively, the mass density and temperature in a reference state. As β_1 at an arbitrary value of T must asymptotically approaches $5 \left(\frac{k_B}{m} \right)^2 T^2 \rho$ in the rarefied-gas limit, we obtain $C_2(\rho_0, T, T_0) = 0$. Now β_1 has been determined within the approximation adopted here, we get the explicit form of h_4 from (2.43)₄. β_2 and β_3 can be determined in a similar way. We can easily check the consistency that β_2 and β_3 obtained in this way satisfy the remaining relations (2.43)_{5,6}. Then we can obtain a relation between L and K as follows: $L = \frac{5}{6} K$.

Substituting the equations of state (2.76) with (2.77) into (2.42) and (2.43), we obtain the first correction of h_2, h_3, h_4 and K with respect to ρ :

$$\begin{aligned} h_2 &= \frac{k_B}{m} T^2 \rho \left(\frac{15B_2 + 20TB_2' + 4T^2B_2''}{18} \rho + O(\rho^2) \right), \\ h_3 &= -\frac{k_B}{m} T^2 \rho (1 + B_2 \rho + O(\rho^2)), \\ h_4 &= -\left(\frac{k_B}{m} \right)^2 T^3 \rho (5 + (5B_2 - T^2B_2'') \rho + O(\rho^2)), \\ K &= \frac{4}{5} + \frac{10TB_2' + 4T^2B_2''}{25} \rho + O(\rho^2). \end{aligned} \quad (2.78)$$

We here make only one remark. When we analyze the concavity condition (2.56), we find that there is a subtle point such that the condition is not always satisfied. As we will see in the next section, the hard-sphere system with constant B_2 is probably the most extreme case

in the sense that the condition is not satisfied for any ρ as far as we adopt the equations of state above. This fact is intimately related to the singularity of the system of field equations mentioned in CASE 1 where the dynamic pressure Π vanishes. Detailed study of such a delicate point will soon be reported elsewhere.

2.7.4 CASE 4: Dense polyatomic gases

The equations of state are expressed as

$$p = \frac{k_B}{m} \rho T + p_\phi(\rho, T), \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T + \varepsilon_{int}(T) + \varepsilon_\phi(\rho, T). \quad (2.79)$$

For later convenience, we introduce

$$c_{v_{ideal}}^*(T) = \frac{d\varepsilon_{ideal}(T)}{dT} / \frac{k_B}{m} = \frac{3}{2} + \frac{d\varepsilon_{int}(T)}{dT} / \frac{k_B}{m}. \quad (2.80)$$

In the same manner with CASE 3, we can determine the integration functions of β_1, β_2 and β_3 as 0. In addition, we can also obtain the relation $L = \frac{5}{6}K$. Then, with the virial expansion form (2.77), we have the first correction of h_2, h_3, h_4 and K with respect to ρ :

$$\begin{aligned} h_2 &= \frac{k_B}{m} T^2 \rho \left[\frac{3 - 2c_{v_{ideal}}^*}{6c_{v_{ideal}}^*} \right. \\ &\quad \left. + \frac{(c_{v_{ideal}}^*)^2 + 6c_{v_{ideal}}^* B_2 + 6(1 + c_{v_{ideal}}^*)TB_2' + 3T^2 B_2''}{6c_{v_{ideal}}^{*2}} \rho + O(\rho^2) \right], \\ h_3 &= -\frac{k_B}{m} T^2 \rho (1 + B_2 \rho + O(\rho^2)), \\ h_4 &= -2 \left(\frac{k_B}{m} \right)^2 T^3 \rho \left[1 + c_{v_{ideal}}^* + \left((1 + c_{v_{ideal}}^*)B_2 - \frac{1}{2}T^2 B_2'' \right) \rho + O(\rho^2) \right], \\ K &= \frac{2}{c_{v_{ideal}}^* + 1} + \frac{(c_{v_{ideal}}^* + 1)TB_2' + T^2 B_2''}{(c_{v_{ideal}}^* + 1)^2} \rho + O(\rho^2). \end{aligned} \quad (2.81)$$

The CASE 4 has been totally unexplored by ET until now. This case is also highly expected to be studied by the present ET theory.

2.8 Application to special systems

In the previous sections (Section 7.3 and Section 7.4), we have seen only the features of dense gases by the application to the system with the virial equations of state. In the present section the general theory is applied to two physically important systems: (i) a hard-sphere system, and (ii) a van der Waals fluid. The analysis of the first system shows explicitly the corrections to the results in rarefied gas system when the system is no more dilute enough. As a hard-sphere system plays an important role in the perturbation theory in liquid-state physics [62, 63, 64],

it seems to be interesting for the researchers in this field to understand ET of the system. A van der Waals fluid is the well-known simple model that can describe real-gas effects including gas-liquid phase transitions.

2.8.1 Hard-sphere system

The thermal and caloric equations of state are given by

$$\begin{aligned} p &= \frac{k_B}{\omega} T \eta \Gamma(\eta), \\ \varepsilon &= \frac{D}{2} \frac{k_B}{m} T, \end{aligned} \quad (2.82)$$

where η is the packing fraction related to the mass density ρ by

$$\eta = \frac{\rho \omega}{m}, \quad (2.83)$$

and $\Gamma(\eta)$ is a function of η determined explicitly by computer experiments [62]. Here ω is the volume of a hard sphere. In this subsection, we use η instead of ρ . Throughout the present section, the specific heat is assumed to be constant, that is, only polytropic fluids are studied. Therefore the caloric equation of state (2.82) is expressed by the degrees of freedom of a molecule D ($D = 3 + f$ where 3 corresponds to the translational motion in the 3-dimensional space and f is the internal degrees of freedom).

Using the expressions of the coefficients in the constitutive equations derived in the same way as above, we obtain the constitutive equations:

$$\begin{aligned} M_{iik} &= \frac{10 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{D\eta\Gamma + 2 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}} q_k, \\ M_{\langle ij \rangle k} &= \frac{4 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{D\eta\Gamma + 2 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}} q_{\langle i} \delta_{j \rangle k}, \\ m_{ppik} &= \frac{k_B}{m} T \left[\frac{k_B}{\omega} \eta T \left(D\Gamma + \Gamma^2 + \frac{1}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right) \right. \\ &\quad \left. + \left\{ D + 2\Gamma - \frac{6D\Gamma^2 + \frac{2}{\eta}(-5D + 6\Gamma) \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma'} \right\} \Pi \right] \delta_{ik} \\ &\quad - \frac{k_B}{m} T \left(D + 2\Gamma + \frac{2}{\eta\Gamma} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right) S_{\langle ik \rangle}, \\ P_{ii} &= - \frac{9D\zeta}{\frac{k_B}{\omega} \eta T^2 (2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma')} \Pi, \\ P_{\langle ij \rangle} &= \frac{\sigma}{2 \frac{k_B}{\omega} \eta T^2 \Gamma} S_{\langle ij \rangle}, \\ Q_i &= - \frac{\tau}{\left(\frac{k_B}{m} \right)^2 \frac{m}{\omega} \eta T^3 \left(D\Gamma + \frac{2}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right)} q_i, \end{aligned} \quad (2.84)$$

where $\Gamma' = d\Gamma(\eta)/d\eta$.

The closed system of field equations can be obtained by using above constitutive equations. We omit its expression for simplicity. The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\begin{aligned}\mu &= p\tau_S, \\ \nu &= \frac{1}{3D} \frac{k_B}{\omega} \eta T (2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma') \tau_{\Pi}, \\ \kappa &= \left(\frac{k_B}{m}\right)^2 \frac{m}{\omega} \eta \frac{T}{2} \left(D\Gamma + \frac{2}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}\right) \tau_q.\end{aligned}\tag{2.85}$$

The concavity condition of the entropy density in this case can be expressed by only one inequality:

$$-\frac{\Gamma}{3} + \frac{\Gamma^2}{D} + \frac{\eta\Gamma'}{2} < 0.\tag{2.86}$$

Then we find that there is a critical packing fraction η_C such that the above condition is satisfied in the region $0 < \eta < \eta_C$. In the case of $D = 5$, for example, we can estimate $\eta_C = 0.0447$ by adopting the following functional form of Γ [65]:

$$\Gamma(\eta) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}.\tag{2.87}$$

The dependence of η_C on D is shown in Fig. 1. It is remarkable that $\eta_C = 0$ in the case of $D = 3$.

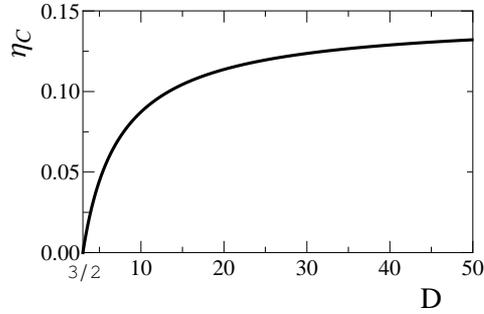


Figure 2.2: Dependence of the critical packing fraction η_C on the degrees of freedom D .

2.8.2 van der Waals fluid

The thermal and caloric equations of state are given by

$$\begin{aligned}p &= \frac{k_B}{m} \frac{T\rho}{1 - b\rho} - a\rho^2, \\ \varepsilon &= \frac{D}{2} \frac{k_B}{m} T - a\rho,\end{aligned}\tag{2.88}$$

where the material-dependent constants a and b represent, respectively, a measure of the attraction between the constituent molecules and the effective volume (or exclusion volume) of a molecule.

The constitutive equations are obtained by using the same procedure as above:

$$\begin{aligned}
 M_{iik} &= 10 \frac{\frac{k_B T}{m} + \frac{a}{b^2 \rho} (1 - b\rho)(b\rho + \log(1 - b\rho))}{(D + 2) \frac{k_B T}{m} - D(1 - b\rho)a\rho} q_k, \\
 M_{\langle ij \rangle k} &= 4 \frac{\frac{k_B T}{m} + \frac{a}{b^2 \rho} (1 - b\rho)(b\rho + \log(1 - b\rho))}{(D + 2) \frac{k_B T}{m} - D(1 - b\rho)a\rho} q_{\langle i} \delta_{j \rangle k}, \\
 m_{ppik} &= \frac{k_B T}{m} \left[(D + 2)p + \frac{k_B T}{m} \frac{b\rho^2}{(1 - b\rho)^2} - 2a\rho^2 \frac{1 + b\rho}{1 - b\rho} + \frac{8}{3} \frac{a^2 \rho^3}{\frac{k_B T}{m}} \right. \\
 &\quad + \left\{ \frac{k_B T}{m} \frac{2(D - 3)(D + 4) - (7D^2 + 18D - 12)b\rho + 5D(D + 2)b^2 \rho^2}{1 - b\rho} \right. \\
 &\quad + \frac{a}{b} (D(1 - b\rho)^2(10 + Db\rho) + 12b\rho(2 + Db\rho)) - 4D \frac{a^2 \rho^2}{\frac{k_B T}{m}} (1 - b\rho)^2 \\
 &\quad \left. \left. + 10D \frac{a}{b^2 \rho} (1 - b\rho)^2 \log(1 - b\rho) \right\} \Pi \right. \\
 &\quad \left. / \left\{ \frac{k_B T}{m} (2(D - 3) - 5Db\rho) + Da\rho(1 - b\rho)^2 \right\} \right] \delta_{ik} \tag{2.89} \\
 &\quad - \frac{k_B T}{m} \left\{ \frac{k_B T}{m} \frac{D + 4 - (D + 2)b\rho}{1 - b\rho} + \frac{a}{b} (2 - (D + 8)b\rho + Db^2 \rho^2) \right. \\
 &\quad \left. + 4 \frac{a^2 \rho^2}{\frac{k_B T}{m}} (1 - b\rho) + 2 \frac{a}{b^2 \rho} (1 - b\rho) \log(1 - b\rho) \right\} S_{\langle ik \rangle} \\
 &\quad / \left\{ \frac{k_B T}{m} - a\rho(1 - b\rho) \right\}, \\
 P_{ii} &= - \frac{9D(1 - b\rho)^2}{\frac{k_B}{m} \rho T^2 (2(D - 3) - 5Db\rho) + Da\rho^2 T(1 - b\rho)^2} \zeta \Pi, \\
 P_{\langle ij \rangle} &= \frac{1 - b\rho}{2 \frac{k_B}{m} \rho T^2 - 2a\rho^2 T(1 - b\rho)} \sigma S_{\langle ij \rangle}, \\
 Q_i &= - \frac{(1 - b\rho)}{\left(\frac{k_B}{m} \right)^2 (D + 2) \rho T^3 - \frac{k_B}{m} D \rho^2 T^2 a(1 - b\rho)} \tau q_i.
 \end{aligned}$$

The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\begin{aligned}
 \mu &= p\tau_S, \\
 \nu &= \left(\frac{k_B}{m} \frac{\rho T}{3D(1 - b\rho)^2} (2(D - 3) - 5Db\rho) + \frac{a\rho^2}{3} \right) \tau_{\Pi}, \tag{2.90} \\
 \kappa &= \frac{1}{2} \left(\left(\frac{k_B}{m} \right)^2 \frac{D + 2}{1 - b\rho} \rho T - \frac{k_B}{m} D a \rho^2 \right) \tau_q.
 \end{aligned}$$

We now study the concavity condition of the entropy density (2.56). For later convenience,

we introduce the dimensionless variables:

$$\hat{p} = \frac{p}{p_{cr}}, \quad \hat{\rho} = \frac{\rho}{\rho_{cr}}, \quad \hat{T} = \frac{T}{T_{cr}}, \quad (2.91)$$

where $\rho_{cr} = 1/(3b)$, $p_{cr} = a/(27b^2)$ and $T_{cr} = 8a/(27\frac{k_B}{m}b)$ are, respectively, the mass density, the pressure and the temperature at the critical point. Then the thermal and caloric equations of state are rewritten in terms of the dimensionless quantities as

$$\hat{p} = \frac{8\hat{T}\hat{\rho}}{3 - \hat{\rho}} - 3\hat{\rho}^2, \quad \hat{\varepsilon} = \frac{\rho_{cr}}{p_{cr}}\varepsilon = \frac{4D\hat{T}}{3} - 3\hat{\rho}. \quad (2.92)$$

As the inequality (2.56)₂ is always satisfied, the concavity condition is now expressed as

$$\begin{aligned} \frac{8\hat{T}\hat{\rho}}{3 - \hat{\rho}} - 3\hat{\rho}^2 > 0, \quad \frac{8\hat{T}}{(3 - \hat{\rho})^2} - 2\hat{\rho} > 0, \\ \frac{18 + D(5\hat{\rho} - 6)}{D(\hat{\rho} - 3)^2}\hat{T}^2\hat{\rho} - \frac{3}{8}\hat{T}\hat{\rho}^2 < 0, \quad \frac{8(D + 2)\hat{T} + 3D(\hat{\rho} - 3)\hat{\rho}}{(\hat{\rho} - 3)}\hat{T}^2\hat{\rho} < 0. \end{aligned} \quad (2.93)$$

The condition is satisfied in the shaded regions in Fig. 2 for several values of D .

