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# Kinetic Theory of Irreversible Processes in a System of Radiation and Matter

by

KEFEI MAO

Department of Physics McGill University Montreal, Quebec, Canada August, 1993

A Thesis submitted to the Faculty of Graduate Studies and Research of McGill University in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

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# Kinetic Theory of Irrever. Processes in a System of Radiation and Matter

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#### Abstract

Thermodynamics of irreversible processes in a radiation field is formulated, based on kinetic theory, by treating nonequilibrium radiation as a nonequilibrium photon gas interacting with matter. The generalized hydrodynamic equations for macroscopic variables necessary for describing temporal and spatial evolution of irreversible processes in the system of matter and radiation are derived from kinetic equations by using the modified moment method. The method rigorously yields the conclusion that entropy differential is not an exact differential when the system is away from equilibrium. Therefore, an extended Gibbs relation for the entropy density does not hold valid. However, an extended Gibbs relation-like equation holds for the compensation differential which has been shown to be an exact differential. The entropy balance equation is cast into an equivalent form in terms of a new function called the Boltzmann function. In the context of the present formalism the light-induc. 1 viscous flow is theoretically explained for the entire range of pressure. The modified moment method has been extended to the covariant Boltzmann equation in order to formulate a theory of relativistic irreversible thermodynamics. Furthermore, the kinetic theory foundations for relativistic irreversible thermodynamics for the system of radiation and matter are provided. The statistical mechanical formulas are obtained for various material and radiative transport coefficients. The radiative transport coefficients stand in simple ratios independent of material parameters. The ratios calculated are in agreement with those used in the phenomenological theory using the Rosseland mean.

#### Résumé

La thermodynamique des processus irréversibles dans un champ de radiations a été exprimée, sur la base de la théorie cinétique, en considerant les radiations hors de l'équilibre comme étant un gaz de photons interagissant avec la matière. Les équations hydrodynamiques généralisées pour les variables nécéssaires à la description temporelle et spatiale de l'évolution des processus irréversibles dans le système de matière et de radiation, ont été dérivées de la théorique cinétique en utilisant la théorie des moments modifiés. Cette méthode a permis de conclure qu'en toute rigueur, la différentielle d'entropie n'était pas exacte pour un système loin de l'équilibre. Par conséquent, l'extension des relations de Gibbs ne peut être valide. De toutes façons, une relation de Gibbs étendue remplace la différentielle de compensation qui, elle, est exacte. L'équation de continuité pour l'entropie a été exprimée en termes d'une nouvelle fonction appelée fonction de Boltzmann. Dans ce formalisme, l'écoulement visqueux induit par la lumière a été expliqué théoriquement pour toute l'échelle de pressions. La méthode des moments modifiés a été étendue à l'équation covariante de Boltzmann pour formuler une théorie relativiste de la thermodynamique irréversible. De plus, les bases de la théorie pour la thermodynamique irréversible relativiste des systèmes de radiation et de matière ont été établies. Les formules statistiques ont été obtenues pour des nombreux matériaux et de coefficients de transport radiatives. Les coefficients de transport sont liés dans un rapport simple indépendant des paramètres des matériaux. Les rapports calculés sont en accord avec ceux utilisés dans la théorie phénomènologique qui considère la moyenne de Rosseland.

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#### Chapter 1

## Introduction

It is well known that radiation, especially, equilibrium (black-body) radiation, has played a germinal role in the development of modern physics [1, 2]. Planck's pioneering work on blackbody radiation lay down the foundation of quantum mechanics. Einstein's celebrated paper in 1917 [3] first introduced the concept of the stimulated emission of radiation by atoms which has led to the invention of modern laser technology. Since then many progresses have been made both for understanding radiation and its applications which are major tools to investigate microscopic structures of matter.

Radiation we encounter in the laboratory and nature is generally in a nonequilibrium state; in other words, a strictly thermal radiation field, namely, an isotropic Planck distribution of photons, is hardly ever found in open systems from which photons escape. Nonequilibrium radiation occurs in various contexts such as laser physics [4], astrophysics [5], plasma physics [6], atomic physics [7a], photochemistry [7b] and solar energy conversion [7c] etc. Thermodynamics of equilibrium radiation is described by an equilibrium Gibbs relation for entropy change in a way completely parallel to equilibrium thermodynamics of matter. Since there is nonequilibrium thermodynamics of matter, we would ask a natural question: is there also a parallel formalism for nonequilibrium radiation? One of the aim of this thesis is to answer this question.

Since radiation cannot reach equilibrium by itself but requires interactions with matter to do so, understanding irreversible phenomena of radiation would require study of the macroscopic behavior of radiation and matter as a single system and, in particular, the irreversible thermodynamics of matter interacting with radiation. Despite the important roles which radiation has played in physical sciences, abundant studies commensurate to the roles played, and recent works reported in the literature ([8] and also see, for example, ref. [9]), there is still a considerable need for study in the area of nonequilibrium radiation.

In the hope to put the theory of irreversible processes in a radiation field on a par with that for matter alone, Wilt [10] carried out studies on the question of irreversible thermodynamics for radiation from mid fifties until the early seventies. He presented an entropy balance equation for radiation, but did not develop the theory further to construct a theory of irreversible processes in the presence of radiation although such a theory would be necessary to answer the questions of local thermodynamic equilibrium, etc., raised in his papers. Essex [11] also addressed his study to an aspect of thermodynamics; he extended the principle of the minimum entropy production to include radiation. The subject is briefly treated from a kinetic theory viewpoint in the monograph by de Groot et al. [8] in terms of Compton scattering of electrons in the relativistic formalism, but not enough to form a basis to carry on with further studies of irreversible thermodynamics. Radiation thermodynamics is also discussed by Kremer and Müller [12].

Quite recently, the combination of laser physics and gas kinetic theory has produced some interesting phenomena such as laser-cooling [13] and light-induced kinetic effects [14] etc. G. Nienhuis and his coworkers developed a kinetic theory of gas in the presence of light [9], which extended the well known Chapman-Enskog method to include the interactions between atomic (molecular) gas and light.

From an astrophysical viewpoint nonequilibrium radiation has been discussed by using radiative energy transfer equations. An extensive study on the solution of radiative energy transfer equation for various boundary conditions and the astrophysical implications of the solution is covered in Chandrasekhar's monograph [2]. As Weinberg pointed out that since the discovery of the 2.7 K radiation background an increased attention has been paid to the possible cosmological role of dissipative processes [15]. A more substantial study of radiative transport problems can be found in the monographs of Oxenius [6] and Mihalas and Mihalas [5]. This phenomenological theory of radiative transport does not provide dynamical foundations for nonequilibrium radiation.

The theory of irreversible processes of radiation has not as yet reached even the formative level achieved [16] for that of matter. It has some way to go before a satisfactory maturity is achieved as a theory, especially when the system is removed far from equilibrium. In the works mentioned earlier, radiation is not put on the same footing as matter at the kinetic level, since it is treated by means of a phenomenological equation of radiative energy transfer and the evolution of radiation entropy is inadequately treated as to allow a practicable theory of irreversible thermodynamics of radiation. Since the radiative energy transfer equations taken in these works are not coupled to the kinetic equation for matter which may be away from equilibrium, one is not able to follow the irreversible evolution of radiation and matter together. In this thesis we approach the problem by starting from the kinetic theory viewpoint that takes radiation and matter as a mixture of particulate photons and material particles which evolves from a nonequilibrium state to an equilibrium state.

We assume a semiclassical Boltzmann equation for photons which is coupled to the Boltzmann equations for material particles [17]. The quantum effect of photons is contained in the collision integral of the Boltzmann-Uehling-Uhlenbeck equation for bosons. This way, the system of radiation and matter is viewed as a mixture of photons and material particles which interact with each other according to the laws of mechanics. The major motivation for this approach is in the desire to formulate irreversible thermodynamics of radiation and matter on equal footing and in a unified manner. Instead of the Chapman-Enskog method [18] and the Grad moment method [19], we employ the modified moment method [20] to solve the Boltzmann equations of photons and material particles. The distinctive features of this method are follows. Firstly, it is capable of treating nonequilibrium processes occurring far from equilibrium. The conventional methods are only valid in the linear regime or near-equilibrium states. Secondly, it allows to establish an exact irreversible thermodynamic structure. The H theorem for the system of radiation and matter is a natural outcome of the kinetic equations. The second law of thermodynamics is rigorously satisfied in the context of the modified moment method.

In addition, the present formalism shows that the extended Gibbs relation for entropy change used in the extended irreversible thermodynamics [21] does not hold valid. However, there is the compensation differential which is an exact differential in the irreversible thermodynamics that satisfies the extended Gibbs relation-like equation, but this means a revision of the logical structure of the extended irreversible thermodynamics is necessary. A new form of local H theorem is derived in terms of the Boltzmann function introduced as a Legendre transformation of the entropy density.

The kinetic theory permits deeper insight into irreversibility and thermodynamics of radiation: for example, the classical theory of blackbody radiation is recovered from the formalism presented here; it also enables us, from the kinetic theory and thermodynamic viewpoints, to look at the celebrated theory [3] of Einstein, by which the Planck distribution function was shown to be consistent with the Boltzmann distribution function for matter. The present theory in fact allows to make a nonequilibrium correction to the Planck distribution function, which is not possible to obtain if the steady state argument is used as in Einstein's theory. It will be shown that the consistency between the Planck distribution function for radiation and Boltzmann distribution function for matter is a result of the H theorem and therefore of the second law of thermodynamics. The equilibrium distribution functions so obtained are unique because of the H theorem.

One of the most important aspects of kinetic theory is that it can provide a way to derive the expression for the nonequilibrium distribution function. Since the interaction of photons with particles via emission, absorption and scattering leads to an exchange of energy and momentum between radiation field and material gas, photons and particles are, in general, in nonequilibrium state. What is the nonequilibrium distribution function for a radiation field? We should answer this question from both theoretical and experimental aspects. The theoretical formula of nonequilibrium distribution function is obtained in the context of the modified moment method which can be reduced to the Chapman-Enskog result in the linear regime.

With the help of distribution functions we can define a set of moments which basically belong to two different classes. One subset contains all the conserved variables such as mass, kinetic energy and hydrodynamic velocity which are collisional invariants. Another subset consists of all the nonconserved variables (fluxes). Of course, determining the distribution function is equivalent to determining these infinite number of moments. However, it is hopeless to find solutions for this infinite set of moments in general. On the other hand experimental measurable quantities are finite. A practicable theory should be constructed in terms of a finite number of physical quantities. This means that we have to truncate the set of moments according to physical demands of an event. The truncation procedure leads from a microscopic description in terms of the distribution function to a hydrodynamic description in terms of a finite number of moments. The evolution of the system will be determined by the governing equations for the physically meaningful moments. Since these moments also appear in the expression of entropy density, the evolution equations of the moments are coupled to the entropy balance equation. The second law of thermodynamics plays role as the constraint to select physically acceptable solutions of the moment evolution equations.

The present kinetic theory formalism establishes a bridge which links the experimental measurable quantities (macroscopic level) of a system and the dynamic mechanism of constituent particles (atomic or molecular level). This makes it possible to evaluate macroscopic variables in terms of particle interactions under nonequilibrium conditions. In this sense, the generalized hydrodynamic equations of radiation and matter have been derived from the coupled Boltzmann equations for photons and material particles by the modified moment method. Solving these generalized hydrodynamic equations under certain initial and boundary conditions will give us the values of the macroscopic quantities which are necessary to describe the system of radiation and matter.

The evolution of a system consisting of matter and a radiation field viewed as a gas-kinetic mixture of material particles and photons has a great advantage. This opens the way to employ the apparatus of gas kinetics for describing the system, where the microscopic evolution equation has the form of a Boltzmann equation. Since interacting systems of matter and radiation cover a broad class of problems under active study, such as laser-cooling [13], optical piston [14] and light-induced viscous flow [22], etc., the kinetic theory of such systems would be necessary to understand the experimental results.

Light can exert forces on atom because photons carry momentum. The exchange of photon momentum with an atom can occur incoherently, as in the case of absorption and reemission of photons, or coherently, as in the case of redistribution (or lensing) of the incident field by the atom. By utilizing photon momentum, it is possible to manipulate atoms by light. Many of the successes in atom manipulation have occurred because not only laser can exert powerful forces on atoms but also techniques have been found to cool these particles to low temperature which are still in the vapor phase. Once the atoms are cooled to temperatures on the order of 1 millikelvin, the electric and magnetic dipole forces can easily overcome thermal motion, and these feeble forces become sufficient to control the atoms. Therefore the atoms, which originally had an equilibrium velocity distribution with a high average kinetic energy, end up in a nonequilibrium state with a narrow velocity distribution and a low average kinetic energy. It is apparent that light is able to lower the entropy of matter. In order to provide a molecular theory of irreversible thermodynamical properties, for example, efficiency rate of a cooling process, a kinetic

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theory would be necessary. Laser cooling and trapping are finding applications in a number of areas [23]. An application that is receiving considerable attention is the construction of better time standards in the microwave or optical domain. A variety of precision measurements will benefit from the long measurement times possible with laser-cooled atoms. Perhaps the most exciting applications in the field of laser cooling and trapping will come out of the ability to study problems in the polymer physics and biology on a single molecular basis.

A completely different mechanism for affecting the motion of atoms by applying a resonant light is light-induced kinetic effects. These are due to the combination of a state-dependent collision cross section and a velocity-selective excitation of atoms by laser. The most studied manifestation of light-induced kinetic effects is the light-induced drift. Because of the Doppler effect, a traveling laser beam produces velocity-selective excitation of atoms. In other words, the excitation rate differs from zero only when the component of particle velocities along the laser propagation direction is near the Doppler-selected velocity  $v_o = (\omega_l - \omega_o)/k_l$ , with  $\omega_l$  the central frequency of radiation,  $\omega_o$  the transition frequency of the particles, and  $k_l$  the wave number. Since particles can only be excited within this narrow group, it is natural to expect that the distribution functions of excited and ground state contain a narrow structure around  $v_o$ . This velocity selection yields opposing fluxes of excited and ground state atoms. Because of the momentum conservation law these two fluxes will cancel each other if there is no buffer ges in a system. However, both fluxes feel different diffusion resistances in the optically inactive buffer gas which is not affected by the light field since the collision cross section of an excited atom is generally larger than that of the ground state atom. In particular, an optical piston effect has been observed in the experiment for an optically dense system [24]. When the laser frequency is tuned in the red Doppler wing the drift velocity is in the laser propagation direction, therefore the light can penetrate the optically dense system farther and farther, sweeping the active atoms to the dark end of the tube. This is the so-called optical piston action or front formation. There are some other light-induced kinetic phenomena which have been observed in onecomponent gas system (without a buffer gas), for instance, surface light-induced drift [25] and light-induced viscous flow [22], etc.

At this point it is worthwhile to mention some applications of the light-induced kinetic effects. The optical piston effect has been used for isotope separation; surface light-induced drift may provide a tool to analyze the mechanism of particle-wall interaction; light-induced viscous flow makes it possible to determine internal particle interactions by measuring the macroscopic drift and there would still be some more potential applications. The underlying mechanism of surface-light drift is quite different from that of optical piston; it is due to state-dependent molecule-surface interactions whereas the light-induced viscous flow is the result of the combination of a state-dependent collision cross section and nonuniform illumination which produces stresses in the gases and gives rise to a particle flow.

However, the experimental results on light-induced viscous fiow can not be well understood by using a linearized kinetic theory. More specifically, in 1989 Hoogeveen et al. [22] reported on an experimental result which demonstrated a gas flow induced in a capillary by a Doppler-broadened laser beam whose intensity is radially distributed. The flow generates a pressure difference and a stress in the capillary. By measuring the pressure difference by a differential manometer and plotting it against the gas pressure, they were able to show that the normal pressure regime behavior follows the classical Navier-Stokes theory prediction, namely, the Hagen-Poiseuille volume flow rate which accounts for the flow rate of a gas through a tube under a pressure gradient when the pressure is in the normal range. However, as the pressure was decreased down to the rarefied gas regime, the curve for the pressure difference vs. pressure started to decrease in contrast to the Hagen-Poiseuille theory prediction. In other words, there appears a maximum in the curve at some low pressure.

In fact, this abnormal behavior is very closely related to the so-called Knudsen paradox. M. Knudsen [26] in 1909 observed that the volume flow rate of gas through a capillary under a pressure difference increases as the pressure diminishes below a value in the rarefied gas regime, in contrast to the classical Navier-Stokes theory prediction that the flow rate should vanish. Since this was reproducible [27] but not possible to explain by the classical Navier-Stokes theory, the phenomenon was called the Knudsen paradox. It is not a paradox, but an indication of the inadequacy of the Navier-Stokes theory which cannot properly handle flows of gases in the range of large Knudsen numbers (0.1 typically or larger). It has recently been explained adequately by using the generalized hydrodynamic theory [28]. The basic physical reason for the phenomenon is that as the gas density diminishes, the mean free path in the gas becomes very long, thus the range of momentum transfer becomes accordingly long, and, as a consequence, the gas behaves as if it is a non-Newtonian fluid in the sense that the viscosity of a rarefied gas depends on the shear rate. Such a fluid has a vanishing viscosity at the wall of the tube which results in a plug flow. The ultimate consequence of this is that a non-energy-dissipating collimated beam is formed in the capillary at low pressure and thus the molecule moves axially and ballistically along the tube under a pressure difference. This phenomenon will be explained by applying the results of the kinetic theory of radiation and matter [29] described later. The basic idea of this theory has also been applied by Enk and Nienhuis [30] to analyze some irreversible processes in connection with the light-induced kinetic effects.

In the proceeding discussions nonrelativistic kinetic theory of radiation and matter and its applications have been presented. However, there are some problems, particularly in astrophysics and nuclear physics (heavy ion collision), where a relativistic description is necessary [8]. Therefore, we need to develop a relativistic kinetic theory which is parallel to the nonrelativistic counterpart as we mentioned earlier in order to understand nonequilibrium behavior of many-body systems consisting of high speed particles. The relativistic irreversible thermodynamics and its applications were presented by Müller [31] and other people [32]. The relativistic Boltzmann equation was also used to study irreversible processes in relativistic gases by employing either the Chapman-Enskog method or the Maxwell-Grad moment method to approximately solve the kinetic equation [8]. Especially, these methods were used as means to obtain or justify a macroscopic theory of irreversible processes in the relativistic framework. When we aim to formulate a theory of irreversible processes, the question of the nature of entropy unavoidably arises, but relativistic kinetic theory has not as yet yielded a satisfactory answer to the question. The range of validity of the existing approximate relativistic thermodynamic theories depends on the answer to this question.

The modified moment method has been extended to solve the relativistic Boltzmann equation [33]. This extension is able to yield a rigorous answer to the question of whether the entropy differential for irreversible processes is exact or not. The answer turns out to be that it is not an exact differential if the system is away from equilibrium. This means that the extended Gibbs relation forming the basis of extended relativistic irreversible thermodynamics (EIT) does not hold valid at least from the viewpoint of the covariant Boltzmann equation. However, there is a differential form called the compensation differential that looks like the extended Gibbs relation used in EIT, but this means a revision of the existing EIT formalism and its logical structure. There are a number of theoretical results that the present quest for the answer has produced: the generalized hydrodynamic equations of relativistic fluids; the question of temperature in relativistic kinetic theory. The present formalism in essence puts the statistical mechanics of nonequilibrium thermodynamics on a par with the Gibbs ensemble theory of equilibrium statistical mechanics. All the macroscopic evolution equations are presented in such a form that they consist of terms which are easily identifiable with the corresponding terms in their nonrelativistic versions and purely relativistic terms which vanish in the nonrelativistic limit. Thus, the relativistic corrections to the classical generalized hydrodynamic equations are clearly identified and made easy to obtain.

It is worthwhile to point out that the relativistic form of the generalized hydrodynamic equations is, mathematically speaking, hyperbolic differential equations which give the speed of the wave solution less than the speed of light. However, conventional hydrodynamic equations such as the Navier-Stokes equations or the relativistic Navier-Stokes equations are parabolic differential equations which give an infinite speed of propagation. This is against the principle of relativity. This problem is discussed in the framework of relativistic irreversible thermodynamics which is derived from relativistic Boltzmann equation by using the Chapman-Enskog method or the Grad moment method.

By using the relativistic kinetic theory it is possible to formulate a nonequilibrium statistical mechanical theory for the systems consisting of photons and relativistic particles which interact with each other in a nonequilibrium condition [34]. The covariant Boltzmann equations for photons and material particles have been solved by means of the modified moment method which seeks the solution of kinetic equations in a way consistent with the thermodynamic laws. The physical motivations to have a covariant kinetic theory of radiation and matter are following. The generalized hydrodynamic equations derived from nonrelativistic Boltzmann equation are not explicitly Lorentz covariant. Therefore, the whole theory is rendered awkward by treating particles as nonrelativistic particles and making Doppler shift corrections for photon frequencies in the treatment of photons. It is also difficult to make sure that the definitions of statistical formulas for macroscopic variables are correctly made with regard to the relativistic correction and the evolution equations have correct relativistic extensions. These awkward features can be easily removed if a covariant theory is formulated. There are some physical problems where a relativistic formalism is unavoidable, for example, if particles move at high speed and interact with radiation.

The theory of transport processes is developed for a system of photons and material particles [35]. The statistical mechanical formulas are obtained for material and radiative transport coefficients. In contrast to the phenomenological theory which is based on the radiative energy transfer equation there are no free parameters in the expressions of transport coefficients of nonequilibrium radiation field. Various radiative transport coefficients stand in simple ratios that are independent of material parameters. The ratios calculated are in agreement with those used in the phenomenological theory by using the Rosseland mean for the radiative absorption coefficient. For explicit calculations of the transport coefficients a photon-electron system is considered with the Compton scattering as the elementary dynamical processes underlying the transport process. The agreement with the phenomenological theory is found to be excellent, supporting the soundness of the underlying kinetic theory of radiation and matter.

Finally, the organization of this thesis is summarized as follows. In chapter 2 the nonrelativistic kinetic theory and irreversible thermodynamics of radiation and matter are presented. Special attention is focused on the theoretical foundation. An application of this theory to the light-induced viscous flow is given in chapter 3. The relativistic kinetic theory and the modified moment method are presented in chapter 4. The covariant kinetic theory of radiation and matter is discussed in chapter 5. The calculation of transport coefficients of photon gas is carried out in chapter 6. Concluding remarks and discussion are given in chapter 7.

#### Chapter 2

# Kinetic theory approach to irreversible thermodynamics of radiation and matter

We present the nonrelativistic kinetic theory for an interacting system of matter and radiation. The kinetic equations are constructed in the spirit of the Boltzmann equation on the basis of a model for interaction between matter and radiation [17]. The H theorem is proved therewith and various aspects of nonequilibrium radiation and its equilibrium limit are discussed. Since the coupled kinetic equations of matter and radiation are nonlinear, an approximate method of solving these kinetic equations is unavoidable. The modified moment method has been used to solve the Boltzmann equations of matter and radiation. The most important differences of the modified moment method with the conventional Chapman-Enskog method and the Maxwell-Grad moment method are as follows. It seeks the solution of Boltzmann equation in such a way that the second law of thermodynamics is satisfied at the order of approximation made. Secondly, it can be applied to analyze nonlinear behavior of gas flow in a thermodynamically consistent manner whereas the nonlinear order solutions by the Chapman-Enskog or the Maxwell-Grad moment method are not generally consistent with the second law of thermodynamics. With these kinetic equations the various macroscopic variables necessary for nonequilibrium matter and radiation are defined and their evolution equations can be derived in the local rest frame moving at fluid velocity **u**.

## 2.1 Kinetic equations

Let us assume a system of photons and a dilute gas consisting of particles with internal degrees of freedom so that they can make transition from one internal state to another on absorption or emission of a photon [17]. The material particles in different internal quantum states will be regarded as different species. These material particles scatter, absorb or emit photons. Since the gas is dilute, the particle correlations may be neglected. Therefore, the particle distribution in the phase space is adequately described by a singlet distribution function alone. Since the point of interest here is in irreversible phenomena but not in some questions in dense fluid kinetic theory, singlet distribution functions obeying some irreversible kinetic equations (e.g., Boltzmann equations) are sufficient. As to photons, since they do not interact with each other owing to the linear nature of the electrodynamic equations (Maxwell's equations), the equilibrium state of photons is attained only by their interaction with matter. If we view radiation as consisting of particulate photons, the absence of photon-photon interactions suggests that a singlet distribution function should be adequate for the photon distribution. But this photon distribution function is not independent of the distribution functions of matter since photons interact with the material particles; in fact, the distribution functions obey a set of coupled kinetic equations. The material particles henceforth will be called simply the particles whenever confusion will not arise thereby.

The material gas consists of species  $a, b, c, \cdots$ ; these species labels are assigned a dual role to indicate both the species and the internal state in which the particular particle is found. The subscript or superscript r on a distribution function or macroscopic variables will refer to radiation (photons). The singlet distribution function for species a will be denoted by  $f_a(\mathbf{v}_a, \mathbf{r}; t)$  where  $\mathbf{v}_a$  is the velocity of a particle of species a and  $\mathbf{r}$  its position at time t. Similarly, the photon distribution function will be denoted by  $f_r(\mathbf{k}_r, \mathbf{r}; t)$  where  $\mathbf{k}_r$  is the wave vector of radiation. The distribution functions are normalized such that they give the number density at position  $\mathbf{r}$  and time t. We will find it convenient for uniformity of notation to use the wave vector  $\mathbf{k}_a$  instead of  $\mathbf{v}_a$  for particle species  $a: m_a \mathbf{v}_a = \hbar \mathbf{k}_a$  where  $m_a$ is mass of species a and  $\hbar$  is the Planck constant/ $2\pi$ .

Then the change in the distribution function of species a in a small elementary phase volume around point  $(\mathbf{r}, \mathbf{k}_{n})$  is assumed to be described by the Boltzmann equation [18]

$$[\partial_t + (\hbar \mathbf{k}_a/m_a) \cdot \nabla + (m_a \mathbf{F}_a/\hbar) \cdot \nabla_k] f_a(\mathbf{k}_a, \mathbf{r}, t) = (\partial f_a)_{coll}$$
(2.1)

where  $\partial_t = \partial/\partial t$ ,  $\nabla_k = \partial/\partial \mathbf{k}_a$ , and  $\mathbf{F}_a$  is the external force on unit mass of species a, which may be taken to be the Lorentz force

$$\mathbf{F}_a = z_a (\mathbf{E} + c^{-1} \mathbf{v}_a \times \mathbf{B}) \tag{2.2}$$

with  $z_a$  denoting the charge number per unit mass of species a:  $z_a = r_a/m_a$  if the species is charged. The right-hand side of (2.1) represents the Boltzmann collision term accounting for the change in the distribution function due to collisions of particles of species a with other particles including photons. To be specific about the processes, we will consider the following models for photon-matter interactions:

$$a + \hbar \omega \rightleftharpoons a + \hbar \omega$$
 (M.1)

$$a + \hbar\omega \rightleftharpoons a^* + \hbar\omega^* \tag{M.2}$$

$$a + \hbar \omega \rightleftharpoons b + \hbar \omega^* \tag{M.3}$$

where the asterisk denotes the post-collision value. Mechanism (M.1) describes an elastic collision between a particle of species a and a photon frequency  $\omega$ ; mechanism (M.2) describes an inelastic collision by which the photon frequency and the kinetic energy of particle a change through, for example, Compton scattering; and the mechanism (M.3) describes a "reactive collision" by which both the material particle and the photon change to another material particle (i.e., a particle of another quantum state) and a photon of a different frequency, respectively. This "reactive collision" is an inelastic collision in which material particles a and b change their internal quantum state on absorbing or emitting a photon. If a photon of frequency,  $\omega$  is absorbed by the material particle a which is transformed to another species b, then  $\omega^* = 0$ . The reverse of this process will be a spontaneous emission of  $\hbar\omega$ 

by a material particle b which subsequently becomes another material particle a. The mechanisms presented leave out the process in which a photon is created or destroyed during a two-body collision between particles, say, a and b. This process requires a three-body collision in the present approach and is possible to take into account if the kinetic equations are generalized to include the three-particle collision operator. Its inclusion, however, would not yield a new insight that warrants the mathematical complication incurred thereby.

To study irreversible thermodynamics of radiation and matter from the kinetic theory viewpoint, precise details of dynamical processes of how radiation interacts with matter is not essential except for the fact that the kinetic equations involved are irreversible and there are well-defined processes for which relevant collision cross sections can be calculated from the mechanical principles, either classical or quantum mechanical, based on the mechanism postulated as, for example, in (M.1)-(M.3). Therefore, it is sufficient to assume that the transition probabilities, which will be denoted by  $W_{ai}^{(e)}$  and  $W_{ai;bj}^{(r)}$ , are known for elastic as well as inelastic and "reactive" collision processes, satisfy certain symmetry relations elaborated later, and have collisional invariants such as mass, momentum and energy. For brevity of notation the distribution function  $f_a(\mathbf{k}_a, \mathbf{r}, t)$  will be abbreviated simply by  $f_a$ . Then the Boltzmann collision term corresponding to the aforementioned elastic, inelastic and "reactive" collision may be written in the form [17]

$$(\partial_l f_a)_{coll} = \sum_{i=a}^r C_e(f_a, f_i) + \sum_{k_r^*} \sum_{i=a}^l C_r(f_a f_r | f_i^* f_{r^*}^*)$$
(2.3)

where the term for i = r is understood to be over photon wave numbers, the prime on the summation sign means the exclusion of the photon species, and

$$C_{\epsilon}(f_{a},f_{i}) = (2\pi)^{3}G_{i}\int d\mathbf{k}_{i}\int d\Omega W_{ai}^{(\epsilon)}(\mathbf{k}_{a},\mathbf{k}_{i}|\mathbf{k}_{a}^{*},\mathbf{k}_{i}^{*}) \times$$

$$\{f_{a}^{*}f_{i}^{*}[1+\epsilon_{a}f_{a}][1+\epsilon_{i}f_{i}] - f_{a}f_{i}[1+\epsilon_{a}f_{a}^{*}][1+\epsilon_{i}f_{i}^{*}]\}, \qquad (2.4a)$$

$$C_{r}(f_{a}f_{r}|f_{i}^{*}f_{r^{*}}^{*}) = (2\pi)^{3}G_{r}\int d\mathbf{k}_{r}\int d\Omega W_{ar;ir^{*}}^{(r)}(\mathbf{k}_{a},\mathbf{k}_{r}|\mathbf{k}_{i}^{*},\mathbf{k}_{r}^{*}) \times$$

$$\{f_i^* f_{r^*}^* [1 + \epsilon_a f_a] [1 + \epsilon_r f_r] - f_a f_r [1 + \epsilon_i f_i^*] [1 + \epsilon_r f_{r^*}^*] \}$$
(2.4b)

where  $d\Omega = sin\theta d\theta d\phi$  is the scattering solid angle,  $G_i$  denotes the statistical weight for species *i* and  $G_r$  denotes the statistical weight for photon. The asterisk denotes the post-collision value. The symbol  $\epsilon_i$  is defined as follows:

$$\epsilon_i = \begin{cases} 0, & \text{if i is a particle;} \\ 1, & \text{if i is a photon.} \end{cases}$$

In defining  $\epsilon_i$  as above, the implicit assumption is made that the particles obey the Boltzmann statistics while the photons obey the Bose-Einstein statistics. The righthand side of (2.4a) accounts for the elastic and inelastic collision effects for species aand i ( $i = a, b, \dots, r$ ). The additional factor in the collision term  $[1 + \epsilon_a f_a][1 + \epsilon_i f_i]$ or  $[1 + \epsilon_a f_{a*}][1 + \epsilon_i f_i^*]$  represents the quantum effect (the indistinguishability of identical particles) that affects the number of final or initial states allowed. The right-hand side of (2.4b) accounts for the contribution to the population change in species a due to a "reactive" collision of a photon and particle a. The quantum effect is taken into account also in this case. This kind of quantum form for the Boltzmann collision operator was first used by Nordheim [36] in 1928 and later by Uehling and Uhlenbeck[37] in their study on quantum gases. It was also applied to study carrier mobilities in semiconductors by Eu [38].