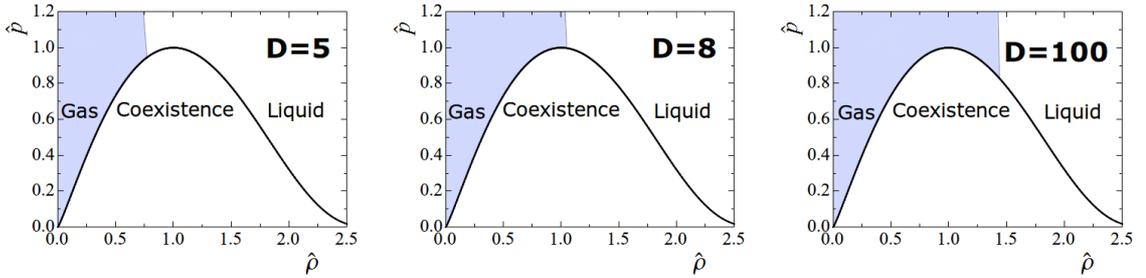


Figure 2.3: The concavity condition (2.93) is satisfied in the shaded region. The degrees of freedom: $D = 5, 8$ and 100 . The curve represents the coexistence curve.

2.9 Concluding remarks

In conclusion we make the following two remarks:

(i) We have proposed and explained a possible phenomenological model of ET of dense gases. The model has been constructed with no reference to microscopic details of the system such as the internal motion of molecules, i.e., molecular rotation and vibration. In this respect, the standpoint of the present work is purely phenomenological and is quite different from that of the previous works dealing with so-called molecular ET [50, 51, 52].

(ii) As discussed in the previous sections, we have understood a subtle point in the present theory in the case of monatomic gases with $c_v^* = 3/2$. This point seems to be interesting from both physical and mathematical viewpoints, and is worthy of further study. This will be the future subject.

Chapter 3

Linear Waves in Rarefied Polyatomic Gases Based on Extended Thermodynamics

Based on the extended thermodynamics for dense gases, the dispersion relation for sound in rarefied polyatomic gases is studied. Through the comparison with experimental data and Navier-Stokes Fourier theory, the validity of extended thermodynamics for dense gases is clarified. Moreover the estimations of the bulk viscosity and relaxation times are studied.

3.1 Introduction

ET of dense gases are proposed and discussed in Chapter 2. This is the theory of 14 fields of mass density, velocity, temperature, viscous stress, dynamic pressure, and heat flux with two parallel hierarchical series of field equations of balance type. The constitutive equations are determined explicitly by the thermal and caloric equations of state. As we have already seen, the theory includes naturally the theory of *rarefied polyatomic* gases as a special case. Now, owing to the establishment of the theory, both the class of gases and the conditions for gases to which ET is applicable have been enlarged enormously.

The purpose of the present chapter is to understand explicitly the validity and the features of the new theory through studying the dispersion relation for sound. We firstly derive the dispersion relation, and secondly compare the results with those obtained in experiments and by the classical Navier-Stokes Fourier (NSF) theory based on the local equilibrium assumption. We will, however, confine our analysis within the sound in some rarefied diatomic gases because suitable experimental data are scarce and are mainly restricted to rarefied gases. The study of the dispersion relation for sound in general dense gases with and without internal degrees

of freedom is, therefore, remained to be a future work.

The organization of the present chapter is as follows: In Section 2, we summarize the basic equations necessary for the present analysis. In Section 3, the dispersion relation is derived and its high-frequency limit is studied. In Section 4, the dispersion relations in hydrogen, deuterium and hydrogen deuteride gases are compared with both experimental data and those derived from the NSF theory. We also evaluate the relaxation times and the bulk viscosity. The last section is devoted to the summary and concluding remarks.

3.2 Basic equations

In this section, we summarize the basic equations for the present analysis. We assume that a nonequilibrium state can be characterized by the 14 independent field variables $\mathbf{u} \equiv (\rho, v_i, T, S_{\langle ij \rangle}, \Pi, q_i)$ where v_i , $S_{\langle ij \rangle}$, $\Pi (= -S_{ii}/3)$ and q_i are, respectively, the velocity, symmetric traceless part of the viscous stress, dynamic pressure and heat flux. In Chapter 2, we have already obtained the closed field equations of these.

We concentrate our attention to rarefied polyatomic gases (Chapter 2, Section 7.2), that is, in the case that the thermal and caloric equations of state are given by (2.67):

$$p = \frac{k_B}{m} \rho T \quad \text{and} \quad \varepsilon = \varepsilon(T), \quad (3.1)$$

where p , ρ , T and ε are the pressure, mass density, absolute temperature and specific internal energy, respectively, and k_B and m being the Boltzmann constant and the mass of a molecule. Note that gases are, in general, non-polytropic, that is, the specific heat at constant volume

$$c_v = \frac{d\varepsilon}{dT} \quad (3.2)$$

is, in general, not constant but depends on the temperature.

Let $\mathbf{u}_0 \equiv (\rho_0, 0, T_0, 0, 0, 0)$ be a constant equilibrium state, then the linearized system in

the neighborhood of \mathbf{u}_0 for the perturbed field \mathbf{u} reads:

$$\begin{aligned}
 \dot{\rho} + \rho_0 \frac{\partial v_k}{\partial x_k} &= 0, \\
 \rho_0 \dot{v}_i + \frac{k_B}{m} T_0 \frac{\partial \rho}{\partial x_i} + \frac{k_B}{m} \rho_0 \frac{\partial T}{\partial x_i} - \frac{\partial S_{\langle ij \rangle}}{\partial x_j} + \frac{\partial \Pi}{\partial x_i} &= 0, \\
 \frac{k_B}{m} \rho_0 c_v^* \dot{T} + \frac{k_B}{m} \rho_0 T_0 \frac{\partial v_k}{\partial x_k} + \frac{\partial q_k}{\partial x_k} &= 0, \\
 \dot{S}_{\langle ij \rangle} - 2 \frac{k_B}{m} \rho_0 T_0 \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} - \frac{2}{1 + c_v^*} \frac{\partial q_{\langle i}}{\partial x_{j \rangle}} &= -\frac{1}{\tau_S} S_{\langle ij \rangle}, \\
 \dot{\Pi} + \left(\frac{2}{3} - \frac{1}{c_v^*} \right) \frac{k_B}{m} \rho_0 T_0 \frac{\partial v_k}{\partial x_k} + \frac{2c_v^* - 3}{3c_v^*(1 + c_v^*)} \frac{\partial q_k}{\partial x_k} &= -\frac{1}{\tau_{\Pi}} \Pi, \\
 \dot{q}_i + (1 + c_v^*) \left(\frac{k_B}{m} \right)^2 \rho_0 T_0 \frac{\partial T}{\partial x_i} - \frac{k_B}{m} T_0 \frac{\partial S_{\langle ik \rangle}}{\partial x_k} + \frac{k_B}{m} T_0 \frac{\partial \Pi}{\partial x_i} &= -\frac{1}{\tau_q} q_i,
 \end{aligned} \tag{3.3}$$

where a dot on a quantity indicates the material time derivative, and c_v^* is the dimensionless specific heat at the reference equilibrium state:

$$c_v^* = \frac{(c_v)_{T=T_0}}{k_B/m}. \tag{3.4}$$

The relaxation times τ_S , τ_{Π} and τ_q in Eq. (3.3) are also evaluated at the reference equilibrium state.

By the Maxwellian iteration [8, 66, 67, 46], we obtain the relations between the relaxation times and the shear viscosity μ , bulk viscosity ν and heat conductivity κ :

$$\mu = \frac{k_B}{m} \rho_0 T_0 \tau_S, \quad \nu = \left(\frac{2}{3} - \frac{1}{c_v^*} \right) \frac{k_B}{m} \rho_0 T_0 \tau_{\Pi}, \quad \kappa = (1 + c_v^*) \left(\frac{k_B}{m} \right)^2 \rho_0 T_0 \tau_q. \tag{3.5}$$

Let us consider a one-dimensional problem and assume:

$$v_i \equiv \begin{pmatrix} v \\ 0 \\ 0 \end{pmatrix}, \quad S_{\langle ij \rangle} \equiv \begin{pmatrix} S & 0 & 0 \\ 0 & -\frac{1}{2}S & 0 \\ 0 & 0 & -\frac{1}{2}S \end{pmatrix}, \quad q_i \equiv \begin{pmatrix} q \\ 0 \\ 0 \end{pmatrix}. \tag{3.6}$$

Then, from Eq. (3.3), the linearized basic field equations are neatly written as

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{A}_0 \frac{\partial \mathbf{u}}{\partial x} = \mathbf{B}_0 \mathbf{u}, \tag{3.7}$$

where \mathbf{A}_0 and \mathbf{B}_0 are given by

$$\mathbf{A}_0 = \begin{pmatrix} 0 & \rho_0 & 0 & 0 & 0 & 0 \\ \frac{k_B T_0}{m \rho_0} & 0 & \frac{k_B}{m} & -\frac{1}{\rho_0} & \frac{1}{\rho_0} & 0 \\ 0 & \frac{T_0}{c_v^*} & 0 & 0 & 0 & \frac{1}{\frac{k_B c_v^* \rho_0}{m}} \\ 0 & -\frac{4}{3} \frac{k_B}{m} \rho_0 T_0 & 0 & 0 & 0 & -\frac{3(1+c_v^*)}{4} \\ 0 & \left(\frac{2}{3} - \frac{1}{c_v^*}\right) \frac{k_B}{m} \rho_0 T_0 & 0 & 0 & 0 & \frac{2c_v^* - 3}{3c_v^*(1+c_v^*)} \\ 0 & 0 & (1+c_v^*) \left(\frac{k_B}{m}\right)^2 \rho_0 T_0 & -\frac{k_B}{m} T_0 & \frac{k_B}{m} T_0 & 0 \end{pmatrix}, \quad (3.8)$$

$$\mathbf{B}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{\tau_S} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{\tau_{\Pi}} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{\tau_q} \end{pmatrix}. \quad (3.9)$$

3.3 Dispersion relation for sound

In this section, we deduce the dispersion relation, and then obtain the high-frequency limit of the phase velocity and the attenuation factor.

3.3.1 Dispersion relation, phase velocity and attenuation factor

We study a plane harmonic wave propagating in the positive x -direction with the frequency ω and the complex wave number $k = k_r + ik_i$ ($k_r = \Re(k)$, $k_i = \Im(k)$) such that

$$\mathbf{u} = \mathbf{w} e^{i(\omega t - kx)}, \quad (3.10)$$

where \mathbf{w} is a constant amplitude vector. From Eq. (3.7), the dispersion relation is expressed by [68]:

$$\det \left(\mathbf{I} - z \mathbf{A}_0 + \frac{i}{\omega} \mathbf{B}_0 \right) = 0, \quad (3.11)$$

where $z \equiv k/\omega$ and \mathbf{I} is the unit matrix. Then the phase velocity v_{ph} and the attenuation factor α are calculated as the functions of the frequency ω :

$$v_{ph}(\omega) = \frac{\omega}{\Re(k)} = \frac{1}{\Re(z)}, \quad (3.12)$$

$$\alpha(\omega) = -\Im(k) = -\omega\Im(z). \quad (3.13)$$

By introducing the dimensionless parameters defined by

$$\Omega = \tau_S \omega, \quad \tau_{qs} = \frac{\tau_q}{\tau_S}, \quad \tau_{ps} = \frac{\tau_{\Pi}}{\tau_S}, \quad (3.14)$$

the dispersion relation (4.8) is shown explicitly as

$$\begin{aligned} & \frac{c_v^*(c_0 z)^4}{3\Omega^2(1+c_v^*)^2\tau_{ps}} \left(-3(1+c_v^*) - i\Omega(3+7c_v^*+5c_v^*\tau_{ps}) + 9\Omega^2c_v^*\tau_{ps} \right) \\ & + \frac{(c_0 z)^2}{3\Omega^3(1+c_v^*)^2\tau_{qs}\tau_{ps}} \left[-3i(1+c_v^*)^2 + \Omega(1+c_v^*)(3+7c_v^*+5c_v^*\tau_{ps}+6(1+c_v^*)\tau_{qs}) \right. \\ & \left. + i\Omega^2 \left(2(3+10c_v^*+5c_v^{*2})\tau_{qs} + 9c_v^*(1+c_v^*)\tau_{ps} + c_v^*(13+8c_v^*)\tau_{qs}\tau_{ps} \right) - 3\Omega^3c_v^*(7+4c_v^*)\tau_{ps}\tau_{qs} \right] \\ & + \frac{(\Omega-i)(\tau_{ps}\Omega-i)(\tau_{qs}\Omega-i)}{\Omega^3\tau_{ps}\tau_{qs}} = 0 \end{aligned} \quad (3.15)$$

with c_0 being the sound velocity in equilibrium:

$$c_0 = \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_0 + \frac{T_0 \left(\frac{\partial p}{\partial T} \right)_0^2}{\rho_0^2 \left(\frac{\partial \varepsilon}{\partial T} \right)_0}} = \sqrt{aT_0 \left(1 + \frac{1}{c_v^*} \right)}, \quad (3.16)$$

where the suffix 0 indicates the values at the reference equilibrium state. Therefore, for given c_v^* , τ_{qs} and τ_{ps} , the quantity $c_0 z (= c_0 k/\omega)$ is calculated from Eq. (3.15) as the function of $\Omega (= \tau_S \omega)$. Hereafter in the present chapter, we will confine our study within the *fastest* sound wave because the experiments discussed in Section 4 give us the data on this wave.

3.3.2 High frequency limit of the phase velocity and the attenuation factor

From the general theory [8, 68], we have the relations:

$$v_{ph}^{(\infty)} \equiv \lim_{\omega \rightarrow \infty} v_{ph}(\omega) = \lambda_0, \quad (3.17)$$

$$\alpha^{(\infty)} \lambda_0 \equiv \lim_{\omega \rightarrow \infty} \alpha(\omega) \lambda_0 = -\mathbf{l}_0 \cdot \mathbf{B}_0 \cdot \mathbf{d}_0, \quad (3.18)$$

where the characteristic velocity λ_0 is the largest eigenvalue of \mathbf{A}_0 , and \mathbf{l}_0 and \mathbf{d}_0 are the corresponding left and right eigenvectors of \mathbf{A}_0 . Then we obtain the limits in the present case:

$$v_{ph}^{(\infty)} = \sqrt{\frac{aT_0(4c_v^* + 7 + F)}{2(1 + c_v^*)}}, \quad (3.19)$$

$$\alpha^{(\infty)} = \frac{\sqrt{2(1 + c_v^*)^3} (F(4 + c_v^*) - 22 - 11c_v^* + 2c_v^{*2})}{9c_v^* \tau_S \sqrt{aT_0} \sqrt{7 + 4c_v^* + F} (7 + 4c_v^* - F)^2 F} \left(4c_v^* + \frac{3c_v^* (8 + 2c_v^* - F)}{\tau_{qs}} + \frac{-3 + 2c_v^*}{\tau_{ps}} \right), \quad (3.20)$$

where F is given by

$$F = \sqrt{37 + 32c_v^* + 4c_v^{*2}}. \quad (3.21)$$

The dependence of the phase velocity $v_{ph}^{(\infty)}$ on c_v^* is shown in Fig. 3.1. In a rarefied monatomic gas with $c_v^* = 3/2$, the phase velocity $v_{ph}^{(\infty)}$ is given by $2.13051\sqrt{aT_0}$ [8]. For large c_v^* , it approaches $\sqrt{3aT_0}$. On the other hand, the attenuation factor $\alpha^{(\infty)}$ depends not

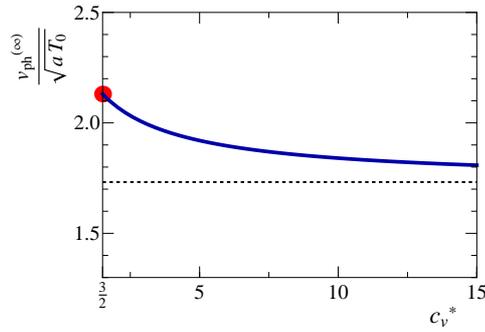


Figure 3.1: Dependence of the phase velocity in the high frequency limit $v_{ph}^{(\infty)}$ on the dimensionless specific heat c_v^* . Rarefied monatomic gases correspond to the case with $c_v^* = 3/2$. The dotted line is the asymptote.

only on c_v^* but also on the relaxation times. In a rarefied monatomic gas, the attenuation factor $\alpha^{(\infty)}$ is given by $(0.0951852 + 0.0931368/\tau_{qs}) / (\tau_S \sqrt{aT_0})$ [8]. For large c_v^* , it approaches $(1 + 2\tau_{ps}) / (9\sqrt{3}\tau_{ps}\tau_S\sqrt{aT_0})$.

3.4 Comparison with experimental data

The dispersion relation obtained above, in particular, the phase velocity v_{ph} and the attenuation factor α as the functions of the frequency ω are compared with the experimental data on normal hydrogen (n-H₂), para hydrogen (p-H₂), normal deuterium (n-D₂), ortho deuterium (o-D₂) and hydrogen deuteride (HD) gases at temperatures 77.3K, 90.2K and the room temperatures [69, 70]. The comparison is also made with the predictions by the classical NSF theory.

Before discussing the subject, we need to make preliminary calculations for determining the values of c_v^* , τ_{qs} and τ_{ps} defined in (3.4) and (3.14) at the reference equilibrium state.

3.4.1 Preliminary calculations

Specific heat

We calculate the specific heat c_v^* of hydrogen, deuterium and hydrogen deuteride gases on the basis of statistical mechanics [71, 72]. As we may safely neglect the contribution of internal vibrational modes in a molecule to the specific heat in the temperature range under consideration, we take only the translational and rotational modes into account. We assume also that the translational mode satisfies the equipartition law of energy. Then c_v^* is expressed as

$$c_v^* = \frac{3}{2} + c_{v,\text{rot}}^*, \quad c_{v,\text{rot}}^* = \beta^2 \frac{\partial^2 \log Z_{\text{rot}}}{\partial \beta^2}, \quad \left(\beta \equiv \frac{1}{k_B T} \right) \quad (3.22)$$

where $c_{v,\text{rot}}^*$ and Z_{rot} are the specific heat and the partition function due to the rotational modes.

For gases composed of heteronuclear diatomic molecules (HD), the partition function is given by

$$Z_{\text{rot}} = \sum_{l=0}^{\infty} (2l+1) \exp[-\beta B l(l+1)], \quad (3.23)$$

where l is the quantum number of the orbital angular momentum and $B = \hbar^2/2I$ with I and \hbar being the moment of inertia of a molecule and the Planck constant divided by 2π , respectively. While, for gases composed of diatomic homonuclear molecules (H_2 and D_2), the partition function is given by

$$\begin{aligned} Z_{\text{rot}} &= Z_g^{g_g} Z_u^{g_u}, \\ Z_g &= \sum_{l=\text{even}} (2l+1) \exp[-\beta B l(l+1)], \\ Z_u &= \sum_{l=\text{odd}} (2l+1) \exp[-\beta B l(l+1)], \end{aligned} \quad (3.24)$$

where g_g and g_u are defined by

$$\text{H}_2 \begin{cases} \text{normal - H}_2 : & g_u = 3/4, & g_g = 1/4 \\ \text{para - H}_2 : & g_u = 0, & g_g = 1 \end{cases}, \quad \text{D}_2 \begin{cases} \text{normal - D}_2 : & g_u = 1/3, & g_g = 2/3 \\ \text{ortho - D}_2 : & g_u = 0, & g_g = 1 \end{cases}. \quad (3.25)$$

Numerically calculated values of c_v^* are shown in Table 3.1 and in Fig. 3.2. The values of B of H_2 , D_2 and HD adopted are 12.09×10^{-22} [J], 6.047×10^{-22} [J] and 9.068×10^{-22} [J], respectively [73].

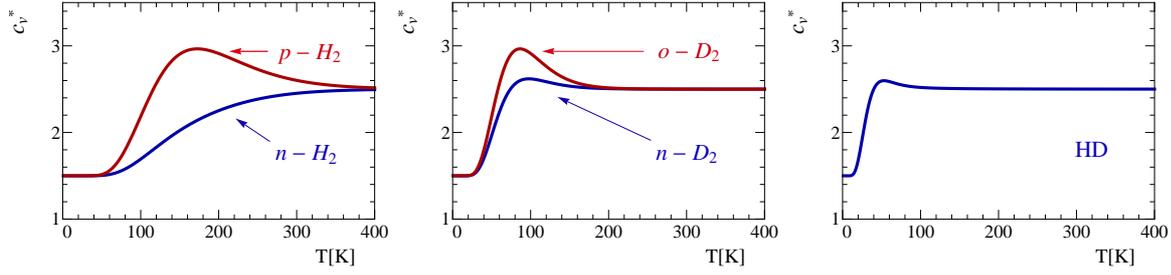


Figure 3.2: Dependence of the dimensionless specific heat c_v^* for n-H₂ and p-H₂ (left), n-D₂ and o-D₂ (center), and HD (right) on the temperature T .

Relaxation times

From (3.5), we have the following relations for the ratios τ_{qs} and τ_{ps} :

$$\tau_{qs} = (1 + c_v^*)^{-1} \frac{\kappa}{\frac{k_B}{m} \mu}, \quad (3.26)$$

$$\tau_{ps} = \left(\frac{2}{3} - \frac{1}{c_v^*} \right)^{-1} \frac{\nu}{\mu}. \quad (3.27)$$

Therefore, in principle, with the help of the experimental data on μ , κ and ν , we can estimate the values of τ_{qs} and τ_{ps} . However, at present, as we have the reliable data only on μ and κ [70], we adopt, in the analysis below, an adjustable parameter:

$$\varphi = \frac{\nu}{\mu}. \quad (3.28)$$

We summarize the adopted values of c_v^* , c_0 , μ , κ , τ_{qs} and the evaluated values of φ and τ_{ps} in Table 3.1, details of which will be discussed in the next subsection.

3.4.2 Experimental data and theoretical predictions for the dispersion relation

Hydrogen gases: n-H₂ and p-H₂

For n-H₂, the dimensionless phase velocity, v_{ph}/c_0 , and the dimensionless attenuation factor, $c_0 \tau_S \alpha$, are shown as the functions of the dimensionless frequency Ω in Fig. 3.3. We see the experimental data on the phase velocity at $T_0 = 273.5, 296.8\text{K}$ by Rhodes [69] and on the attenuation factor at $T_0 = 293\text{K}$ by Sluijter et al. [70] accompanied by the theoretical results at $T_0 = 293\text{K}$ predicted by the ET theory and the NSF theory.

Noticeable points from Fig. 3.3 are summarized as follows: (i) In the region with small Ω , as is expected, the predictions by the two theories coincide with each other. The value of the parameter φ is determined to be 37 as the best fit with the experimental data in this region.

Table 3.1: Values of the temperature T_0 , dimensionless specific heat c_v^* , sound speed in equilibrium c_0 , shear viscosity μ [70], heat conductivity κ [70] and the ratio of the relaxation times of the heat flux and the deviatoric part of the viscous stress τ_{qs} adopted in the present analysis. And the values of the parameter φ , bulk viscosity ν , and the ratio of the relaxation times of the bulk viscosity and the deviatoric part of the viscous stress τ_{ps} evaluated by the present analysis.

Gas	T_0 [K]	c_v^*	c_0 [$\frac{\text{m}}{\text{s}}$]	μ [$\mu\text{Pa} \cdot \text{s}$]	κ [$\frac{\text{mW}}{\text{m} \cdot \text{K}}$]	τ_{qs}	φ	ν [$\mu\text{Pa} \cdot \text{s}$]	τ_{ps}
n – H ₂	77.3	1.57	723	3.50	49.8	1.34	28	98.0	988
	293	2.45	1300	8.82	182	1.46	37	326	144
p – H ₂	77.3	1.76	707	3.50	52.7	1.33	76	266	783
	90.2	1.99	748	3.97	63.6	1.30	76	302	465
	293	2.61	1290	8.82	192	1.46	31	273	109
n – D ₂	77.3	2.54	472	4.82	45.6	1.30	36	174	132
	293	2.50	920	12.3	131	1.47	22	271	82.5
o – D ₂	77.3	2.93	463	4.82	49.4	1.26	44	212	135
	90.2	2.96	499	5.50	55.6	1.24	33	182	100
	293	2.50	920	12.3	131	1.47	22	271	82.5
HD	77.3	2.55	544	4.21	51.9	1.26	1.4	5.89	5.11
	293	2.50	1060	10.8	149	1.43	2.4	25.9	8.99

This procedure of determining φ will be adopted throughout the present chapter. (ii) When we go into the ultrasonic frequency region with larger Ω , the prediction by the ET theory is evidently superior to that by the NSF theory. The difference between the two theories emerges around $\Omega = \omega\tau_s = 10^{-3}$. We will evaluate τ_s , which depends on T_0 and p_0 , later. (iii) The ET theory seems to be valid at least up to the experimental data with the maximum dimensionless frequency $\Omega = 10^{-1}$. (iv) The large value of φ means that $\nu \gg \mu$. We will discuss its physical meaning below.

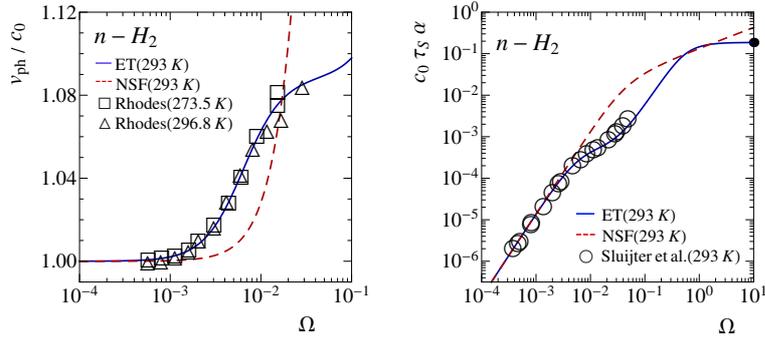


Figure 3.3: Dependence of the dimensionless phase velocity v_{ph}/c_0 (left) and the attenuation factor $c_0\tau_s\alpha$ (right) on the dimensionless frequency Ω for n-H₂. The squares and triangles in the left figure are the experimental data at $T_0 = 273.5$ and 296.8 K, respectively, by Rhodes [69], and the circles in the right figure are those at $T_0 = 293$ K by Sluijter et al. [70]. The solid and dashed lines are predictions at 293K by the ET and NSF theories, respectively. The black circle on the right vertical line in the right figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi = 37$.

For p-H₂, we compare the theoretical predictions with the experimental data on the phase velocity at $T_0 = 273.8, 298.4$ K by Rhodes [69] and on the attenuation factor at $T_0 = 293$ K by Sluijter et al. [70]. We have a similar result as shown in Fig. 3.4, where the selected value of the parameter φ is 31. Remarkable points in this case are qualitatively the same as in the case of n-H₂ above.

Hereafter we focus our discussion only on the attenuation factor because of the lack of the experimental data on the phase velocity for the purpose of the present study. In Fig. 3.5, the attenuation factors for n-H₂ at $T_0 = 77.3$ K and for p-H₂ at $T_0 = 77.3, 90.2$ K are shown. We see again that the present theory can describe the experimental data very well. The values of the parameter φ are selected to be 28, 76 and 76, respectively. These values are again very large.

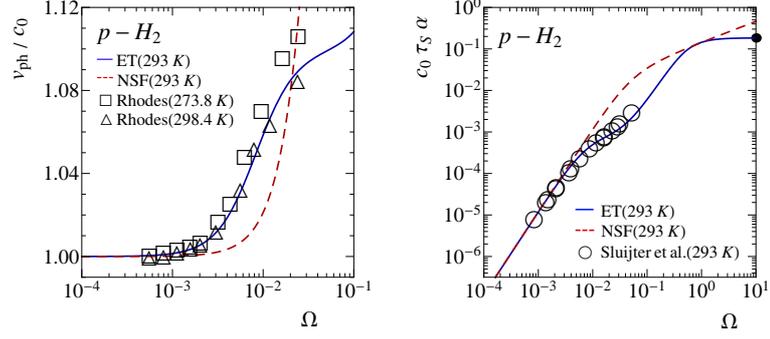


Figure 3.4: Dependence of the dimensionless phase velocity v_{ph}/c_0 (left) and the attenuation factor $c_0\tau_S\alpha$ (right) on the dimensionless frequency Ω for p- H_2 . The squares and triangles in the left figure are the experimental data at $T_0 = 273.8$ and 298.4 K, respectively, by Rhodes [69], and the circles in the right figure are those at $T_0 = 293$ K by Sluijter et al. [70]. The solid and dashed lines are predictions at 293K by the ET and NSF theories, respectively. The black circle on the right vertical line in the right figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi = 31$.