If the wave vector is written as  $\mathbf{k}_r = k_r \hat{\mathbf{k}}_r$ , where  $k_r = |\mathbf{k}_r| = \omega/c$  (c is the speed of light,  $\omega$  the angular frequency and  $\hat{\mathbf{k}}_r$  the unit vector in the direction of propagation), the Boltzmann equation for the photon distribution function  $f_r(\mathbf{k}_r, \mathbf{r}, \mathbf{t})$ coupled to (2.1) is

$$(\partial_t + c\hat{\mathbf{k}}_r \cdot \nabla) f_r(\mathbf{k}_r, \mathbf{r}, t) = (\partial_t f_r)_{(coll)}.$$
(2.5)

Here the collision term on the right-hand side consists of contributions arising from elastic, inelastic and "reactive" scattering of photons by particles. It consists of forms similar to the terms in (2.4a, b):

$$(\partial_t f_r)_{call} = \sum_{i=a}^{\prime} \{ C_e(f_r, f_i) + \sum_{j=a}^{\prime} \sum_{k_r^*} C_r(f_r f_i | f_{r^*}^* f_j^*) \}$$
(2.6a)

where

$$C_{\epsilon}(f_r f_i) = (2\pi)^3 G_i \int d\mathbf{k}_i \int d\Omega W_{ri}^{(\epsilon)}(\mathbf{k}_r, \mathbf{k}_i | \mathbf{k}_r^*, \mathbf{k}_i^*) \times \{f_r^*(\mathbf{k}_r^*) f_i^* [1 + \epsilon_r f_r(\mathbf{k}_r)] [1 + \epsilon_i f_i] - f_r(\mathbf{k}_r) f_i [1 + \epsilon_r f_r^*(\mathbf{k}_r^*)] [1 + \epsilon_i f_i^*]\}, \quad (2.6b)$$

and

$$C_{r}(f_{r}(\mathbf{k}_{r})f_{i}|f_{r^{*}}^{*}(\mathbf{k}_{r^{*}}^{*})f_{j}^{*}) = (2\pi)^{3}G_{i}\int d\mathbf{k}_{i}\int d\Omega W_{ri;jr^{*}}(\mathbf{k}_{r},\mathbf{k}_{i}|\mathbf{k}_{r}^{*},\mathbf{k}_{j}^{*}) \times \{f_{r^{*}}^{*}(\mathbf{k}_{r}^{*})f_{j}^{*}[1+\epsilon_{i}f_{i}][1+\epsilon_{r}f_{r}] - f_{i}f_{r}(\mathbf{k}_{r})[1+\epsilon_{j}f_{j}^{*}][1+\epsilon_{r^{*}}f_{r^{*}}^{*}(\mathbf{k}_{r}^{*})]\}.$$
 (2.6c)

The sum over i in (2.6a) must be excluded in the case of i = r since photons do not interact with each other. This means that photons cannot reach equilibrium by themselves if they do not interact with matter. Therefore, the theory of irreversible thermodynamics of radiation cannot be formulated independently of the corresponding theory for matter with which the former is in interaction.

The restriction on the summation sign mentioned earlier can be removed if we formally introduce the transition probabilities:

$$W_{rr}^{(e)}(\mathbf{k}_r, \mathbf{k}_r | \mathbf{k}_r^*, \mathbf{k}_r^*) = 0, \quad W_{rr, r^* r^*}^{(r)}(\mathbf{k}_r, \mathbf{k}_r | \mathbf{k}_r^*, \mathbf{k}_r^*) = 0$$

identically. Furthermore, if we also define  $\mathbf{F}_r = 0$ , then the Boltzmann equation for photons becomes formally similar to the Boltzmann equations for material particles (2.1). Thus, we summarize the Boltzmann equations for the system consisting of photons and material particles by the unified equation

$$\begin{aligned} &[\partial_t + (\hbar \mathbf{k}_i/m_i) \cdot \nabla + (m_i \mathbf{F}_i/\hbar) \cdot \nabla_k] f_i(\mathbf{k}_i, \mathbf{r}, \mathbf{t}) \\ &= \sum_{j=a}^r \{ C_e(f_i, f_j) + \sum_k^r \sum_{l=1}^r C_r(f_i f_j | f_k^* f_l^*) \} \\ &\equiv \Re_i[f_i] \equiv \sum_{j=a}^r \Re_{ji}[f_j f_i] \end{aligned}$$
(2.7)

where the subscript *i* runs over all species, matter and photon,  $\hbar k_r/m_r$  must be understood to be  $c\hat{k}_r$ , and  $m_r$  is a fictitious photon mass defined later. In connection with the Boltzmann equation we note the following properties of the transition probabilities:

$$W_{ai}^{(v)} = W_{ia}^{(v)}$$

$$W_{ai;kl}^{(v)} = W_{kl;ai}^{(v)}.$$
(2.8)

These relations stem from the principle of microscopic reversibility and will be used for proving the H theorem for the kinetic equations postulated.

In the existing works [2, 5, 6, 10, 11] on radiation mentioned earlier, a radiation energy transfer equation is used, which is a linear evolution equation for the intensity  $I_{\nu}$  of radiation of frequency  $\nu$ . For example, if we quote Wildt[10], the radiation energy transfer equation is

$$c^{-1}\frac{\partial}{\partial t}I_{\nu} + \sum_{s}\mu_{s}\frac{\partial}{\partial x_{s}}I_{\nu} = -(\kappa_{\nu} + \sigma_{\nu})I_{\nu} + \sigma_{\nu}I_{\nu0} + \epsilon_{\nu0}$$
(2.9)

where  $\mu_s$  is a direction cosine,  $\kappa_{\nu}$  the absorption coefficient,  $\sigma_{\nu}$  the (isotropic) scattering coefficient,  $\epsilon_{\nu 0}$  the spontaneous emission coefficient and  $I_{\nu 0}$  the integral of  $I_{\nu}$  over angles (i.e., the energy density). This is a prototype of radiation energy transfer equations used in the existing theories of radiation. The radiation intensity  $I_{\nu}$  is linearly proportional to the photon distribution function  $f_r(\mathbf{k}_r, \mathbf{r}; t)$ ,

$$f_r(\mathbf{k}_r, \mathbf{r}; t) = (c^2 / h^4 \nu^3) I_{\nu}(\mathbf{k}_r, \mathbf{r}; t).$$
(2.10)

Therefore, the left-hand side of (2.9) is basically the same as that of (2.5). However, the right-hand side of (2.9) differs from that of (2.5) as given by (2.6a) and (2.6b) in that the former is linear in  $I_{\nu}$  whereas the latter is nonlinear in photon distribution functions. It must be noted, though, that their physical significances share the same origin since both account for a photon population change due to interactions between matter and radiation one way or another. Nevertheless, there is one very important difference: that is, the kinetic equation (2.5) together with (2.1) naturally yields the (equilibrium) Planck distribution as a consequence of the H theorem as will be shown in section 2.2. In contrast to this, the radiation energy transfer equation (2.9) requires the frequency-dependent source function defined by  $I_{\nu}^{*} \equiv \epsilon_{\nu 0}/\kappa_{\nu}$  as an input obtained by some other physical considerations, and this  $I_{\nu}^{*}$  is taken to be the Planck distribution function. It is easy to see that although the equilibrium solution for (2.9) should be the intensity of black radiation (the Planck distribution), such a solution is merely implicit, being hidden in the coefficients  $\epsilon_{\nu 0}$ and  $\kappa_{\nu}$  that must be chosen in an *ad hoc* manner by an auxiliary theory outside the framework of the theory in question. For the purpose of formulating a theory of irreversible thermodynamics for radiation this aspect of equations like (2.9) is a major weakness that is not present in the kinetic theory.

#### 2.2 The H theorem, entropy and Planck's law

The kinetic equations for the system of matter and radiation admit an H functional with which an entropy can be defined. The entropy so defined can be shown to increase with time, reaching a maximum at equilibrium. We define the entropy of the system by the formula

$$S(t) = S_m(t) + S_r(t)$$
 (2.11)

with

$$S_m(t) = -k_B \sum_i' (2\pi)^{-3} G_i \int d\mathbf{r} \int d\mathbf{k}_i f_i (lnf_i - 1)$$
 (2.12a)

$$S_r(t) = -k_B (2\pi)^{-3} G_r \int d\mathbf{r} \int d\mathbf{k}_r \{ f_r ln f_r - [1+f_r] ln [1+f_r] \}$$
(2.12b)

where  $S_m$  and  $S_r$  are respectively the entropy of matter and of radiation. Note that the sum over *i* in (2.12a) is only for the material species. We shall abbreviate the averaging operation with angular brackets,

$$(2\pi)^{-3}G_i\int d\mathbf{k}_i\cdots\equiv\langle\cdots\rangle_i$$

$$(2\pi)^{-3}G_r\int d\mathbf{k}_r\cdots\equiv\langle\cdots\rangle_r$$

from which the subscrip i or r will be dropped whenever there is no possibility of notational confusion. Differentiation of S(t) with time yields

$$\frac{dS}{dt} = \frac{dS_m}{dt} + \frac{dS_r}{dt}$$

$$= -k_B \sum_i' \int d\mathbf{r} \langle \ln f_i \partial_t f_i \rangle$$

$$-k_B \int d\mathbf{r} \langle \{\ln f_r - \ln[1 + f_r]\} \partial_t f_r \rangle.$$
(2.13)

By introducing the symbol  $\epsilon_i$  defined before, we can cast the entropy derivative in a simpler, unified form

$$\frac{dS}{dt} = -k_B \sum_{i}^{r} \int d\mathbf{r} \langle \{ lnf_i - ln[1 + \epsilon_i f_i] \} \partial_t f_i \rangle$$
(2.14)

where the sum over i is now material species as well as radiation. On substitution of the kinetic equation (2.7) and integrations by parts we can put (2.14) in the form

$$\frac{dS}{dt} = k_B \sum_{i}^{r} \int d\mathbf{r} \langle ln[\epsilon_i + f_i^{-1}] \Re_i \rangle$$

$$= k_B \sum_{j}^{r} \sum_{i}^{r} \int d\mathbf{r} \langle ln[\epsilon_i + f_i^{-1}] \Re_{ji} \rangle$$

$$= \frac{1}{2} k_B \sum_{j}^{r} \sum_{i}^{r} \int d\mathbf{r} \langle ln\{[\epsilon_j + f_j^{-1}][\epsilon_i + f_i^{-1}]\} \Re_{ji} \rangle$$

$$= \frac{1}{4} k_B \sum_{j}^{r} \sum_{i}^{r} \int d\mathbf{r} \langle ln\{f_j^* f_i^*[1 + \epsilon_i f_i][1 + \epsilon_j f_j] \\
/f_j f_i[1 + \epsilon_i f_i^*][1 + \epsilon_j f_j^*]\} \Re_{ji} \rangle$$

$$\geq 0 \qquad (2.15)$$

where the third equality is due to the symmetrization with respect to particle indices and the fourth equality is the result of symmetrizing collision integrals by using the microscopic reversibility expressed by (2.8). Cast in such a form, the right-hand

or

side of the fourth equality is seen to be always positive and we conclude that the entropy time derivative is always positive: it is the H theorem. The equality holds at equilibrium where hold the relations

$$ln(f_{aeg}^*f_{ieg}^*) = ln(f_{aeq}f_{ieq}) \qquad (a, i \neq r), \tag{2.16a}$$

$$ln\{f_{aeq}^{*}f_{req}^{*}[1+f_{req}]\} = ln\{f_{aeq}f_{req}[1+f_{req}^{*}]\} \qquad (a \neq r),$$
(2.16b)

where  $f_{aeq}$ , etc., mean the equilibrium distribution functions. Eqs. (2.16a, b) imply that the logarithmic functions of the equilibrium functions are summational invari---ants. Since there are only five summational invariants such as mass, momentum and energy,  $ln f_{aeq}$ , etc., must be functions of the summational invariants. By using the usual procedure [18] taken for constructing the equilibrium solution for the Boltzmann equation, we easily deduce

$$f_{aeq} = exp[-\beta(H_a - \mu_a^o)] \tag{2.17a}$$

$$exp(-\beta\mu_a^o) = n_a^{-1} \langle exp(-\beta H_a) \rangle$$
(2.17b)

where  $H_a$  is the kinetic energy,  $\beta = 1/k_BT$ , T being the absolute temperature, and  $\mu_a^o$  the normalization factor which is simply the equilibrium chemical potential. We will elaborate on these quantities later when local equilibrium distribution functions are introduced. Since different internal states of material species are counted as different species and the kinetic equations postulated do not contain an internal state evolution operator, they do not permit determination of population distributions of various species over internal states. This defect may be cured if the Hamiltonian of the system is given by  $H_i = m_i c_i^2/2 + \epsilon_{is}^o$ ,  $\epsilon_{is}^o$  corresponding to the internal energy,  $c_i$  peculiar velocity defined  $c_i = v_i - u$  where u is the so-called hydrodynamic velocity:

$$\mathbf{u} = \frac{1}{\rho} \sum_{i}^{\prime} \int d\mathbf{v}_{i} m_{i} \mathbf{v}_{i} f_{i}(\mathbf{v}_{i}, \mathbf{r}; t)$$

and  $\rho$  the total mass density of material particles. With the help of the hydrodynamic velocity **u**, we define the substantial time derivative as following:

$$\frac{d}{dt} = \partial_t + \mathbf{u} \cdot \nabla.$$

The normalization factor  $\beta \mu_i^o$  is also added a factor, say,  $-lnq_i$  where

$$q_i = \sum_{s} exp(-\beta \epsilon_{is}^o),$$

the sum is being over the internal states of species s.

Eq. (2.16b) may be recast as follows:

$$ln\{f_{aeq}^*[1+f_{req}^{-1}]\} = ln\{f_a[1+f_{req}^{*-1}]\}$$

and with the definition

$$exp(W_r^o) = 1 + f_{reg}^{-1}$$
 (2.18)

it takes the form

$$ln\{f_{aeq}^{*}exp[-W_{r}^{o*}]\} = ln\{f_{aeq}exp[-W_{r}^{o}]\}.$$
(2.19)

Since this relation then is in exactly the same form as (2.16a), it is possible to deduce that  $W_r^o$  consists of summation invariants only: in fact, it is sufficient to take in the laboratory frame

$$W_r^o = \beta(\hbar\omega - \mu_r^o) \tag{2.20}$$

where  $\mu_r^o$  is the exponent of the normalization factor which will turn out to be equal to zero if the photon number is variable. From (2.18) and (2.20) we find

$$f_{req}(\omega) = \{ exp[(\hbar\omega - \mu_r^o)\beta] - 1 \}^{-1}.$$
 (2.21)

It is easy to show  $\mu_r^o = 0$  if the photon number is variable. The equilibrium number density of photon is given by

$$n_r = N_r/V = \langle f_{reg}(\omega) \rangle$$
  
=  $\pi^{-2}c^{-3} \int_0^\infty d\omega \omega^2 \{ exp[(\hbar\omega - \mu_r^o)\beta] - 1 \}^{-1}.$  (2.22)

This number changes as  $\mu_r^o$  and  $\beta$  change. If the radiation pressure is denoted by  $p_r$ , the thermodynamic potential in the grand canonical ensemble  $\Omega_r = -p_r V$  may be written as

$$\Omega_r = (V/\pi^2 c^3 \beta) \int_0^\infty d\omega \omega^2 ln \{1 - exp[(\mu_r^o - \hbar \omega)\beta]\}.$$
 (2.23)

In that case, the number density  $n_r$  is given by

$$n_r = -(\partial \Omega_r / \partial \mu)_{T,V} \tag{2.24}$$

where  $\mu$  is the chemical potential and, moreover, the differentiation of  $\Omega$ , with respect to  $\mu_r^o$  exactly yields (2.22). We thus identify  $\mu_r^o$  with the chemical potential  $\mu$ 

$$\mu_r^o = \mu. \tag{2.25}$$

Furthermore

$$\mu = (\partial A_r^o / \partial n_r)_{T,V} = -T(\partial S_r^o / \partial n_r)_{T,V}$$
(2.26)

where  $A_r^0$  is the work function, and if  $A_r^o$  is required to be a minimum as it is varied with respect to  $n_r$ , we must have

$$(\partial A_r^o/\partial n_r)_{T,V} = 0 \tag{2.27a}$$

which implica

$$\mu_r^o = 0. \tag{2.27b}$$

That is, equilibrium radiation has a vanishing chemical potential. Therefore, the equilibrium distribution function takes the form

$$f_{req}(\omega) = [exp(\hbar\omega\beta) - 1]^{-1}.$$
(2.28)

In order to determine the parameter  $\beta$  we proceed as follows: According to the Stefan-Boltzmann law [39] the radiation energy density is given by

$$E_r^o = 4\sigma_{SB}T^4/c \tag{2.29}$$

where  $\sigma_{SB}$  is the Stefan-Boltzmann constant. We now calculate  $E_r^o$  by using  $f_{req}$  given in (2.28) and equate the result with the one in (2.29),

$$4\sigma_{SB}T^4/c = \pi^2/15(hc)^3\beta^4.$$
 (2.30)

Thus, we find

$$(\beta T)^{-4} = (60\hbar c^3/\pi^2)\sigma_{SB} \tag{2.31}$$

which must be a universal constant since  $\sigma_{SB}$  is universal as verified experimentally, namely, by the Kirchhoff law [1, 39]. This universal constant turns out to be the Boltzmann constant raised to the fourth power and hence there follows the relation

$$\beta = 1/k_B T$$

This identification of  $\beta$  also agrees with the meaning of  $\beta$  obtained from the definition of temperature in terms of the equilibrium distribution function  $f_{aeq}$  for species  $a \neq r$ . The existence of a single parameter  $\beta$  for both radiation and matter must be emphasized. This way, we have identified  $\beta$  from the viewpoint of radiation in a completely consistent manner with that of matter, and the distribution function so determined is the well known form for black body radiation, namely, the Planck formula. In the present framework it is a unique equilibrium solution for the kinetic equation (2.7) since there is only one linear combination of the summational invariants satisfying (2.16), and this uniqueness is ultimately due to the H theorem. Moreover, this solution (2.28) and Maxwell distribution function (2.17) are mutually consistent with each other. This mutual consistency between the Planck distribution function for radiation and the Boltzmann distribution function for matter was first shown by Einstein in his well known paper [3] of 1917 where stimulated emission was also introduced. A term corresponding to the stimulated emission appears as the quantum effect term in the collision integral in the present theory. Einstein exploited the detailed balance to show that the Planck distribution function could be derived alternatively to the original derivation. Here, the kinetic theory derivation shows that the aforementioned consistency is deeply rooted in the H theorem and therefore the second law of thermodynamics.

Since the equilibrium distribution functions are known, it is possible to calculate equilibrium thermodynamics quantities [39] with them. Here we only make a few relevant remarks helpful for the calculation required. Firstly, note that

$$d\mathbf{k}_r = k_r^2 dk_r d\hat{\mathbf{k}}_r = c^{-3} \omega^2 d\omega d\hat{\mathbf{k}}_r$$

and, secondly,  $G_r = 2$  for photons. Then, it is straightforward to show that

$$S_r^o = 4V \bar{E}_r^o / 3T.$$
 (2.32)

The radiation energy density is given by

$$E_r^o = \pi^2 (k_B T)^4 / 15(\hbar c)^3 \tag{2.33}$$

which, on substitution into (2.32), yields

$$S_r^o = 16\sigma_{SB}T^3 V/3c. (2.32')$$

A similar calculation may be made for  $\Omega_r$  with  $\mu_r^o = 0$  and we find

$$p_r = \bar{E}_r^o/3 \tag{2.34}$$

for the radiation pressure. Note that  $S_r^o$  is independent of  $n_r$ . Let us cast (2.32), by using (2.43), into the form

$$S_r^o = (E_r^o + p_r V)/T \qquad (E_r^o = \bar{E}_r^o V)$$

which implies that the radiation enthalpy is simply given by

$$H_r^o = TS_r^o$$
This means that the radiation Gibbs free energy is equal to zero, and it agrees with the fact that the radiation chemical potential is equal to zero.

In the case of gases obeying the Boltzmann statistics the thermodynamic temperature is defined by

$$1/T = (\partial S/\partial E)_V \tag{2.35}$$

where S and E are the entropy and the internal energy of the system, respectively. In the case of equilibrium radiation we have defined the temperature through the Stefan-Boltzmann law. This procedure can be shown to be consistent with the thermodynamic definition of temperature given above. It is straightforward to see that there holds the equilibrium Gibbs relation for radiation [1, 39]

$$TdS_r^o = dE_r^o + p_r dV. \tag{2.36}$$

This relation is deeply rooted in the Stefan-Boltzmann law of radiation and it is a motivation for defining the radiation temperature by means of the aforementioned law.

# 2.3 Nonequilibrium distribution functions and macroscopic evolution equations

The H theorem makes it possible to determine uniquely the mutually consistent equilibrium distribution functions (2.17) and (2.28). There remains the problem of determining the nonequilibrium distribution functions obeying (2.7). Since the kinetic equations (2.7) are nonlinear integro-differential equations which may not be solvable exactly, approximate solutions must be sought after. It is emphasized that any approximate methods should satisfy the second law of thermodynamics. The modified moment method has been shown to satisfy the strict requirement [20, 40] in the case of material gases. In this method the nonequilibrium distribution functions are sought after in an exponential form,

$$f_i = exp[-\beta(H_i + H_i^{(1)} - \mu_i)]$$
(2.37)

where  $\mu_i$  is the normalization factor defined by

$$exp(-\beta\mu_i) = n_i^{-1} \langle exp[-\beta(H_i + H_i^{(1)})] \rangle$$
 (2.38a)

and  $H_i^{(1)}$ , the nonequilibrium part of the distribution function, is written in the form

$$H_i^{(1)} = \sum_{\alpha \ge 1} X_i^{(\alpha)} \odot h_i^{(\alpha)}.$$
(2.38b)

Here,  $X_i^{(\alpha)}$  are as yet undetermined functions of macroscopic variables only and  $h_i^{(\alpha)}$  are expressible in terms of tensor Hermite polynomials of peculiar velocity  $\mathbf{c}_i = \hbar \mathbf{k}_i / m_i - \mathbf{u}$  with  $\mathbf{u}$  denoting the mean fluid velocity, which will be statistically defined later. The symbol  $\odot$  means a scalar product of vectors or tensors. Here we list some physically relevant terms of  $h_i^{(\alpha)}$  as follows

$$h_{i}^{(1)} = [m_{i}\mathbf{c}_{i}\mathbf{c}_{i}]^{(2)}, \qquad h_{i}^{(2)} = \frac{1}{3}Tr(m_{i}\mathbf{c}_{i}\mathbf{c}_{i}) - p_{i}/n_{i},$$
  
$$h_{i}^{(3)} = (\frac{1}{2}m_{i}c_{i}^{2} + \epsilon_{i}^{o} - \hat{h}_{i})\mathbf{c}_{i}, \qquad h_{i}^{(4)} = m_{i}\mathbf{c}_{i}, \qquad (2.39)$$

where  $[]^{(2)}$  denotes the traceless symmetric part of the second rank tensor,  $p_i$ is the static pressure of material species *i* and  $n_i$  its density, and  $\hat{h}_i$  the enthalpy defined by  $\hat{h}_i = E_i + p_i v_i$ . It is apparent that  $h_i^{(\alpha)}$  are the microscopic expressions of hydrodynamic variables, since when averaged over the velocity distribution,  $h_i^{(\alpha)}$ will give the shear stress, the excess trace part of the stress, the heat flux and mass flux, etc. The details are given, for example, in ref. [40]. Since radiation part is our main subject, we will pay much attention to them.

The nonequilibrium distribution function of radiation may be constructed in a form similar to the Planck distribution function as follows

$$f_r(\omega) \equiv f_r(\mathbf{k}_r, \mathbf{r}, \mathbf{t}) = \{exp[\beta \bar{W}_r(\mathbf{k}_r)] - 1\}^{-1}$$
(2.40)

where  $\tilde{W_r}$  is a function of  $\omega$ ,  $\hat{k}_r$ , r and t. As well known, the equilibrium Planck distribution satisfies Wien's law [1, 39], that is,  $f_{reg}$  is a function of dimensionless

variable  $x \equiv \hbar \omega / k_B T$  only, in the labratory frame. Since Wien's law is a scaling law, it is likely to remain valid even for nonequilibrium radiation. Therefore, we use Wien's law to define the nonequilibrium temperature of radiation which will give rise to a sensible structure for irreversible thermodynamics. Let us introduce dimensionless vector  $\mathbf{x} \equiv \hbar \mathbf{k}_r / k_B T = x \hat{\mathbf{x}}$ , then  $W_r$  is looked for in such a way that

$$\beta \bar{W}_r(\omega, \hat{\mathbf{k}}_r) = W_r(\mathbf{x}) \tag{2.41}$$

that is,  $W_r(\mathbf{x})$  is not an explicit function of T but the reduced variable  $\mathbf{x}$ . By using this form of the distribution function the energy density of nonequilibrium radiation is

$$\bar{E}_{r} = V^{-1}E_{r} = 2(2\pi)^{-3} \int d\mathbf{k}_{r} \hbar \omega \{exp[W_{r}(\mathbf{x})] - 1\}^{-1}$$
$$= (k_{B}T)^{4}F_{E}$$
(2.42)

where

$$F_E = \int d\mathbf{x} x \{ exp[W_r(\mathbf{x})] - 1 \}^{-1}$$

which is a function independent of temperture T.

Since a system of radiation and matter is considered as a gaseous mixture of photons and material particles, the kinetic temperature of this system should be defined such that

$$\frac{3}{2}nk_BT = \langle \sum_i' \frac{1}{2}m_i v_i^2 f_i \rangle + \langle \hbar \omega f_r \rangle = \langle \sum_i' \frac{1}{2}m_i v_i^2 f_{ieq} \rangle + \langle \hbar \omega f_{req} \rangle$$
(2.43a)

where n is the total number density of material particles and photons:  $n = \sum_{i=1}^{n} n_{i} + n_{r}$ . The radiation distribution function then must be consistent with the matter distribution functions determined such that (2.43a) holds in addition to two other conditions,

$$\sum_{i}^{\prime} \rho_{i} = \left\langle \sum_{i}^{\prime} m_{i} f_{i} \right\rangle = \left\langle \sum_{i}^{\prime} m_{i} f_{ieq} \right\rangle$$
(2.43b)

$$\rho \mathbf{u} \equiv \sum_{i}^{\prime} \rho_{i} \mathbf{u}_{i} = \langle \sum_{i}^{\prime} m_{i} \mathbf{v}_{i} f_{i} \rangle = \langle \sum_{i}^{\prime} m_{i} \mathbf{v}_{i} f_{ieq} \rangle.$$
(2.43c)

These conditions are the so-called matching conditions which give the operational meanings of temperature, mass density and hydrodynamic velocity. We remark that these kinetic definitions of macroscopic variables are consistent with the thermodynamic definitions. In some works on kinetic theory of gaseous mixtures, a multi-temperature is introduced, that is, different temperatures are assigned to different species. But such temperatures do not have thermodynamically operational meaning. For instance, if a cavity contains nonequilibrium gas and radiation, it is impossible to determine, and meaningless to talk about, the gas and radiation temperature separately since the gas and the radiation interact with each other and hence there is no way to measure the temperature of each species directly and independently. Therefore, it is necessary to formulate a kinetic theory in terms of a common temperature for an interacting system of radiation and matter. Such a temperature is generally space and time dependent for a nonequilibrium system.