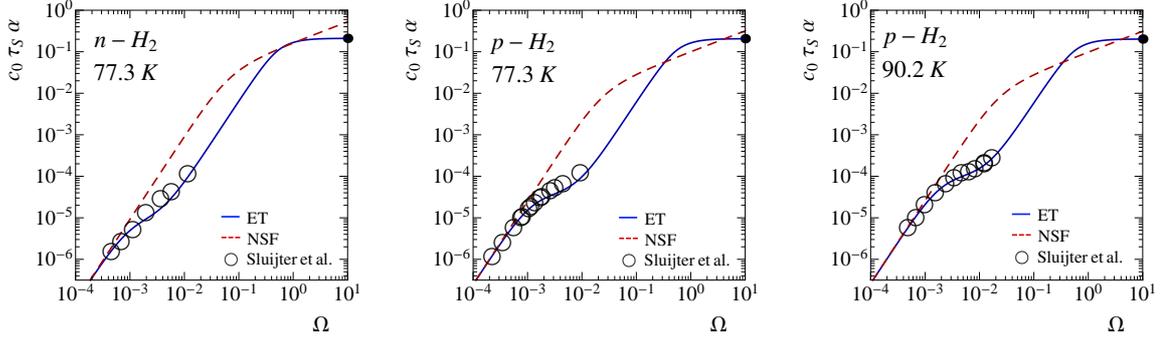


Figure 3.5: Dependence of the dimensionless attenuation factor $c_0\tau_S\alpha$ on the dimensionless frequency Ω for n- H_2 at $T_0 = 77.3$ K (left), and for p- H_2 at $T_0 = 77.3$ K (center) and 90.2 K (right). The circles are the experimental data by Sluijter et al. [70]. The solid and dashed lines are predictions by the ET and NSF theories, respectively. The black circle on the right vertical line in each figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi=28, 76$ and 76 from left to right.

Deuterium gases: n- D_2 and o- D_2

Comparisons are also made for n- D_2 at $T_0 = 77.3$ and 293 K with $\varphi=36$ and 22 in Fig. 3.6, and for o- D_2 at $T_0 = 77.3, 90.2$ and 293 K with $\varphi=44, 33$ and 22 in Fig. 3.7. From these figures, we have qualitatively the same observations as those in the case of hydrogen gases.

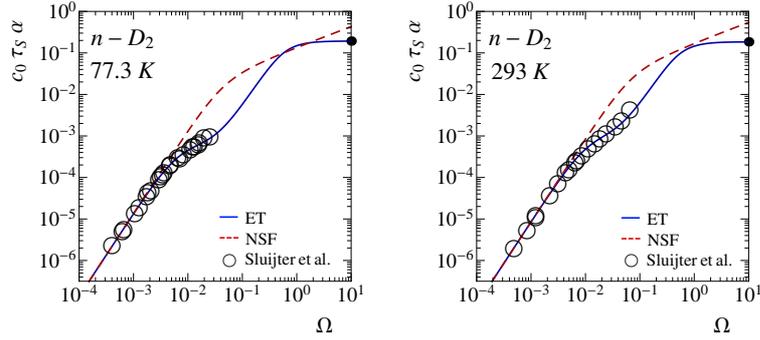


Figure 3.6: Dependence of the dimensionless attenuation factor $c_0 \tau_S \alpha$ on the dimensionless frequency Ω for $n\text{-D}_2$ at $T_0=77.3\text{K}$ (left) and 293K (right). The circles are the experimental data by Sluijter et al. [70]. The solid and dashed lines are predictions by the ET and NSF theories, respectively. The black circle on the right vertical line in each figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi=36$ (left) and 22 (right).

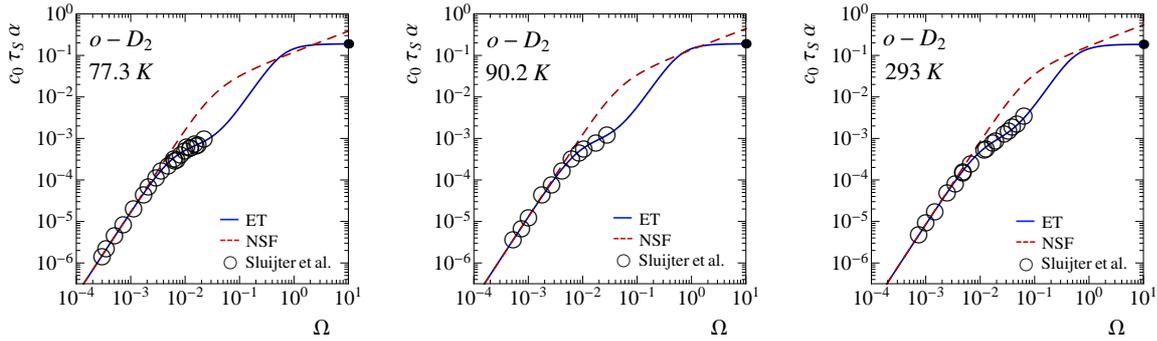


Figure 3.7: Dependence of the dimensionless attenuation factor $c_0 \tau_S \alpha$ on the dimensionless frequency Ω for $o\text{-D}_2$ at $T_0 = 77.3\text{K}$ (left), 90.2K (center) and 293K (right). The circles are the experimental data by Sluijter et al. [70]. The solid and dashed lines are predictions by the ET and NSF theories, respectively. The black circle on the right vertical line in each figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi = 44, 33$ and 22 from left to right.

Hydrogen deuteride gases: HD

Lastly we show the results of HD gases at $T_0 = 77.3$ and 293K in Fig. 3.8. We notice the following points: (i) The difference between the two theories is small and the theoretical predictions are consistent with the experimental data in the range: $\Omega \leq 10^{-1}$. This means that the local equilibrium assumption holds well up to $\Omega \doteq 10^{-1}$, while for the other gases analyzed above the assumption holds until $\Omega \doteq 10^{-3}$. (ii) The values of φ adopted here are 1.4 and 2.4 . These values are $O(1)$, that is, $\nu \sim \mu$, and are very small compared with those

obtained for the other gases discussed above. We will discuss this interesting fact below.

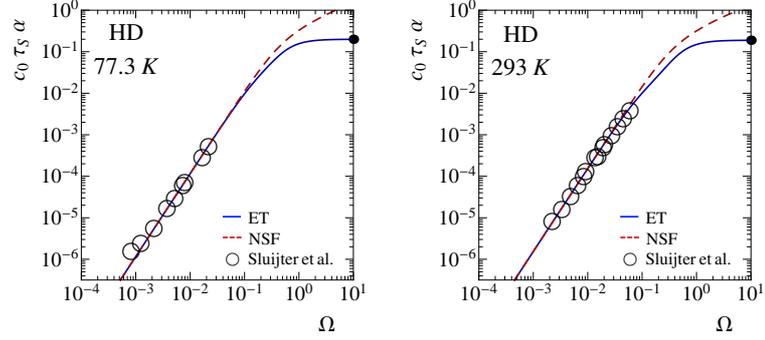


Figure 3.8: Dependence of the dimensionless attenuation factor $c_0\tau_S\alpha$ on the dimensionless frequency Ω for HD at $T_0=77.3\text{K}$ (left) and 293K (right). The circles are the experimental data by Sluijter et al. [70]. The solid and dashed lines are predictions by the ET and NSF theories, respectively. The black circle on the right vertical line in each figure corresponds to $\alpha^{(\infty)}$. We adopt $\varphi = 1.4$ (left) and 2.4 (right).

3.4.3 Remarks

Three remarks (A)-(C) are made below.

(A) We have seen clearly that the present theory of ET is consistent with the experimental data even in the high frequency range where the local equilibrium assumption is no more valid. Although the comparisons with the experimental data have been made only for the rarefied diatomic gases, the consistency gives us a strong confidence that the ET theory for dense gases [66, 67] deserves further studies. There are potentially many research fields where the ET theory may play a crucial role, for example, fields of acoustics [74] and gas dynamics [7].

(B) From the values of the ratios τ_{qs} and τ_{ps} in Table 3.1, we have noticed an interesting fact that, except for HD gases, τ_{II} is much larger than τ_S , while τ_S and τ_q are comparable with each other. This fact was reported also in some kinetic theoretical studies [75, 76]. By using the result summarized in Table 3.2, the relaxation times for given T_0 and p_0 can be estimated. For example, the relaxation times in a n- H_2 gas at $p_0 = 10^3$ [Pa] and $T_0 = 77.3$ [K] can be calculated: $\tau_S = 3.50 \times 10^{-9}$ [s], $\tau_{\text{II}} = 3.46 \times 10^{-6}$ [s] and $\tau_q = 4.70 \times 10^{-9}$ [s].

In the next chapter, it was pointed out that the relaxation time τ_{II} is in the same order of magnitude as the relaxation time of the energy exchange between the molecular translational mode and the internal modes, which, in the present case, are the rotational modes. The results obtained above suggest that the sharp temperature change of the specific heat due to the rotational modes $c_{v,\text{rot}}^*$ depicted in Fig. 3.2 is somehow related to the emergence of the large

value of τ_{Π} . The detailed study of this subject is, however, beyond the scope of the present phenomenological study, and its statistical-mechanical or kinetic-theoretical study by taking into account the realistic collision processes between the constituent molecules is required.

Table 3.2: Relaxation times of the deviatoric part of the viscous stress τ_S , dynamic pressure τ_{Π} and heat flux τ_q multiplied by the pressure p_0 for several values of T_0 in H_2 , D_2 and HD gases.

Gas	T_0 [K]	$\tau_S p_0$ [s · μ Pa]	$\tau_{\Pi} p_0$ [s · μ Pa]	$\tau_q p_0$ [s · μ Pa]
n – H_2	77.3	3.50	3460	4.70
	293	8.82	1270	12.8
p – H_2	77.3	3.50	2740	4.64
	90.2	3.97	1850	5.16
	293	8.82	962	12.9
n – D_2	77.3	4.82	637	6.25
	293	12.3	1010	18.1
o – D_2	77.3	4.82	652	6.09
	90.2	5.50	552	6.81
	293	12.3	1010	18.1
HD	77.3	4.21	21.5	5.32
	293	10.8	97.1	15.5

(C) From the values of φ in Table 3.1, we have also noticed a similar fact that, except for HD gases, the bulk viscosity ν is much larger than the shear viscosity μ . The similarity is natural because there are relations between the viscosities and the relaxation times as shown in Eq. (3.5). A point to be emphasized here is that, as the direct experiments to measure the bulk viscosity are usually difficult, the method for the evaluation of the bulk viscosity utilized here through analyzing the dispersion relation on the basis of the ET theory is quite useful. The values of ν thus evaluated are summarized in Table 3.1. We hope that present thermodynamic approach contributes to the recent studies of the bulk viscosity [77, 78, 79, 80, 81].

3.5 Summary and concluding remarks

To sum up, we have studied the dispersion relations in rarefied polyatomic gases, that is, hydrogen, deuterium and hydrogen deuteride gases, basing on the ET theory of dense gases. We have properly taken the temperature dependence of the specific heats, c_v , of these gases into

the dispersion relations. The comparison of the theoretical predictions with experimental data on the phase velocity and the attenuation factor has revealed that the ET theory is valid even in nonequilibrium states out of local equilibrium. We have also evaluated the bulk viscosity and the relaxation times.

Finally some concluding remarks are made:

(i) There is a phenomenological theory of the dispersion relation for sound, the basic equations of which are composed of the relaxation equations for some nonequilibrium parameters and the Euler (or NSF) equations for the conservation laws [2, 82]. One crucial point is that the theory is based on the local equilibrium assumption. In this respect, this may be regarded as a theory in the framework of thermodynamics of irreversible processes [2]. Because of this, in the present chapter, we have compared the ET theory only with the NSF theory as a representative one. In Ref. [83], the relationship between the simplified ET theory and the theory with one relaxation equation was studied in detail.

(ii) We have analyzed the experimental data on rarefied hydrogen, deuterium and hydrogen deuteride gases in the temperature range where the rotational modes in a molecule play an important role. The ET theory can be applied to many other rarefied polyatomic gases in a wider temperature range where the rotational and/or vibrational modes in a molecule play a role. Comprehensive study of this must be a promising future work.

(iii) As is mentioned in the first section, it is interesting to study the dispersion relation for sound in dense gases. As a first step, we are now studying it in a gas prescribed by the virial equations of state.

(iv) In order to study the effect of the large value of the relaxation time τ_{Π} on various nonequilibrium phenomena such as shock wave phenomena, it seems to be appropriate to adopt a simpler model than the one adopted here. The theory with only 6 independent field variables (ρ, v_i, T, Π) developed in the next chapter [83] may play an important role in such studies.

Chapter 4

Extended Thermodynamics of Dense Gases with 6 Fields: An extension of Meixner's theory

In the previous chapter, we have seen the case that the relaxation time related to bulk viscosity is much larger than other relaxation times. To study such phenomenon, it is useful to consider the simplest theory in the framework of ET of dense gases, that is, ET with 6 fields; mass density, velocity, temperature and dynamic pressure. Such ET theory plays a role as an extension of Meixner's theory, that is, the thermodynamic theory with energy transfer from molecular translational mode to internal modes.

4.1 Introduction

Energy transfer from molecular translational mode to internal modes, such as rotational and vibrational modes, affects the propagation speed and attenuation of a sound in a gas composed of polyatomic molecules. Especially when the frequency ω of the sound is in the same order of magnitude as the inverse of the relaxation time of the energy transfer, $1/\tau$, the effect on the sound is prominent. Such non-equilibrium phenomena are usually observed in the ultrasonic frequency range.

The thermodynamic theory with non-equilibrium parameters governed by the relaxation equations [5, 6, 2] has been utilized to describe the phenomena for many years. In order to grasp the essence of the theory, let us consider the simplest case where only one relaxation equation for a non-equilibrium parameter ξ is present in addition to the system of Euler equations for a gas that expresses the mass, momentum and energy conservation laws. That is, we neglect all dissipative processes but we take into account the relaxation process. The relaxation equation

is introduced in such a way that

$$\dot{\xi} = -\beta A, \quad (4.1)$$

where a dot on ξ represents the material time derivative, β is a positive coefficient, and A is the affinity of the relaxation process of the energy transfer that depends not only on ξ but also on other thermodynamic quantities, say, the mass density and the entropy density. When $\omega\tau \ll 1$, it was proved that the relaxation process may be interpreted in terms of the dynamic pressure Π , which is related to the gas velocity \mathbf{v} as

$$\Pi = -\nu^{\text{eff}} \text{div } \mathbf{v}$$

with ν^{eff} being the effective bulk viscosity.

Although Meixner's theory mentioned above seems to be natural, there remain some problems that should be overcome: (i) In Meixner's theory, the relaxation equation (4.1) is not fully congruous with the Euler equations. It has not been introduced on the same ground of the Euler equations as one of the general thermodynamic basic field equations. In fact, in a rarefied gas limit, the relaxation equation is not consistent with its counterpart of the moment equations derived from the kinetic theory of gases [52]. See also section 4.4.2 below. (ii) Meixner's theory is formulated within the framework of thermodynamics of irreversible processes [2]. The local equilibrium assumption is premised from the beginning. However, in such phenomena as ultrasonic wave propagation where temporal and spatial changes are rapid and steep, this assumption is not well-satisfied (see Chapter 3 and [84]).

In this chapter, we propose a fully-consistent thermodynamic theory of the sound propagation in a gas with the energy transfer where the local equilibrium assumption is not necessarily valid, and thereby try to extend Meixner's theory. We adopt the theory of extended thermodynamics (ET) (Chapter 2 and [66, 67]). As before, the essence of our theory can be most clearly shown by studying the simplest case where only one dissipative process due to the dynamic pressure exists. In section 2, we derive the closed system of field equations for gases. In section 3, we study the dispersion relation for sound and compare it with that derived from Meixner's theory. The last section is devoted to concluding remarks with the discussions of subsystems and the kinetic theoretical basis of the present theory.

4.2 Extended thermodynamics of real gases with 6 fields

As we have seen in Chap. 2, ET of dense gases has been constructed based on balance equations with binary hierarchy structure by using only general principles such as the Galilean invariance and the entropy principle, we proved that the system of field equations can be closed with respect to the independent field variables and the constitutive functions are determined explicitly by the equilibrium thermal and caloric equations of state.

In this section, we restrict our study within the simplest case of 6 independent field variables, that is,

$$\begin{aligned}
 \text{mass density:} & & F \quad (= \rho), \\
 \text{momentum density:} & & F_i \quad (= \rho v_i), \\
 \text{energy density:} & & G_{ii} \\
 \text{trace part of momentum flux:} & & F_{ii}.
 \end{aligned}$$

4.2.1 Binary hierarchy of the differential equations

We adopt the following binary hierarchy (F-series and G-series, see also section 4.4.2.) of the balance equations [66, 67]:

$$\begin{aligned}
 \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\
 \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\
 \frac{\partial G_{ii}}{\partial t} + \frac{\partial G_{iik}}{\partial x_k} &= 0, \\
 \frac{\partial F_{ii}}{\partial t} + \frac{\partial F_{iik}}{\partial x_k} &= P_{ii}
 \end{aligned} \tag{4.2}$$

where F_{ik} is the momentum flux, F_{iik} is the flux of F_{ii} , G_{iik} is the energy flux, and P_{ii} is the production with respect to F_{ii} . The equations with no production term represent the mass, momentum and energy conservation laws.

As the balance equations (4.2) should be invariant under the *Galilean transformation*, the dependence of the quantities on the velocity can be expressed as follows [49]:

$$\begin{aligned}
 F_{ij} &= \rho v_i v_j + M_{ij}, \\
 G_{ii} &= \rho v_i v_i + m_{ii}, \\
 F_{iik} &= \rho v_i v_i v_k + 3M_{(ik} v_i) + M_{iik}, \\
 G_{iik} &= \rho v_i v_i v_k + m_{ii} v_k + 2M_{ik} v_i + m_{iik},
 \end{aligned} \tag{4.3}$$

where M_{ij} , m_{ii} , M_{iik} and m_{iik} do not depend on the velocity. Parentheses around a set of indices represent the symmetrization with respect to the indices. The production P_{ii} is also independent of the velocity.

With Eq. (4.3), the balance equations (4.2) can be rewritten as

$$\begin{aligned}
 \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
 \rho \dot{v}_i + \frac{\partial M_{ij}}{\partial x_j} &= 0, \\
 \dot{m}_{ii} + m_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= 0, \\
 \dot{M}_{ii} + M_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= P_{ii}.
 \end{aligned} \tag{4.4}$$

We notice that the quantities M_{ij} , m_{ii} and m_{ppi} have the following conventional meanings:

$$\begin{aligned}
 \text{stress:} & & t_{ij} &= -M_{ij} \quad (= -(p + \Pi) \delta_{ij} + M_{\langle ij \rangle}), \\
 \text{specific internal energy:} & & \varepsilon &= \frac{1}{2\rho} m_{ii}, \\
 \text{heat flux:} & & q_i &= \frac{1}{2} m_{ppi},
 \end{aligned}$$

where the pressure p depends only on ρ and m_{ii} , Π is the dynamic pressure, and angular brackets denote the symmetric traceless part.

We may now adopt $\{\rho, v_i, m_{ii}, \Pi\}$ as a set of independent variables instead of $\{F, F_i, G_{ii}, F_{ii}\}$. The balance equation of M_{ii} (Eq. (4.4)₄) is then rewritten as

$$\begin{aligned}
 \dot{\Pi} + \left(\frac{5}{3} p - \rho \left(\frac{\partial p}{\partial \rho} \right)_{m_{ii}} - (m_{rr} + 2p) \left(\frac{\partial p}{\partial m_{qq}} \right)_{\rho} \right) \frac{\partial v_k}{\partial x_k} \\
 + \left(\frac{5}{3} - 2 \left(\frac{\partial p}{\partial m_{qq}} \right)_{\rho} \right) \Pi \frac{\partial v_k}{\partial x_k} + 2 \left(\frac{1}{3} - \left(\frac{\partial p}{\partial m_{qq}} \right)_{\rho} \right) \frac{\partial v_r}{\partial x_k} M_{\langle rk \rangle} \\
 + \frac{1}{3} \frac{\partial M_{rrk}}{\partial x_k} - \left(\frac{\partial p}{\partial m_{qq}} \right)_{\rho} \frac{\partial m_{rrk}}{\partial x_k} = \frac{P_{rr}}{3}.
 \end{aligned}$$

4.2.2 Constitutive equations

We need the constitutive equations in order to set up the closed system of field equations. We assume that the constitutive equations at one point and time depend on the independent fields at that point and time. Therefore the constitutive quantities $\{M_{\langle ij \rangle}, M_{iik}, m_{iik}, P_{ii}\}$ are expressed as functions of

$$(\rho, m_{ii}, \Pi).$$

We apply the constitutive theory of ET [8] where the following universal physical principles (A)-(C) are imposed on the constitutive equations: (A) *Material frame indifference principle*: This requires that constitutive equations are independent of an observer. This principle and the Galilean invariance for the balance laws constitute the objectivity principle (the principle

of relativity). (B) *Entropy principle*: All solutions of the system of field equations must satisfy the entropy balance law:

$$\frac{\partial h}{\partial t} + \frac{\partial(hv_k + \varphi_k)}{\partial x_k} = \Sigma \geq 0 \Leftrightarrow \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \varphi_k}{\partial x_k} = \Sigma \geq 0$$

where h is the entropy density, h_k is the entropy flux ($h_k = hv_k + \varphi_k$: φ_k is the non-convective entropy flux), and Σ is the entropy production. Here h and φ_k are constitutive quantities:

$$h \equiv \hat{h}(\rho, m_{ii}, \Pi), \quad \varphi_k \equiv \hat{\varphi}_k(\rho, m_{ii}, \Pi).$$

(C) *Causality*: This requires the concavity of the entropy density and guarantees the hyperbolicity of the system of field equations. This also ensures the well-posedness (local in time) of a Cauchy problem and the finiteness of the propagation speeds of disturbances.

As the result of the universal principles, in the neighborhood of equilibrium, we obtain the constitutive equations:

$$M_{\langle ij \rangle} = 0, \quad M_{iik} = 0, \quad m_{iik} = 0, \quad P_{ii} = -\frac{3\zeta}{Ta_1}\Pi, \quad (4.5)$$

where ζ is a positive function of the density ρ and the temperature T , and a_1 is given by [66, 67]

$$a_1 = \frac{5}{3}p - \rho \left(\frac{\partial p}{\partial \rho} \right)_T - \frac{T}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho^2 \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1}.$$

The entropy density and entropy flux are given by

$$h = h^E - \frac{1}{2Ta_1}\Pi^2, \quad \varphi_k = 0, \quad (4.6)$$

where h^E is the entropy density in equilibrium. From (4.6), we obtain the concavity conditions at an equilibrium state:

$$\left(\frac{\partial \varepsilon}{\partial T} \right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho} \right)_T > 0, \quad a_1 > 0.$$

4.2.3 Field equations

The closed system of field equations is obtained by substituting the constitutive equations (4.5) into the system (4.4):

$$\begin{aligned} \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\ \rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} &= 0, \\ \rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \dot{T} + \left[p + \Pi - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \frac{\partial v_k}{\partial x_k} &= 0, \\ \dot{\Pi} + (a_1 + a_2\Pi) \frac{\partial v_k}{\partial x_k} &= -\frac{1}{\tau_\Pi}\Pi, \end{aligned} \quad (4.7)$$

where the relaxation time τ_{Π} and a_2 are given by

$$\tau_{\Pi} = \frac{Ta_1}{\zeta}, \quad a_2 = \frac{5}{3} - \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_{\rho} \left(\frac{\partial \varepsilon}{\partial T} \right)_{\rho}^{-1}.$$

The evolution equation (4.7)₄ for Π is now obtained consistently, which may be seen as the counterpart of the relaxation equation in Meixner's theory.

If we apply the Maxwellian iteration [8, 46] to the system (4.7), the first iterate $\Pi^{(1)}$ is obtained by the substitution of the 0th iterate $\Pi^{(0)} = 0$ into the left hand side of (4.7)₄:

$$\Pi^{(1)} = -a_1 \tau_{\Pi} \frac{\partial v_k}{\partial x_k},$$

from which the bulk viscosity ν is given by

$$\nu = a_1 \tau_{\Pi} = \frac{Ta_1^2}{\zeta}.$$

Therefore we can calculate ζ from the experimental data of ν .

4.3 Dispersion relation for sound: comparison with Meixner's theory

In this section, we study a linear plane harmonic wave and obtain its dispersion relation. The result obtained is compared with that from Meixner's theory.

Without loss of generality, we may study the wave in the following form:

$$\mathbf{u} = \mathbf{u}_0 + \bar{\mathbf{u}}$$

where $\mathbf{u} = (\rho, v, T, \Pi)^T$ is a state vector with v being the x -component of the velocity \mathbf{v} , $\mathbf{u}_0 = (\rho_0, 0, T_0, 0)^T$ is a state vector at a reference equilibrium state, and $\bar{\mathbf{u}} = (\bar{\rho}, \bar{v}, \bar{T}, \bar{\Pi})^T$ is the deviation from \mathbf{u}_0 expressed as

$$\bar{\mathbf{u}} = \mathbf{w} e^{i(\omega t - kx)}.$$

Here \mathbf{w} is the amplitude, ω is the frequency, and k is the complex wave number such that $k = k_r + ik_i$ ($k_r = \Re(k)$, $k_i = \Im(k)$).

From the linearized system of field equations, which is obtained by linearizing (4.7) with respect to $\bar{\mathbf{u}}$, we can easily obtain the dispersion relation [8]:

$$\det \left(\mathbf{I} - z \mathbf{A}_0 + \frac{i}{\omega} \mathbf{B}_0 \right) = 0, \quad (4.8)$$

where $z = k/\omega$, \mathbf{I} is the unit matrix, and

$$\mathbf{A}_0 = \begin{pmatrix} 0 & \rho & 0 & 0 \\ \frac{1}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_T & 0 & \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho & \frac{1}{\rho} \\ 0 & \frac{p - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} & 0 & 0 \\ 0 & a_1 & 0 & 0 \end{pmatrix}_0, \quad \mathbf{B}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{\tau_{\Pi}} \end{pmatrix}_0.$$

The index 0 indicates the values at the reference state.

From the dispersion relation, the phase velocity v_{ph} and the attenuation factor α are obtained as the functions of ω :

$$v_{\text{ph}} = \frac{\omega}{\Re(k)} = \frac{1}{\Re(z)}, \quad \alpha = -\Im(k) = -\omega \Im(z).$$

By the requirement of the linear stability, α must be positive (negative) for the waves traveling to the x -positive (negative) direction.

The high-frequency limits of v_{ph} and α are given by [8, 68] :

$$\lim_{\omega \rightarrow \infty} v_{\text{ph}}(\omega) = \lambda_0 = \sqrt{\frac{5p_0}{3\rho_0}}, \quad \lim_{\omega \rightarrow \infty} \alpha(\omega)\lambda_0 = -\mathbf{l}_0 \cdot \mathbf{B}_0 \cdot \mathbf{d}_0, \quad (4.9)$$

where the characteristic velocity λ_0 is the non-zero eigenvalue of \mathbf{A}_0 , and \mathbf{l}_0 and \mathbf{d}_0 are the left and right eigenvectors of \mathbf{A}_0 , respectively. It is remarkable that, even for polyatomic gases, the high frequency limit $v_{\text{ph}}(\infty)$ does not depend on the internal degrees of freedom in a rarefied gas limit. The attenuation factor is given by

$$\alpha(\infty) = \pm \frac{1}{2\tau_{\Pi}} \sqrt{\frac{3\rho_0}{5p_0}} \left(1 - \frac{3}{5} c_0^2 \frac{\rho_0}{p_0} \right),$$

where c_0 is the sound velocity in the reference state:

$$c_0^2 = \left(\left(\frac{\partial p}{\partial \rho} \right)_T + \frac{\left(\frac{\partial p}{\partial T} \right)_\rho^2 T}{\left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \rho^2} \right)_0.$$

Finally let us compare the dispersion relation (4.8) with that of Meixner's theory. The relation (4.8) can be rewritten as

$$(c_0 z)^2 \left(-\frac{5p_0}{3c_0^2 \rho_0} + \frac{i}{\tau_{\Pi} \omega} \right) + 1 - \frac{i}{\tau_{\Pi} \omega} = 0.$$

While the dispersion relation derived from Meixner's theory is given by [2]

$$(c_0 z)^2 \left(-\frac{v_{\text{ph}}(\infty)^2}{c_0^2} + \frac{i}{\tau \omega} \right) + 1 - \frac{i}{\tau \omega} = 0.$$

By taking the relation (4.9)₁ into account, it is easy to show that, if $\tau_{\Pi} = \tau$, both dispersion relations coincide with each other.

4.4 Subsystems and kinetic theory

We have shown in the above that, through studying the simplest case, a fully-consistent thermodynamic theory of sounds in a gas with the energy transfer can be established on the basis of ET. This is valid even in the region beyond the local equilibrium assumption. The relationship between the present theory with 6 independent variables and Meixner's theory is also shown. It is found that, as far as the dispersion relation for a weak sound propagating in an equilibrium state is concerned, both theories predict the same expression of the relation.

Lastly we make four concluding remarks 4.4.1-4.4.4:

4.4.1 ET of 14 fields and the concept of subsystems

The extended thermodynamic theory of dense gases that takes into account not only the dynamic pressure but also the shear stress and heat flux has already been proposed in Chap. 2 and in [66, 67]. This is the theory of real gases with 14 field variables. In this respect, it is important to recognize that the theory with 6 variables presented above is a *main subsystem* of the 14-variable theory according to the definition which we have seen in Chapter 1, Section 3.2 (and see Boillat and Ruggeri [48]). We may, therefore, assert that the 6-variable theory is the simplest variant among dissipative systems from the non-dissipative Euler system. In contrast to the well-known Navier-Stokes-Fourier model that is of parabolic type, the present variant is of hyperbolic type. To sum up, the present 6-variable system is the simplest non-trivial hyperbolic one next to the system of Euler equations.