In order to derive evolution equations for the macroscopic variables for the photon gas we first introduce the energy-momentum tensor T which is define statistically by the formula

$$T^{ij} = 2ch^{-3} \int \frac{d^3\mathbf{p}}{p^0} p^i p^j f_r(\mathbf{p})$$
(2.44)

where  $p^0 = (\mathbf{p} \cdot \mathbf{p})^{1/2}$  for photons. Under the Lorentz transformation  $p \to p'$  [the four-momentum  $p \equiv p^{\mu} = (\mathbf{p}, p^0)$ ], it can be shown,

$$\frac{d^3\mathbf{p}}{p^0}f_r(\mathbf{p}) = \frac{d^3\mathbf{p}'}{p^{0\prime}}f_r'(\mathbf{p}') = invariant.$$
(2.45)

Since the distribution function is a Lorentz scalar

$$f_r(\mathbf{p}) = f'_r(\mathbf{p}'),$$

the energy-momentum tensor  $T^{ij}$  transforms as a second rank tensor,

$$\bar{T}^{ij} = 2ch^{-3} \int \frac{d^3 \mathbf{p}'}{p^{0\prime}} p^{i\prime} p^{j\prime} f_r'(\mathbf{p}')$$
  
=  $2ch^{-3} \int \frac{d^3 \mathbf{p}}{p^0} p^{i\prime} p^{j\prime} f_r(\mathbf{p}).$  (2.46)

Under the Lorentz transformation the frequency transforms as

$$\nu' = \gamma_u \nu (1 - \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) \tag{2.47}$$

where

$$\gamma_u = (1 - u^2/c^2)^{-1/2}, \quad \hat{\mathbf{k}}_r = \mathbf{k}_r/k_r$$

Eq. (2.47) can be reduced to the nonrelativistic Doppler formula

$$\nu' \approx \nu (1 - \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) \tag{2.47'}$$

if the high order terms of  $O(c^{-2})$  are neglected. The aberration formula for  $\hat{\mathbf{k}}_r$  is given by

$$\hat{\mathbf{k}}_r' = [\gamma_u(1 - \hat{\mathbf{k}} \cdot \mathbf{u}/c)]^{-1} \{ \hat{\mathbf{k}} - (\mathbf{u}/c)[\gamma_u + \hat{\mathbf{k}} \cdot \mathbf{u}/c(1 + \gamma_u)] \}.$$
(2.48)

In consistency with the nonrelativistic approximation neglecting the terms  $O(c^{-2})$  or higher, (2.48) may be written as

$$\hat{\mathbf{k}}_r' \approx (\hat{\mathbf{k}}_r - \mathbf{u}/c)(1 - \hat{\mathbf{k}}_r \cdot \mathbf{u}/c)^{-1}.$$
(2.48')

Then it is easy to show that in the local rest frame radiation energy density can be given by the statistical formula

$$\bar{E}_{\mathbf{r}} = 2h^{-3} \int d^3 \mathbf{p} \hbar \omega (1 - 2\hat{\mathbf{k}}_{\mathbf{r}} \cdot \mathbf{u}/c) f_{\mathbf{r}}(\mathbf{p}, \mathbf{r}, t).$$
(2.49a)

Under the aforementioned nonrelativistic approximation we may put  $\bar{E}_r$  in a following form

$$\bar{E}_r = \langle \hbar \omega (\hat{\mathbf{k}}_r - \mathbf{u}/c) \cdot (c\hat{\mathbf{k}}_r - \mathbf{u}) f_r \rangle \qquad (2.49a')$$

where

$$\langle Af_r \rangle = 2h^{-3} \int d^3 \mathbf{p} Af_r.$$

Other macroscopic quantities which are necessary to describe the system, such as heat flux, pressure tensor, etc. are defined accordingly

$$\mathbf{Q}_r = \langle \hbar \omega (1 - \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) (c \hat{\mathbf{k}}_r - \mathbf{u}) f_r \rangle$$
(2.49b)

$$\mathbf{P}_r = \langle \hbar \omega (\hat{\mathbf{k}}_r - \mathbf{u}/c) (\hat{\mathbf{k}}_r - \mathbf{u}/c) f_r \rangle.$$
(2.49c)

The hydrodynamic pressure of photon gas is defined by

$$p_{r} = \frac{1}{3}\bar{E}^{o} = (2/3h^{3})\int d^{3}\mathbf{p}\hbar\omega(\hat{\mathbf{k}}_{r} - \mathbf{u}/c) \cdot (\hat{\mathbf{k}}_{r} - \mathbf{u}/c)f_{reg}.$$
 (2.49d)

These statistical mechanical quantities of radiation are in close correspondence with their matter counterparts defined in terms of the peculiar velocity with respect to the hydrodynamic velocity  $\mathbf{u}$ .

According to the modified moment method,  $W_r$  is taken to be the following form in the local rest frame moving with the velocity **u** 

$$W_r = \beta \{ \hbar \omega (1 + \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) + \sum_{\delta} X_r^{(\delta)} \odot h_r^{(\delta)} - \mu_r \}$$
(2.50*a*)

where  $\mu_r$  is the exponent of normalization factor for the radiation distribution function,

$$n_r = \langle f_r \rangle; \tag{2.50b}$$

 $X_r^{(\delta)}$  are functions of macroscopic variables such as stress tensors, heat flux, etc., which will be determined from the kinetic equations postulated; and finally  $h_r^{(\delta)}$  are defined in such a way that they give relavent macroscopic variables when averaged with the distribution function

$$h_r^{(1)} = \hbar \omega [(\hat{\mathbf{k}}_r - \mathbf{u}/c)(\hat{\mathbf{k}}_r - \mathbf{u}/c)]^{(2)}, \qquad (2.51a)$$

$$h_r^{(2)} = (\hbar\omega/3)Tr[(\hat{\mathbf{k}}_r - \mathbf{u}/c)(\hat{\mathbf{k}}_r - \mathbf{u}/c)] - p_r/n_r, \qquad (2.51b)$$

$$h_r^{(3)} = [\hbar\omega(1 - \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) - \bar{\epsilon}_r](c\hat{\mathbf{k}}_r - \mathbf{u}/c), \qquad (2.51c)$$

$$h_r^{(4)} = c\hat{\mathbf{k}}_r - \mathbf{u},\tag{2.51d}$$

$$h_r^{(5)} = \hbar \omega P_3(\hat{\mathbf{k}}_r - \mathbf{u}/c), \quad etc.$$
(2.51e)

where  $\bar{\varepsilon}_r = \bar{E}_r/n_r = \pi^4 k_B T/30\zeta(3)$  is the mean energy per photon and  $P_3(z)$  is the Legendre polynomial of order 3 and  $\zeta(3) = 1.202$  is a Riemann zeta function. Higher order moments may consist of higher order Legendre polynomials. At this point it is useful to make the following comments in connection with the moments defined in (2.51). Firstly, the Doppler effect has been taken into account although the nonrelativistic approximation is used. Secondly, in the phenomenological theory the radiative energy transfer equation (2.9) is solved by taking the Eddington diffusion approximation [2, 5]. It is nothing but the lowest order approximation in a moment method for the equation, which is generalized by including in principle a complete set of spherical harmonics of  $\hat{\mathbf{k}}_r$ . In other words, this generalization is a moment method for the radiative energy transfer equation. The present moment method has some important distinguishing aspects: (1) Our starting point is the Boltzmann-type kinetic equation for photon gas instead of a radiative energy transfer equation. This formalism establishes a bridge between the dynamical theory and the macroscopic phenomenological theory; in other words, once we know the differential cross section of particle interactions the physically measurable quantities can be computed in principle. There is no phenomenological parameter at all; (2) We impose the second law of thermodynamics as a constraint to ensure that the theory and its approximate solutions satisfy the requirements of the thermodynamic laws, and the acquisition thereby of a theory of irreversible thermodynamics for radiation and matter.

The macroscopic quantities such as shear stress tensor, excess trace part of pressure tensor, heat flux, etc., associated with radiation now can be calculated with the corresponding moments introduced:

$$\Phi_r^{(1)} \equiv \Pi_r = \langle h_r^{(1)} f_r \rangle, \qquad (2.52a)$$

$$\Phi_r^{(2)} \equiv \Delta_r = \langle h_r^{(2)} f_r \rangle, \qquad (2.52b)$$

$$\Phi_r^{(3)} \equiv \mathbf{Q}_r' = \mathbf{Q}_r - \hat{\varepsilon}_r \mathbf{J}_r = \langle h_r^{(3)} f_r \rangle, \qquad (2.52c)$$

$$\Phi_r^{(4)} \equiv \mathbf{J}_r / m_r = \langle h_r^{(4)} f_r \rangle = \langle (c \hat{\mathbf{k}}_r - \mathbf{u}) f_r \rangle, \qquad (2.52d)$$

$$\Phi_r^{(5)} \equiv \Gamma_r = \langle h_r^{(5)} f_r \rangle, \qquad (2.52e)$$

where  $\hat{\varepsilon}_r = \bar{\varepsilon}_r/m_r$  and a fictitious photon mass  $m_r$  is introduced by the relation

 $m_r = 4V\sigma_{SB}T^4/c^3$ , which has the numerical value 7.5646  $\times 10^{-16}Jm^{-3}K^{-4}$ . The final outcome of the theory will be inconsequential to the choice of this fictitious mass as long as it is a constant, and the definition made above seems reasonable.

One of the purposes of the present kinetic theory is to derive the evolution equations for the macroscopic variables of matter and radiation. Although this procedure is standard as one used in the case of matter alone [20], we should notice that there exist the source terms in the balance equations because of the energy and momentum exchange between photons and particles. Here we will not repeat the derivation process, but present the final results below [17]:

Matter part :

$$\partial_t \rho = -\nabla \cdot \rho \mathbf{u} \tag{2.53a}$$

$$\rho d_t c_i = -\nabla \cdot \mathbf{J}_i + \Lambda_i^{(n)} \tag{2.53b}$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P}_m + \sum_i' \rho \mathbf{F}_i + \Lambda_m^{(u)}$$
(2.53c)

$$\rho d_t \varepsilon_m = -\nabla \cdot \mathbf{Q}_m - \mathbf{P}_m : \nabla \mathbf{u} + \sum_i' \mathbf{F}_i \cdot \mathbf{J}_i + \Lambda_m^{(e)}$$
(2.53d)

$$\rho d_i \hat{\Phi}_i^{(\alpha)} = Z_i^{(\alpha)} + \Lambda_i^{(\alpha)}$$
(2.53e)

where the mass density, stress tensor, heat flux, internal energy density of matter are, respectively, denoted by

$$\rho = \sum_{i}^{\prime} \rho_{i}, \quad \mathbf{P}_{m} = \sum_{i}^{\prime} \mathbf{P}_{i}, \quad \mathbf{Q}_{m} = \sum_{i}^{\prime} \mathbf{Q}_{i}, \quad \varepsilon_{m} = \sum_{i}^{\prime} \varepsilon_{i},$$

the summation being over all material species; other symbols are defined as follows:

$$\Lambda_i^{(n)} = \langle m_i \Re_i \rangle, \tag{2.54a}$$

$$\Lambda_m^{(e)} = \sum_i' \langle (\frac{1}{2}m_i c_i^2 + \epsilon_i^0) \Re_i \rangle, \qquad (2.54b)$$

$$\Lambda_m^{(u)} = \sum_i' \langle m_i \mathbf{v}_i \Re_i \rangle, \qquad (2.54c)$$

$$\Lambda_i^{(\alpha)} = \langle h_i^{(\alpha)} \Re_i \rangle, \qquad (2.54d)$$

$$\Phi_i^{(\alpha)} = \rho \hat{\Phi}_i^{(\alpha)} = \langle h_i^{(\alpha)} f_i \rangle, \qquad (2.55a)$$

$$Z_i^{(\alpha)} = -\nabla \cdot \langle \mathbf{c}_i h_i^{(\alpha)} f_i \rangle + \langle f_i [d_t + \mathbf{c}_i \cdot \nabla + (m_i \mathbf{F}_l / \hbar) \cdot \nabla_k] h_i^{(\alpha)} \rangle.$$
(2.55b)

We arrange the various fluxes in the following order:

$$lpha: 1, 2, 3, 4, \ldots, \Phi_i^{(lpha)}: \Pi_i, \Delta_i, Q_i', J_i, \ldots,$$

where  $\mathbf{Q}'_i = \mathbf{Q}_i - \hat{h}_i \mathbf{J}_i$ ,  $\hat{h}_i$  being the enthalpy per unit mass of material species *i*. The dissipation terms  $\Lambda_i^{(\alpha)}$ , etc., are related to the entropy production which we will discuss later on. The streaming terms  $Z_i^{(\alpha)}$  can be written in a more explicit form for the leading moments as follows:

$$Z_{i}^{(1)} = -\nabla \cdot \psi_{i}^{(1)} - 2[\mathbf{P}_{i} \cdot \nabla \mathbf{u}]^{(2)} - 2[\mathbf{J}_{i}(d_{t}\mathbf{u} - \mathbf{F}_{i})]^{(2)}, \qquad (2.56a)$$

$$Z_i^{(2)} = -\nabla \cdot \psi_i^{(2)} - \frac{2}{3}\Pi_i : \nabla \mathbf{u} - \frac{2}{3}\Delta_i \nabla \cdot \mathbf{u} - \frac{2}{3}\mathbf{J}_i \cdot (d_t \mathbf{u} - \mathbf{F}_i) - p_i d_t ln(p_i v^{5/3}/c_i) - \mathbf{J}_i \cdot \nabla (p_i/\rho_i), \qquad (2.56b)$$

$$Z_i^{(3)} = -\nabla \cdot \psi_i^{(3)} - \mathbf{Q}_i' \cdot \nabla \mathbf{u} - (d_t \mathbf{u} - \mathbf{F}_i) \cdot (\mathbf{P}_i - p_i \mathbf{U}) - \varphi_i^{(3)} : \nabla \mathbf{u} - \mathbf{J}_i d_t \hat{h}_i - \mathbf{P}_i \cdot \nabla \mathbf{u}, \qquad (2.56c)$$

$$Z_i^{(4)} = -\nabla \cdot \mathbf{P}_i - \rho_i (d_t \mathbf{u} - \mathbf{F}_i) - \mathbf{J}_i \cdot \nabla \mathbf{u}, \qquad (2.56d)$$

where

$$\psi_i^{(\alpha)} = \langle \mathbf{c}_i h_i^{(\alpha)} f_i \rangle,$$
$$\varphi_i^{(3)} = \langle \mathbf{c}_i \mathbf{c}_i \mathbf{c}_i f_i \rangle,$$

and U is the unit second rank tensor.

Radiation part :

$$\rho d_t c_r = -\nabla \cdot \mathbf{J}_r + \Lambda_r^{(n)}, \qquad (2.57a)$$

$$\rho d_t \hat{\phi}_r = -\nabla \cdot \mathbf{P}_r + \Lambda_r, \qquad (2.57b)$$

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and

$$\rho d_t \varepsilon_r = -\nabla \cdot \mathbf{Q}_r - \mathbf{P}_r : \nabla \mathbf{u} - \mathbf{u} \cdot \nabla \cdot \mathbf{P}_r + \Lambda_r^{(e)}, \qquad (2.57c)$$

$$\rho d_t \hat{\Phi}_r^{(\alpha)} = Z_r^{(\alpha)} + \Lambda_r^{(\alpha)}, \qquad (2.57d)$$

where  $c_r = m_r n_r / \rho$ ,  $\hat{\phi}_r = \phi_r / \rho = \mathbf{Q}_r / c^2 \rho$ ,  $\varepsilon_r = \bar{E}_r / \rho$ ,  $\hat{\Phi}_r^{(\alpha)} = \Phi_r^{(\alpha)} / \rho$ , and the streaming term as well as the dissipative terms are defined, respectively,

$$Z_r^{(\alpha)} = -\nabla \cdot \langle (c\hat{\mathbf{k}}_r - \mathbf{u})h_r^{(\alpha)}f_r \rangle + \langle f_r[d_t + (c\hat{\mathbf{k}}_r - \mathbf{u}) \cdot \nabla]h_r^{(\alpha)} \rangle, \quad (2.58a)$$

$$\Lambda_r^{(n)} = \langle m_r \Re_r \rangle, \tag{2.58b}$$

$$\Lambda_r^{(\mathbf{u})} = \langle (\hbar\omega/c)(\hat{\mathbf{k}}_r - \mathbf{u}/c)\Re_r \rangle, \qquad (2.58c)$$

$$\Lambda_r^{(e)} = \langle \hbar \omega (\hat{\mathbf{k}}_r - \mathbf{u}/c) \cdot (\hat{\mathbf{k}}_r - \mathbf{u}/c) \Re_r \rangle, \qquad (2.58d)$$

$$\Lambda_r^{(\alpha)} = \langle h_r^{(\alpha)} \Re_r \rangle. \tag{2.58e}$$

We will point out the meaning of the dissipation terms in a later section. Here we write the streaming terms in a more explicit form:

$$Z_r^{(1)} = -\nabla \cdot \psi_r^{(1)} - 2[\mathbf{P}_r \cdot \nabla \mathbf{u}]^{(2)}, \qquad (2.56'a)$$

$$Z_r^{(2)} = -\nabla \cdot \psi_r^{(2)} - 2(\mathbf{P}_r - p_r \mathbf{U}) : \nabla \mathbf{u} - p_r d_t ln(p_r v^3/c_r) - \mathbf{J}_r \cdot \nabla(p_r/\rho_r), \qquad (2.56'b)$$

$$Z_r^{(3)} = -\nabla \cdot \psi_r^{(3)} - \mathbf{Q}_r' \cdot \nabla \mathbf{u} - d_t \mathbf{u} \cdot \mathbf{P}_r - \mathbf{P}_r \cdot \nabla \hat{\varepsilon}_r - \mathbf{J}_r d_t \hat{\varepsilon}_r, \quad (2.56'c)$$

$$Z_r^{(4)} = -c^{-2} \nabla \cdot \mathbf{P}_r - \rho_r d_t \mathbf{u} - \mathbf{J}_r \cdot \nabla \mathbf{u}, \qquad (2.56'd)$$

$$Z_r^{(5)} = -\nabla \cdot \psi_r^{(5)} - 3\Phi_r^{(5)} \cdot \nabla \mathbf{u}, \qquad (2.56'e)$$

etc.

where

$$\begin{split} \psi_r^{(\alpha)} &= \langle (c\hat{\mathbf{k}}_r - \mathbf{u}) h_r^{(\alpha)} f_r \rangle, \\ \varphi_r^{(3)} &= c^{-2} \langle (c\hat{\mathbf{k}}_r - \mathbf{u}) (c\hat{\mathbf{k}}_r - \mathbf{u}) (c\hat{\mathbf{k}}_r - \mathbf{u}) f_r \rangle. \end{split}$$

The nonrelativistic approximation has been used to derive the evolution equations for the radiation part (2.57) and (2.58). It is emphasized that the evolution equations for radiation and matter are coupled through the source terms and they are also coupled to the entropy balance equation which will be presented later. This set of evolution equations are called the generalized hydrodynamic equations for radiation and matter. By solving these equations we can determine the nonequilibrium distribution functions for radiation and matter.

We now calculate the normalization factor  $\mu_r$  which is closely related to the chemical potential of photon gas. As mentioned earlier, the equilibrium chemical potential of photon gas is equal to zero, therefore a nonvanishing chemical potential is one of the characteristics of nonequilibrium radiation. With the help of (2.50b) we have

$$n_r = \langle [exp(W_r) - 1]^{-1} \rangle,$$

where  $W_r$  is given by (2.50a). Since  $f_r$  must be positive,  $W_r$  is positive for all  $\beta$ and  $\omega$ . With the help of Taylor expansion we may write  $n_r$  in the form

$$n_r = \sum_{q \ge 1} \langle exp(-qW_r) \rangle \tag{2.59}$$

where

$$W_r = \beta(\mathcal{H} - \mu_r), \qquad (2.60a)$$

$$\mathcal{H} = \hbar\omega(1 + \hat{\mathbf{k}}_r \cdot \mathbf{u}/c) + \sum_{\alpha} X_r^{(\alpha)} \odot h_r^{(\alpha)}.$$
(2.60b)

It is convenient to introduce the following symbols:

$$z = exp(\beta\mu_r) - 1, \qquad (2.61a)$$

$$y_q = \langle exp(-q\beta \mathcal{H}) \rangle \quad (q \ge 1),$$
 (2.61b)

then, (2.59) may be cast into the form

$$n_r = \sum_{q \ge 1} y_q (z+1)^q.$$
 (2.62)

It can be recast into

$$n_r - \sum_{q \ge 1} y_q = z (\sum_{q \ge 1} q y_q + \sum_{q \ge 1} 2^{-1} q (q-1) y_q z + \dots + \sum_{q \ge 1} y_q z^{q-1}).$$
(2.62')

Let us further define

$$\tau = n_r - \sum_{q \ge 1} y_q, \tag{2.63}$$

$$\varphi^{-1}(z,\beta) = \sum_{q\geq 1} qy_q + \sum_{q\geq 1} 2^{-1}q(q-1)y_qz + \dots + \sum_{q\geq 1} y_qz^{q-1}.$$
 (2.64)

We should point out that  $\varphi$  is a well-defined function of z and  $\beta$  since  $y_q$  are explicitly calculable with  $\mathcal{H}$  given in (2.60b). With these notations, (2.62') can be simply recast in the form

$$z = \tau \varphi(z, \beta). \tag{2.65}$$

By solving this equation for z we will get the chemical potential of nonequilibrium radiation. With the help of the Lagrange theorem [41] we find the solution to be

$$z = \sum_{j=1}^{\infty} \frac{\tau^{j}}{j!} (d^{j-1} \varphi^{j} / dz^{j-1})_{z=0}.$$
 (2.66)

Therefore the chemical potential is given by

$$\beta \mu_r = \ln\{1 + \sum_{j=1}^{\infty} \frac{\tau^j}{j!} (d^{j-1} \varphi^j / dz^{j-1})_{z=0}\}.$$
 (2.67)

Here it is worthwhile to discuss more about the chemical potential of nonequilibrium radiation. Since  $\varphi(z,\beta)$  is a very complicated function, it is difficult to find solutions of (2.67). Therefore it would be more practicable to seek the lowest order approximation which is given by the formula

$$\beta \mu_r = \ln[1 + \tau \varphi(0, \beta)] = \ln[1 + (n_r - \sum_{q \ge 1} y_q) / \sum_{q \ge 1} q y_q].$$
(2.68)

This equation gives the dependence of the chemical potential on the nonequilibrium correction for the distribution function. Note that  $n_r$  is a function of  $\beta$  only,

$$n_r = \frac{2\zeta(3)(k_B T)^3}{\pi^2 (\hbar c)^3}.$$
(2.69)

The high order approximations can be evaluated iteratively from the lowest order approximation if it is necessary for the real problems. At this point we will examine the behavior of  $\mu_r$  when the system approaches equilibrium. At equilibrium state all the fluxes are equal to zero, that is,  $\mathcal{H} \to \hbar \omega$ , and consequently  $\tau \to 0$ . In this limit the chemical potential vanishes:

$$\mu_r \rightarrow 0$$

which is in accord with the fact that the equilibrium chemical potential  $\mu_r^0$  equals zero as shown before. This consistency with the physical requirement confirms that our formula for the chemical potential of nonequilibrium radiation  $\mu_r$  is correct.

Until now the dissipation terms  $\Lambda_i^{(\alpha)}$ , etc. which appear in the entropy production and the flux evolution equations have not been calculated explicitly. In order to put the flux evolution equations in a more transparent form with regards to the  $X_i^{(\alpha)}$  dependence, we may apply the cumulant expansion method to evaluate the dissipation terms. The most important and physically relevant results can be covered by the first order cumulant approximation for the entropy production. In that approximation we find

$$\Lambda_i^{(\alpha)} = (\beta g)^{-1} \sum_j^r \sum_{\gamma} R_{ij}^{(\alpha\gamma)} \odot X_j^{(\gamma)} q_e(X), \qquad (2.70)$$

$$g = (m/2k_BT)^{1/2}/(nd)^2,$$
 (2.71)

$$q_{\epsilon}(X) = \sinh[\kappa(X)]/\kappa(X), \qquad (2.72)$$

$$\kappa(X) = \left(\sum_{i}^{r} \sum_{j}^{r} \sum_{\alpha}^{r} \sum_{\gamma}^{r} X_{i}^{(\alpha)} \odot R_{ij}^{(\alpha\gamma)} \odot X_{j}^{(\gamma)}\right)^{1/2}, \qquad (2.73)$$

where  $R_{ij}^{(\alpha\gamma)}$  are the collision bracket integrals appearing in the Chapman-Enskog theory [18]; their explicit forms will be given later on. In addition, d is the mean size parameter and m is a mass and the factor g scales the Boltzmann collision integral to a dimensionless form. Here we give the details of the derivation of (2.70). The entropy production for the system of radiation and matter is defined by

$$\sigma = k_B g^{-1} \sum_{i}^{r} \langle ln(\epsilon_i + f_i^{-1})g\Re_i \rangle.$$
(2.74)

By substituting the distribution functions (2.37) and (2.40) into the definition of the entropy production and taking into account various collisional invariants, we can cast  $\sigma$  in the form:

$$\sigma = T^{-1} \left( \sum_{i}^{\prime} \sum_{\alpha} X_{i}^{(\alpha)} \odot \Lambda_{i}^{(\alpha)} + \sum_{\alpha} X_{r}^{(\alpha)} \odot \Lambda_{r}^{(\alpha)} \right)$$
$$- T^{-1} \left( \sum_{i}^{\prime} \hat{\mu}_{i} \Lambda_{i}^{(n)} + \hat{\mu}_{r} \Lambda_{r}^{(n)} \right)$$
$$= T^{-1} \sum_{i}^{r} \sum_{\alpha} X_{i}^{(\alpha)} \odot \Lambda_{i}^{(\alpha)} - T^{-1} \left( \sum_{i}^{\prime} \hat{\mu}_{i} \Lambda_{i}^{(n)} + \hat{\mu}_{r} \Lambda_{r}^{(n)} \right). \quad (2.74')$$

Writing  $\Re_i$  more explicitly and defining the dimensionless collisional average by  $\langle \rangle_c$ ,

$$\langle \cdots \rangle_{c} = (2\pi)^{-3} G_{j} \int d\mathbf{k}_{j} \int d\Omega (W_{ij}^{(e)} \delta_{ik} \delta_{jl} + W_{ij;kl}^{(r)}) \cdots, \qquad (2.75)$$

we recast (2.74) in the following form:

$$\sigma = k_B g^{-1} \hat{\sigma}, \qquad (2.76a)$$

$$\hat{\sigma} = -\sum_{i}^{r} \sum_{j}^{r} \sum_{k}^{r} \sum_{l}^{r} \langle f_{k}^{*} f_{l}^{*} f_{i} f_{j} [(\epsilon_{k} + f_{k}^{*-1})(\epsilon_{l} + f_{l}^{*-1}) - (\epsilon_{i} + f_{i})(\epsilon_{j} + f_{j})] ln(\epsilon_{i} + f_{i}^{-1}) \rangle_{c}.$$
(2.76b)

Here  $\hat{\sigma}$  is a dimensionless (or reduced) entropy production. By substituting the distribution functions

$$f_i = [exp(W_i) - \epsilon_i]^{-1}$$

into (2.76b),  $\hat{\sigma}$  can be expressed in the form

$$\hat{\sigma} = \frac{1}{4} \sum_{i}^{r} \sum_{j}^{r} \langle (W_{ij} - W_{kl}^{*}) [exp(-W_{kl}^{*}) - exp(-W_{ij})] C_{q} \rangle_{c}, \qquad (2.77a)$$

where

$$C_q = \{ [1 - \epsilon_i exp(-W_i)] [1 - \epsilon_j exp(-W_j)] [1 - \epsilon_k exp(-W_k^*)] \times [1 - \epsilon_l exp(-W_l^*)] \}^{-1}, \qquad (2.77b)$$

$$W_{ij} = W_i + W_j, \quad etc. \tag{2.77c}$$

Note that  $C_q$  is the quantum effect contribution to the entropy production which will be put equal to unity in the classical limit; In that case, (2.77a) reduces to the same form as the classical formula for a gas mixture. At the lowest order approximation  $C_q$  will be approximated by replacing  $W_i$ , etc., with  $W_i^0$ , namely, the exponent of the local equilibrium distribution function:

$$C_q^0 = C_q(W_i^0, W_j^0). (2.78)$$

Then we apply a cumulant expansion method [20] to evaluate  $\hat{\sigma}$ . Let us define

$$\kappa = \frac{1}{2} \left( \sum_{i}^{r} \sum_{j}^{r} \sum_{k}^{r} \sum_{l}^{r} \langle \langle (W_{ij} - W_{kl}^{*})^{2} \rangle \rangle_{ij;kl} \right)^{1/2}, \qquad (2.79a)$$

where

$$\langle \langle \cdots \rangle \rangle_{ij;kl} = \langle \cdots C_q^0 \rangle_c.$$
 (2.79b)

This collisional average has two distinctive components: elastic (together with inelastic contribution) and reactive. The former will be expressed as  $[\cdots]_{ij}$  and the latter  $[\cdots]_{ij;kl}$ . By using the same cumulant expansion method as in ref. [20], we obtain  $\hat{\sigma}$  to the first order cumulant approximation:

$$\hat{\sigma} = \kappa \sinh(\kappa). \tag{2.80}$$

Here the dissipation function  $\kappa^2$  may be written as

$$\kappa^{2} = \frac{1}{4} \sum_{i}^{r} \sum_{j}^{r} [(W_{ij}^{*} - W_{ij})^{2}]_{ij} + \frac{1}{4} \sum_{i}^{r} \sum_{j}^{r} \sum_{k}^{r} \sum_{l}^{r} [(W_{kl}^{*} - W_{ij})^{2}]_{ij;kl}$$
  
$$\equiv \kappa_{e}^{2} + \kappa_{r}^{2}. \qquad (2.81)$$

The elastic part  $\kappa_e^2$  of the collision integral involves the transition probability  $W_{ij}^{(e)}$ while the reactive part  $\kappa_r^2$  involves the transition probability  $W_{ij;kl}^{(r)}$ . Since

$$W_i = W_i^0 + \sum_{\alpha} X_i^{(\alpha)} \odot h_i^{(\alpha)} - \mu_i$$

and  $W_i^0$  is a collisional invariant, we find

$$W_{kl}^{*} - W_{ij} = \beta \sum_{\alpha} (X_{k}^{(\alpha)} \odot h_{k}^{(\alpha)^{*}} + X_{l}^{(\alpha)} \odot h_{l}^{(\alpha)^{*}} - X_{i}^{(\alpha)} \odot h_{i}^{(\alpha)} - X_{j}^{(\alpha)} \odot h_{j}^{(\alpha)}) - \beta (\mu_{k}^{*} + \mu_{l}^{*} - \mu_{i} - \mu_{j}).$$
(2.82)

On the substitution of this result into the elastic part in (2.81), we obtain  $\kappa_e^2$  in the following form:

$$\kappa_e^2 = \sum_i^r \sum_j^r \sum_{\alpha} \sum_{\gamma} X_i^{(\alpha)} \odot \Re_{ij}^{(\alpha\gamma)} \odot X_j^{(\alpha)}.$$
(2.83*a*)

The reactive collision operator is symmetric with respect to the interchange of reactant particles or product particles and to the reversal of the collision processes. When the symmetry properties are exploited, the reactive part  $\kappa_r^2$  of the dissipation function can be written as

$$\kappa_r^2 = \sum_i^r \sum_{\alpha} \sum_{\gamma} (X_i^{(\alpha)} \odot \mathfrak{S}_{ii}^{(\alpha\gamma)} \odot X_i^{(\alpha)} + \sum_{j \neq i}^r X_i^{(\alpha)} \odot \mathfrak{S}_{ij}^{(\alpha\gamma)} \odot X_j^{(\alpha)}) + \sum_i^r \mathcal{A}_i^2 \mathfrak{S}_i^{(0)}$$
(2.83b)

where the coefficients  $\Re_{ij}^{(\alpha\gamma)}$ , etc., can be cast in terms of the collision bracket integrals:

$$\Re_{ii}^{(\alpha\gamma)} = \frac{1}{4}\beta^{2} [(h_{i}^{(\alpha)*} + h_{i'}^{(\alpha)*} - h_{i}^{(\alpha)} - h_{i'}^{(\alpha)*})(h_{i}^{(\gamma)*} + h_{i'}^{(\gamma)*} - h_{i}^{(\gamma)} - h_{i'}^{(\gamma)})]_{ii'} + \frac{1}{2}\beta^{2} \sum_{j\neq i} [(h_{i}^{(\alpha)*} - h_{i}^{(\alpha)})(h_{i}^{(\gamma)*} - h_{i}^{(\gamma)})]_{ij}, \qquad (2.84a)$$

$$\Re_{ij}^{(\alpha\gamma)} = \frac{1}{2}\beta^2 [(h_i^{(\alpha)*} - h_i^{(\alpha)})(h_i^{(\gamma)*} - h_i^{(\gamma)})]_{ij} \quad (i \neq j).$$
(2.84b)

We have affixed a prime on one of the subscripts i's in (2.84a) to indicate another particle of species *i*, while the coefficients  $\Im_{ij}^{(\alpha\gamma)}$  etc., are defined by the collision bracket integrals as follows:

$$\Im_{ii}^{(\alpha\gamma)} = \frac{1}{2}\beta^2 \sum_{k}^{r} \sum_{l}^{r} \{ [h_i^{(\alpha)} h_i^{(\gamma)}]_{ii;kl} + \sum_{j}^{r} [h_i^{(\alpha)} h_i^{(\gamma)}]_{ij;kl} \},$$
(2.85*a*)

$$\Im_{ij}^{(\alpha\gamma)} = \frac{1}{2}\beta^2 \sum_{k}^{r} \sum_{l}^{r} \{ [h_i^{(\alpha)} h_j^{(\gamma)}]_{ij;kl} - 2[h_i^{(\alpha)} h_i^{(\gamma)}]_{ij;kl} \} \quad (i \neq j), \quad (2.85b)$$

$$\Im_i^{(0)} = \frac{1}{4} \beta^2 [\mathbf{1}]_{ij;kl}, \qquad (2.85c)$$

$$\mathcal{A}_{i} = -(\mu_{k}^{*} + \mu_{l}^{*} - \mu_{i} - \mu_{j}).$$
(2.85d)

Here,  $\Im_i^0$  is the reaction rate constant which is simply the equilibrium average of the transition probability of reaction  $i + j \rightleftharpoons k + l$  (note that one of the species is a photon.), and  $\mathcal{A}_i$  the corresponding affinity. Since the number of internal states are the same as the number of species in the present model, the sum of the reactive contribution to  $\kappa_r^2$  runs over all species.

The summation of the elastic and inelastic components of the dissipation function leads to

$$R_{ij}^{(\alpha\gamma)} = \Re_{ij}^{(\alpha\gamma)} + \Im_{ij}^{(\alpha\gamma)}$$
(2.86)

which is related to transport coefficients and, therefore,  $\Im_{ij}^{\alpha\gamma}$  represent the corrections to the transport coefficients which arise from the "reactive" collisions between material particles and photons. The entropy production may be written in the form

$$\sigma = k_B g^{-1} \kappa^2 \sinh(\kappa) / \kappa.$$

Comparing this expression of  $\sigma$  with (2.74'), we can easily identify  $\Lambda_i^{(\alpha)}$ , etc. with the help of the dissipation function obtained above:

$$\Lambda_i^{(\alpha)} = (\beta g)^{-1} \sum_j^r \sum_{\gamma} R_{ij}^{(\alpha\gamma)} \odot X_j^{(\gamma)} sinh(\kappa) / \kappa, \qquad (2.87)$$

and

$$\Lambda_i^{(n)} = -(\beta g)^{-1} \mathcal{A}_i \Im_i^{(0)}.$$
 (2.88)

These results are very useful when we deal with hydrodynamic problems, and they are also essential for evaluating transport coefficients. We will discuss these issues in the later sections.

#### 2.4 Irreversible thermodynamics of radiation and matter

The key quantities in the study of irreversible thermodynamics are the entropy, entropy flux, and entropy production. Following the modified moment method [40] used for the case of matter alone, we formulate a local theory of irreversible thermodynamics of radiation and matter. For this purpose it is necessary to introduce local entropy and related variables. In the local frame the local entropy density Sis defined as an additive sum of contribution from matter and radiation:

$$\rho S(\mathbf{r},t) = \rho S_m(\mathbf{r},t) + \rho S_r(\mathbf{r},t), \qquad (2.89a)$$

$$\rho S_m(\mathbf{r},t) = -k_B \sum_i' \langle f_i(lnf_i - 1) \rangle, \qquad (2.89b)$$

$$\rho \mathcal{S}_r(\mathbf{r},t) = -k_B \langle [f_r ln f_r - (1+f_r) ln(1+f_r)] \rangle, \qquad (2.89c)$$

where  $\rho$  is the local mass density of matter. It is emphasized that the rationale for the definition of entropy in (2.89a) is as follows. Treating the total entropy as the sum of radiation and matter entropies is motivated by the general aim of the present thesis to unify the thermodynamics of radiation and matter. As we mentioned earlier, a system consisting of radiation and matter is considered as a gas-mixture of photons regarded as different species and material particles. Since entropy is an extensive quantity, the total entropy of system must be the sum of the entropies of the total constituent particles. The different expressions for radiation and matter entropy are due to the fact that photons are quantum particles satisfying Bose-Einstein statistics whereas material particles are classical. The manner of defining the radiation entropy density S as well as other macroscopic variables in terms of unit mass of matter with which radiation is in interaction may be justified. It is most appropriate from the kinetic theory viewpoint to define macroscopic variable densities on the basis of the total mass density. However, photons have zero rest mass. For this reason we define the radiation entropy density per unit mass of matter. It also gives operationally meaningful quantities, especially when the evolution equations for various radiation-related macroscopic variables are defined in the local rest frame moving at the hydrodynamic velocity **u** and, consequently, the matter-related quantities such as the velocity gradient appear in the evolution equations for radiation variables. At this point we need to mention that with the help of the fictitious photon mass the total mass density may be defined as the sum of the particle mass density and the fictitious mass density of the photon in order to evaluate the densities of macroscopic variables, but their evolution equations become rather messy because of the temperature dependence of the fictitious photon mass.

It is straightforward to derive the entropy balance equation from kinetic equations (2.7). On differentiation of  $\rho S$  in (2.89) with respect to time and substitution of the kinetic equations into it there results the entropy balance equation in the form

$$\rho d_t \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}_s + \sigma(\mathbf{r}, t). \tag{2.90a}$$

According to the H theorem shown earlier, the entropy production of the system satisfies

$$\sigma(\mathbf{r},t) \ge 0 \tag{2.90b}$$

with the equality holding at equilibrium. This is a statistical mechanical representation of the second law of thermodynamics. The various definitions for the entropy flux  $J_s$  and the entropy production  $\sigma$  are as follows:

$$\mathbf{J}_{s} = \mathbf{J}_{s}^{(r)} + \mathbf{J}_{s}^{(m)}, \tag{2.91a}$$

$$\sigma = \sigma_r + \sigma_m, \tag{2.91b}$$

$$\mathbf{J}_{s}^{(m)} = -k_{B} \sum_{i}^{\prime} \langle f_{i} \mathbf{c}_{i} (lnf_{i} - 1) \rangle, \qquad (2.91c)$$

$$\mathbf{J}_{r}^{(r)} = -k_{B} \langle (c\hat{\mathbf{k}}_{r} - \mathbf{u}) [f_{r} ln f_{r} - (1 + f_{r}) ln (1 + f_{r})] \rangle, \qquad (2.91d)$$

$$\sigma_m = -k_B \sum_i' \langle ln f_i \Re_i \rangle, \qquad (2.91e)$$

$$\sigma_r = -k_B \langle [lnf_r - ln(1+f_r)] \Re_r \rangle.$$
(2.91f)

Here the subscripts or the superscripts m and r stand for the matter part and the radiation part, respectively. The matter parts of the entropy flux and entropy production are the same as those in the case of matter alone whereas radiation parts contain the quantum contributions of photons. Since we have chosen the local rest frame moving at hydrodynamic velocity  $\mathbf{u}$ , the Doppler effect should be taken into account for photons, that is, there is a term  $(c\hat{\mathbf{k}}_r - \mathbf{u})$  appearing in the radiation entropy flux. The consideration of the Doppler effect makes the present formalism better balanced between the matter and radiation parts. It is useful to interpret (2.91d) that the radiation entropy flux is basically the average value of  $k_B(c\hat{\mathbf{k}}_r - \mathbf{u})[(1 + f_r^{-1})ln(1 + f_r) - lnf_r]$  with respect to the distribution function  $f_r$  in the local rest frame, and this interpretation is also applying in computing the entropy flux in terms of radiation heat flux, etc.

The evolution equations (2.53a)-(2.53e) and (2.57a)-(2.57d) for macroscopic variables must be subordinated to the entropy balance equation (2.90a), or more specially, the H theorem (2.90b). Since the kinetic equations cannot be solved exactly, seeking an approximate solutions for the distribution function is inevitable. The H theorem requires that the approximate forms for various dissipation terms  $\Lambda_i^{(\alpha)}$  and  $\Lambda_r^{(\alpha)}$ , etc. in the evolution equations should be taken in such a way that the entropy production remains always positive semidefinite. By this way, the evolution equations or generalized hydrodynamic equations for radiation and matter are made rigorously consistent with the H theorem, that is, the second law of thermodynamics. This is the basic strategy of the modified moment method. As shown earlier, the entropy production can be written as

$$\sigma = T^{-1} \sum_{i} \sum_{\alpha} X_{i}^{(\alpha)} \odot \Lambda_{i}^{(\alpha)} - T^{-1} (\sum_{i}' \hat{\mu}_{i} \Lambda_{i}^{(n)} + \hat{\mu}_{r} \Lambda_{r}^{(n)}).$$
(2.92)

With the same distribution functions as for the entropy production the entropy flux can be directly derived from its definition. The matter part is given by

$$\mathbf{J}_{s}^{(m)} = T^{-1} \sum_{i}^{\prime} (\mathbf{Q}_{i} - \hat{\mu}_{i} \mathbf{J}_{i} + \sum_{\alpha} X_{i}^{(\alpha)} \odot \psi_{i}^{(\alpha)} + p_{i} \mathbf{J}_{i} / \rho_{i})$$
(2.93)

where

$$p_i = n_i k_B T, \quad \hat{\mu}_i = \mu_i / m_i,$$

and

$$\psi_i^{(\alpha)} = \langle \mathbf{c}_i h_i^{(\alpha)} f_i \rangle. \tag{2.94}$$

The entropy flux for the radiation part can be recast in the following form

$$\mathbf{J}_{s}^{(r)} = T^{-1}(\mathbf{Q}_{r} - \hat{\mu}_{r}\mathbf{J}_{r} + \sum_{\alpha} X_{r}^{(\alpha)} \odot \psi_{r}^{(\alpha)}) + p_{r}\phi_{r}/\rho_{r} + \mathbf{J}_{sq}^{(r)}, \qquad (2.95)$$

where

$$\psi_r^{(\alpha)} = \langle (c\hat{\mathbf{k}}_r - \mathbf{u})h_r^{(\alpha)}f_r \rangle, \quad \phi_r = c^{-2}\mathbf{Q}_r, \qquad (2.96a)$$

$$\mathbf{J}_{sq}^{(r)} = -k_B \langle (c\hat{\mathbf{k}}_r - \mathbf{u}) ln [1 - exp(-W_r)] \rangle.$$
(2.96b)

Note that the local rest frame forms for  $h_r^{(\alpha)}$  are used in this calculation, and the radiation entropy flux has an additional term  $J_{sq}^{(r)}$  due to the quantum character of photon gas. We observe that the radiation entropy flux is rather similar to its matter counterpart. Therefore, the total entropy flux may be written as

$$\mathbf{J}_{s} = T^{-1} \sum_{i}^{\prime} (\mathbf{Q}_{i} - \hat{\mu}_{i} \mathbf{J}_{i}) + T^{-1} (\mathbf{Q}_{r} - \hat{\mu}_{r} \mathbf{J}_{r}) + \mathbf{J}_{sn}.$$
(2.97)

In comparison with the Chapman-Enskog result for the entropy flux, there is an additional term  $J_{sn}$  which contains the nonlinear contributions of matter and radiation and the quantum contribution of photons to the entropy flux:

$$\mathbf{J}_{sn} = T^{-1} \sum_{i}' \sum_{\alpha} X_{i}^{(\alpha)} \odot \psi_{i}^{(\alpha)} + T^{-1} \sum_{\alpha} X_{r}^{(\alpha)} \odot \psi_{r}^{(\alpha)} + \sum_{i}' p_{i} \mathbf{J}_{i} / \rho_{i} + p_{r} \phi_{r} / \rho_{r} + \mathbf{J}_{sq}^{(r)}.$$
(2.98)

Once the entropy flux and entropy production are known the entropy density for the system of radiation and matter can be calculated.

In order to analyze the relation between the time derivative of the entropy density and other independent macroscopic variables we will cast the entropy balance equation into a more explicit form that indicates the macroscopic variable dependence of S. Such a similar relation exists in equilibrium statistical mechanics, namely, the Gibbs relation. For nonequilibrium systems the so-called extended Gibbs relation was shown to be valid in the linear regime. The question is: does this relation hold for systems that are far away from equilibrium? The answer is not. To show that this is the case, we substitute the entropy production (2.92) and the entropy flux (2.97) into the entropy balance equation (2.90a); we then eliminate the gradients of the heat fluxes  $\mathbf{Q}_m$  and  $\mathbf{Q}_r$  and fluxes  $\mathbf{J}_m$  and  $\mathbf{J}_r$  with the help of the energy balance equations (2.53d) and (2.57c) and the mass fraction balance equations (2.53b) and (2.57a). The dissipation terms  $\Lambda_m^{(\alpha)}$  and  $\Lambda_r^{(\alpha)}$  appearing in the entropy production are also eliminated by using the flux evolution equations (2.53e) and (2.57d). The final result of this long calculation is

$$d_{t}S = T^{-1}(d_{t}\varepsilon_{m} + d_{t}\varepsilon_{r} + (p_{m} + p_{r})d_{t}V - \sum_{i}^{\prime}\hat{\mu}_{i}d_{t}c_{i} - \hat{\mu}_{r}d_{t}c_{r}$$

$$+ \sum_{i}^{\prime}\sum_{\alpha}X_{i}^{(\alpha)} \odot d_{t}\hat{\Phi}_{i}^{(\alpha)} + \sum_{\alpha}X_{r}^{(\alpha)} \odot d_{t}\hat{\Phi}_{r}^{(\alpha)}) + \aleph$$

$$= T^{-1}(d_{t}\varepsilon + pd_{t}V - \sum_{i}^{r}\hat{\mu}_{i}d_{t}c_{i} + \sum_{i}^{r}\sum_{\alpha}X_{i}^{(\alpha)} \odot d_{t}\hat{\Phi}_{i}^{(\alpha)}) + \aleph, \quad (2.99)$$

where

$$\varepsilon = \varepsilon_m + \varepsilon_r, \qquad p = p_m + p_r,$$
 (2.100)

$$\begin{split} &\aleph = -\rho^{-1} (\nabla \cdot \mathbf{J}_{sn} + T^{-1} \sum_{i}' \sum_{\alpha} X_{i}^{(\alpha)} \odot Z_{i}^{(\alpha)} + T^{-1} \sum_{\alpha} X_{r}^{(\alpha)} \odot Z_{r}^{(\alpha)}) \\ &+ (\rho T)^{-1} ((\Pi_{m} + \Pi_{r}) : \nabla \mathbf{u} + T^{-1} (\Delta_{m} + \Delta_{r}) \nabla \cdot \mathbf{u} \\ &+ T^{-1} (\mathbf{Q}_{m} + \mathbf{Q}_{r}) \cdot \nabla ln T + \sum_{i}' \mathbf{J}_{i} \cdot [\nabla (\hat{\mu}_{i}/T) - \mathbf{F}_{i}/T] \\ &+ \mathbf{J}_{r} \cdot \nabla (\hat{\mu}_{r}/T)). \end{split}$$
(2.101)

Here the matter and radiation parts are combined into a single term in the spirit that treats radiation as if it is another species of matter. It is clear that  $\aleph$  does not equal zero for the nonequilibrium system where the values of various macroscopic quantities and their spatial gradient terms will be dependent on the path taken by the system evolving from one state to another in the Gibbs space. Therefore,  $d_t S$  is not an exact differential as is the case for an equilibrium system for which the equilibrium Gibbs relation holds for  $d_t S$ . It is well known that the Gibbs relation is one of the most important result in the equilibrium thermodynamics since it provides a way to calculate the thermodynamic functions. One hopes that a similar relation may hold for nonequilibrium systems, if then irreversible thermodynamics can be formulated in parallel to equilibrium thermodynamics. To achieve this aim we define the following differential:

$$Td_t\Psi = d_t\varepsilon + pd_tV - \sum_i^r \hat{\mu}_i d_tc_i + \sum_i^r \sum_\alpha X_i^{(\alpha)} \odot d_t\Phi_i^{(\alpha)}, \qquad (2.102)$$

which is called the *compensation differential*. It must be noted that the matter and radiation parts are combined in this compensation differential. The physical meaning of the compensation differential is that it describes the transfer of energy and matter between an elementary volume enclosing matter and radiation and its surroundings. After imposing the integrability conditions the compensation differential becomes exact. It means that the various thermodynamic functions can be evaluated by using the compensation differential and its integrability conditions. With  $d_t\Psi$  so defined as in (2.102), the entropy balance equation takes the form

$$d_t \mathcal{S} = d_t \Psi + \aleph. \tag{2.103}$$

The implication of this equation is that the entropy differential  $d_tS$  becomes the compensation differential  $d_t\Psi$  and thus an exact differential if and only if  $\aleph \equiv 0$ . The circumstance happens only for equilibrium systems or for linear irreversible processes in which linear thermodynamic force-flux relations replace the constitutive equations for fluxes  $\Phi_i^{(\alpha)}$  (2.53e) and (2.57d). In the former case the equilibrium Gibbs relation holds for the system of radiation and matter and in the latter case there exists the local equilibrium Gibbs relation. Except for these two cases the entropy differential is not an exact differential for systems that are away from equilibrium.

The physical significance of S can be better understood by the following analysis. First we rewrite the kinetic equations of matter and radiation in the forms:

$$f_i[d_t + \mathbf{c}_i \cdot \nabla + (m_i \mathbf{F}_i/\hbar) \cdot \nabla_k] ln(f_i/f_{ieq}) = \Re_i(f_i), \qquad (2.104a)$$

$$f_r[d_t + (c\hat{\mathbf{k}}_r - \mathbf{u}) \cdot \nabla] ln[(1 + f_r^{-1})/(1 + f_{req}^{-1})] = -(1 + f_r)^{-1} \Re_r(f_r), \quad (2.104b)$$

where  $i = a, b, \dots$ , excluding r and the equilibrium distribution functions satisfy

$$[d_i + \mathbf{c}_i \cdot \nabla + (m_i \mathbf{F}_i/\hbar) \cdot \nabla_k] f_{ieq} = 0, \qquad (2.105a)$$

$$[d_t + (c\hat{\mathbf{k}}_r - \mathbf{u}) \cdot \nabla] f_{req} = 0. \qquad (2.105b)$$

For the macroscopic variables of equilibrium or local equilibrium states, there exits the Gibbs-Duhem relation

$$\sum_{i}' c_{i} d_{t}(\hat{\mu}_{i}^{0}/T) = V d_{t}(p_{m}/T) + \varepsilon_{m} d_{t}(1/T).$$
(2.106)

Then, together with the formulae (2.56) and (2.58a) for  $Z_i^{(\alpha)}$  and  $Z_r^{(\alpha)}$ , respectively, and also the nonclassical part  $J_{sn}$  of the entropy flux, we finally obtain

$$\begin{split} &\aleph = \sum_{i}^{r} \left( \sum_{\alpha} \hat{\Phi}_{i}^{(\alpha)} \odot d_{t} X_{i}^{(\alpha)} - d_{t}(\hat{\mu}_{i}/T) \right) + \varepsilon_{m} d_{t}(1/T) + V d_{t}(p_{m}/T) - \hat{\sigma}_{L} \\ &- \rho^{-1} k_{B} \sum_{i}^{\prime} \left\langle \nabla \cdot \left\langle \mathbf{v}_{i} f_{i} \right\rangle + \rho^{-1} k_{B} \nabla \cdot \left\langle (c \hat{\mathbf{k}}_{r} - \mathbf{u}) ln[1 - exp(-W_{r})] \right\rangle \\ &+ \rho^{-1} k_{B} \sum_{i}^{\prime} \left\langle f_{i}[d_{t} + \mathbf{v}_{i} \cdot \nabla + (m_{i} \mathbf{F}_{i}/\hbar) \cdot \nabla_{k}] ln(f_{i}/f_{ieq}) \right\rangle \\ &+ \rho^{-1} k_{B} \left\langle f_{r}[d_{t} + (c \hat{\mathbf{k}}_{r} - \mathbf{u}) \cdot \nabla] ln[(1 + f_{req}^{-1})/(1 + f_{r}^{-1})] \right\rangle, \end{split}$$
(2.107)

where

$$\bar{X}_{i}^{(\alpha)} = X_{i}^{(\alpha)}/T,$$

$$\hat{\sigma}_{L} = -(\rho T)^{-1} \{ (\Pi_{m} + \Pi_{r}) : \nabla \mathbf{u} + T^{-1} (\Delta_{m} + \Delta_{r}) \nabla \cdot \mathbf{u} + T^{-1} (\mathbf{Q}_{m} + \mathbf{Q}_{r}) \cdot \nabla ln T + \sum_{i}^{\prime} \mathbf{J}_{i} \cdot [\nabla (\hat{\mu}_{i}^{0}/T) + \mathbf{F}_{i}/T] \}. \quad (2.108)$$

Here  $\hat{\sigma}_L$  is the linear entropy production per unit density which includes the contributions from both radiation and matter. The last term in (2.108) does not have a radiation component since the chemical potential of equilibrium radiation is equal to zero and also  $\mathbf{F}_r = 0$ . With the help of the equation (2.104a), the second last term in (2.107) can be recast into

$$\rho^{-1}k_B \sum_{i}' \langle f_i[d_t + \mathbf{c}_i \cdot \nabla + (m_i \mathbf{F}_i/\hbar) \cdot \nabla_k] ln(f_i/f_{ieq}) \rangle$$
  
=  $\rho^{-1}k_B \sum_{i}' \langle \Re_i \rangle.$  (2.109)

The last term in (2.107) may be written in a similar form by using (2.104b)

$$\rho^{-1}k_B \langle f_r[d_t + (c\hat{\mathbf{k}}_r - \mathbf{u}) \cdot \nabla] ln[(1 + f_{reg}^{-1})/(1 + f_r^{-1})] \rangle$$
  
=  $\rho^{-1}k_B \langle (1 + f_r)^{-1} \Re_r \rangle = \rho^{-1}k_B \langle [1 - exp(-W_r)] \Re_r \rangle.$  (2.110)

Since

$$\sum_{i}^{\prime} \langle \Re_{i} \rangle + \langle \Re_{r} \rangle = 0$$
 (2.111)

and also

$$-\sum_{i}^{\prime} \nabla \cdot \langle \mathbf{c}_{i} f_{i} \rangle - \nabla \cdot \langle (c \hat{\mathbf{k}}_{r} - \mathbf{u}) f_{r} \rangle$$
  
=  $\rho \sum_{i}^{r} d_{t}(c_{i}/m_{i}) - \sum_{i}^{\prime} \Lambda_{i}^{(n)}/m_{i} - \Lambda_{r}^{(n)}/m_{r}$   
=  $\rho \sum_{i}^{r} d_{t}(c_{i}/m_{i}) = 0.$ 

We obtain

$$\begin{split} \aleph &= \sum_{i}^{r} \left[ \sum_{\alpha} \hat{\Phi}_{i}^{(\alpha)} \odot d_{t} X_{i}^{(\alpha)} - c_{i} d_{t} (\hat{\mu}_{i}/T) \right] + \varepsilon_{m} d_{t} (1/T) \\ &+ V d_{t} (p_{m}/T) - \hat{\sigma}_{L} + \aleph_{q} \end{split}$$

where

$$\Re_q \equiv \rho^{-1} k_B \{ \nabla \cdot \langle (c \hat{\mathbf{k}}_r - \mathbf{u}) \{ exp(-W_r) [1 - exp(-W_r)]^{-1} \\ + \ln[1 - exp(-W_r)] \} \rangle + \sum_i' \langle \Re_i \rangle + \langle [1 - exp(-W_r)] \Re_r \rangle \}.$$
(2.112)

It represents a quantum contribution of photons to the entropy flux. Note that when  $\aleph_q = 0$ , the classical form of the entropy flux  $\aleph$  is recovered. Since the equilibrium radiation has no chemical potential, the corresponding Gibbs-Duhem equation is

$$\epsilon_r d_t(1/T) + V d_t(p_r/T) = 0$$
 (2.113)

we are finally able to write  $\aleph$  in the form

$$\aleph = \varepsilon d_t (1/T) + V d_t (p/T) + \sum_i^r \left( \sum_{\alpha} \hat{\Phi}_i^{(\alpha)} \odot d_t \bar{X}_i^{(\alpha)} - c_i d_t (\hat{\mu}_i/T) \right)$$
  
-  $\hat{\sigma} + \aleph_q.$  (2.114)

When the system is at equilibrium, the time and space derivative of intensive macroscopic variables such as T, p/T, etc., are equal to zero and various fluxes as well as  $\aleph$  also vanish. Therefore  $\aleph$  vanishes at equilibrium. However, as demonstrated earlier,  $\aleph$  is not equal to zero generally for the system away from equilibrium. In order to reveal the physical meaning of  $\aleph$ , let us introduced a new function, the so-called Boltzmann function

$$\mathcal{B} = \mathcal{S} - T^{-1}(\varepsilon + pV - \sum_{i}^{r} c_{i}\hat{\mu}_{i} + \sum_{i}^{r} \sum_{\alpha} \hat{\Phi}_{i}^{(\alpha)} \odot X_{i}^{(\alpha)}), \qquad (2.115)$$

then the entropy balance equation is transformed into the form

$$d_t \mathcal{B} = -\hat{\sigma}_L + \aleph_q. \tag{2.116}$$

This is an equivalent form of the entropy balance equation. Since  $\hat{\sigma}_L$  is positive semidefinite, the differential equation (2.116) can be regarded as a local form of the H theorem, if the sign of  $\aleph_q$  is the same as that of  $-\hat{\sigma}_L$  or it is absent. However, it seems at first glance that a definite sign of  $\aleph$  can no longer be attached to (2.116) unlike the case of classical monatomic gases. The term  $\aleph_q$  originates from the quantum nature of the photon gas.

The aim to have a local form of H theorem for a quantum gas can be achieved by introducing a suitable function as follows [42]:

$$\Gamma = \rho \hat{\Gamma} = k_B \sum_{i}^{r} \langle [1 - f_i^{-1} ln(1 + f_i^{-1})] f_i \rangle.$$
(2.117)

Differentiating  $\Gamma$  respect to time and using the kinetic equation (2.7), we find the equation for  $\Gamma$ ,

$$\rho \frac{d\hat{\Gamma}}{dt} = -k_B \sum_{j=1}^{r} \nabla \cdot \langle \mathbf{c}_j [1 - f_j^{-1} ln(1+f_j)] f_j \rangle + \sum_{i}^{r} \langle \Re_i \rangle + k_B \sum_{i}^{r} \sum_{j=1}^{r} \langle f_j (1+f_j)^{-1} \Re_j (f_i f_j) \rangle.$$
(2.118)

By virtue of the collisional invariance of the Boltzmann collision integral, it follows from (2.118) that

$$\aleph_q = -\frac{d\tilde{\Gamma}}{dt}.$$
 (2.119)

Therefore, by defining a new Boltzmann function  $\mathcal{B}_{\Gamma}$  for the quantum system by the formula

$$\mathcal{B}_{\Gamma} = \mathcal{B} + \tilde{\Gamma}, \qquad (2.120a)$$

we can recast the differential equation for  $\mathcal{B}_{\Gamma}$  in a form similar to the one for classical gases,

$$\frac{d}{dt}\mathcal{B}_{\Gamma} = -\hat{\sigma}_L. \tag{2.120b}$$

Since  $\hat{\sigma} \geq 0$ , the derivative on the left-hand side of this equation has a definite sign and the Boltzmann function  $\mathcal{B}_{\Gamma}$  is a decreasing function of time. Eq. (2.119) means that the entropy density acquires a quantum correction term in addition to the contributions known in the case of classical gases.

Up to now our discussions are limited to the boson gas, but it is necessary to extend these results to fermions such as electron gas in semiconductor, etc.. The kinetic equation for the fermions is the Boltzmann-Nordheim equation; in this case  $\aleph_q$  is given by

$$\Re_{q} = \rho k_{B} \sum_{j=1}^{r} \nabla \cdot \langle \mathbf{c}_{j} [1 + f_{j}^{-1} ln(1 - f_{j})] f_{j} \rangle + \sum_{i=1}^{r} \langle \Re_{i} \rangle + \rho^{-1} k_{B} \sum_{i=1}^{r} \sum_{j=1}^{r} \langle f_{j} (1 + f_{j})^{-1} \Re_{j} (f_{i} f_{j}) \rangle.$$
(2.121)

Then, on definition of  $\Gamma$  by the formula

$$\Gamma = \rho \hat{\Gamma} = k_B \sum_{j=1}^{r} \langle [1 + f_j^{-1} ln(1 - f_j)] f_j \rangle, \qquad (2.122)$$

the evolution equation for  $\hat{\Gamma}$  can be shown to be

$$\rho \frac{d\hat{\Gamma}}{dt} = -k_B \sum_{j=1}^{r} \nabla \cdot \langle \mathbf{c}_j [1 + f_j^{-1} ln(1 - f_j)] f_j \rangle - k_B \sum_{i=1}^{r} \sum_{j=1}^{r} \langle f_j (1 + f_j)^{-1} \Re_j (f_i f_j), \qquad (2.123)$$

which implies that the Boltzmann function  $\mathcal{B}_{\Gamma}$  defined by

$$\mathcal{B}_{\Gamma} = \mathcal{S} - T^{-1} \left( \varepsilon + V - \sum_{i=1}^{r} c_i \hat{\mu}_i + \sum_{i=1}^{r} \sum_{\alpha} X_i^{(\alpha)} \odot \hat{\Phi}_i^{(\alpha)} \right) + \hat{\Gamma}$$
(2.124)

obeys the same equation as (2.120b). The only difference between the boson and fermion gases is in the definition of  $\Gamma$ .