4.4.2 Consistency with the kinetic theory of polyatomic gases

Let us study the system (4.7) in the rarefied gas limit, and adopt the thermal and caloric equations of state:

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{D}{2} \frac{k_B}{m} T, \quad (4.10)$$

where k_B and m are the Boltzmann constant and the mass of a molecule, and the constant D is the degrees of freedom of a molecule, i.e., $D = 3 + f$ where 3 corresponds to the translational motion and f is the internal degrees of freedom. The system of field equations is expressed as

$$\begin{aligned} \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\ \rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} &= 0, \\ \dot{T} + \frac{2}{D \frac{k_B}{m} \rho} (p + \Pi) \frac{\partial v_k}{\partial x_k} &= 0, \\ \dot{\Pi} + \frac{2(D-3)}{3D} p \frac{\partial v_k}{\partial x_k} + \frac{5D-6}{3D} \Pi \frac{\partial v_k}{\partial x_k} &= -\frac{1}{\tau_\Pi} \Pi. \end{aligned} \quad (4.11)$$

The relaxation time τ_{Π} and the bulk viscosity ν are given by

$$\tau_{\Pi} = \frac{2(D-3)pT}{3D\zeta}, \quad \nu = \frac{2(D-3)}{3D}p\tau_{\Pi}.$$

For monatomic gases ($D = 3$), as is expected, ν vanishes and the evolution equation (4.11)₄ for Π has now no role.

In this subsection, we show that above results are fully consistent with the kinetic theory. That is, the balance equations for rarefied polyatomic gases (4.11) can be obtained via the kinetic theory [14] in which the internal energy of a molecule I is taken into account. Physical quantities are expressed as the moments of a one-body distribution function $f(x_i, c_i, t, I)$ with c_i being the velocity of a molecule. The mass density ρ and the momentum density ρv_i are expressed as

$$\begin{aligned} \rho &= \int m f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \\ \rho v_i &= \int m c_i f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \end{aligned} \quad (4.12)$$

where $\varphi(I)dI$ is a nonnegative measure. We adopt $\varphi(I) = I^\sigma$ [14], where σ will be related to the degrees of freedom D below. The integration range is taken as $[0, \infty)$ for I and $(-\infty, \infty)$ for c_1, c_2 and c_3 . By using the peculiar velocity C_i defined by

$$C_i \equiv c_i - v_i,$$

the internal energy ε , and the sum of the pressure p and the dynamic pressure Π are expressed as

$$\begin{aligned} 2\rho\varepsilon &= \int (mC^2 + 2I) f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \\ 3(p + \Pi) &= \int mC^2 f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \end{aligned} \quad (4.13)$$

where $C^2 = C_i C_i$. It is noticeable that there exist two kinds of second order moments: the energy density and the momentum flux, which appear in the binary structure introduced in section 2. Therefore, as proposed in [13], the moments of the F-series and G-series can be obtained at the kinetic level:

$$\begin{aligned} F_{i_1 i_2 \dots i_n} &= \int m c_{i_1} c_{i_2} \dots c_{i_n} f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \\ G_{i_1 i_2 \dots i_n ll} &= \int (m c^2 + 2I) c_{i_1} c_{i_2} \dots c_{i_n} f(x_i, c_i, t, I) \varphi(I) dI dc_1 dc_2 dc_3, \end{aligned}$$

where $c^2 = c_i c_i$.

We adopt the Bhatnagar-Gross-Krook (BGK) equation [85] as the basic equation in the kinetic approach:

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = -\frac{f - f_E}{\tau'},$$

where τ' is the relaxation time and f_E is the local equilibrium distribution function given by [14]

$$f_E = \frac{n}{q(T)} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{1}{k_B T} \left(\frac{m}{2} C^2 + I \right)} \quad (4.14)$$

with n being the number density ($n = \rho/m$) and $q(T)$ the normalization function defined by

$$q(T) = \int \varphi(I) e^{-\frac{I}{k_B T}} dI.$$

Inserting (4.14) into (4.13), we have the relation $\sigma = (D - 5)/2$ due to the consistency between (4.13) and (4.10).

Multiplying the BGK equation by $m\Phi(c_i, I) \equiv m(1, c_i, (c^2 + 2I/m), c^2)$ and integrating over the whole space, we have the balance equations of 6 moments $\mathbf{u} \equiv (F, F_i, G_{ii}, F_{ii})$, which are certainly the same as (4.2) with the collision term:

$$P_{ii} = -(1/\tau') \int m c^2 (f - f_E) \varphi(I) dI d c_1 d c_2 d c_3.$$

Concerning the closure at the kinetic level, we adopt the maximum entropy principle (MEP) that we have seen in Chapter 1, Section 2.2 (see also for rarefied monatomic gases [61, 8] and for polyatomic ones [13]). Under MEP, the distribution function is calculated by maximizing the entropy, which is a functional of f , under the constraints of fixed values for the moments. In the neighborhood of equilibrium the distribution function is given by [48, 12]

$$f = f_E \left(1 - \frac{m}{k_B} \tilde{\Lambda} \cdot \Phi(c_i, I) \right), \quad (4.15)$$

where $\tilde{\Lambda}$ is the non-equilibrium part of Lagrange multiplier. The non-equilibrium part of \mathbf{u} is thus given by

$$\mathbf{u} - \mathbf{u}_E = -\frac{m^2}{k_B} \int f_E \tilde{\Lambda} \cdot \Phi(c_i, I) \Phi(c_i, I) \varphi(I) dI d c_1 d c_2 d c_3,$$

where \mathbf{u}_E is the equilibrium part. On the other hand, from the definitions of (4.12) and (4.13), we know that $\mathbf{u} - \mathbf{u}_E \equiv (0, 0, 0, 3\Pi)$. Therefore we obtain $\tilde{\Lambda}$ in terms of the independent variables. By using the distribution function (4.15) with this $\tilde{\Lambda}$, all moments are expressed in closed forms. These are the same, if $\tau' = \tau_{II}$, as the constitutive equations used in (4.11).

In this way, we have confirmed in the case of rarefied polyatomic gases that our macroscopic thermodynamic theory is perfectly in agreement with the kinetic theory and also in this case the entropy principle gives the same results of the MEP as in the case of monatomic gases [48]. The compatibility between two different approaches supports the validity of the present macroscopic ET theory for any real gases given by the general system (4.7).

Finally we recall that the basic system of differential equations can be written in a symmetric form by using the main field Λ that, in the case of rarefied polyatomic gases, coincides

with the Lagrange multiplier vector $\tilde{\Lambda} + \Lambda_E$ (see [48] and references therein):

$$\begin{aligned}\Lambda_E &\equiv \frac{1}{T} \left(-g + \frac{v^2}{2}, -v_i, \frac{1}{2}, 0 \right) \\ \tilde{\Lambda} &\equiv \frac{m}{k_B \rho T^2} \Pi \left(-\frac{v^2}{2}, v_i, \frac{3}{2(D-3)}, -\frac{D}{2(D-3)} \right)\end{aligned}\tag{4.16}$$

with g being the chemical potential.

4.4.3 Characteristic velocities and hyperbolic region

In a general non-equilibrium state, the characteristic velocities are given by

$$\lambda = v_n \text{ (multiplicity 4)}, \quad \lambda = v_n \pm \sqrt{\frac{5}{3} \frac{p + \Pi}{\rho}}$$

where $v_n = \mathbf{v} \cdot \mathbf{n}$ with \mathbf{n} being the unit normal of the wave front. The condition of hyperbolicity is then expressed by $\Pi > -p$.

Chapter 5

Fluctuating hydrodynamics based on ET

Based on ET, the fluctuating hydrodynamics theory, which can be applied to beyond the assumption of local equilibrium, is proposed. In particular, ET for rarefied monatomic gases with 13 fields (mass density, velocity, temperature, viscous stress and heat flux) are studied. The hierarchy structure of hydrodynamic fluctuations are discussed, in particular, the relation between ET and Navier-Stokes Fourier theory is considered.

5.1 Introduction

Landau and Lifshitz developed the theory of fluctuating hydrodynamics for viscous, heat-conducting fluids with constitutive equations of Navier-Stokes and Fourier type [86, 24, 87] basing on thermodynamics of irreversible processes (TIP). They introduced additional stochastic flux terms (generalized random forces) into the constitutive equations of the viscous stress and the heat flux by applying the fluctuation-dissipation theorem [25, 26, 27, 28]. As we have seen in Chapter 1, the Landau-Lifshitz (LL) theory has been applied to nano-technology [32, 33] and molecular biology [34, 35]. In addition, the fluctuating-hydrodynamic approach plays an effective role in the field of non-equilibrium statistical mechanics [31, 43, 44].

However, as TIP rests essentially on the local equilibrium assumption that is valid for nonequilibrium phenomena near equilibrium, it is highly probable that TIP may no longer be valid for highly nonequilibrium cases such as the cases where nanoflows are involved, or the cases where rarefied gases play a role. As for the discussion on the validity criterion of the assumption, see, for example, Ref. [89]. Extended thermodynamics (ET) is a generalized theory being applicable to such cases.

The purpose of the present chapter is to develop a theory of fluctuating hydrodynamics

based on ET. In particular we study for ET with the 13-fields of rarefied monatomic gases (ET-13) shown in Chapter 1, Section 3, as a representative case. After establishing the relationship between the present theory and the LL theory, the hierarchy structure of the hydrodynamic fluctuations will be discussed.

5.2 Theory of fluctuating hydrodynamics based on ET

The basic equations in the present study are the linearized equations of ET-13 for a monatomic rarefied gas around an equilibrium state. The independent variables are the mass density ρ , velocity v_i , temperature T , shear stress $S_{\langle ij \rangle}$, and heat flux q_i . Note that the dynamic pressure vanishes identically in this case.

$$\begin{aligned}
 \frac{\partial \rho}{\partial t} + \rho_0 \frac{\partial v_i}{\partial x_i} &= 0, \\
 \frac{\partial v_i}{\partial t} + \frac{aT_0}{\rho_0} \frac{\partial \rho}{\partial x_i} + a \frac{\partial T}{\partial x_i} - \frac{1}{\rho_0} \frac{\partial S_{\langle ij \rangle}}{\partial x_j} &= 0, \\
 a \frac{\partial T}{\partial t} + \frac{2}{3} a T_0 \frac{\partial v_k}{\partial x_k} + \frac{2}{3 \rho_0} \frac{\partial q_k}{\partial x_k} &= 0, \\
 \frac{\partial S_{\langle ij \rangle}}{\partial t} - \frac{4}{5} \frac{\partial q_{\langle i}}{\partial x_j \rangle} - 2a \rho_0 T_0 \frac{\partial v_{\langle i}}{\partial x_j \rangle} &= -P_{\langle ij \rangle}, \\
 \frac{\partial q_i}{\partial t} - a T_0 \frac{\partial S_{\langle ij \rangle}}{\partial x_j} + \frac{5}{2} a^2 \rho_0 T_0 \frac{\partial T}{\partial x_i} &= \frac{P_i}{2},
 \end{aligned} \tag{5.1}$$

where $a \equiv k_B/m$ with k_B being the Boltzmann constant and m the mass of a molecule, and $P_{\langle ij \rangle}$ and P_i are the source terms. The quantities with and without the suffix 0 are, respectively, the quantities at the equilibrium state and the deviations from the equilibrium state. The first three equations represent, respectively, the mass, momentum and energy conservation laws, and the last two are the equations of balance type for the irreversible fluxes $S_{\langle ij \rangle}$ and q_i . Owing to the presence of the second part that have been neglected in the traditional hydrodynamic analysis, the rapidly changing (deterministic) modes can be taken into account. We may call these modes fast modes. The specific entropy production Σ is obtained as follows:

$$\Sigma = \lambda_{\langle ij \rangle} P_{\langle ij \rangle} + \lambda_{ppi} P_{qqi} \geq 0, \tag{5.2}$$

where $\lambda_{\langle ij \rangle}$ and λ_{ppi} are Lagrange multipliers (see (1.135)).

Within the linear constitutive equations, we have

$$P_{\langle ij \rangle} = \sigma \lambda_{\langle ij \rangle}, \quad P_i = \tau \lambda_{ppi}, \tag{5.3}$$

where σ and τ are positive coefficients and evaluated at the reference equilibrium state. Furthermore we have already known the relations between the lagrange multipliers and original fields (Eqs. (1.157)) :

$$\lambda_{\langle ij \rangle} = \frac{1}{2a\rho_0 T_0^2} S_{\langle ij \rangle}, \quad \lambda_{ppi} = -\frac{1}{5a^2 \rho_0 T_0^3} q_i. \tag{5.4}$$

Let us now try to introduce the random forces into ET in a similar way in Chapter 1. Section 2.3. We recall the generic fluctuation-dissipation theorem. The specific entropy production is given by Eq. (1.64):

$$\Sigma = -\dot{x}_a X_a \quad (5.5)$$

and where we assume the linear constitutive equation between \dot{x}_a and X_a with the phenomenological coefficient C_{ab} , we can introduce the Gaussian white random force \mathbf{f}_a into the constitutive equation in such a way that

$$\dot{x}_a = -C_{ab}X_b + \mathbf{f}_a, \quad (5.6)$$

where the mean of \mathbf{f}_a vanishes and its correlation is given by

$$\langle \mathbf{f}_a(\mathbf{x}, t) \mathbf{f}_b(\mathbf{x}', t') \rangle = k_B (C_{ab} + C_{ba}) \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'). \quad (5.7)$$

Now we easily notice the following correspondence relationship between the generic case above and the present case:

$$\dot{x}_a \rightarrow \{P_{\langle ij \rangle}, P_i\}, \quad X_a \rightarrow \{-\lambda_{\langle ij \rangle}, -\lambda_{ppi}\}. \quad (5.8)$$

And we can introduce the Gaussian white random forces $\mathbf{r}_{\langle ij \rangle}$ and \mathbf{s}_i into Eq. (5.3) as follows:

$$P_{\langle ij \rangle} = \sigma \lambda_{\langle ij \rangle} + \mathbf{r}_{\langle ij \rangle}, \quad P_i = \tau \lambda_{ppi} + \mathbf{s}_i, \quad (5.9)$$

where the means of $\mathbf{r}_{\langle ij \rangle}$ and \mathbf{s}_i vanish, and their correlations are given by

$$\begin{aligned} \langle \mathbf{r}_{\langle ij \rangle}(\mathbf{x}, t) \mathbf{r}_{\langle mn \rangle}(\mathbf{x}', t') \rangle &= k_B \sigma (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm} - \frac{2}{3} \delta_{ij} \delta_{mn}) \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'), \\ \langle \mathbf{s}_i(\mathbf{x}, t) \mathbf{s}_j(\mathbf{x}', t') \rangle &= 2k_B \tau \delta_{ij} \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'), \\ \langle \mathbf{r}_{\langle ij \rangle}(\mathbf{x}, t) \mathbf{s}_m(\mathbf{x}', t') \rangle &= 0. \end{aligned} \quad (5.10)$$