## 2.5 Nonequilibrium corrections for distribution functions

Since the thermodynamic structure is universal as we have presented earlier, it has the same form for all systems. However, calculation of physical measurable quantities requires the knowledge of dynamic interactions, namely, the differential cross sections from the kinetic theory viewpoint. In the context of the present formalism the dynamic information is contained in the unknowns  $X_i^{(\alpha)}$  and  $X_r^{(\alpha)}$ . Therefore, a complete kinetic theory should provide a method to determine  $X_i^{(\alpha)}$  and  $X_r^{(\alpha)}$  in a way consistent with thermodynamic laws. Since the Boltzmann equations cannot be solved exactly in closed analytical form, these unknown functions can only be determined approximately. The most obvious way is to substitute (2.37) and (2.40) for the distribution functions into the kinetic equations (2.1) as well as (2.5) and generate the evolution equations for  $X_i^{(\alpha)}$  and  $X_r^{(\alpha)}$ , which may be solved together with other evolution equations for macroscopic variables already presented. Since this method is very complicated, we look for another more direct method, albeit approximate. As we know the distribution function can be expanded in terms of a complete set of moments as in the conventional moment method for material gases, the same expansion is also valid for photon gas,

$$f_i = f_{ieq}(1 + \sum_{\alpha} A_i^{(\alpha)} \odot h_i^{(\alpha)}), \qquad (2.125a)$$

$$f_r = f_{req} (1 + \sum_{\alpha} A_r^{(\alpha)} \odot h_r^{(\alpha)}), \qquad (2.125b)$$

where the coeffients  $A_i^{(\alpha)}$  and  $A_r^{(\alpha)}$  are functions of macroscopic variables such as temperature, fluxes, etc. If one tries to construct a theory of irreversible processes with the forms (2.125a) and (2.125b), the attempt will be frustrated because these forms are not appropriate for calculating the entropy, entropy flux and entropy production which is always positive semidefinite. Nevertheless, it is a mathematically acceptable way of expressing the nonequilibrium distribution function. The nonequilibrium canonical form used in the modified moment method allows us to avoid the aforementioned difficulty associated with the entropy and related quantities. The nonequilibrium canonical forms and the moment expansions (2.125) share the same sets of material and photon moments. This means that the unknows  $X_i^{(\alpha)}$ and  $X_r^{(\alpha)}$  in the nonequilibrium canonical forms can be determined from (2.125) by equating them and solving the equation for the unknowns. We thereby obtain the equations:

$$k_{B}^{-1}(\Delta \bar{\mu}_{i} - \sum_{\alpha \ge 1} X_{i}^{(\alpha)} \odot h_{i}^{(\alpha)}) = \ln(1 + \sum_{\gamma \ge 1} A_{i}^{(\gamma)} \odot h_{i}^{(\gamma)})$$
(2.126*a*)

and

$$\left\{ exp[\beta(\bar{W}_r^0 + \sum_{\alpha} X_r^{(\alpha)} \odot h_r^{(\alpha)} - \mu_r)] - 1 \right\}^{-1}$$
  
=  $f_{req}(1 + \sum_{\alpha} A_r^{(\alpha)} \odot h_r^{(\alpha)})$  (2.126b)

where

$$f_{req} = \{exp(\beta \bar{W}_r^0) - 1\}^{-1}, \qquad \bar{W}_r^0 = \hbar \omega (1 + \hat{\mathbf{k}}_r \cdot \mathbf{u}/c).$$

Firstly, we consider matter part. Since the moments  $h_i^{(\alpha)}$  are chosen such that they are orthogonal in the following sense

$$\langle h_i^{(\alpha)} h_i^{(\gamma)} f_{ieq} \rangle = \delta_{\alpha\gamma} \langle h_i^{(\alpha)} h_i^{(\alpha)} f_{ieq} \rangle$$
(2.127)

 $A_i^{(\alpha)}$  can be given in terms of fluxes as follows:

$$\Phi_i^{(\alpha)} = \langle f_{ieq} h_i^{(\alpha)} (1 + \sum_{\gamma \ge 1} A_i^{\gamma)} \odot h_i^{(\gamma)}) \rangle = A_i^{(\alpha)} \odot \langle f_{ieq} h_i^{(\alpha)} h_i^{(\alpha)} \rangle.$$
(2.128)

Note that the fluxes on the left-hand side are determined from the flux evolution equations. The quantity in the angular brackets in (2.128) is a function of temperature only. This means that the coefficient  $A_i^{(\alpha)}$  is directly proportional to  $\Phi_i^{(\alpha)}$ . The calculations of the angular brackets are straightforward. We simply present the results for a few leading moments:

$$A_{i}^{(1)} = \beta \Phi_{i}^{(1)} / p_{i}, \quad A_{i}^{(2)} = 0,$$

$$A_{i}^{(3)} = \beta (8/5\rho_{i})(m_{i}/2k_{B}T)^{1/2} \Phi_{i}^{(3)},$$

$$A_{i}^{(4)} = \beta [2/n_{i}(2m_{i}k_{B}T)^{1/2}] \Phi_{i}^{(4)}.$$
(2.129a)

Then, the unknowns  $X_i^{(\alpha)}$  can be obtained from (2.125a) in terms of the coefficients  $A_i^{(\alpha)}$ . To the lowest order approximation the results are

$$X_{i}^{(1)} = -\Phi_{i}^{(1)}/2p_{i}, \quad X_{i}^{(2)} = -2\Phi_{i}^{(2)}/3p_{i} = 0,$$
  

$$X_{i}^{(3)} = -\Phi_{i}^{(3)}/p_{i}\hat{h}_{i}, \quad X_{i}^{(4)} = -\Phi_{i}^{(4)}/\rho_{i}.$$
(2.129b)

The radiation part requires fresh consideration because the distribution function is different from those for the matter part owing to the quantum nature of photons. By multiplying  $h_r^{(\alpha)}$  to (2.125b) and integrating over  $\mathbf{k}_r$ , we obtain

$$\Phi_r^{(\gamma)} = \langle f_{reg}(1 + \sum_{\alpha} A_r^{(\alpha)} \odot h_r^{(\alpha)}) h_r^{(\gamma)} \rangle.$$
(2.130)

To evaluate the integrals in (2.130), it is convenient to change the variable of integration by transformations

$$\hat{\mathbf{q}} = \hat{\mathbf{k}}_{\mathbf{r}} - \mathbf{u}/c, \qquad \mathbf{q} = (\omega/c)\hat{\mathbf{q}} + \omega\mathbf{u}/c^2.$$

Then, by using the properties of integrals of Cartesian tensors, we find that the same rules of calculation apply as for those for the matter part. It is possible to show that

$$\langle f_{req} h_r^{(\alpha)} \rangle = 0 \tag{2.131}$$

since the fluxes vanish at equilibrium. With the help of the orthogonality relation of a completed set of photon moments,

$$\langle f_{req} h_r^{(\alpha)} h_r^{(\gamma)} \rangle = \delta_{\alpha\gamma} \langle f_{req} h_r^{(\gamma)} h_r^{(\gamma)} \rangle, \qquad (2.132)$$

we find

$$A_r^{(\gamma)} \odot \langle f_{req} h_r^{(\gamma)} h_r^{(\gamma)} \rangle = \Phi_r^{(\gamma)}.$$
(2.133)

Since the integrals are functions of temperature only, the coefficients  $A_r^{(\alpha)}$  are proportional to the fluxes  $\Phi_r^{(\alpha)}$ . The calculation of these integrals is rather technical, so we simply present the results:

$$A_r^{(1)} = \beta \Phi_r^{(1)} / 0.488 \pi p_r, \qquad A_r^{(2)} = \beta \Phi_r^{(2)} / 5.196 \pi p_r,$$
  

$$A_r^{(3)} = \beta \Phi_r^{(3)} / 1.200 \pi p_r, \qquad A_r^{(4)} = 3 \Phi_r^{(4)} / n_r,$$
  

$$A_r^{(5)} = \beta \Phi_r^{(5)} / 0.523 \pi p_r.$$
(2.134)

The unknows  $X_r^{(\alpha)}$  of the radiation part can be expressed in terms of  $A_r^{(\alpha)}$ . The procedure is different from that of the matter part because of the quantum nature of photons. We will give the details. We rewrite the distribution function of nonequilibrium photon gas in the form

$$exp(-W_r) = 1 - (1 + f_r)^{-1}.$$
 (2.135)

On substitution of the canonical form for  $f_r$  into (2.135) and taking the logarithm yields the equation

$$\sum_{\alpha} X_r^{(\alpha)} \odot h_r^{(\alpha)} = \mu_r - k_B T ln \Big( \frac{1 + \sum_{\alpha} A_r^{(\alpha)} \odot h_r^{(\alpha)}}{1 + exp(-\beta \bar{W}_r^0) \sum_{\alpha} A_r^{(\alpha)} \odot h_r^{(\alpha)}} \Big).$$

Multiplying  $h_r^{(\gamma)}$  and  $f_{req}$  and integrating over  $\mathbf{k}_r$ , we obtain

$$X_{r}^{(\alpha)} \odot \langle f_{req} h_{r}^{(\gamma)} h_{r}^{(\gamma)} \rangle$$
  
=  $-k_{B}T \langle f_{r} h_{r}^{(\gamma)} ln \Big( \frac{1 + \sum_{\alpha} A_{r}^{(\alpha)} \odot h_{r}^{(\alpha)}}{1 + exp(-\beta \bar{W}_{r}^{0}) \sum_{\alpha} A_{r}^{(\alpha)} \odot h_{r}^{(\alpha)}} \Big) \rangle.$  (2.136)

Approximate results for  $X_r^{(\alpha)}$  can be obtained by expanding the logarithmic function. To the lowest order approximation, we find

$$X_r^{(\alpha)} = -k_B T A_r^{(\alpha)}. \tag{2.137}$$

The second order and high order approximations may be evaluated by an iterative method. To the lowest order approximation, the unknowns  $X_r^{(\alpha)}$  for radiation are given by

$$X_{r}^{(1)} = -\Phi_{r}^{(1)}/0.488\pi p_{r}, \qquad X_{r}^{(2)} = -\Phi_{r}^{(2)}/5.196\pi p_{r},$$

$$X_{r}^{(3)} = -\Phi_{r}^{(3)}/1.200\pi p_{r}, \qquad X_{r}^{(4)} = -3\beta \Phi_{r}^{(4)}/n_{r},$$

$$X_{r}^{(5)} = -\Phi_{r}^{(5)}/0.523\pi p_{r}. \qquad (2.138)$$

These approximate results (2.129b) and (2.138) for  $X_i^{(\alpha)}$  and  $X_r^{(\alpha)}$  are essential for calculating the dissipative terms  $\Lambda_i^{(\alpha)}$  and  $\Lambda_r^{(\alpha)}$ , etc., whose first order cumulant approximants have already been presented earlier. The dissipation terms thus calculated, the macroscopic evolution equations (2.53a)-(2.53e) and (2.57a)-(2.57d) are closed and solutions can be obtained from them, subject to initial and boundary conditions appropriate for the hydrodynamic problem in hand. We will call these coupled partial differential equations the generalized hydrodynamic equations of radiation of 1 matter. The macroscopic variables which are necessary for describing the irreversible processes in question, of course, appear in the entropy balance equation. Therefore, the solutions of the generalized hydrodynamic equations must be subject to the entropy balance equation. In the sense that the entropy production  $\sigma$  is positive semidefinite, that is,  $\Lambda_i^{(\alpha)}$  and  $\Lambda_r^{(\alpha)}$  are such that  $\sigma \geq 0$ , the generalized hydrodynamic equations fully conform with the second law of thermodynamics. Under the present formalism of kinetic theory, one of the remaining tasks in macroscopic physics is hydrodynamic and thermodynamic. It requires solution of the generalized hydrodynamic equations and study of irreversible thermodynamic relations between various macroscopic properties. Of course, calculation of the transport coefficients is another task. We will discuss these issues in later sections.

## 2.6 Discussion and concluding remarks

A nonrelativistic kinetic theory for a system consisting of photons and material particles which interact with each other is formulated. Instead of the conventional equation of radiation energy transfer we have proposed a semiclassical Boltzmann equation for photons which is coupled to the Boltzmann equations for material particles. In this theory, the system of matter and radiation is viewed as a gaseous mixture of material particles and photons. The advantage of this consideration is in formulating irreversible thermodynamics of matter and radiation on equal footing and in a unified manner. The kinetic theory enables us to show that the Planck distribution function for equilibrium radiation is consistent with the Boltzmann distribution function for material particles and that they are unique. Furthermore, the mathematical structure of irreversible thermodynamics and the radiation hydrodynamic equations in a rather general form, namely, the generalized hydrodynamic equations for matter and radiation, have been derived. In addition, the present theory shows that instead of the extended Gibbs relation used for  $d_iS$  in the local equilibrium assumption approach there exists the compensation differential  $d_t\Psi$ , which plays the same role as the entropy density in the local equilibrium approach and reduces to  $d_t S$  at equilibrium. With the compensation differential we may introduce the Boltzmann function such that a local form of H theorem is obtained. By solving the evolution equations for fluxes such as radiation stress tensor, radiation heat flux, etc., the radiative transport coefficients can be computed even if the system is removed far away from equilibrium since the modified moment method exceeds the limit of validity of the first-order Chapman-Enskog theory [18] for solving the Boltzmann equation.

The local H theorem (2.120b) for  $\mathcal{B}$  and the calculation of the compensation differential is exact within the nonrelativistic kinetic framework since no approximation is made for the involved equations and the related quantities. This means that the extended Gibbs relation for the entropy density does not hold valid, at least from the kinetic theory viewpoint, for the systems away from equilibrium unless there occur some special circumstances in which  $\aleph = 0$  identically. These particular cases include the equilibrium state itself and linear irreversible processes which can be described by linear force-flux relations.

In equilibrium statistical mechanics of Gibbs, an exact but formal theory is developed for equilibrium thermodynamics in terms of partition functions or an equilibrium distribution function, and various thermodynamic functions and relations thereof are calculated. In the present formalism, a comparable formal theory is attained for nonequilibrium processes described by a set of Boltzmann equations, and the unknows  $X_i^{(\alpha)}$  occupy the place of the partition function in equilibrium statistical mechanics which must be computed explicitly in terms of temperature, density, and other system parameters. Thus, we have in essence acquired a formal theory of irreversible processes comparable to equilibrium statistical thermodynamics of Gibbs.

The moment method used here for radiation has a feature in common with the spherical harmonics approximation [43] for the radiation energy transfer equation,

but the use of the H theorem and an exponential form (2.40) for the distribution function of photons is a distinctive feature that has important consequences in the quest for a mathematical theory of irreversible processes in a system of radiation and matter. It makes the present formalism fill up the lacunae left at the level of irreversible thermodynamics by the existing theories of radiative energy transfer. The most important aspect of the modified moment method is capable of treating nonequilibrium processes occurring far from equilibrium. Therefore, it is reasonable to expect that the theory presented here for radiation and matter holds valid far from equilibrium. Applications of the theory to realistic problems and comparing with experiments are the only way to justify the theory. We will present the result of applying the generalized hydrodynamic equations of radiation and matter to the experiment of light-induced viscous flow in the next chapter.

Finally, we remark that a nonrelativistic approximation is made for photons in the calculations of  $X_r^{(\alpha)}$  and  $J_s^{(r)}$  and in the energy balance equation since we have neglected some small terms of the order  $(u/c)^2$  and higher. Such an awkward feature will disappear if the theory is formulated in a Lorentz covariant form by using relativistic Boltzmann equation. We will present such a study in chapter 5. Our original intention was to have a practicable theory which suitably describes irreversible thermodynamics of systems consisting of atoms (or molecules) and photons. Since atoms (or molecules) move very slowly compared with photons, a nonrelativistic theory is physically acceptable. We believe that the theory presented provides an internally consistent mathematical structure with which to study kinetic theory and irreversible thermodynamics of radiation and matter from a molecular viewpoint.

#### Chapter 3

# Application of the kinetic theory of radiation and matter to the light-induced viscous flow

The irreversible thermodynamics of radiation and matter which is derived from the kinetic theory can cover a broad range of natural phenomena. In this chapter we will present an application of the kinetic theory of radiation and matter presented in the previous chapter to the light-induced kinetic effects [29]. In recent years, laser has been successfully used to manipulate atoms and molecules, or trap them in a volume, or cool a gas [13]. Under the theme of light-induced kinetic effects [14] a number of intriguing experiments have been reported on the action of laser on atoms and molecules. By tuning a narrow-band laser within a Doppler-broadened absorption line of an atomic or molecular gas and inducing velocity-selective excitations of atoms or molecules by means of the Doppler effect, it has been possible to produce macroscopic drifts of particles. These drifts give rise to a number of interesting effects such as an optical piston [24], light-induced viscous flow arising from collisions in the bulk [22] and with the surface [25], etc.

The light-induced kinetic effects are distinguished from those originating from the photon pressure. They are in fact much larger than the latter in magnitude since collisions between the matter particles are intimately related to them and momentum transfer by matter particles are much larger than that by photons. Since the basic physical cause for the velocity drift has been discussed by various authors [9, 44] since the work by Gel'mukhanov and Shalagin [14], we will not dwell on it here. It is interesting to see that light-induced kinetic effects are in essence an outcome of the combination of gas kinetic effects and laser spectroscopy which seem, until recently, to be unrelated fields. In this chapter we present a theory of lightinduced viscous flow in a gas and compare theoretical results with the experiment
by Hoogeveen et al. [22]. The purpose of doing these is twofolds. First of all, it serves as an experimental justification of the kinetic theory of radiation and matter presented in the previous chapter. Secondly, the low pressure behavior of the lightinduced viscous flow has not been explained theoretically. It is necessary to have a theory to better account for the experimental results.

### 3.1 Light-induced viscous flow

More specifically, in 1989 Hoogeveen et al. [22] reported on an experimental result which demonstrated a gas flow induced in a capillary by a Doppler-broadened laser beam. The profile of the laser beam is assumed to be cylindrically symmetric but radially distributed such that the highest intensity is at the center of the tube. The flow generates a pressure difference and a stress in the capillary. By measuring the pressure difference which the flow produces in the capillary by a differential manometer and plotting it against the gas pressure, they were able to show that the normal pressure regime behavior follows the classical Navier-Stokes theory prediction, namely, the Hagen-Poiseuille volume flow rate which accounts for the flow rate of a gas through a tube under a pressure gradient when the pressure is in the normal range. In fact, the linear constitutive relation between the pressure tensor and the velocity gradient has been used in order to obtain the Hagen-Poiseuille volume flow rate. Therefore, it can not be true for nonlinear flow problems. The experiment by Hoogeveen et al. shows that as the pressure is decreased down to the rarefied gas regime, the curve for the pressure difference vs. pressure starts to decrease in a sharp deviation from the Hagen-Poiseuille theory prediction. In other words, there appears a maximum in the curve at some low pressure. This behavior has remained unexplained until now. Let us briefly present the theory of Hoogeveen et al. in an attempt to understand light-induced viscous flow in a one-component molecular gas.

The light-induced kinetic effects are the consequences of the combination of velocity-selective excitations and state-dependent collisions. A traveling laser beam, the frequency of which is slightly tuned off resonance, excites those atoms which are Doppler shifted into resonance; the excitation is thus velocity selective. A hole appears in the ground-state velocity distribution of the absorbing atoms, whereas a peak appears in the excited-state distribution. This results in antiparallel fluxes of excited and ground-state atoms. In the absence of buffer gas these two fluxes cancel because of the momentum conservation law. However, this will not be the case when the atoms are embedded in a buffer gas. In that situation velocity-changing collisions will tend to thermalize the velocity distributions. Since an excited atom usually has a larger collision cross section than a ground-state atom, the average velocity of the excited-state atoms. As a result, the optically active atoms acquire a net drift velocity opposite to that of the Doppler-selected velocity.

The light-induced drift can also happen in a one-component molecular gas where intermolecular collisions dominate. This is the so-called light-induced viscous flow [22]. It seems somewhat unexpected that in a pure gas such the effect happens. The light-induced viscous flow is due to the fact that the combination of a statedependent collision cross section and nonuniform illumination produces stresses in the gas which give rive to a particle flow.

An elementary picture of the light-induced viscous flow is following. Excited particles in the boundary layer near the wall have suffered their last collision, when they are in the range of  $\bar{l}_e$  from the wall whereas the ground state particles collide with the wall at a distance of  $\bar{l}_g$  where  $\bar{l}_e$  and  $\bar{l}_g$  are the mean free path of the excited state particle and the ground state particle, respectively. Since  $\bar{l}_g > \bar{l}_e$ , the excited state particles are located in a relatively dark region of the tube in ground state particles which are in a light regime. Therefore, the peak in the excitedstate distribution is smaller than the dip in the ground-state distribution because of the nonuniformity of the laser intensity. Consequently, the total distribution function of ground state particles and the excited state particles have a dip around the Doppler-selected velocity  $v_0 = (\omega_l - \omega_0)/k_l$  mentioned earlier. This means that there is a net parallel momentum transfer to the wall. As a result, a net particle flow appears in the moving direction of the excited particles whose cross section is larger than that of the ground state particles. Moreover, this process is not confined to the boundary layer. In the same elementary mean-free-path picture, each layer of gas transfers momentum to the adjacent layer closer to the wall. This will produce a stress in the gas, therefore a particle flow in the bulk of the gas.

In the theoretical description of this phenomenon, two-level model for molecule is assumed. For simplicity, the homogeneous linewidth of the transition will be considered to be very small so that only molecules having a velocity very close to the Doppler-selected velocity  $v_0$  are excited by a narrow-band laser. To analyze the gas flow, Hoogeveen et al. used a modification of the Chapman-Enskog method in which the distribution function is expanded around a Maxwellian distribution of the gas in equilibrium with the wall of the tube:

$$f_{eq}(\mathbf{v}) = n(m/2\pi k_B T)^{3/2} exp(-mv^2/2k_B T)$$
  
=  $ng_{eq}(v_x)g_{eq}(v_r)g_{eq}(v_{\phi}),$  (3.1a)

where

$$g_{eq}(v_i) = (m/2\pi k_B T)^{1/2} exp(-mv_i^2/2k_B T).$$
(3.1b)

Since the velocity-selective excitation can make a hole in the ground state of a molecule and create a peak in the excited state, the approximation for the distribution function must take care of both the Chapman-Enskog correction terms and the Bennett dip and peak [22]. In the scheme of linear approximation, one may write the distribution functions for the ground and excited states as follows:

$$f_g(\mathbf{v}) = f_{eq}(\mathbf{v}) \left[ 1 + \Phi - A(r, v_r) \delta(v_z - v_0) \right], \qquad (3.2)$$

$$f_e(\mathbf{v}) = f_{eq}(\mathbf{v})B(r, v_r)\delta(v_z - v_0). \tag{3.3}$$

Here, laser propagation direction is taken as z-axis,  $\Phi$  is the Chapman-Enskog correction term while  $A(r, v_r)$  and  $B(r, v_r)$  denote the ground-state Bennett dip and the excited-state peak, respectively. After solving the Boltzmann equation, it is possible to get

$$A(r,v_r) = \frac{P(r)}{\nu_g} - \frac{v_r}{\nu_g^2} \frac{dP(r)}{dr},$$
(3.4)

to the linear order of  $v_r$ , and similarly for B. With the distribution function calculated, the stress is given by

$$\Pi_{zr} = -\eta_0 \frac{du(r)}{dr} + nk_B T v_0 g_{eq}(v_0) \Big[ \frac{1}{\nu_g^2} - \frac{1}{\nu_e^2} \Big] \frac{dP(r)}{dr}.$$
(3.5)

Here  $\eta_0$  is shear viscosity,  $\nu_g$  and  $\nu_e$  are the collision frequency of ground-state and excited-state in BGK model [18], u(r) is the velocity profile and P(r) accounts for the probability rate of the radiative-excitation process. Since under hydrodynamic conditions the flow velocity vanishes at the wall [u(R) = 0], one finds

$$u(r) = \frac{1}{2}\pi v_0 \frac{\Delta \nu}{\nu} \left[ \frac{n_e(r)}{n} - \frac{n_e(R)}{n} \right]$$
(3.6)

where the number density  $n_e$  of excited molecules is given by

$$n_{\epsilon}(r) = nP(r)g_{\epsilon q}(v_0)/\nu.$$
 (3.7)

Since  $\nu_e$  differs little from  $\nu_g$ ,

$$\nu_g^{-2} - \nu_e^{-2} \approx 2(\nu_e - \nu_g)/\nu^3 \equiv 2\Delta\nu/\nu^3.$$

On the other hand, the flow of particle in a closed tube gives rise to a pressure difference  $\delta p$  along the tube. This pressure difference will generate a pipe flow which may be described by the Hagen-Poiseuille volume flow rate:

$$Q_{HP} = \frac{\pi R^4}{8\eta_0 L} \delta p. \tag{3.8}$$

Here, L is the length of the capillary, R is the radius of the capillary and  $\delta p$  is the pressure difference at ends of the capillary.

According to the experimental arrangement, the light-induced flow has to be balanced by the Poiseuille back flow:

$$\int_0^R dr 2\pi r u(r) - \frac{\pi R^4}{8\eta_0 L} \delta p = 0.$$
 (3.9)

From this equation it may seem that explicit knowledge about the laser-beam profile (or more precisely, the excitation profile) is required. However, if it is assumed that the excited-state fraction near wall approaches zero,  $\delta p$  can be expressed in terms of the excited-state fraction  $\bar{n}_e/n$  averaged over the tube cross section, since both contain an integration over the same radial dependence. With the assumption  $n_e(R) = 0$  one arrives at

$$\frac{\delta p}{p} = 16 \frac{L}{R} \frac{\bar{l}}{\bar{R}} \frac{v_0}{\bar{v}} \frac{\Delta \nu}{\nu} \frac{\bar{n}_e}{n}, \qquad (3.10a)$$

where

$$\frac{\bar{n}_{e}}{n} = \frac{1}{\pi R^{2}} \int_{0}^{R} dr 2\pi r \frac{n_{e}(r)}{n}, \qquad (3.10b)$$

and  $\bar{v} = \nu \bar{l} = (8k_B T/\pi m)^{1/2}$  is the mean thermal speed. The theoretical result and experimental data have been shown in the Fig. 1. It is clear to see that in the near-hydrodynamic pressure regime,  $p \ge 40$  Pa or Knudsen number  $N_k = \frac{\bar{l}}{R} \le \frac{1}{8}$ , the values of  $(\delta p_m/p)/(\bar{n}_e/n)$  are found to be inversely proportional to the pressure, which is expected from (3.10a) because of  $\bar{l} \propto p^{-1}$ . Unlike in the hydrodynamic pressure regime, the Hagen-Poiseuille prediction completely fails for the low-pressure data ( $p \leq 20$  Pa or  $N_k \geq 0.25$ ). The physical reason will be found in the following sections.

#### 3.2 The Knudsen problem

M. Knudsen [26] in 1909 observed that the volume flow rate of a gas through a capillary under a pressure difference increases as the pressure diminishes below a value into the rarefield gas regime, in contrast to the classical Navier-Stokes theory prediction that the flow rate should vanish. Therefore, there is a minimum value of  $Q_k$  at a nonzero value of pressure p as shown in Fig. 2. Knudsen was able to fit his experimental data for the volume flow rate per unit pressure difference  $Q_k$  to the empirical formula [26]:

$$Q_k = a_1 p + a_2 \frac{1 + c_1 p}{1 + c_2 p} \tag{3.11a}$$

where

$$a_1 = \pi R^4 / 8L\eta_0, \quad a_2 = 4\sqrt{2\pi}R^3 / 3L\sqrt{\rho_1},$$
 (3.11b)

and  $c_1$  and  $c_2$  are numerical constants;  $\rho_1$  is the specific density of the gas at temperature T when the pressure is equal to  $1 \ dyn/cm^2$ . Since this was reproducible [27] but not possible to explain by the classical Navier-Stokes theory, the phenomenon was called the Knudsen paradox. It is not a paradox, but an indication of the inadequacy of the Navier-Stokes theory which cannot properly handle flows of gases in the range of large Knudsen numbers ( $\approx 0.1$  typically or larger).

The Knudsen problem was studied theoretically in the case of plane Poiseuille flow [45, 46]. Since experiments were performed in a circular-tube flow geometry, it was not possible to compare the aforementioned theoretical results with experimental results, but their results predicted the existence of a minimum in the volume flow rate. The BGK kinetic equation was used to the plane Poiseuille flow geometry and subjected to the slip boundary conditions in ref. [45, 46]. There is, however, no theoretical study available for the problem in a circular-tube flow geometry.

Recently the Knudsen problem has been explained adequately by using the generalized hydrodynamic theory [28]. The basic physical reason for the phenomenon is that as the gas density diminishes, the mean free path in the gas becomes very long, thus the range of momentum transfer becomes accordingly long, and as a consequence, the gas behaves as if it is a non-Newtonian fluid in the sense that the viscosity of a rarefied gas depends on the shear rate. Such a fluid has a vanishing viscosity at the wall of the tube which results in a plug flow. The ultimate consequence of this is that a non-energy-dissipating collimated beam is formed in the capillary at low pressure and thus the molecules move axially and ballistically along the tube under a pressure difference.

It is assumed that a fluid is laminarly flowing in a circular tube of length Land radius R, subject to a longitudinal pressure gradient. The pressure difference between the entrance and exit of the tube is denoted by  $\delta p = p_i - p_f$  where  $p_i$  and  $p_f$  are the pressure at the entrance and exit of the tube, respectively. The fluid is maintained at a constant uniform temperature and therefore there is no heat flux. The generalized hydrodynamic equations are given by (2.53a)-(2.53e),

$$\frac{\partial}{\partial t}\rho = -\nabla \cdot \rho \mathbf{u},\tag{3.12}$$

$$\rho \frac{d}{dt} \mathbf{u} = -\nabla p - \nabla \cdot \mathbf{\Pi}, \qquad (3.13)$$

$$\rho \frac{d}{dt} \hat{\boldsymbol{\Pi}} = -2p[\nabla \mathbf{u}]^{(2)} - (p/\eta_0) \boldsymbol{\Pi} q_e(\kappa).$$
(3.14)

Since the flow is assumed to be in a steady state, time derivatives are set equal to zero. Considering the symmetry properties of circular-tube flow, the generalized hydrodynamic equations in the cylindrical coordinates are reduced to

$$\frac{\partial}{\partial r}(\rho r u_r) = 0 \tag{3.15a}$$

$$\frac{\partial p}{\partial z} + \frac{1}{r}\frac{\partial}{\partial r}r\Pi = 0$$
(3.15b)

$$\Pi q_{\epsilon}(\Pi) = -2\eta_0 \gamma \tag{3.16}$$

where

$$q_e(\Pi) = \sinh(\kappa)/\kappa, \tag{3.17}$$

$$\kappa = \tau \Pi / \eta_0, \tag{3.18}$$

$$\tau = [2\eta_0 (m_r k_B T/2)^{1/2}]^{1/2} / \sqrt{2} n k_B T \sigma, \qquad (3.19)$$

$$\gamma = \frac{1}{2} (\partial u_z / \partial r), \qquad (3.20)$$

with  $\eta_0$  denoting the Chapman-Enskog (Newtonian) shear viscosity,  $m_r$  and  $\sigma$  the reduced mass and the size parameter of molecule. It is easy to find the velocity profile by solving (3.12)-(3.14) as follows:

$$u_z(r) = (R/\tau\theta)[\cosh\theta - \cosh(\theta r/R)]$$
(3.21)

where

$$\theta = \tau R \delta p / 2L \eta_0. \tag{3.22}$$

The velocity profile (3.21) reduces to the well-known Hagen-Poiseuille velocity profile

$$u_z(r) = \frac{\delta p}{4L\eta_0} (R^2 - r^2)$$
 (3.23)

as the parameter  $\theta$  gets small.