We obtain the expressions for $P_{\langle ij \rangle}$ and P_i in terms of $S_{\langle ij \rangle}$, q_i and the random forces $\mathbf{r}_{\langle ij \rangle}$, \mathbf{s}_i :

$$\begin{aligned} P_{\langle ij \rangle} &= \frac{1}{\tau_S} S_{\langle ij \rangle} + \mathbf{r}_{\langle ij \rangle}, \\ P_i &= -\frac{2}{\tau_q} q_i + \mathbf{s}_i, \end{aligned} \quad (5.11)$$

where τ_S and τ_q are the relaxation times at a reference equilibrium state corresponding to (1.167):

$$\tau_S = \frac{2a\rho_0 T_0^2}{\sigma}, \quad \tau_q = \frac{10a^2\rho_0 T_0^3}{\tau}. \quad (5.12)$$

The means of the random forces $\mathbf{r}_{\langle ij \rangle}$ and \mathbf{s}_i vanish. And their correlations are given by

$$\begin{aligned} \langle \mathbf{r}_{\langle ij \rangle}(\mathbf{x}, t) \mathbf{r}_{\langle mn \rangle}(\mathbf{x}', t') \rangle &= k_B \frac{2a\rho_0 T_0^2}{\tau_S} (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm} - \frac{2}{3} \delta_{ij} \delta_{mn}) \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'), \\ \langle \mathbf{s}_i(\mathbf{x}, t) \mathbf{s}_j(\mathbf{x}', t') \rangle &= k_B \frac{20a^2\rho_0 T_0^3}{\tau_q} \delta_{ij} \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'), \\ \langle \mathbf{r}_{\langle ij \rangle}(\mathbf{x}, t) \mathbf{s}_m(\mathbf{x}', t') \rangle &= 0, \end{aligned} \quad (5.13)$$

where the brackets $\langle \ \rangle$ in the left-hand side stand for the statistical average at the reference equilibrium state.

Equations (5.1) with (5.11) and (5.13) constitute *the basic system of equations for fluctuating hydrodynamics based on ET (ET-13)*.

The relaxation times τ_S and τ_q can be evaluated by experiments or kinetic-theoretical analyses. For gases with Maxwellian interatomic potential, in particular, we have the relation $3\tau_S = 2\tau_q$ [8]. Other realistic monatomic gases satisfy this relation approximately.

5.3 Two subsystems of the stochastic field equations

The basic system of equations obtained above may be decomposed into two uncoupled subsystems, that is, the subsystem composed of longitudinal modes (System-L) and the subsystem of transverse modes (System-T).

System-L

The relevant quantities of the system are given by

$$\begin{aligned} \rho, \quad T, \quad \psi \left(\equiv \frac{\partial v_i}{\partial x_i} \right), \quad \xi \left(\equiv \frac{\partial^2 S_{\langle ij \rangle}}{\partial x_i \partial x_j} \right), \quad \varphi \left(\equiv \frac{\partial q_i}{\partial x_i} \right), \\ \mathbf{v} \left(\equiv -\frac{\partial^2 \mathbf{r}_{\langle ij \rangle}}{\partial x_i \partial x_j} \right), \quad \text{and} \quad \mathbf{w} \left(\equiv \frac{1}{2} \frac{\partial \mathbf{s}_i}{\partial x_i} \right). \end{aligned} \quad (5.14)$$

The spatial Fourier transform of the system is the system of the rate-type differential equations in the space of the wave number \mathbf{k} and time t ($\mathbf{k}t$ -representation) as follows:

$$\begin{aligned} \frac{\partial \rho(\mathbf{k}, t)}{\partial t} + \rho_0 \psi(\mathbf{k}, t) &= 0, \\ \frac{\partial \psi(\mathbf{k}, t)}{\partial t} - \frac{aT_0 k^2}{\rho_0} \rho(\mathbf{k}, t) - ak^2 T(\mathbf{k}, t) - \frac{1}{\rho_0} \xi(\mathbf{k}, t) &= 0, \\ a \frac{\partial T(\mathbf{k}, t)}{\partial t} + \frac{2}{3} aT_0 \psi(\mathbf{k}, t) + \frac{2}{3\rho_0} \varphi(\mathbf{k}, t) &= 0, \\ \frac{\partial \xi(\mathbf{k}, t)}{\partial t} + \frac{8}{15} k^2 \varphi(\mathbf{k}, t) + \frac{4}{3} a\rho_0 T_0 k^2 \psi(\mathbf{k}, t) &= -\frac{1}{\tau_S} \xi(\mathbf{k}, t) + \mathbf{v}(\mathbf{k}, t), \\ \frac{\partial \varphi(\mathbf{k}, t)}{\partial t} - aT_0 \xi(\mathbf{k}, t) - \frac{5}{2} a^2 \rho_0 T_0 k^2 T(\mathbf{k}, t) &= -\frac{1}{\tau_q} \varphi(\mathbf{k}, t) + \mathbf{w}(\mathbf{k}, t), \end{aligned} \quad (5.15)$$

where $\rho(\mathbf{k}, t)$ is the spatial Fourier transform of $\rho(\mathbf{x}, t)$ defined as

$$\rho(\mathbf{k}, t) \equiv \frac{1}{(2\pi)^3} \int \rho(\mathbf{x}, t) \exp(-i\mathbf{k} \cdot \mathbf{x}) d\mathbf{x}, \quad (5.16)$$

and the other quantities are similarly defined.

From Eq. (5.13), the quantities $\mathbf{v}(\mathbf{k}, t)$ and $\mathbf{w}(\mathbf{k}, t)$ are the Gaussian white random forces

with null means and correlations:

$$\begin{aligned}
 \langle \mathbf{v}(\mathbf{k}, t) \mathbf{v}(\mathbf{k}', t') \rangle &= k_B \frac{a\rho_0 T_0^2}{3\pi^3 \tau_S} k^4 \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\
 \langle \mathbf{w}(\mathbf{k}, t) \mathbf{w}(\mathbf{k}', t') \rangle &= k_B \frac{5a^2 \rho_0 T_0^3}{8\pi^3 \tau_q} k^2 \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\
 \langle \mathbf{v}(\mathbf{k}, t) \mathbf{w}(\mathbf{k}', t') \rangle &= 0.
 \end{aligned} \tag{5.17}$$

System-T

The relevant quantities of the system are given by

$$\begin{aligned}
 \omega_i (\equiv (\text{curl} \mathbf{v})_i), \quad \sigma_i \left(\equiv \epsilon_{ijk} \frac{\partial^2 S_{\langle kn \rangle}}{\partial x_j \partial x_n} \right), \quad \pi_i (\equiv (\text{curl} \mathbf{q})_i), \\
 \mathfrak{r}_i \left(\equiv -\epsilon_{ijk} \frac{\partial^2 \mathfrak{r}_{\langle kn \rangle}}{\partial x_j \partial x_n} \right), \quad \text{and} \quad \mathfrak{v}_i \left(\equiv \frac{1}{2} (\text{curl} \mathfrak{s})_i \right).
 \end{aligned} \tag{5.18}$$

The field equations in the $\mathbf{k}t$ -representation are as follows:

$$\begin{aligned}
 \frac{\partial \omega_i(\mathbf{k}, t)}{\partial t} - \frac{1}{\rho_0} \sigma_i(\mathbf{k}, t) &= 0, \\
 \frac{\partial \sigma_i(\mathbf{k}, t)}{\partial t} + \frac{2}{5} k^2 \pi_i(\mathbf{k}, t) + a\rho_0 T_0 k^2 \omega_i(\mathbf{k}, t) &= -\frac{1}{\tau_S} \sigma_i(\mathbf{k}, t) + \mathfrak{r}_i(\mathbf{k}, t), \\
 \frac{\partial \pi_i(\mathbf{k}, t)}{\partial t} - aT_0 \sigma_i(\mathbf{k}, t) &= -\frac{1}{\tau_q} \pi_i(\mathbf{k}, t) + \mathfrak{v}_i(\mathbf{k}, t).
 \end{aligned} \tag{5.19}$$

Note that, for given \mathfrak{r}_i and \mathfrak{v}_i , the equations for the set of variables $(\omega_i, \sigma_i, \pi_i)$ with the same suffix i can be solved separately from those with the different suffix $j (\neq i)$. In view of Eq. (5.13), \mathfrak{r}_i and \mathfrak{v}_i are the Gaussian white random forces with null means and correlations:

$$\begin{aligned}
 \langle \mathfrak{r}_i(\mathbf{k}, t) \mathfrak{r}_m(\mathbf{k}', t') \rangle &= k_B \frac{a\rho_0 T_0^2}{4\pi^3 \tau_S} k^4 \left(\delta_{im} - \frac{k_i k_m}{k^2} \right) \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\
 \langle \mathfrak{v}_i(\mathbf{k}, t) \mathfrak{v}_m(\mathbf{k}', t') \rangle &= k_B \frac{5a^2 \rho_0 T_0^3}{8\pi^3 \tau_q} k^2 \left(\delta_{im} - \frac{k_i k_m}{k^2} \right) \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\
 \langle \mathfrak{r}_i(\mathbf{k}, t) \mathfrak{v}_m(\mathbf{k}', t') \rangle &= 0.
 \end{aligned} \tag{5.20}$$

5.4 Elimination of the fast modes

Let us express the shear stress and the heat flux in terms of the other quantities so as to eliminate the fast modes in the basic system of equations. We solve the last two equations of (5.15) and (5.19) with respect to (ξ, φ) and (σ_i, π_i) , respectively, assuming, for the moment, that the other 3 variables in the case of Eq. (5.15) (or 1 variable in the case of Eq. (5.19)) are some given functions of \mathbf{k} and t .

The solutions can be expressed in a generic way because the last two equations of both the systems can be written in the following matrix form:

$$\frac{d\mathbf{y}(\mathbf{k}, t)}{dt} + \mathbf{M}(\mathbf{k}) \cdot \mathbf{y}(\mathbf{k}, t) = \mathbf{d}(\mathbf{k}, t) + \mathbf{a}(\mathbf{k}, t), \tag{5.21}$$

where $\mathbf{y}(\mathbf{k}, t)$, $\mathbf{M}(\mathbf{k})$, $\mathbf{d}(\mathbf{k}, t)$ and $\mathbf{a}(\mathbf{k}, t)$ are given explicitly in Eq. (5.32) or (5.35) below. The quantity $\mathbf{a}(\mathbf{k}, t)$ is a Gaussian white random force vector with two components. It is important to notice that the matrix $\mathbf{M}(\mathbf{k})$ satisfies the relation: $\mathbf{M}(-\mathbf{k}) = \mathbf{M}(\mathbf{k})$.

The solution of (5.21) is given by

$$\begin{aligned} \mathbf{y}(\mathbf{k}, t) &= \exp[-(t - t_0)\mathbf{M}(\mathbf{k})] \cdot \mathbf{y}(\mathbf{k}, t_0) \\ &+ \int_{t_0}^t d\theta \exp[-(t - \theta)\mathbf{M}(\mathbf{k})] \cdot \mathbf{d}(\mathbf{k}, \theta) \\ &+ \int_{t_0}^t d\theta \exp[-(t - \theta)\mathbf{M}(\mathbf{k})] \cdot \mathbf{a}(\mathbf{k}, \theta), \end{aligned} \quad (5.22)$$

where t_0 is an initial time. The third term on the right-hand side may be regarded as a Gaussian random force, which is denoted by \mathbf{b} , i.e.,

$$\mathbf{b}(\mathbf{k}, t) \equiv \int_{t_0}^t d\theta \exp[-(t - \theta)\mathbf{M}(\mathbf{k})] \cdot \mathbf{a}(\mathbf{k}, \theta). \quad (5.23)$$

The random force \mathbf{b} is, in general, not white.

The correlation matrix $\hat{\chi}(\mathbf{k}_2, \mathbf{k}_1, t_2, t_1)$ ($t_2 > t_1$) of the random force \mathbf{b} is given by

$$\begin{aligned} \hat{\chi}_{ij}(\mathbf{k}_2, \mathbf{k}_1, t_2, t_1) & \\ &\equiv \langle \mathbf{b}_i(\mathbf{k}_2, t_2) \mathbf{b}_j(\mathbf{k}_1, t_1) \rangle \\ &= \int_{t_0}^{t_2} d\theta_2 \int_{t_0}^{t_1} d\theta_1 (\exp[-(t_2 - \theta_2)\mathbf{M}(\mathbf{k}_2)])_{il} \langle \mathbf{a}_l(\mathbf{k}_2, \theta_2) \mathbf{a}_k(\mathbf{k}_1, \theta_1) \rangle (\exp[-(t_1 - \theta_1)\mathbf{M}(\mathbf{k}_1)])_{jk}, \end{aligned} \quad (5.24)$$

where the correlation matrix of the random force \mathbf{a} is given in the following form:

$$\langle \mathbf{a}_l(\mathbf{k}_2, \theta_2) \mathbf{a}_k(\mathbf{k}_1, \theta_1) \rangle = C_{lk}(\mathbf{k}_1) \delta(\mathbf{k}_2 + \mathbf{k}_1) \delta(\theta_2 - \theta_1) \quad (5.25)$$

with a matrix \mathbf{C} . See the relations (5.17) and (5.20).

After some calculations, we may summarize the solution compactly as follows [90]: The solution \mathbf{y} is expressed by

$$\mathbf{y}(\mathbf{k}, t) = \int_{-\infty}^t d\theta \Phi(\mathbf{k}, t - \theta) \cdot \mathbf{d}(\mathbf{k}, \theta) + \mathbf{b}(\mathbf{k}, t) \quad (5.26)$$

with the memory function given by

$$\Phi(\mathbf{k}, t) = \exp[-t\mathbf{M}(\mathbf{k})]. \quad (5.27)$$

Here we have neglected the transient effect that depends on an initial condition by taking the limit: $t_0 \rightarrow -\infty$. The mean of the random force \mathbf{b} vanishes. And its correlation matrix is expressed by

$$\chi(\mathbf{k}_1, t_2 - t_1) = \Phi(\mathbf{k}_1, t_2 - t_1) \chi^0(\mathbf{k}_1), \quad (5.28)$$

where the quantity χ is introduced by the relation:

$$\hat{\chi}(\mathbf{k}_2, \mathbf{k}_1, t_2, t_1) = \chi(\mathbf{k}_1, t_2 - t_1) \delta(\mathbf{k}_2 + \mathbf{k}_1), \quad (5.29)$$

and

$$\chi^0(\mathbf{k}_1) = \chi(\mathbf{k}_1, 0). \quad (5.30)$$

Finally the relation between χ^0 and \mathbf{C} is given by

$$\mathbf{M}(\mathbf{k})\chi^0(\mathbf{k}) + \chi^0(\mathbf{k})\mathbf{M}(\mathbf{k})^T = \mathbf{C}(\mathbf{k}). \quad (5.31)$$

We summarize some noticeable points:

(i) We may regard the relation (5.26) as a constitutive relation between \mathbf{y} and \mathbf{d} with the random force \mathbf{b} . The quantity \mathbf{y} is the functional of the history of the quantity \mathbf{d} . It should be emphasized that the constitutive relation has been obtained from the dynamic equations of the fast modes by neglecting the dependence on the initial condition. Such constitutive relations have been proposed in the theory of so-called *generalized hydrodynamics* where the transport coefficients, in general, take into account the effect of non-locality in space and time.