The volume flow of particles in the tube in unit time is given by the formula

$$Q_0(\delta p) = 2\pi \int_0^R dr r u_z(r). \tag{3.24}$$

By substituting the velocity profile (3.21) and performing the integration, we obtain

$$Q_{0}(\delta p) = (2\pi/\tau\theta) [\frac{1}{2} \cosh\theta + \theta^{-2} (\cosh\theta - 1) - \theta^{-1} \sinh\theta]$$
  
=  $\frac{\pi R^{4} \delta p}{8L\eta_{0}} (1 + \delta Q)$   
=  $Q_{HP}(1 + \delta Q)$  (3.25)

where

$$\delta Q = 8\theta^{-2} \left[ \frac{1}{2} \cosh\theta + \theta^{-2} (\cosh\theta - 1) - \theta^{-1} \sinh\theta \right] - 1$$
 (3.26)

and

$$Q_{HP} = \frac{\pi R^4 \delta p}{8L\eta_0}.$$
(3.27)

Since  $\tau$  is inversely proportional to p, so is  $\theta$ . Therefore,  $\delta Q$  vanishes as  $\theta \to 0$  and thus Q becomes a linear function of p in this limit, that is,  $Q_0(\delta p)$  is reduced to  $Q_{HP}$  which predicts  $Q_{HP} = 0$  at p = 0. This is contradictory with the experiments by Knudsen [26] and Gaede [27]. It is easy to see that the formula (3.25) has an asymptotic behavior as

$$Q_0(\delta p) \to pexp(\theta_0/p) \quad as \quad p \to 0$$

where

$$\theta_0 = p\theta = \tau_0 R\delta p/2L\eta_0,$$
  
$$\tau_0 = [2\eta_0 (m_r k_B T/2)^{1/2}]^{1/2}/\sqrt{2}\sigma.$$

The minimum value of  $Q_0(\delta p)$  can be determined by the equation:

$$\frac{d}{d\theta} \{ \theta^{-3} [\frac{1}{2} \cosh\theta + \theta^{-2} (\cosh\theta - 1) - \theta^{-1} \sinh\theta] \} = 0$$

it is the transcendental equation for  $\theta_m$  at the minimum

$$\theta_m(10+\theta_m^2)sinh\theta_m - 5(2+\theta_m^2)cosh\theta_m + 10 = 0$$

the approximate solution of this equation is

$$\theta_m \approx 2.30$$

therefore the pressure at the minimum is given by

$$p_m = \theta_0 / \theta_m.$$

The basic reason for the appearance of the minimum is that the effective viscosity diminishes as the parameter  $\theta$  increases, and thereby the gas density or the mean pressure decreases. The Navier-Stokes equation does not have a mechanism for a diminishing viscosity, and the absence of such a mechanism is the reason for the Hagen-Poiscuille result being in variance with experiment at low pressure. By introducing  $Q(p) - Q_0(\delta p)p/\delta p$ , we obtain a formula for Q(p) from (3.25), (3.26) and (3.27):

$$Q(p) = \frac{\pi R^4}{8L\eta_0} 8(\theta_0/p)^{-2} \{ \frac{1}{2} \cosh(\theta_0/p) + (\theta_0/p)^{-2} [\cosh(\theta_0/p) - 1] - (\theta_0/p)^{-1} \sinh(\theta_0/p) \} p.$$
(3.25')

The theoretical result based on the (3.25') for  $\theta_0 = 0.1$  and the experimental result are shown in Fig. 2.

There is, however, a difference between the theoretical result and the experimental data at very low pressure regime as shown in in Fig. 2 although the theoretical result is qualitatively correct. The physical reason is that in the calculation of the flow rate Q we have used the lowest order approximation for the nonequilibrium distribution function which may not suitably describe the systems far away from equilibrium. The higher order approximations for the nonequilibrium distribution can be evaluated in the scheme of the modified moment method [47] but that makes the analytic calculation of the flow rate impossible. Here we present a semiempirical approach which can improve the behavior of the flow rate in the very low pressure regime. This can be done by changing the p in (3.25') to p' = p + 0.02. The result for the flow rate Q'(p') is has been shown in the Fig. 3 which gives better fitting to the experimental data.

#### 3.3 Theory of light-induced viscous flow in a gas

The kinetic theory of photons and material particles given in the previous

chapter yields a set of the generalized hydrodynamic equations and lays the kinetic theory foundation for a theory of irreversible thermodynamics of radiation and matter. The basic idea of the theory developed here has been applied by van Enk and Nienhuis [30] to analyze some irreversible processes in connection with the lightinduced kinetic effects. Here we apply the generalized hydrodynamic equations to study the experimental result by Hoogeveen et al. [22].

Since the experiment was done in a single-component gas under the condition of a uniform temperature, it is sufficient to consider only the stress evolution equations together with the momentum and mass balance equations. In the case of the flow geometry and condition for the experiment, the mass balance equation is trivially integrated and thus does not play a significant role in solving the generalized hydrodynamic equations. We assume that the molecule has only two internal states, and treat the molecules of different internal states as different species. This treatment is reasonable since the excited molecules interact with slightly different cross sections from the ground state molecules and thus are distinguishable. Therefore, there are three species in the system, because the photons are treated as another species in the aforementioned kinetic theory of radiation and matter [17]. Since the radiated system is in a stagnant state and thus any deviation from equilibrium is initially small, it is appropriate to take linearized stress evolution equations (2.53e) and (2.57d) for  $\alpha = 1$ 

$$\rho \frac{d}{dt} \hat{\Pi}_a = -2p_a \underline{\gamma} - \sum_{b=1}^r p_a \mathcal{R}_{ab} \Pi_b, \qquad (3.28)$$

where the subscript *a* denotes the species 1, 2, and *r*, *r* being reserved for the photon,  $\Pi_a = \rho \hat{\Pi}_a$  is the shear stress tensor,  $\underline{\gamma} = [\nabla \mathbf{u} + (\nabla \mathbf{u})^t]/2 - \mathbf{U}\nabla \cdot \mathbf{u}/3$ , **u** being the hydrodynamic velocity and **U** the unit tensor, and the summation in (3.28) runs over 1, 2, and *r*. The coefficients  $\mathcal{R}_{ab}$  are related to the collision bracket

integrals  $R_{ab}$  as follows:

$$\mathcal{R}_{ab} = (2\beta g p_a p_b)^{-1} R_{ab} \tag{3.29a}$$

with  $\beta = 1/k_B T$  and g denoting the parameter defined in the previous chapter. Considering the symmetry of the flow geometry, (3.29a) can be reduced to the scalar form (one component):

$$\rho \frac{d}{dt} \hat{\Pi}_a = -2p_a \gamma - \sum_{b=1}^r p_a \mathcal{R}_{ab} \Pi_b \tag{3.29b}$$

where  $\Pi_a = \rho \hat{\Pi}_a$  is a nonvanishing component of  $\Pi_a$ ,  $\gamma = \frac{1}{2} [\partial u_z(r) / \partial r]$ , and  $u_z(r)$  is z-component of the hydrodynamic velocity.

Since the experiment was performed under a steady state condition, it is sufficient to consider the steady-state form of (3.29b):

$$2p_1\gamma + p_1(\mathcal{R}_{11}\Pi_1 + \mathcal{R}_{12}\Pi_2 + \mathcal{R}_{1r}\Pi_r) = 0,$$
  

$$2p_2\gamma + p_2(\mathcal{R}_{21}\Pi_1 + \mathcal{R}_{22}\Pi_2 + \mathcal{R}_{2r}\Pi_r) = 0.$$
 (3.30)

Solving this equation for  $\Pi_1$  and  $\Pi_2$  and adding them up, we obtain

$$\Pi = \Pi_1 + \Pi_2 = -2\eta_0\gamma + \Pi_L \tag{3.31}$$

where  $\eta_0$  is the shear viscosity of the gas which can be expressed in terms of the collision bracket integrals in the scheme of the present kinetic theory,

$$\eta_0 = (\mathcal{R}_{11} + \mathcal{R}_{22} - 2\mathcal{R}_{12}) / (\mathcal{R}_{11}\mathcal{R}_{22} - \mathcal{R}_{12}^2)$$
(3.32)

and

$$\Pi_L = -[\mathcal{R}_{1r}(\mathcal{R}_{22} - \mathcal{R}_{12}) + \mathcal{R}_{2r}(\mathcal{R}_{11} - \mathcal{R}_{12})](\mathcal{R}_{11}\mathcal{R}_{22} - \mathcal{R}_{12}^2)^{-1}\Pi_r.$$
(3.33)

The  $\Pi_L$  is the stress generated by the laser and is proportional to the light intensity which is distributed radially across the cross section of the capillary. According to the experimental arrangement, the flow generated by the light is exactly balanced by the opposing flow due to the pressure difference in the differential manometer, the matter part of the stress is equal to zero. Therefore, we obtain form (3.31)

$$2\eta_0\gamma = \Pi_L. \tag{3.34}$$

Adopting this equation to the geometry of the flow and integrating the resulting equation where  $\gamma = \frac{1}{2} [\partial u_z(r) / \partial r]$ , we obtain the radial velocity profile in the capillary

$$u_z(r) = \eta_0^{-1} \int_R^r dr \Pi_L(r).$$
 (3.35)

Therefore, the flow rate of the gas in the capillary is given by

$$Q(I) = 2\pi \int_0^R dr r u_z(r) = 2\pi \eta_0^{-1} \int_0^R dr r \int_R^r dr' \Pi_L(r')$$
  
=  $\pi \eta_0^{-1} \int_R^0 dr r^2 \Pi_L(r).$  (3.36)

We may rewrite this integral in the form

$$\pi R^3 \nu \bar{n}_e / n = \pi \eta_0^{-1} \int_R^0 dr r^2 \Pi_L(r)$$
 (3.37)

where  $\nu$  is a parameter of dimension of inverse time related to the collision frequency defined in terms of the collision bracket integrals (this  $\nu$  can be easily identified from (3.37).),  $\bar{n}_e$  the density of the excited species, and n is the total density. The parameter  $\nu$  can be evaluated explicitly, but since we are interested only in the pressure dependence of the flow rate, it will be sufficient to treat it as a semiempirical parameter as was done for equivalent parameter in the work of Hoogeveen et al. [22]. Balancing the laser-generated flow with a pressure difference in a differential manometer is equivalent to opposing the flow with another flow generated by the same pressure difference in the absence of light. Therefore, Q(I) may be equated to the flow rate arising from a pressure difference in the same flow geometry. Such a flow rate is given in the previous chapter in connection with the Knudsen problem. The flow rate  $Q_0$  of a gas through a capillary under a pressure difference was shown to be

$$Q_{0}(\delta p) = (2\pi/\tau\theta) \left[\frac{1}{2}\cosh\theta + \theta^{-2}(\cosh\theta - 1) - \theta^{-1}\sinh\theta\right]$$
$$= Q_{HP}(1 + \delta Q). \tag{3.38}$$

Here  $Q_{HP}$  is the Hagen-Poiseuille flow rate. It is clear that  $Q_0(\delta p)$  approaches  $Q_{HP}$ as  $\theta$  tends to zero, namely, in the Navier-Stokes theory limit. The expression for  $Q_0(\delta p)$  has been used to explain the Knudsen problem. Now, by equating  $Q_0(\delta p)$ with Q(I), we obtain

$$\pi R^3 \nu \bar{n}_e/n = (2\pi/\tau\theta) [\frac{1}{2} \cosh\theta + \theta^{-2} (\cosh\theta - 1) - \theta^{-1} \sinh\theta].$$
(3.39)

This equation can be solved for  $\delta p$ . It may solved by an iterative method. By taking the lowest order approximation by putting  $\delta Q = 0$ , we obtain

$$(\delta p/p)_0 = (8L\eta_0 \nu/R)(\bar{n}_e/n)/p \equiv C/p$$
 (3.40)

where

$$C = (8L\eta_0\nu/R)(\bar{n}_e/n).$$

The relation (3.40) is the classical hydrodynamic result given by Hoogeveen et al. It is a linear relationship between  $(\delta p/p)_0/(\bar{n}_e/n)$  and  $p^{-1}$  as observed in their experiment [22] in the normal pressure regime. By using this result as the zeroth iterate and substituting it into (3.39), we obtain the first iterate:

$$(\delta p/p)_1 = \frac{1}{4}Cb^4 \{b^2 p^3 \sinh^2(b/2p) + p^3 [b\cosh(b/2p) - 2p\sinh(b/2p)]^2\}^{-1} \quad (3.41)$$

where

$$b = [\eta_0 (mk_B T/2)^{1/2}]^{1/2} (RC/2L\eta_0 \sigma).$$
(3.42)

This process of iteration can be continued and the sequence rapidly converges. Therefore, the first iterate is found sufficient in practice. The formula (3.41) is our main theoretical result. The subscript 1 will be dropped from  $(\delta p/p)_1$ . We now test this formula against the experimental data by Hoogeveen et al. [22]. Using the parameters specified for the experiment [22] and fixing the constant C with a data point in the high pressure regime, the pressure difference is calculated as a function of p by using (3.41). The result is shown in Fig. 4. In the normal pressure (high pressure) range this formula reduces to the formula derivable from the Hagen-Poiseuille flow rate and gives an inverse pressure dependence. As the pressure is reduced to the rarefied gas regime, the nonlinear contribution in (3.41) becomes dominant and  $\delta p/p$  begins to diminish after a certain value of p, producing a maximum. However, the  $\delta p/p$  decreases too fast in the very low pressure regime, compared with the experimental data. This may be attributed to the fact  $Q_0(\delta p)$ has been calculated to an approximation by using a lower-order approximate distribution function. It is possible to improve the distribution function by including the higher order approximation, but such a distribution function would not allow an analytic form for  $Q_0(\delta p)$ . In view of this situation, we may take a semiempirical approach by introducing a parameter in (3.41). We find that if p in (3.41) is replaced with p' = p + 3.7, the formula performs much better. Namely, we take instead of (3.41) the following formula:

$$\delta p/p = \frac{1}{4}Cb^4 \{b^2(p+3.7)^3 sinh^2[b/2(p+3.7)] + (p+3.7)^3 \times [bcosh(b/2(p+3.7)) - 2(p+3.7)sinh(b/2(p+3.7))]^2\}^{-1}.$$
 (3.43)

The  $\delta p/p$  value computed with this formula is plotted against p in Fig. 5 which shows an excellent fitting of the experimental data over the entire range of pressure studied. Notice that the maximum position, which is around p = 20 Pa, remains almost unchanged by this shift in p to p'.

The present theoretical result is a product of a combination of the kinetic theory of radiation and matter [17] and the kinetic theory of rarefied gases [28], each of which gives rise to a set of generalized hydrodynamic equations that may be solved appropriately, given the boundary and initial conditions. Especially, in the case of the latter kinetic theory and generalized hydrodynamics one does not need the conventionally used slip boundary conditions since the nonlinear transport processes take care of the slip phenomena, as is evident from the Knudsen problem which is adequately resolved [28] without resorting to the slip boundary conditions. Therefore, the present theory, as an application of the kinetic theory of radiation and matter, not only provides the theoretical explanation of the light-induced kinetic effect observed by Hoogeveen et al. [22] but also provides another credible evidence that the generalized hydrodynamic theory [40] used for gas dynamics is a useful theoretical tool that can adequately treat gas dynamic problems even if slip boundary conditions are not taken as are in the conventional gas dynamics. In any event, the experiment studied here may be viewed as an interesting example of experiments related to the Knudsen problem.

# Figure Captions: Chapter 3

Fig. 3.1 The maximum of the observed pressure difference, normalized by the excited-state fraction as a function of pressure for the transition Q(12, 2) (squares) and Q(12, 3) (circles) for two quartz surfaces; Q(12, 2) transition for surface of stainless steel denoted by crosses. The solid straight line gives the Navier-Stokes result.

Fig. 3.2 Reduced flow rate  $(Q_k \text{ and } Q)$  vs pressure (in units of cm Hg) for  $\delta_0=0.1$ . The dash curve is the result of Knudsen's empirical formula for  $Q_k$  while the solid curve is the result of the generalized hydrodynamic equations for Q.

Fig. 3.3 Reduced flow rate vs pressure (in units of cm Hg). The solid curve is the original result of the generalized hydrodynamic equations. The dash curve is plotted according to Knudsen's empirical formula. The dash-dot curve is the result by using improved formula for Q(p') where p' = p + 0.02.

Fig. 3.4 Scaled pressure difference vs pressure for light-induced flow in a capillary. The dash line is the Navier-Stokes-theory prediction and solid curve is the prediction made by using the present theory. The squares, circles, and crosses are experimental data for the Q(12,2), Q(12,3), and Q(12,2), respectively. The Q(12,2) data were obtained with a stainless-steel capillary, whereas a quartz capillary was used for the Q(12,2) and Q(12,3) data.

Fig. 3.5 Scaled pressure difference vs pressure for light-induced flow in a capillary. The dash line is the Navier-Stokes-theory prediction and solid curve is the prediction made using the improved formula (3.43). The squares, circles, and crosses are experimental data for the Q(12, 2), Q(12, 3), and Q(12, 2), respectively.

The Q(12,2) data were obtained with a stainless-steel capillary, whereas a quartz capillary was used for the Q(12,2) and Q(12,3) data.





















#### Chapter 4

# Relativistic Boltzmann equation and relativistic irreversible thermodynamics

The nonrelativistic form of irreversible thermodynamics and generalized hydrodynamic equations for the system of radiation and matter is presented in the chapter 2. In that theory the material particles are treated nonrelativistically and the Doppler effect for photons are considered in the nonrelativistic approximation while photons are relativistic particles. Therefore, the nonrelativistic formulation leaves an unsatisfactory aftertaste. A nonrelativistic approximation destroys explicit Lorentz covariance of the kinetic equations whereas the covariance of kinetic theory for photons is important. In that scheme we have to carefully consider relativistic corrections for photons. This awkward feature can be removed if a covariant kinetic theory is formulated [34]. Moreover, there are some important problems, particularly in astrophysics and nuclear physics, where a relativistic kinetic theory is required since particles move at high speed. For instance, the theory will be useful in understanding electron and neutrino transport properties in the early universe [8].

Instead of the Chapman-Enskog method and the Grad moment method which are only valid in the linear regime, the modified moment method has been extended to solve the relativistic Boltzmann equation [33]. In this way, the relativistic generalized hydrodynamic equations can be derived from the covariant Boltzmann equation for a relativistic gas mixture. Unlike the Navier-Stokes equations which are parabolic differential equations, the relativistic generalized equations are hyperbolical differential equations which give a finite speed of wave propagation. This is consistent with the principle of relativity. The relativistic irreversible thermodynamics is also constructed based on the kinetic theory. The modified moment method for the covariant Boltzmann equation rigorously shows that the entropy differential is not an exact differential if the system is away from equilibrium. Therefore, an extended Gibbs relation does not hold valid for the entropy density in contrast to the usual surmise taken in the extended irreversible thermodynamics [21]. However, an extended Gibbs relation-like equation holds for the compensation differential as in the case of its nonrelativistic counterpart. The entropy balance equation is east into an equivalent form in terms of a new function called the Boltzmann function. The equation is seen to be a local expression of the H theorem [33]. Together with the generalized hydrodynamic equations for various macroscopic variables, these macroscopic evolution equations form a mathematical structure for a theory of irreversible processes in relativistic monatomic gases. In this chapter, in order to prepare for eventual formulation of a covariant theory of radiation and matter, we will formulate irreversible thermodynamics for material gases first by starting from the relativistic Boltzmann equation. The relativistic kinetic theory for the system of photons and material particles will be presented in the next chapter.

# 4.1 Relativistic kinetic equation

From the kinetic theory viewpoint, when *m*-component mixtures of a relativistic monatomic gases are in a nonequilibrium state, the time evolution of the systems may be described by a relativistic Boltzmann equation. By solving this equation the hydrodynamic and thermodynamic variables are determined. There exist three different ways of solving the relativistic Boltzman equation, namely, the Chapman-Enskog method, the Grad moment method and the modified moment method. The former two methods are well established [8] but they are only valid in the linear regime. Here we present the third method which allows us to obtain an exact irreversible thermodynamics for relativistic gas systems and analyze nonlinear processes in nonequilibrium systems [33]. Before the kinetic equation is introduced is useful to fix the notation and the convention for vectors and tensors appearing in the theory.

A point x in space-time is denoted by a four-vector

$$x \equiv x^{\mu} = (ct, \mathbf{r}) \tag{4.1a}$$

where c is the speed of light, t is time, r is the three-vector for spatial position and index  $\mu$  ranges 0, 1, 2, 3; here 0 is the time component and the rest of the indices are the space components. The corresponding four-momentum of species *i* is

$$p_{i} \equiv p_{i}^{\mu} = (p_{i}^{0}, \mathbf{p}_{i}),$$

$$p_{i}^{0} = (\mathbf{p}_{i}^{2} + m_{i}^{2}c^{2})^{1/2}.$$
(4.1b)

The covariant gradient operator is denoted by

$$\partial_{\mu} = (c^{-1}\partial_t, \nabla)$$

where  $\partial_t = \partial/\partial t$  and  $\nabla = \partial/\partial r$ . In this work the following convention is adopted for the metric

$$g^{\mu\nu} = diag(1, -1, -1, -1). \tag{4.2}$$

If the hydrodynamic velocity is denoted by  $U^{\mu}(x)$ , which will be defined later, then associated with the metric tensor in (4.2) is the projector  $\Delta^{\mu\nu}$ :

$$\Delta^{\mu\nu}(x) = -g^{\mu\nu} + c^{-2}U^{\mu}(x)U^{\nu}(x).$$
(4.3)

Here  $U^{\mu}(x)$  is normalized to c

$$U^{\mu}U_{\mu} = c^2. \tag{4.4}$$

This projector tensor has the following properties:

$$\Delta^{\mu\nu} = \Delta^{\nu\mu}, \tag{4.5a}$$

$$\Delta^{\mu\nu}U_{\nu}=0, \qquad (4.5b)$$

$$\Delta^{\mu\nu}\Delta_{\nu\sigma} = -\Delta^{\mu}_{\sigma}, \qquad (4.5c)$$

$$\Delta^{\mu}_{\mu} = -3. \tag{4.5d}$$

These properties will be frequently used when relativistic macroscopic evolution equations, namely, hydrodynamic equations, are derived from the kinetic equation.

The covariant Boltzman equation for the single distribution function  $f_i(x, p_i)$ may be written in the form

$$p_{i}^{\mu}\partial_{\mu}f_{i}(x,p_{i}) = \sum_{j=1}^{m} C(f_{i},f_{j})$$
(4.6a)

where the collision integral is given by the formula

$$C(f_i, f_j) = G_{ij} \int d^3 \bar{\mathbf{p}}_j d^3 \bar{\mathbf{p}}_i^* d^3 \bar{\mathbf{p}}_j^* W_{ij}(p_i p_j | p_i^* p_j^*) \\ \times [f_i^*(x, p_i^*) f_j^*(x, p_j^*) - f_i(x, p_i) f_j(x, p_j)],$$
(4.6b)

with  $d^3\bar{\mathbf{p}}_j = d^3\mathbf{p}_j/p_j^0, d^3\bar{\mathbf{p}}_j^* = d^3\mathbf{p}_j^*/p_j^{0*}$ , etc. and  $W_{ij}(p_ip_j|p_i^*p_j^*)$  denoting the transition rate for transition from the initial state  $(p_i, p_j)$  to the final state  $(p_i^*, p_j^*)$  as a result of a collision between particles *i* and *j*. The factor  $G_{ij} = 1 - \delta_{ij}/2$  insures that the final state is not counted twice. The asterisk denotes the post-collision value. Note that the subscripts *i* and *j* play a dual role of labeling a species and a particle of that species. The transition rate is a scalar under Lorentz transformation and obeys the microscopic reversibility (detailed balance)

$$W_{ij}(p_i p_j | p_i^* p_j^*) = W_{ij}(p_i^* p_j^* | p_i p_j).$$
(4.7)

This property is important for proving the H theorem.

# 4.2 Mean values and hydrodynamic variables

The distribution function makes it possible to calculate statistical mechanical mean values for observables. First of all, the distribution function is normalized to the number density  $n_i(x)$ 

$$n_i(x) = \int d^3 \mathbf{p}_i f_i(x, p_i). \tag{4.8a}$$

We remark that this should not be confused with the hydrodynamic number density defined later. In the same manner, the particle flux of species i is given by the statistical mechanical formula

$$\mathbf{j}_i(x) = \int d^3 \mathbf{p}_i \mathbf{v}_i f_i(x, p_i)$$
(4,8b)

where  $\mathbf{v}_i = c\mathbf{p}_i/p^0$ , the velocity of particle *i*. With these two quantities a covariant vector, namely, particle four-flow can be constructed:

$$N_i^{\mu}(x) = \langle p_i^{\mu} f_i(x, p_i) \rangle. \tag{4.9}$$

Here the angular brackets are the abbreviation of the integral

$$\langle \cdots \rangle = c \int \frac{d^3 \mathbf{p}_i}{p_i^0} \cdots$$

The covariant energy-momentum tensor of species i is defined by the statistical mechanical formula

$$T_i^{\mu\nu}(x) = \langle p_i^{\mu} p_i^{\nu} f_i(x, p_i) \rangle.$$
(4.10)

Then, the total number four-flow and total energy-momentum are given by

$$N^{\mu} = \sum_{i=1}^{m} N_{i}^{\mu}.$$
 (4.11*a*)

and

$$T^{\mu\nu} = \sum_{i=1}^{m} T_i^{\mu\nu}.$$
 (4.11b)

The definition of hydrodynamic velocity in relativity is not unique. There are two different definitions: one is due to Eckart [48] and the other is due to Landau and Lifshitz [49]. Here the Eckart definition will be adopted since it is simpler and more closely in line with the nonrelativistic counterpart. It is defined by

$$U^{\mu} = c N^{\mu} / (N^{\nu} N_{\nu})^{1/2}. \tag{4.12}$$

This definition clearly satisfies the normalization condition (4.4). With the hydrodynamic velocity we now define the hydrodynamic number density  $\rho_i$  of species *i* by

$$\rho_i = c^{-2} U_\mu N_i^\mu \tag{4.13a}$$

and the total hydrodynamic number density by

$$\rho = \sum_{i=1}^{m} \rho_i = c^{-2} U_{\mu} N^{\mu}, \qquad (4.13b)$$

which implies

$$N^{\mu} = \rho U^{\mu}. \tag{4.14}$$

We remark that  $\rho_i$  is not the same as  $n_i$  and a clear distinction should be made between them to avoid possible confusion that might arise in connection with relativistic hydrodynamic equations and its nonrelativistic counterparts derived from the nonrelativistic Boltzmann equation. It is easy to show the relation between  $\rho$ and n as follows:

$$\rho(x) = n(x)(1 - u^2/c^2)^{-1/2}.$$
(4.15)

The various relevant macroscopic variables such as energy density, heat flux, etc. can be defined in covariant form with the help of the hydrodynamic velocity just defined. The scalar energy density  $\varepsilon_i$  of species *i* is given by

$$E_i = \rho_i \varepsilon_i = c^{-2} U_\mu T_i^{\mu\nu} U_\nu. \tag{4.16}$$

The heat flux  $Q_i^{\mu}$  and diffusion flux  $J_i^{\mu}$  are also expressed in terms of the energymomentum tensor as follows:

$$Q_i^{\mu} = -U_{\nu} T_i^{\nu\sigma} \Delta_{\sigma}^{\mu}, \qquad (4.17)$$

$$J_i^{\mu} = N_i^{\mu} - c_i N^{\mu}, \qquad (4.18a)$$

where  $c_i$  is the number fraction:

$$c_i = \rho_i / \rho, \tag{4.18b}$$

It is more convenient to use a new heat flux defined by

$$Q_i^{\prime \mu} = Q_i^{\mu} - h_i J_i^{\mu}, \qquad (4.19a)$$

where  $h_i$  is the enthalpy per particle of species i:

$$h_i = (+p_i \rho_i^{-1}).$$
 (4.19b)

Here  $p_i$  is the hydrodynamic pressure of species *i*. We will give its statistical definition inter. Clearly, from the definitions of heat flux and diffusion flux it can be shown the useful identities  $U_{\mu}Q_i^{\mu} = 0$  and  $U_{\mu}J_i^{\mu} = 0$ ; consequently,  $U_{\mu}Q_i^{\prime \mu} = 0$ . The total heat flux  $Q^{\mu}$  is a summation of  $Q_i^{\mu}$ 

$$Q^{\mu} = \sum_{i=1}^{m} Q_i^{\mu}.$$

However, owing to the definition of  $J_i^{\mu}$  the diffusion fluxs are not all independent of each other since there holds the relation

$$\sum_{i=1}^m J_i^\mu = 0$$

The stress tensor  $P_i^{\mu\nu}$  is defined as

$$P_i^{\mu\nu} = \Delta_{\sigma}^{\mu} T_i^{\sigma\tau} \Delta_{\tau}^{\nu}. \tag{4.20a}$$

In order to reveal its physical meaning we decompose  $P_i^{\mu\nu}$  into the traceless symmetric part  $\prod_i^{\mu\nu}$ , the excess trace part  $\Delta_i$  and the hydrodynamic pressure  $p_i$  of species *i* as follows:

$$P_i^{\mu\nu} = p_i \Delta^{\mu\nu} + \Delta_i \Delta^{\mu\nu} + \Pi_i^{\mu\nu}. \tag{4.20b}$$

The traceless part is related to the viscous phenomena while the excess trace part is associated with the dilatation (or compression) of the gas. The hydrostatic pressure is defined in terms of equilibrium (or local equilibrium) energy-momentum tensor  $T_{ei}^{\mu\nu}$ :

$$p_i = \frac{1}{3} \Delta_{\mu\nu} T^{\mu\nu}_{ei}.$$
 (4.21a)

Then, it is easy to see that

$$\Delta_{i} = \frac{1}{3} \Delta_{\mu\nu} P_{i}^{\mu\nu} - p_{i} = \frac{1}{3} \Delta_{\mu\nu} T_{i}^{\mu\nu} - p_{i}, \qquad (4.21b)$$

$$\Pi_i^{\mu\nu} = P_i^{\mu\nu} - \frac{1}{3} \Delta_{\sigma\tau} T_i^{\sigma\tau} \Delta^{\mu\nu}.$$
(4.21c)

The component stress tensors add up to the total stress tensor:

$$\Pi^{\mu\nu} = \sum_{i=1}^m \Pi^{\mu\nu}_i, \qquad \Delta = \sum_{i=1}^m \Delta_i, \qquad p = \sum_{i=1}^m p_i$$

Because of this decomposition for  $P_i^{\mu\nu}$ , the energy-momentum tensor can be cast into the form:

$$T_i^{\mu\nu} = c^{-2} E_i U^{\mu} U^{\nu} + c^{-2} (Q_i^{\mu} U^{\nu} + U^{\mu} Q_i^{\nu}) + P_i^{\mu\nu}.$$
(4.22)

In the proceeding discussions the statistical meaning of hydrodynamic variables has been presented. However, the hydrodynamic description must satisfy the thermodynamic laws, particularly, the second law of thermodynamics. In order to formulate irreversible thermodynamics for a relativistic system it is necessary to introduce the entropy four-flow in a covariant form

$$S^{\mu}(x) = \sum_{i=1}^{m} S^{\mu}_{i} = -k_{B} \sum_{i=1}^{m} \langle p^{\mu}_{i} [lnf_{i}(x, p_{i}) - 1] f_{i}(x, p_{i}) \rangle.$$
(4.23)

With the four-vector  $S^{\mu}$  and hydrodynamic velocity  $U^{\mu}$  we can introduce the scalar entropy S(x) or the scalar entropy per particle S as follows:

$$S(x) \equiv \rho S(x) = c^{-2} U_{\mu} S^{\mu}.$$
 (4.24)

This is the quantity we are going to deal with in the theory of irreversible processes that will be constructed on the basis of the covariant Boltzmann equation.