(ii) As we pointed out above, we notice clearly, from Eq. (5.28), that the random force \mathbf{b} is the Gaussian non-white (or colored) random force. And, in accordance with the general considerations [27, 28] on such a case, the memory function Φ defined in Eq. (5.27) plays an essential role in both Eq. (5.26) for the constitutive equation and Eq. (5.28) for the correlation of the random force. In other words, if we adopt some approximation in the form of the memory function, both the constitutive equation and the correlation of the random force are affected by the approximation simultaneously in order to keep the consistency in the theory. See also the remark (iv) below.

(iii) The relation (5.31) is the one that connects the random force \mathbf{b} and the random force \mathbf{a} . This is the key relation in the following analysis of the hierarchy structure of the random forces in different levels of description in fluctuating hydrodynamics.

(iv) In comparison with the characteristic relaxation times for the conserved quantities such as mass, momentum and energy, the fast modes have much smaller relaxation times, and decay quickly. If we describe hydrodynamic phenomena in such a way that the relaxation times τ_S and τ_q for the fast modes are sufficiently small, the memory function can be well approximated by the Dirac's delta function with a suitable proportional constant. See Refs. [91, 92, 93, 94] for such a coarse graining approximation. At the same time, the random force \mathbf{b} in this approximation becomes to be a white random force. This case will be studied in the next section.

5.5 Relationship to the Landau-Lifshitz theory

In what follows, we adopt the coarse graining approximation explained above and show explicitly the coarse-grained solutions for the System-L and System-T [91]. We will see that these solutions are just the ones in the LL theory.

System-L

The quantities in Eq. (5.21) are given by

$$\begin{aligned} \mathbf{y}(\mathbf{k}, t) &= \begin{bmatrix} \xi(\mathbf{k}, t) \\ \varphi(\mathbf{k}, t) \end{bmatrix}, & \mathbf{M}(\mathbf{k}) &= \begin{bmatrix} \frac{1}{\tau_S} & \frac{8}{15}k^2 \\ -aT_0 & \frac{1}{\tau_q} \end{bmatrix}, \\ \mathbf{d}(\mathbf{k}, t) &= \begin{bmatrix} -\frac{4}{3}a\rho_0T_0k^2\psi(\mathbf{k}, t) \\ \frac{5}{2}a^2\rho_0T_0k^2T(\mathbf{k}, t) \end{bmatrix}, & \mathbf{a}(\mathbf{k}, t) &= \begin{bmatrix} \mathbf{v}(\mathbf{k}, t) \\ \mathbf{w}(\mathbf{k}, t) \end{bmatrix}. \end{aligned} \quad (5.32)$$

Denoting $\mathbf{b} = [\mathbf{g}, \mathbf{h}]^T$, we have the following relation up to the leading term with respect to τ_S and τ_q [91]:

$$\begin{bmatrix} \xi(\mathbf{k}, t) \\ \varphi(\mathbf{k}, t) \end{bmatrix} = \begin{bmatrix} -\frac{4}{3}a\rho_0T_0k^2\tau_S\psi(\mathbf{k}, t) + \mathbf{g}(\mathbf{k}, t) \\ \frac{5}{2}a^2\rho_0T_0k^2\tau_qT(\mathbf{k}, t) + \mathbf{h}(\mathbf{k}, t) \end{bmatrix}. \quad (5.33)$$

The Gaussian white random forces \mathbf{g} and \mathbf{h} have null means and correlations:

$$\begin{aligned} \langle \mathbf{g}(\mathbf{k}, t) \mathbf{g}(\mathbf{k}', t') \rangle &= \frac{1}{3\pi^3} k_B a \rho_0 T_0^2 k^4 \tau_S \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\ \langle \mathbf{h}(\mathbf{k}, t) \mathbf{h}(\mathbf{k}', t') \rangle &= \frac{5}{8\pi^3} k_B a^2 \rho_0 T_0^3 k^2 \tau_q \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\ \langle \mathbf{g}(\mathbf{k}, t) \mathbf{h}(\mathbf{k}', t') \rangle &= 0. \end{aligned} \quad (5.34)$$

System-T

The quantities in Eq. (5.21) are given by

$$\begin{aligned} \mathbf{y}(\mathbf{k}, t) &= \begin{bmatrix} \sigma_i(\mathbf{k}, t) \\ \pi_i(\mathbf{k}, t) \end{bmatrix}, & \mathbf{M}(\mathbf{k}) &= \begin{bmatrix} \frac{1}{\tau_S} & \frac{2}{5}k^2 \\ -aT_0 & \frac{1}{\tau_q} \end{bmatrix}, \\ \mathbf{d}(\mathbf{k}, t) &= \begin{bmatrix} -a\rho_0T_0k^2\omega_i(\mathbf{k}, t) \\ 0 \end{bmatrix}, & \mathbf{a}(\mathbf{k}, t) &= \begin{bmatrix} \mathbf{r}_i(\mathbf{k}, t) \\ \mathbf{v}_i(\mathbf{k}, t) \end{bmatrix}. \end{aligned} \quad (5.35)$$

Denoting $\mathbf{b} = [\mathbf{r}_i, \mathbf{v}_i]^T$, we obtain the following relations in a similar way as above [91]:

$$\begin{bmatrix} \sigma_i(\mathbf{k}, t) \\ \pi_i(\mathbf{k}, t) \end{bmatrix} = \begin{bmatrix} -a\rho_0T_0k^2\tau_S\omega_i(\mathbf{k}, t) + \mathbf{r}_i(\mathbf{k}, t) \\ \mathbf{v}_i(\mathbf{k}, t) \end{bmatrix}. \quad (5.36)$$

Note that there is no deterministic part in $\pi_i(\mathbf{k}, t)$, therefore, only the random force plays a role. The correlations between the zero-mean Gaussian white random forces are given by

$$\begin{aligned}\langle \xi_i(\mathbf{k}, t) \xi_m(\mathbf{k}', t') \rangle &= \frac{1}{4\pi^3} k_B a \rho_0 T_0^2 k^4 \tau_S \left(\delta_{im} - \frac{k_i k_m}{k^2} \right) \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\ \langle \iota_i(\mathbf{k}, t) \iota_m(\mathbf{k}', t') \rangle &= \frac{5}{8\pi^3} k_B a^2 \rho_0 T_0^3 k^2 \tau_q \left(\delta_{im} - \frac{k_i k_m}{k^2} \right) \delta(\mathbf{k} + \mathbf{k}') \delta(t - t'), \\ \langle \xi_i(\mathbf{k}, t) \iota_m(\mathbf{k}', t') \rangle &= 0.\end{aligned}\tag{5.37}$$

The relationship between the present theory and the LL theory: We can now confirm that the expressions in Eqs. (5.33), (5.34), (5.36) and (5.37) are exactly the same as those derived from the LL theory where the shear viscosity μ and the heat conductivity κ are identified by the relations (1.170):

$$\mu = a \rho_0 T_0 \tau_S, \quad \kappa = \frac{5}{2} a^2 \rho_0 T_0 \tau_q.\tag{5.38}$$

Thus we have proved that the LL theory can be derived from the present theory by using the coarse graining approximation, and that the LL theory is included in the present theory as a limiting case.

The present theory and the LL theory belong to the two different levels of description of fluctuating hydrodynamics. As we analyzed above, the rapidly changing deterministic modes (fast modes) in ET have been consistently re-normalized into the random forces in the LL theory. Therefore, from a physical point of view, the delta functions appeared in the correlations have their own validity range depending on the spatio-temporal resolution of their description level.

5.6 Discussion and concluding remarks

In the present chapter, we have summarized the recent theory of fluctuating hydrodynamics based on ET. And we have made clear the link between the two levels of description of fluctuating hydrodynamics, that is, the present theory based on ET-13 and the LL theory. This link has been established through introducing another intermediate level of description, which is characterized by the conservation equations with the memory-type constitutive equation and the colored Gaussian random force. In this way, we notice that there are at least three levels of description of fluctuating hydrodynamics in the present work. And we notice, in particular, the explicit hierarchy structure of the random forces.

Generally speaking, there are many such levels. Boillat and Ruggeri [8, 48] found the hierarchy structure of ET and the important concept called the “main subsystem” of field equations. Each main subsystem gives us one level of description with different resolution from each other. And, in a similar way as above, we can develop the corresponding fluctuating hydrodynamics basing on a given main subsystem (Chapter 1, Section 3).

Finally we summarize the concluding remarks:

(i) In ET, Navier-Stokes and Fourier constitutive equations are obtained as its limit case by using an iterative scheme called the Maxwellian iteration [8]. If we apply this scheme formally to the present basic system with random forces, we can also obtain the results of the LL theory.

(ii) In the present chapter, we have studied a monatomic rarefied gas only. Fluctuating hydrodynamics can also be established in a similar way by using ET for polyatomic rarefied gases and for monatomic and polyatomic dense gases proposed in Chapter 2 where the dynamic pressure exists. We hope that we will soon show their details.

(iii) As the basic system of equations in ET is of hyperbolic type, the propagation speed of information is finite. In this respect, ET is in sharp contrast to the traditional theory of Navier-Stokes and Fourier type that predicts infinite speeds for the propagation of heat and shear stress. It is, therefore, quite reasonable to adopt ET in order to develop, in particular, the relativistic fluctuating hydrodynamics. See the pioneering work by Calzetta [95].

(iv) Numerical analyses based on the present theory in various situations are highly expected. We can expect qualitatively different effects predicted by the present theory from those by the LL theory, especially when we study the fluctuations in a small spatio-temporal scale.

Chapter 6

Summary and concluding remarks

In this thesis, we developed the following two theoretical approaches, which opened a new field of non-equilibrium thermodynamics:

1. Extended thermodynamics of dense gases
2. Fluctuating hydrodynamics based on extended thermodynamics

The details and the characteristics of the recently developed theory of ET for dense gases are discussed in Chapter 2. The new approach of ET for dense gases is based on balance equations with two hierarchy series. The constitutive equations are determined by the *entropy inequality*, *concavity* and *material frame indifference*. As a result, we extended the applicable range of ET to rarefied polyatomic gases, dense monatomic gases and dense polyatomic gases, which were not fully explored. This means that there are potentially many research fields where this approach may play a crucial role. As typical dense gases, hard-sphere gases and van der Waals fluids are studied. Moreover, the subtle point with respect to the concavity condition in the case of monatomic gases became apparent.

The validity of the new approach is tested by studying the dispersion relation of sound in rarefied polyatomic gases in Chapter 3. The dispersion relation is compared with experimental data and Navier-Stokes Fourier theory. The results show that ET is valid even in the case of a non-equilibrium state out of local equilibrium. Moreover, the bulk viscosity and the relaxation times were evaluated. Hydrogen, deuterium and hydrogen deuteride gas analyses were performed at several temperatures, and the results strongly suggest that the ET theory for dense gases deserves further attention.

To clarify the role of dynamic pressure, we studied the ET for dense gases with 6 independent fields in Chapter 4. A fully-consistent thermodynamic theory of sound in gases with energy transfer was established on the basis of ET, valid even in the region where the local equilibrium assumption does not hold. The relationship between the theory with 6 independent fields and Meixner's theory was also shown. It was found that, as far as the dispersion

relation of weak sound propagation in equilibrium state is concerned, both theories predict the same expression for dispersion.

Obviously, the consistent thermodynamic theory of dense gases that is valid beyond the local equilibrium assumption is crucially important, for example, in acoustics [74] and gas dynamics [7], and in their various applications in the fields of engineering, biology and so on.

In Chapter 5, we proposed the fluctuating hydrodynamics approach based on ET. We clarified the link between the two levels that describe the fluctuating hydrodynamics, that is, the theory based on the ET for rarefied monatomic gases with 13 independent fields and the Landau-Lifshitz theory. This link has been established by introducing an intermediate level of description, which is characterized by conservation equations with memory-type constitutive equations and the colored Gaussian random force. Consequently, there are at least three levels that describe the fluctuating hydrodynamics in the present work and, in particular, the explicit hierarchy structure of the random forces.

The concluding remarks have as follows:

1. We have clearly demonstrated the usefulness and potential of ET for dense gases and fluctuating hydrodynamics based on ET, and we believe that this new approach will open new fields in modern science and engineering.
2. We have clarified the subtle point of the ET for dense gases in the case of monatomic gases. This point is interesting from a physical and mathematical viewpoints; also, it is worthy of further study and will be considered as the future subject.
3. In ET, Navier-Stokes and Fourier constitutive equations are obtained as the limiting case by using an iterative scheme called the Maxwellian iteration. By applying this scheme to the present basic system with random forces, the results of the Landau-Lifshitz theory can be also obtained.

Lastly we list topics for future work using the developed theoretical approach:

- Analysis of wave propagation phenomena in dense gases.
- Analysis of the propagation of non-linear waves such as acceleration waves and shock waves.
- Extend the ET-based fluctuating hydrodynamics to rarefied polyatomic gases and dense gases.
- Extend the applicable range of the ET for dense gases and the fluctuating hydrodynamics to the relativistic region, and pay particular attention to the effect of dynamic pressure.

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List of Papers

Chapter 2.

- ◇ T. Arima, S. Taniguchi, T. Ruggeri and M. Sugiyama: Extended thermodynamics of dense gases. *Continuum Mechanics and Thermodynamics*, 24, pp.271-292 (2012).
- ◇ T. Arima and M. Sugiyama: CHARACTERISTIC FEATURES OF EXTENDED THERMODYNAMICS OF DENSE GASES. *Atti della Accademia Peloritana dei Pericolanti*, vol 90, pp. 1-15 (2012).

Chapter 3.

- ◇ T. Arima, S. Taniguchi, T. Ruggeri and M. Sugiyama: Dispersion Relation for Sound in Rarefied Polyatomic Gases Based on Extended Thermodynamics. *Continuum Mechanics and Thermodynamics*, DOI 10.1007/s00161-012-0271-8 (2012).

Chapter 4.

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Chapter 5.

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