#### 4.3 Relativistic generalized hydrodynamic equations

The particle number and energy-momentum conservation laws are easily derived from the covariant Boltzmann equation since these quantities are the collisional invariants of the Boltzmann collision integral. The covariant balance equations for the particle number and energy-momentum are, respectively,

$$\partial_{\mu}N^{\mu} = 0 \tag{4.25}$$

and

$$\partial_{\nu}T^{\mu\nu} = 0. \tag{4.26}$$

Various fluid dynamic equations can be obtained from these balance equations. With the definitions of the operators

$$D = U^{\mu} \partial_{\mu}, \tag{4.27a}$$

$$\nabla^{\mu} = -\Delta^{\mu\nu} \partial_{\nu}, \qquad (4.27b)$$

the covariant derivative can be decomposed into two components as below:

$$\partial^{\mu} = c^{-2} U^{\mu} D + \nabla^{\mu}. \tag{4.27c}$$

The operator D will be called convective time derivative, which is analogous to the nonrelativistic substantial time derivative, and  $\nabla^{\mu}$  to the gradient operator.

By using the decomposition of  $\partial^{\mu}$  and various definitions such as hydrodynamic density etc. given earlier, it is possible to derive from the conservation laws (4.25) and (4.26) the following balance equations of density, density fractions, momentum and energy. Since the details are well documented in [8] we list the results only: Equation of continuity:

$$D\rho = -\rho \nabla_{\mu} U^{\mu}. \tag{4.28}$$

Density fraction balance equation: For systems without a chemical reaction

$$\rho D c_i = -\nabla_\mu J_i^\mu + c^{-2} J_i^\mu D U_\mu. \tag{4.29}$$

Momentum balance equation:

$$c^{-2}h\rho DU^{\mu} = \nabla^{\mu}\rho + \Delta^{\mu}_{\sigma}\partial_{\nu}\bar{P}^{\sigma\nu} + c^{-2}(\Delta^{\mu}_{\nu}DQ^{\nu} - Q^{\mu}\nabla_{\nu}U^{\nu} - Q^{\nu}\nabla_{\nu}U^{\mu}) \quad (4.30)$$

where

$$\bar{P}^{\sigma\nu} = \sum_{i=1}^{m} (\Delta_i \Delta^{\sigma\nu} + \Pi_i^{\sigma\nu}) = \Delta \Delta^{\sigma\nu} + \Pi^{\sigma\nu}$$
(4.31*a*)

and h is the enthalpy per particle of the mixture:

$$h = \sum_{i=1}^{m} (\varepsilon_i + p_i \rho_i^{-1}) = \varepsilon + p \rho^{-1}.$$
 (4.31b)

Energy balance equation:

$$\rho D\varepsilon = -\nabla_{\mu}Q^{\mu} - p\nabla_{\mu}U^{\mu} + \bar{P}^{\mu\nu}\nabla_{\nu}U_{\mu} + 2c^{-2}Q^{\mu}DU_{\mu}.$$

$$(4.32)$$

These balance equations contain macroscopic variables such as the stress tensor, heat flux and diffusion fluxes, etc. which require their own evolution equations. We can derive them from the covariant Boltzmann equation. First we introduce a tensor  $\psi_i^{(\alpha)\mu\nu...l}$  defined as the average of its molecular expression  $p_i^{\sigma} h_i^{(\alpha)\mu\nu...l}$  with respect to the distribution function [33]

$$\psi_i^{(\alpha)\mu\nu\dots l\sigma} = \langle p_i^{\sigma} h_i^{(\alpha)\mu\nu\dots l} f_i(x, p_i) \rangle$$
(4.33)

where  $h_i^{(\alpha)\mu\nu\dots l}$  is the  $\alpha$ th element of a set of molecular expressions of moments in terms of which the distribution function may be expanded. The leading moments

relevant to physical applications of the theory developed here are:

$$h_i^{(1)\mu\nu} = c^2 (U_\lambda p_i^\lambda)^{-1} (\Delta^\mu_\sigma \Delta^\nu_r - \frac{1}{3} \Delta_{\sigma\tau} \Delta^{\mu\nu}) p_i^\sigma p_i^\tau, \qquad (4.34a)$$

$$h_i^{(2)} = \frac{1}{3} c^2 (U_\lambda p_i^\lambda)^{-1} \Delta_{\mu\nu} p_i^{\mu} p_i^{\nu} - p_i / \rho_i, \qquad (4.34b)$$

$$h_{i}^{(3)\mu} = -c^{2}(U_{\lambda}p_{i}^{\lambda})^{-1} \{ \Delta_{\sigma}^{\mu}p_{i}^{\nu}p_{i}^{\sigma}U_{\nu} - a_{i}h_{i}[p_{i}^{\mu} - c^{-2}(U_{\lambda}p_{i}^{\lambda})U^{\mu}] \}, \quad (4.34c)$$

$$h_i^{(4)\mu} = c^2 (U_\lambda p_i^\lambda)^{-1} [p_i^\mu - c^{-2} (p_i^\lambda U_\lambda) U^\mu], \qquad (4.34d)$$

etc.

where

$$a_{i} = \Delta^{\mu}_{\sigma} \Delta^{\nu}_{\tau} \langle p^{\sigma}_{i} p^{\tau}_{i} f_{\epsilon i} \rangle g_{\mu\nu} [\Delta^{\mu}_{\sigma} \Delta^{\nu}_{\tau} \langle p^{\sigma}_{i} p^{\tau}_{i} (U_{\lambda} p^{\lambda}_{i})^{-1} f_{\epsilon i} \rangle g_{\mu\nu}]^{-1}.$$
(4.34*e*)

These moments tend to the nonrelativistic moments appearing in the nonrelativistic kinetic theory [20] in the limit of  $u/c \rightarrow 0$ . They are constructed by means of the Schmidt orthogonalization method such that they give rise to physically relevant variables when averaged.

The physical measurable quantities  $\Phi_i^{(\alpha)\mu\nu\dots l\sigma}$ , which are tensors of various ranks, are the constraction of  $\psi_i^{(\alpha)\mu\nu\dots l\sigma}$  with  $U_{\sigma}$ :

$$\Phi_i^{(\alpha)\mu\nu\dots l} = c^{-2} U_\sigma \psi_i^{(\alpha)\mu\nu\dots l\sigma}.$$
(4.35)

It is then easy to show that

$$\Phi_i^{(1)\mu\nu} = \Pi_i^{\mu\nu}; \quad \Phi_i^{(2)} = \Delta_i; \quad \Phi_i^{(3)\mu} = Q_i^{\prime\mu}; \quad \Phi_i^{(4)\mu} = J_i^{\mu}; \quad etc.$$

Thus, we are treating  $\psi_i^{(\alpha)\mu\nu\dots l\sigma}$  as components of a "four-tensor" and macroscopic moments  $\Phi_i^{(\alpha)\mu\nu\dots l}$  are their contractions with the hydrodynamic four-velocity in the sense similar to the scalars such as the number density, entropy density, etc. This way, they are put on equal conceptual footing with the conserved variables and entropy density to which they are related, as will be shown later. The evolution equation for  $\psi_i^{(\alpha)\mu\nu\dots l\sigma}$  is easily derived from the covariant Boltzmann equation:

$$\partial_{\sigma}\psi_{i}^{(\alpha)\mu\nu\dots l\sigma} = \langle p_{i}^{\sigma}\partial_{\sigma}h_{i}^{(\alpha)\mu\nu\dots l}f_{i}(x,p_{i})\rangle + \Lambda_{i}^{(\alpha)\mu\nu\dots l}$$
(4.36)

where the dissipation term

$$\Lambda_i^{(\alpha)\mu\nu\cdots l} = \sum_{j=1}^m \langle h_i^{(\alpha)\mu\nu\cdots l} C(f_i, f_j) \rangle$$
(4.37)

is closely related to the entropy production which we will discuss later. With the definition of  $\hat{\Phi}_i^{(\alpha)\mu\nu\ldots l}$  as  $\Phi_i^{(\alpha)\mu\nu\ldots l}$  per particle,

$$\Phi_i^{(\alpha)\mu\nu\dots l} = \rho \hat{\Phi}_i^{(\alpha)\mu\nu\dots l}, \qquad (4.38)$$

and by making use of (4.35), we obtain

$$\rho D\hat{\Phi}_i^{(\alpha)\mu\nu\dots l} = Z_i^{(\alpha)\mu\nu\dots l} + \Lambda_i^{(\alpha)\mu\nu\dots l}$$
(4.39)

where the kinetic term  $Z_i^{(\alpha)\mu\nu\dots l}$  is given by

$$Z_i^{(\alpha)\mu\nu\dots l} = \langle p_i^{\sigma} \partial_{\sigma} h_i^{(\alpha)\mu\nu\dots l} f_i(x, p_i) \rangle + \partial_{\tau} (\Delta_{\sigma}^{\tau} \psi_i^{(\alpha)\mu\nu\dots l\sigma}).$$
(4.40)

This statistical mechanical formula can be worked out more explicitly for the leading moments as follows:

$$\begin{split} Z_i^{(1)\mu\nu} &= -\nabla_{\sigma}\Omega_i^{(1)\mu\nu\sigma} - 2[\Pi_i \cdot \nabla U]^{(2)\mu\nu} + 2p_i[\nabla U]^{(2)\mu\nu} \\ &+ \langle f_i p_i^{\sigma} p_i^{\tau} p_i^l (p_i^{\epsilon} U_{\epsilon})^{-1} \rangle \nabla_{\sigma} U_{\tau} (\Delta_l^{\mu} U^{\nu} + U^{\mu} \Delta_l^{\nu}) \rangle \\ &+ 2\Delta_i [\nabla U]^{(2)\mu\nu} + \Pi_i^{\mu\nu} \nabla_{\sigma} U^{\sigma} - 2c^{-2} [Q_i D U]^{(2)\mu\nu} \\ &- \frac{1}{3} \langle f_i p_i^{\sigma} p_i^{\tau} p_i^l (p_i^{\epsilon} U_{\epsilon})^{-1} \rangle \Delta_{l\tau} (U^{\mu} \nabla_{\sigma} U^{\nu} + U^{\nu} \nabla_{\sigma} U^{\mu}) \\ &- \frac{1}{3} \langle f_i p_i^{\sigma} p_i^{\tau} p_i^l p_i^{\lambda} c^2 (p_i^{\epsilon} U_{\epsilon})^{-2} \rangle \nabla_{\sigma} U_{\lambda} (\Delta_l^{\mu} \Delta_{\tau}^{\nu} - \frac{1}{3} \Delta_{l\tau} \Delta^{\mu\nu}) \\ &- c^{-2} [(P_i^{\mu\tau} U^{\nu} + P_i^{\nu\tau} U^{\mu}) D U_{\tau} \end{split}$$

$$+ (p_{i} + \Delta_{i})(U^{\mu}DU^{\nu} + U^{\nu}DU^{\mu}) \},$$

$$(4.41a)$$

$$Z_{i}^{(2)} = -\nabla_{\mu}\Omega_{i}^{(2)\mu} + \frac{2}{3}\Pi_{i}^{\mu\nu}[\nabla U]_{\mu\nu}^{(2)} - p_{i}Dln(p_{i}v^{5/3})$$

$$+ \frac{2}{3}\Delta_{i}\nabla_{\nu}U^{\nu} - \nabla_{\mu}(J_{i}^{\mu}p_{i}/\rho_{i}) + \frac{2}{3}c^{-2}Q_{i}^{\mu}DU_{\mu}$$

$$- \frac{1}{3}\langle f_{i}p_{i}^{\sigma}p_{i}^{\tau}p_{i}^{l}p_{i}^{\lambda}c^{2}(p_{i}^{\epsilon}U_{\epsilon})^{-2}\rangle\nabla_{\sigma}U_{\lambda}\Delta_{\tau l},$$

$$(4.41b)$$

$$Z_{i}^{(3)\mu} = -\nabla_{\nu}\Omega_{i}^{(3)\nu\mu} + \Pi_{i}^{\mu\nu}DU_{\nu} - (p_{i} + \Delta_{i})DU^{\mu} - J_{i}^{\mu}Dh_{i}$$

$$+ Q_{i}^{i\nu}\nabla_{\nu}U^{\mu} + a_{i}J_{i}^{\nu}U^{\mu}\nabla_{\nu}h_{i} + (p_{i} + \Delta_{i})U^{\mu}\nabla^{\nu}U_{\nu}$$

$$- U^{\mu}\Pi_{i}^{\nu\sigma}\nabla_{\nu}U_{\sigma} - c^{-2}U^{\mu}Q_{i}^{i\nu}DU_{\nu}$$

$$- a_{i}\langle f_{i}p_{i}^{\nu}p_{i}^{\mu}c^{2}(U_{\epsilon}p_{i}^{\epsilon})^{-1}\rangle\nabla_{\nu}h_{i}$$

$$+ \langle f_{i}p_{i}^{\nu}p_{i}^{\mu}c^{2}(U_{\epsilon}p_{i}^{\epsilon})^{-2}\rangle a_{i}h_{i}\nabla_{\nu}U_{\lambda}$$

$$- \langle f_{i}p_{i}^{\mu}p_{i}^{\sigma}c^{2}(U_{\epsilon}p_{i}^{\epsilon})^{-1}\rangleh_{i}\partial_{\sigma}a_{i} + U^{\mu}N_{i}^{\sigma}h_{i}\partial_{\sigma}a_{i},$$

$$Z_{i}^{(4)\mu} = -\nabla_{\nu}\Omega_{i}^{(4)\mu\nu} - J_{i}^{\nu}\nabla_{\nu}U^{\mu} - \rho_{i}DU^{\mu} - c^{-2}U^{\mu}J_{i}^{\nu}DU_{\nu}$$

$$- \langle f_{i}p_{i}^{\mu}p_{i}^{\sigma}p_{i}^{\lambda}c^{2}(p_{i}^{\epsilon}U_{\epsilon})^{-2}\rangle\nabla_{\sigma}U_{\lambda},$$

$$(4.41d)$$

where

$$\begin{split} [\nabla U]^{(2)\mu\nu} &= \frac{1}{2} (\nabla^{\mu} U^{\nu} + \nabla^{\nu} U^{\mu}) - \frac{1}{3} \Delta^{\mu\nu} \nabla^{\tau} U_{\tau}, \\ [A \cdot B]^{(2)\mu\nu} &= \frac{1}{2} (A^{\mu\sigma} B^{\nu}_{\sigma} + A^{\nu\sigma} B^{\mu}_{\sigma}) - \frac{1}{3} \Delta^{\mu\nu} A^{\sigma\tau} B_{\sigma\tau}, \\ \Omega^{(\alpha)\nu\dots\sigma\mu}_{i} &= \psi^{(\alpha)\nu\dots\sigma\mu}_{i} - \hat{\Phi}^{(\alpha)\nu\dots\sigma}_{i} N^{\mu}. \end{split}$$

We emphasize that the evolution equations (4.39) are coupled to the momentum, energy and concentration balance equations introduced earlier. As in the nonrelativistic kinetic theory this set of equations is open and therefore must be suitably closed by means of a closure relation. When the set is thus closed, it provides relativistic generalized hydrodynamic equations consisting of (4.28)-(4.30), (4.32) and (4.39) with the number of moments limited to a finite value by the closure. The flux evolution equation (4.39) can be easily shown to tend to the nonrelativistic counterpart in the limit of  $c \to \infty$ . The manner in which the moments  $\{\Phi_i^{(\alpha)}\}$  are
defined is significantly different from the one in the conventional moment method [8, 50] and as a consequence their evolution equations are significantly different.

#### 4.4 The H theorem, equilibrium solution, temperature and pressure

With the definitions of the entropy four-flow and the scalar entropy density we can derive the entropy balance equation from the relativistic Boltzmann equation. The covariant form of the entropy balance equation is given by

$$\partial_{\mu}S^{\mu} = \sigma_{ent}(x) \tag{4.42}$$

where

$$\sigma_{ent}(x) = -k_B \sum_{i=1}^{m} \sum_{j=1}^{m} \langle lnf_i(x, p_i)C(f_i, f_j) \rangle.$$
(4.43)

By following the well known procedure [8] based on the symmetry properties of the transition probability, it is easy to show that the entropy production  $\sigma_{ent}(x)$  is positive:

$$\sigma_{ent}(x) \ge 0, \tag{4.44}$$

with the equality applying only at equilibrium. This is the content of the H theorem. It is a statistical mechanical representation of the second law of thermodynamics. In terms of the scalar entropy density we will write the entropy balance equation in a more useful form:

$$\rho DS = -\partial_{\mu} J_{s}^{\mu} + \sigma_{ent}(x) \tag{4.45a}$$

where the entropy flux is given by

$$J_s^{\mu} = S^{\mu} - SN^{\mu} = S^{\mu} - \rho SU^{\mu}.$$
(4.45b)

Various balance equations and flux evolution equations previously introduced are subject to the entropy balance equation in the sense that the entropy production  $\sigma_{ent}(x)$  must remain positive so that the second law of thermodynamics is satisfied. As it stands, the entropy balance equation provides no clue as to how this requirement of the second law is fulfilled. This point is usually clarified by using an approximate distribution function (e.g., the Chapman-Enskog solutions), but since the thermodynamic laws must be satisfied rigorously, any conclusion drawn in that respect on the basis of an approximate solution to the kinetic equation cannot be relied on if the system is removed from equilibrium by an arbitrary degree. We therefore must employ a rigorous approach. The modified moment method [20] meets this stringent constraint. As a further preparation for this method, we now consider the equilibrium solution to the covariant Boltzmann equation.

Owing to the H theorem, the equilibrium solution  $f_{ei}$  to the covariant Boltzmann equation is uniquely determined. The result is the well known Jüttner function [8]

$$f_{ei} = exp[-\beta(p_i^{\mu}U_{\mu} - \mu_i^e)] \tag{4.46}$$

where  $\mu_i^e$  is the normalization factor which turns out to be the chemical potential, and  $\beta$  turns out to be proportional to the inverse temperature:  $\beta \equiv 1/k_BT$ . This parameter  $\beta$  is determined by comparing the thermodynamic entropy, pressure, and internal energy with the statistical mechanical entropy, pressure, and internal energy calculated with the equilibrium solution of the kinetic equation by following the basic strategy of the Gibbs ensemble theory. Since the equilibrium entropy four-flow with  $f_{ei}$  given as in (4.46) is

$$S_{e}^{\mu} = k_{B}\beta \sum_{i=1}^{m} (T_{ei}^{\mu\nu}U_{\nu} + N_{ei}^{\mu}/\beta - \mu_{i}^{e}N_{ei}^{\mu}), \qquad (4.47a)$$

we find the equilibrium scalar entropy in the form

$$S_{\epsilon} = k_{B}\beta[E + \rho/\beta - \sum_{i=1}^{m} \mu_{i}^{\epsilon}\rho_{i}]. \qquad (4.47b)$$

The thermodynamic temperature  $T_t$  is defined by

$$T_t^{-1} = (\partial S_e / \partial E). \tag{4.48}$$

By making  $S_e$  in (4.47) correspond to the thermodynamic entropy, and other terms in it to the energy, pressure and density, respectively, we are able to find the parameter T:  $T_t = T$ . This identifies the physical significance of T. It is the absolute temperature and

$$\beta = 1/k_B T_t = 1/k_B T. \tag{4.49}$$

Henceforth,  $T_t$  and T are interchangeably used. In fact,  $T_t$  means T unless stated otherwise. Since the chemical potential is defined by

$$\mu_i^e/T = -(\partial S_e/\partial \rho_i) \tag{4.50}$$

in thermodynamics, the normalization factor  $\mu_i^{\epsilon}$  is indeed the chemical potential. The ideal gas equation of state is identified by

$$p = \rho k_B T, \quad (v = \rho^{-1}).$$
 (4.51)

It must be remembered that this T is the temperature of the equilibrium system, which will be occasionally denoted by  $T_e$ , if necessary, to make distinction from the nonequilibrium temperature.

The hydrodynamic pressure has been given by (4.21a) in terms of the equilibrium energy-momentum tensor which we will work out more explicitly:

$$p = \sum_{i=1}^{m} p_i = \frac{1}{3} \sum_{i=1}^{m} \Delta_{\mu\nu} T_{ei}^{\mu\nu} = \frac{1}{3} \sum_{i=1}^{m} \Delta_{\mu\nu} \langle p_i^{\mu} p_i^{\nu} \rangle.$$
(4.52a)

Substituting the equilibrium distribution function (4.46) into it, we find

$$p = \sum_{i=1}^{m} 4\pi m_i^2 c\beta^{-2} K_2(m_i c^2 \beta) exp(\beta \mu_i^e)$$
(4.52b)

where  $K_2(z)$  is a modified Bessel function [48] of the second kind. The density  $\rho$  may be similarly calculated:

$$\rho = c^{-2} U_{\mu} N^{\mu} = \sum_{i=1}^{m} 4\pi m_i^2 c \beta^{-1} K_2(m_i c \beta) exp(\beta \mu_i^{\epsilon}).$$
(4.53)

This, together with (4.52b), implies the equation of state (4.51). Therefore, the thermodynamically defined pressure through the equation of state (4.51) is consistent with the statistical mechanical definition of p in (4.52a). The situation thus is seen to be the same as in the nonrelativistic kinetic theory in that the kinetically and the thermodynamically defined pressure are identical. However, this is not the case for the internal energy.

In the nonrelativistic kinetic theory the temperature is defined such that the following relation holds true between the internal energy and the temperature [18]

$$\varepsilon = \frac{3}{2}k_B T. \tag{4.54}$$

The temperature defined in this manner is called the kinetic temperature and coincides with the thermodynamic temperature defined through the thermodynamic relation

$$T^{-1} = (\partial S_e / \partial E). \tag{4.55}$$

However, in the relativistic theory the situation is altered significantly since if the kinetic temperature is defined by (4.54), then it does not agree with the thermodynamic temperature defined by means of (4.55). Nevertheless, (4.55) is consistent with (4.51). One recovers the coincidence between (4.54) and (4.55) in the limit of  $u/c \rightarrow 0$ , in which the term  $mc^2$  is neglected; see ref. [8] for expression for  $\epsilon$ . However, it would be preferable to have the thermodynamic temperature coincide with the kinetic temperature in the relativistic kinetic theory as well, since the kinetic theory should be a molecular representation of thermodynamics underlying macroscopic processes. Here we define the kinetic temperature for a system of particles with finite masses such that it precisely coincides with the thermodynamic temperature as follows:

$$\frac{3}{2}\rho k_B T_e = \sum_{i=1}^m (2c^2)^{-1} \langle (p_i^{\mu} p_i^{\nu} U_{e\mu} U_{e\nu} - m_i^2 c^4) f_{ei}(x, p_i) \rangle.$$
(4.56)

This definition yields a correct nonrelativistic limit. It is rooted basically in the idea that the temperature is a measure of kinetic energy. Since the integrand in (4.56) is scalar, that is, its value is independent of frame, it is convenient to choose the local rest frame where  $U_{\mu} = (c, 0, 0, 0)$  to evaluate the integral. Then,

$$f_{ei} = exp[-\beta(cp_i^0 - \mu_i^e)]$$
(4.57)

where  $\beta = 1/k_B T_t$  with the subscript t restored to mean the thermodynamic temperature. Thus, we find

$$\frac{3}{2}\rho k_B T_e = \sum_{i=1}^m \frac{1}{2} exp(\beta \mu_i^e) \int d^3 \mathbf{p}_i (e_i - m_i^2 c^4 / e_i) exp(-\beta e_i)$$
(4.58a)

where

$$e_i = cp_i^0 = (c^2 \mathbf{p}_i^2 + m_i^2 c^4)^{1/2}.$$
 (4.58b)

With the transformations

$$z_i = m_i c^2 \beta, \qquad \tau_i = \beta e_i,$$

(4.58a) may be put in the form

$$\frac{3}{2}\rho k_B T_e = \sum_{i=1}^m exp(\beta\mu_i^e) 2\pi c^{-3} \beta^{-4} \frac{4!}{2^2 2!} z_i^2 K_2(z_i).$$
(4.59)

In view of the fact that the chemical potential is given by

$$exp(-\beta\mu_i^e) = 4\pi m_i^2 c(\rho_i\beta)^{-1} K_2(z_i),$$

it follows from (4.59) that

$$T_{t} = T_{t}$$

since the right-hand side of (4.59) is equal to  $3\rho k_B T_t/2$ . This proves the coincidence of the kinetic temperature with the thermodynamic temperature, if the kinetic temperature is defined as stated in (4.56). It must be noted that Eq. (4.56) is another way of expressing Tolman's equipartition theorem [52]. Therefore, the definition of temperature by (4.56) is seen to be based on the equipartition law. In other words, the relativistic kinetic temperature may be defined by means of the equipartition theorem of Tolman, which equally holds for both nonrelativistic and relativistic theories. This interpretation of the definition of kinetic temperature provides us with a universal way of defining temperature for both nonrelativistic and relativistic theories: the equipartition law of Tolman.

The local rest frame version of the definition (4.56) of kinetic temperature in relativity was suggested by ter Haar and Wergeland [53], and it was later taken by Menon and Agrawal [54], but as pointed out by Landsberg [55], their definition is preceded by Tolman [52]. On the other hand, in the Chapman-Enskog theory [8] the kinetic temperature is defined such that the equation of state in thermodynamics and in kinetic theory coincide with each other. Therefore, there appear to be two different modes of defining the temperature, but, in fact, they are identical at least in the case of dilute gases. Since,

$$p_i^{\mu} p_i^{\nu} U_{e\mu} U_{e\nu} - m_i^2 c^4 = c^2 p_i^{\mu} p_i^{\nu} \Delta_{\nu\mu}$$

substitution of this relation into (4.56) yields

$$\frac{\frac{3}{2}}{\rho}k_B T_e = \frac{1}{2} \Delta_{\sigma\mu} T_e^{\mu\sigma}$$
$$= \frac{3}{2}p$$

which implies the equation of state. This result elaborates on what has been said earlier in connection with the matching conditions used in the Chapman-Enskog theory.

### 4.5 Modified moment method

With the equilibrium distribution function uniquely determined by the H theorem and the parameter therein identified with the thermodynamic temperature and chemical potential, it is now possible to develop a method to determine the nonequilibrium distribution function such that it is consistent with the H theorem. In the nonrelativistic kinetic theory the determination of a nonequilibrium distribution function is made possible by the modified moment method [20]. Here we extend the same method to solve the relativistic Boltzmann equation. This extension allows us to establish rigorously the irreversible thermodynamics for relativistic systems [33]. To begin with, the following consideration is helpful for adopting a general strategy.

Since the nonequilibrium distribution function must be reduced to the equilibrium distribution function as the system tends toward equilibrium, it is natural to construct the former based on the latter. Therefore, we look for the nonequilibrium distribution function in the form

$$f_i = f_i^0(\beta_e, \rho_e, U_e^{\mu}) \Delta f_i$$

where  $f_i^0 = f_i^0(\beta_e, \rho_e, U_e^{\mu})$  is the equilibrium distribution function already determined and  $\Delta f_i$  is the nonequilibrium correction. This correction term may be expressed in a variety of ways corresponding to different ways to solve the Boltzmann equation. In order to have a operational meaning for the parameters appearing in the distribution function, the nonequilibrium distribution function will be determined to satisfy the matching conditions. There exist three different matching conditions which are used in the literature:

Eckart's matching conditions [48]:

$$\rho_e = \rho, \qquad U_e^\mu = U^\mu, \qquad E_e = E;$$

Landau and Lifshitz's matching conditions [51]:

$$\rho_e = \rho, \qquad E_e U_e^\mu = E U^\mu - Q^\mu;$$

Stewart's matching conditions [50]:

$$\rho_e = \rho, \qquad U_e^{\mu} = U^{\mu}, \qquad E_e - 3p_e = E - 3p$$

In nonrelativistic kinetic theory the energy matching condition automatically matches the nonequilibrium temperature to the equilibrium temperature appearing in the distribution function. This matching condition in fact serves simultaneously as the statistical mechanical definition of the nonequilibrium temperature. In the matching conditions of the relativistic kinetic theory mentioned earlier we notice that none of them can serve as the statistical mechanical definition of nonequilibrium temperature since the internal energy is not equal to  $3k_BT/2$  for a monatomic gas if the particle is relativistic. Therefore, the kinetic theories using the aforementioned matching conditions do not unequivocally and mathematically identify the nonequilibrium temperature appearing in the nonequilibrium distribution function. We believe that it is not sufficient to simply call the temperature in the equilibrium solution of the kinetic equation local and dependent on space-time and then use it in the nonequilibrium distribution function as is usually done in the literature since then it is not statistically defined within the framework of the nonequilibrium theory in hand. Since we need to fix the statistical mechanical meaning of nonequilibrium temperature for the nonequilibrium distribution function of a relativistic gas, we propose for the matching conditions meeting the requirement we set for them in connection with temperature as follows:

$$c^{-2} \langle p_i^{\mu} U_{\mu} f_i \rangle = c^{-2} \langle p_i^{\mu} U_{\mu} f_{ei} \rangle, \qquad (4.60a)$$

$$\sum_{i=1}^{m} \langle p_i^{\mu} f_i \rangle = \sum_{i=1}^{m} \langle p_i^{\mu} f_{ei} \rangle, \qquad (4.60b)$$

$$\sum_{i=1}^{m} c^{-2} \langle p_{i}^{\mu} p_{i}^{\nu} f_{i} \rangle U_{\mu} U_{\nu} = \sum_{i=1}^{m} c^{-2} \langle p_{i}^{\mu} p_{i}^{\nu} f_{\epsilon i} \rangle U_{\mu} U_{\nu}, \qquad (4.60c)$$

$$\sum_{i=1}^{m} \frac{1}{3} \langle p_{i}^{\mu} p_{i}^{\nu} f_{i} \rangle \Delta_{\mu\nu} = \sum_{i=1}^{m} \frac{1}{3} \langle p_{i}^{\mu} p_{i}^{\nu} f_{ei} \rangle \Delta_{\mu\nu}.$$
(4.60*d*)

The first two conditions are the same as those in the matching conditions of Eckart and Stewart and the third matches the internal energies. The last condition simultaneously serves as the temperature matching condition. Notice that (4.60c) and (4.60d) are the matching conditions for the projections of the energy-momentum tensor onto two different directions. These conditions imply that  $f_i$  is determined in terms of  $\rho, U^{\mu}$ , and T or p among other macroscopic variables, and that the nonequilibrium part of  $f_i$  is such that

if  $f_i$  is written as

$$f_i = f_i^0 (1 + \phi_i).$$

It must be pointed out that in the Chapman-Enskog method of solution for the covariant Boltzmann equation, condition (4.60d) is not explicitly imposed for the nonequilibrium distribution function. In the present relativistic kinetic theory (4.60d) defines the kinetic temperature. The relativistic version of the generalized hydrodynamic equations remains basically unchanged by the various matching conditions presented in this work, although some details of the generalized hydrodynamic equations get modified to some extent because some macroscopic quantities become modified depending on what we mean by nonequilibrium temperature.

Now, the nonequilibrium distribution function is matched with  $f_{ei}$  as described and written in an exponential form

$$f_i = exp[-\beta(p_i^{\mu}U_{\mu} + H_i^{(1)} - \mu_i)]$$
(4.61a)

where

$$H_{i}^{(1)} = \sum_{\alpha \ge 1} X_{i\mu\nu\dots l}^{(\alpha)} h_{i}^{(\alpha)l\dots\nu\mu}$$
$$\equiv \sum_{\alpha \ge 1} X_{i}^{(\alpha)} \odot h_{i}^{(\alpha)}$$
(4.61b)

and  $\mu_i$  is the normalization factor given by the formula

$$exp(-\beta\mu_{i}) = \rho_{i}^{-1} \langle c^{-2} p_{i}^{\lambda} U_{\lambda} exp[-\beta(p_{i}^{\mu} U_{\mu} + \sum_{\alpha \geq 1} X_{i\mu\nu...l}^{(\alpha)} h_{i}^{(\alpha)l...\nu\mu})] \rangle.$$
(4.61c)

The parameter  $\beta = 1/k_B T$  has the meaning as fixed by (4.60d) and elaborated earlier. The tensors  $X_{i\mu\nu\dots l}^{(\alpha)}$  are as yet undetermined functions of macroscopic variables, but will be determined such that (4.61a) satisfies the kinetic equation and any approximation to them does not violate the H theorem. Consequently, the resulting formalism for irreversible processes remains consistent with the second law of thermodynamics. To construct such a formalism, we assume that  $X_i^{(\alpha)}$  are somehow known and then proceed to construct the formalism. (In this sense the attitude taken here is similar to that by the Gibbs ensemble theory where the partition function is assumed to be known and with it thermodynamic functions and their relations are sought after.) By making sure that the entropy production remains positive to the approximation to be made in the future to the unknown  $X_i^{(\alpha)}$ , the consistency of the formalism with the second law of thermodynamics is preserved. For  $\alpha = 1$  the unknown is the second rank tensor; for  $\alpha = 2$  it is a scalar; while for  $\alpha = 3$  and 4 the unknowns are vectors. The sum over  $\alpha$  in (4.61b) in principle runs over any number of terms, but it must be such that  $f_i$  is normalizable. Only this restriction is necessary in formulating the theory since the distribution function is explicitly used only to define macroscopic observable in the moment method, and once that is done, its role in the kinetic theory is basically over except for the entropy production for which the restriction just mentioned is sufficient. The exponential form for  $f_i$  will be called the nonequilibrium canonical form.

Substitution of the nonequilibrium canonical form for  $f_i$  into (4.43) for the entropy production yields the formula

$$\sigma_{ent} = T^{-1} \sum_{i=1}^{m} \sum_{\alpha \ge 1} X_{i\mu\nu\dots l}^{(\alpha)} \Lambda_{i}^{(\alpha)l\dots\nu\mu}$$
$$= T^{-1} \sum_{i=1}^{m} \sum_{\alpha \ge 1} X_{i}^{(\alpha)} \odot \Lambda_{i}^{(\alpha)}$$
(4.62)

for which the collisional invariants of the Boltzmann collision integral are exploited. As in the case of its nonrelativistic version [20], the entropy production in this form suggests that energy dissipation arises owing to the dissipative evolution of nonconserved macroscopic variables  $\Phi_i^{(\alpha)\mu\nu\dots l}$ . As it stands in (4.62),  $\sigma_{ent}$  is easily seen to remain positive no matter what approximation is made to the unknown  $X_i^{(\alpha)}$ , thanks to the H theorem and the nonequilibrium canonical form for  $f_i$ . Since it is not possible to determine  $X_i^{(\alpha)}$  exactly, the positivity of  $\sigma_{ent}$  is a very useful property to have in formulating a thermodynamically consistent theory of irreversible processes. This is made possible by the nonequilibrium canonical form for the distribution function. The entropy balance equation (4.45a), as it stands, does not reveal how the second law works to conform irreversible processes to it. With the nonequilibrium canonical form, the situation is greatly improved and we are now able to calculate the entropy differential accompanying irreversible processes in a way consistent with the second law.

On substitution of the nonequilibrium canonical form into the statistical mechanical formula (4.23) and the entropy flux (4.45b) and use of the decomposition (4.22) for  $T_i^{\mu\nu}$ , we obtain the entropy flux of four-vector in the form

$$J_{s}^{\mu} = T^{-1} \sum_{i=1}^{m} (Q_{i}^{\mu} - \mu_{i} J_{i}^{\mu}) + T^{-1} \sum_{i=1}^{m} \sum_{\alpha \ge 1} X_{i\sigma...\nu}^{(\alpha)} \Omega_{i}^{(\alpha)\nu...\sigma\mu}$$
(4.63*a*)

where

$$\Omega_{i}^{(\alpha)\nu\dots\sigma\mu} = \psi_{i}^{(\alpha)\nu\dots\sigma\mu} - \hat{\Phi}_{i}^{(\alpha)\nu\dots\sigma}N^{\mu}$$
$$= -\psi_{i}^{(\alpha)\nu\dots\sigma\tau}\Delta_{\tau}^{\mu}. \qquad (4.63b)$$

Now, by subtituting (4.63a) and (4.63b) into the entropy balance equation (4.8) and eliminating the dissipation term  $\Lambda_i^{(\alpha)}$  and the divergences of  $Q_i^{\mu}$  and  $J_i^{\mu}$  with the help of the evolution equation for  $\hat{\Phi}_i^{(\alpha)}$  and the balance equations, we obtain DS in the form

$$DS = T^{-1}(D\varepsilon + pDv - \sum_{i=1}^{m} \mu_i Dc_i + \sum_{i=1}^{m} \sum_{\alpha \ge 1} X_i^{(\alpha)} \odot D\hat{\Phi}_i^{(\alpha)} - c^{-2}\hat{Q}^{\mu} DU_{\mu}) + \aleph$$

$$(4.64)$$

where

$$\aleph = \aleph_d - \aleph_c, \tag{4.65a}$$
$$\aleph_d = (\rho T)^{-1} \sum_{i}^{m} (-\Pi_i^{\mu\nu} \nabla_{\nu} U_{\mu} - \Delta_i \Delta^{\mu\nu} \nabla_{\nu} U_{\mu}$$

$$+ Q_i^{\mu} \partial_{\mu} lnT + J_i^{\mu} T \partial_{\mu} \bar{\mu}_i), \qquad (4.65b)$$

$$\aleph_c = \rho^{-1} \sum_{i=1}^m \sum_{\alpha \ge 1} [\partial_\mu (\bar{X}_i^{(\alpha)} \odot \Omega_i^{(\alpha)\mu}) + \bar{X}_i^{(\alpha)} \odot Z_i^{\alpha)}], \qquad (4.65c)$$

$$\bar{X}_i^{(\alpha)} = X_i^{(\alpha)}/T; \quad \bar{\mu}_i = \mu_i/T; \quad v = \rho^{-1}; \quad \hat{Q}^{\mu} = Q^{\mu}/\rho.$$
 (4.66)

i=1

Here we define the compensation differential

$$D\Psi = T^{-1}(D\varepsilon + pDv - \sum_{i=1}^{m} \mu_i Dc_i + \sum_{i=1}^{m} \sum_{\alpha \ge 1} X_i^{(\alpha)} \odot D\hat{\Phi}_i^{(\alpha)} - c^{-2}\hat{Q}^{\mu} DU_{\mu}) \quad (4.67)$$

which differs from the nonrelativistic formula only by the appearance of the velocity derivative term that is  $O(c^{-2})$  and thus vanishes in the nonrelativistic limit. It is interesting to see that in relativistic theory the fluid velocity appears explicitly as a Gibbs variable in contrast to the nonrelativistic theory.

Since the term  $\aleph$  does not vanish when the system is away from equilibrium, owing to the fact that the fluxes do not vanish in a nonequilibrium condition, the entropy differential DS is not equal to the compensation differential  $D\Psi$  and hence does not become a Pfaffian form [57]. Eq. (4.64) presages the invalidity of the extended Gibbs relation for DS unless  $\aleph = 0$  identically. To answer this question, we examine  $\aleph$  in detail.

The nonequilibrium contribution  $\aleph$  may be cast into a more transparent and useful form. To this end, the following relations are useful. The nonequilibrium canonical form for  $f_i$  may be recast into the form

$$\sum_{\alpha \ge 1} \bar{X}_i^{(\alpha)} \odot h_i^{(\alpha)} = \Delta \bar{\mu}_i - k_B ln(f_i/f_i^0), \qquad (4.68)$$

where

$$\Delta \mu_i = \bar{\mu}_i - \bar{\mu}_i^0, \qquad \bar{\mu}_i^e = \mu_i^e/T.$$

By using the kinetic equation and formula (4.40), it is possible to show that

$$\sum_{i=1}^{m} \sum_{\alpha \ge 1} \bar{X}_{i}^{(\alpha)} \odot Z_{i}^{(\alpha)} = \sum_{i=1}^{m} \sum_{\alpha \ge 1} [\langle f_{i} p_{i}^{\mu} \partial_{\mu} (\bar{X}_{i}^{(\alpha)} \odot h_{i}^{(\alpha)}) \rangle + \partial_{\mu} (\Delta_{\nu}^{\mu} \bar{X}_{i}^{(\alpha)} \odot \psi_{i}^{(\alpha)\nu})] - \sum_{i=1}^{m} \sum_{\alpha \ge 1} [\langle f_{i} p_{i}^{\mu} (\partial_{\mu} \bar{X}_{i}^{(\alpha)}) \odot h_{i}^{(\alpha)} \rangle + (\partial_{\mu} \bar{X}_{i}^{(\alpha)}) \odot \Delta_{\nu}^{\mu} \psi_{i}^{(\alpha)\nu}].$$
(4.69)

From the kinetic equation

$$\sum_{i=1}^{m} \langle f_i p_i^{\mu} \partial_{\mu} ln(f_i/f_i^0) \rangle = 0$$
(4.70)

and, in view of (4.28) and the decomposition  $\partial^{\mu} = c^{-2}U^{\mu}D + \nabla^{\mu}$ , we get

$$\langle f_i p_i^{\mu}(\partial_{\mu} \bar{X}_i^{(\alpha)}) \odot h_i^{(\alpha)} \rangle + (\partial_{\mu} X_i^{(\alpha)}) \odot \Delta_{\nu}^{\mu} \psi_i^{(\alpha)\nu}$$

$$= (\partial_{\mu} X_i^{(\alpha)}) \odot \psi_i^{(\alpha)\mu} + \Delta_{\nu}^{\mu} (\partial_{\mu} X_i^{(\alpha)}) \odot \psi_i^{(\alpha)\nu}$$

$$= (c^{-2} U_{\mu} D + \nabla_{\mu}) X_i^{(\alpha)} \odot \psi_i^{(\alpha)\mu} - (\nabla_{\mu} \bar{X}_i^{(\alpha)}) \odot \psi_i^{(\alpha)\mu}$$

$$= c^{-2} U_{\mu} \psi_i^{(\alpha)\mu} \odot D \bar{X}_i^{(\alpha)}$$

$$= \Phi_i^{(\alpha)} \odot D \bar{X}_i^{(\alpha)},$$

$$(4.71)$$

then there follows the relation

$$\begin{aligned} \aleph_{c} &= \rho^{-1} \sum_{i=1}^{m} [N_{i}^{\mu} \partial_{\mu} \Delta \bar{\mu}_{i} - \Phi_{i}^{(\alpha)} \odot D \bar{X}_{i}^{(\alpha)}] \\ &= \rho^{-1} \sum_{i=1}^{m} J_{i}^{\mu} \nabla_{\mu} \Delta \bar{\mu}_{i} - \sum_{i=1}^{m} [\sum_{\alpha \geq 1} \hat{\Phi}_{i}^{(\alpha)} \odot D \bar{X}_{i}^{(\alpha)} - c_{i} D \Delta \bar{\mu}_{i}]. \end{aligned}$$
(4.72)

The Gibbs-Duhem relation following from the statistical mechanical definition of  $\mu_i^e$  may be written in the form

$$\sum_{i=1}^{m} c_i D\bar{\mu}_i^e = \varepsilon D(1/T) + v D(p/T).$$
(4.73)

With (4.72) for  $\aleph_c$  and (4.73),  $\aleph$  can be recast into a more transparent form

$$\aleph = \sum_{i=1}^{m} \left( \sum_{\alpha \ge 1} \hat{\Phi}_{i}^{(\alpha)} \odot D\bar{X}_{i}^{(\alpha)} - c_{i} D\Delta\bar{\mu}_{i} \right) + \varepsilon D(1/T) + v D(p/T) - \hat{\sigma}_{L}$$
(4.74)

where

$$\hat{\sigma}_{L} = -(\rho T)^{-1} \sum_{i=1}^{m} (-\Pi_{i}^{\mu\nu} \nabla_{\nu} U_{\mu} + \Delta_{i} \nabla^{\mu} U_{\mu} + Q_{i}^{\mu} \nabla_{\mu} ln T + J_{i}^{\mu} T \nabla_{\mu} \bar{\mu}_{i}^{e}).$$
(4.75)

Note that this quantity is a measure of energy dissipation due to irreversible processes in the system. By defining the Boltzmann function  $\mathcal{B}$ 

$$\mathcal{B} = \mathcal{S} - T^{-1}(\varepsilon + pv - \sum_{i=1}^{m} c_i \mu_i - \sum_{i=1}^{m} \sum_{\alpha \ge 1} \hat{\Phi}_i^{(\alpha)} \odot \bar{X}_i^{(\alpha)})$$
(4.76)

and combining (4.64) with (4.74), we finally obtain a differential equation for  $\mathcal{B}$  which is equivalent to the entropy balance equation (4.45a):

$$D\mathcal{B} = -\hat{\sigma}_L - c^{-2}T^{-1}\hat{Q}^{\mu}DU^{\mu}.$$
(4.77)

This equation differs from the nonrelativistic analog [20] by the last term which vanishes in the nonrelativistic limit. By using the the momentum balance equation, we may write (4.77) in the form

$$D\mathcal{B} = -\Xi_d \tag{4.78}$$

where

$$\Xi_{d} = -(\rho T)^{-1} \sum_{i=1}^{m} [-\Pi_{i}^{\mu\nu} \nabla_{\nu} U_{\mu} + \Delta_{i} \nabla^{\mu} U_{\mu} + Q_{i}^{\mu} (\nabla_{\mu} ln T + h^{-1} \nabla_{\mu} p) + J_{i}^{\mu} T \nabla_{\mu} \bar{\mu}_{i}^{\epsilon}] - T^{-1} \hat{Q}^{\mu} [\Delta_{\mu\sigma} \partial_{\nu} \bar{P}^{\sigma\nu} + c^{-2} (\Delta_{\mu\nu} D Q^{\nu} - Q_{\mu} \nabla_{\nu} U^{\nu} - Q^{\nu} \nabla_{\nu} U_{\mu})].$$
(4.79)

The dissipation term  $\Xi_d$  contains terms quadratic in fluxes such as  $Q^{\mu}$  and  $\bar{P}^{\sigma\nu}$  which are one order higher than the terms in  $\hat{\sigma}_L$ ; they are relativistic effects.

The dissipation term  $\Xi_d$  does not vanish if there is an irreversible process present in the system, and consequently  $DB \neq 0$  except at equilibrium. This means that DS is not an exact differential and not equal to the compensation differential  $D\Psi$  away from equilibrium. That is, the extended Gibbs relation for DS does not exist if the system is away from equilibrium, in contradiction with the premise made in the relativistic version of extended irreversible thermodynamics. This is a rigorous result based on the covariant Boltzmann equation and does not require an explicit solution for the unknowns  $X_i^{(\alpha)}$  for its validity as long as the latter exist. There exists a differential form for the compensation function  $\Psi$  that looks like an extended Gibbs relation, however. It may be used to construct a thermodynamic theory of irreversible processes in a way parallel to equilibrium thermodynamics. The theory will provide various relations between nonequilibrium thermodynamic quantities that can be related to experimental observables. In any case, the present result on DS calls for revision of the exiting notions of nonequilibrium entropy and entropy fluxes and of the applications thereof in extended irreversible thermodynamics [21], including its relativistic version.

# 4.6 Cumulant expansion for the dissipation terms $\Lambda_i^{(\alpha)}$

The dissipation terms  $\Lambda_i^{(\alpha)}$  defined in (4.37) must be calculated in terms of macroscopic variables before the evolution equations for  $\Phi_i^{(\alpha)}$  are solved for specific flow problems. Since  $\Lambda_i^{(\alpha)}$  are intimately related to the entropy production and the latter must remain positive regardless of the approximation made to  $\Lambda_i^{(\alpha)}$ , it is best to calculate the dissipation terms through the entropy production that is manifestly positive. As in the nonrelativistic kinetic theory, the aim is nicely achieved if a cumulant expansion is employed.

To this end, we first write the distribution function in the form

$$f_i = f_i^0 exp(-\omega_i) \tag{4.80}$$

where  $f_i^0$  is the local Jüttner (equilibrium distribution) function

$$f_i^0 = exp[-\beta(p_i^{\mu}U_{\mu} - \mu_i^e)], \qquad (4.81a)$$

$$exp(-\beta\mu_i^e) = \rho_i^{-1} \langle c^{-2} p_i^{\nu} U_{\nu} exp(-\beta p_i^{\mu} U_{\mu}) \rangle, \qquad (4.81b)$$

$$\omega_i = \beta (H_i^{(1)} - \Delta \mu_i). \tag{4.81c}$$

We also define the abbreviation

$$x_{ij} = \omega_i + \omega_j, \qquad y_{ij} = \omega_i^* + \omega_j^*, \qquad (4.82)$$

and the following reduced variables

$$\pi_i^{\mu} = c p_i^{\mu} \beta, \qquad \bar{U}^{\mu} = U^{\mu} / c.$$
 (4.83)

The distribution function may be scaled with the factor  $\rho/(mk_BT)^{3/2}$  where m is the mean rest mass of the mixture; that is,

$$f_i^0 = \left[\rho/(mk_B T)^{3/2}\right] \bar{f}_i^0. \tag{4.84}$$

Therefore,  $\tilde{f}_i^0$  is dimensionless. The transition rate  $W_{ij}$  is scaled by  $\lambda^2/mk_BT$  where  $\lambda$  is a parameter with the dimension of length. We may take  $\lambda$  to be the mean free path or the interaction range or the size parameter. Thus, we write

$$W_{ij} = \bar{W}_{ij} (\lambda^2 / m k_B T) \tag{4.85}$$

so that  $\bar{W}_{ij}$  is dimensionless. It is then convenient to define the parameter

$$g = (mc^2/k_B T)^4/c\lambda^2 \rho^2$$
 (4.86)

which has a dimension of volume  $\times$  time. If this parameter is multiplied to the collision integral for the entropy production, it is rendered dimensionless as follows:

$$\sigma_{ent}(x) = k_B \hat{\sigma}_{ent}(x)/g \tag{4.87}$$

where the dimensionless reduced entropy production  $\hat{\sigma}_{ent}(x)$  is given by the integral

$$\hat{\sigma}_{ent}(x) = \frac{1}{4} \sum_{i=1}^{m} \sum_{j=1}^{m} \ll (x_{ij} - y_{ij}) [exp(-y_{ij}) - exp(-x_{ij})] \gg$$
(4.88)

where

$$\ll \ldots \gg = G_{ij} \int d^3 \bar{\pi}_i d^3 \bar{\pi}_j d^3 \bar{\pi}_i^* d^3 \bar{\pi}_j^* \bar{f}_i^0 \bar{f}_j^0 \bar{W}_{ij} \dots, \qquad (4.89)$$

with  $d^3 \bar{\pi}_i = d^3 \pi_i / \pi_i^0$ . Then, with the definitions

$$\Theta^{(+)}(\varepsilon) = \sum_{i=1}^{m} \sum_{j=1}^{m} \ll (x_{ij} - y_{ij})[exp(-\varepsilon y_{ij}) - 1] \gg, \qquad (4.90a)$$

$$\Theta^{(-)}(\varepsilon) = \sum_{i=1}^{m} \sum_{j=1}^{m} \ll (x_{ij} - y_{ij})[exp(-\varepsilon x_{ij}) - 1] \gg, \qquad (4.90b)$$

the reduced entropy production may be written as

$$\hat{\sigma}_{ent}(x) = \frac{1}{4} [\Theta^{(+)}(\varepsilon) - \Theta^{(-)}(\varepsilon)]_{\varepsilon=1}.$$
(4.91)

Now, the factors  $\Theta^{(\pm)}(\varepsilon)$  are in exactly the same form as the factors appearing in the nonrelativistic version of the modified moment method for the entropy production. We can, therefore, apply the same cumulant expansion method as for the nonrelativistic version to obtain the cumulant expansion for  $\hat{\sigma}_{ent}(x)$ . Since the method is well documented [56], we will simply list the result. Let

$$\kappa = \ll \frac{1}{4} \sum_{i=1}^{m} \sum_{j=1}^{m} (x_{ij} - y_{ij})^2 \gg^{1/2}, \qquad (4.92a)$$

$$\kappa_2 = \ll \frac{1}{4} \sum_{i=1}^m \sum_{j=1}^m (x_{ij} - y_{ij})^2 (x_{ij} + y_{ij}) \gg, \qquad (4.92b)$$

$$\kappa_3 = \ll \frac{1}{4} \sum_{i=1}^m \sum_{j=1}^m (x_{ij} - y_{ij})^2 (x_{ij}^2 + x_{ij}y_{ij} + y_{ij}^2) \gg, \quad etc.$$
(4.92c)

Then, we find to the first order cumulant approximation the reduced entropy production has the form

$$\hat{\sigma}_{ent}(x) = \kappa \sinh \kappa \ge 0. \tag{4.93}$$

It is easy to see that  $\hat{\sigma}_{ent}(x)$  is always positive and therefore the second law of thermodynamics is satisfied completely. The higher order cumulant approximations can also be obtained in a similar procedure. First, let us observe that  $\kappa$  may be expressed in the quadratic form

$$\kappa = \left[\sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{\alpha, \gamma \ge 1} X_i^{(\alpha)} \odot R_{ij}^{(\alpha\gamma)} \odot X_j^{(\gamma)}\right]^{1/2}$$
(4.94)

where  $R_{ij}^{(\alpha\gamma)}$  are the collision bracket integrals appearing in the Chapman-Enskog method. To write them explicitly, we define the brackets as follows:

$$[A \odot B]_{ij} = G_{ij} \int d^3 \overline{\pi}_i d^3 \overline{\pi}_j d^3 \overline{\pi}_i^* d^3 \overline{\pi}_j^* \overline{f}_i^0 \overline{f}_j^0 \overline{W}_{ij} A \odot B.$$

Then, the collision bracket integrals are:

$$R_{ii}^{(\alpha\gamma)} = \frac{1}{4}\beta^{2} [(h_{i}^{(\alpha)} + h_{i'}^{(\alpha)} - h_{i}^{(\alpha)*} - h_{i'}^{(\alpha)*})(h_{i}^{(\gamma)} + h_{i'}^{(\gamma)} - h_{i}^{(\gamma)*} - h_{i'}^{(\gamma)*})]_{ii'} + \frac{1}{2}\beta^{2} \sum_{j\neq i} [(h_{i}^{(\alpha)} - h_{i'}^{(\alpha)*})(h_{i}^{(\gamma)} - h_{i}^{(\gamma)*})]_{ij}, \qquad (4.95a)$$

$$R_{ij}^{(\alpha\gamma)} = \beta^2 \sum_{j \neq i} [(h_i^{(\alpha)} - h_j^{(\alpha)*})(h_i^{(\gamma)} - h_j^{(\gamma)*})]_{ij}, \quad (i \neq j).$$
(4.95b)

These integrals satisfy the Onsager reciprocal relations. We remark that  $\kappa^2$  is intimately related to the Rayleigh-Onsager dissipation function which is quadratic in fluxes.

By using (4.94) in (4.93) and comparing the latter with (4.62), we find the dissipation terms to the first order cumulant approximation:

$$\Lambda_i^{(\alpha)} = (\beta g)^{-1} \sum_{j=1}^m \sum_{\gamma \ge 1} R_{ij}^{(\alpha \gamma)} \odot X_j^{(\gamma)}(\sinh \kappa / \kappa).$$
(4.96)

This form of dissipation terms is completely consistent with the second law of thermodynamics inasmuch as the entropy production in (4.93) is positive. Higher order forms  $\Lambda_i^{(\alpha)}$  can be similarly found from the higher cumulant approximations for  $\hat{\sigma}_{ent}$ .

# 4.7 Determination of the unknowns $X_i^{(\alpha)}$

With various thermodynamically consistent macroscopic evolution equations and the entropy balance equation in place in the theory, there now remains the task of determining the unknowns  $X_i^{(\alpha)}$  appearing in the nonequilibrium canonical form of the distribution function. They can be determined in a manner completely parallel to the case of the nonrelativistic theory. Nevertheless, since the equations involved are different, it is necessary to elaborate on the method.

Since the distribution function can be expanded into moments as in the conventional moment method, we may write

$$f_{i} = f_{i}^{0} (1 + \sum_{\alpha \ge 1} A_{i}^{(\alpha)} \odot h_{i}^{(\alpha)})$$
(4.97)

where the coefficients  $A_i^{(\alpha)}$  are functions of macroscopic variables such as temperature, fluxes, etc. as will be shown presently. It must be noted that the construction of an irreversible thermodynamic theory with the form (4.97), particularly when the system is away from equilibrium, is not appropriate since the entropy production can not be positive beyond the linear order. However, the moment expansion for the nonequilibrium distribution function is mathematically acceptable. On the other hand, the nonequilibrium canonical form and the moment expansion share the same set of moments. This means that we can calculate the unknowns  $X_i^{(\alpha)}$  in the nonequilibrium canonical form with the help of the moment expansion (4.97). By equating (4.61a) and (4.97) and taking logarithm, we obtain the equation

$$k_{B}^{-1}(\Delta \bar{\mu}_{i} - \sum_{\alpha \ge 1} X_{i}^{(\alpha)} \odot h_{i}^{(\alpha)}) = \ln(1 + \sum_{\gamma \ge 1} A_{i}^{(\gamma)} \odot h_{i}^{(\gamma)}).$$
(4.98)

Since the moments  $h_i^{(\alpha)}$  are chosen such that they are orthogonal in the following sense

$$\langle f_i^0(p_i^{\lambda}U_{\lambda})^{-1}\bar{h}_i^{(\alpha)}\bar{h}_i^{(\gamma)}\rangle = \delta_{\alpha\gamma}\langle f_i^0(p_i^{\lambda}U_{\lambda})^{-1}\bar{h}_i^{(\alpha)}\bar{h}_i^{(\alpha)}\rangle$$
(4.99)

where  $\bar{h}_i^{(\alpha)}$  are defined by

$$\bar{h}_{i}^{(\alpha)} = c^{-2} U_{\sigma} p_{i}^{\sigma} h_{i}^{(\alpha)}.$$
(4.100)

 $A_i^{(\alpha)}$  are given in terms of fluxes as follows:

$$\Phi_i^{(\alpha)\mu\nu\dots l} = \langle f_i^0 \bar{h}_i^{(\alpha)\mu\nu\dots l} (1 + \sum_{\gamma \ge 1} A_i^{(\gamma)} \odot h_i^{(\gamma)}) \rangle$$

$$= A_{i}^{(\alpha)} \odot \sum_{\gamma \ge 1} \langle f_{i}^{0} \bar{h}_{i}^{(\alpha)\mu\nu\dots l} h_{i}^{(\gamma)} \rangle$$
  
$$= A_{i}^{(\alpha)} \odot \langle f_{i}^{0} \bar{h}_{i}^{(\alpha)\mu\nu\dots l} h_{i}^{(\alpha)} \rangle.$$
(4.101)

Note that the fluxes on the left-hand side are determined from the flux evolution equations. The quantity in the angular brackets in (4.101) is a function of temperature only. Therefore, the coefficients  $A_i^{(\alpha)}$  are directly proportional to  $\Phi_i^{(\alpha)\mu\nu\dots l}$ . In fact, it is possible to write

$$A_i^{(1)\mu\nu} = \frac{1}{5} \Phi_i^{(1)\mu\nu} / \langle f_i^0 \bar{h}_i^{(1)} : h_i^{(1)} \rangle, \qquad (4.102a)$$

$$A_{i}^{(2)} = \Phi_{i}^{(2)} / \langle f_{i}^{0} \bar{h}_{i}^{(2)} h_{i}^{(2)} \rangle, \qquad (4.102b)$$

$$A_i^{(3)\mu} = \frac{1}{3} \Phi_i^{(3)\mu} / \langle f_i^0 \bar{h}_i^{(3)} \cdot h_i^{(3)} \rangle, \qquad (4.102c)$$

$$A_i^{(4)\mu} = \frac{1}{3} \Phi_i^{(4)\mu} / \langle f_i^0 \bar{h}_i^{(4)} \cdot h_i^{(4)} \rangle, \quad etc.$$
(4.102d)

By applying the same procedure as for (4.101), we obtain from (4.98) the  $X_i^{(\alpha)}$  in terms of  $A_i^{(\gamma)}$ :

$$-\beta X_i^{(\alpha)} \langle f_i^0 \bar{h}_i^{(\alpha)} \odot h_i^{(\alpha)} \rangle = A_i^{(\alpha)} \langle f_i^0 \bar{h}_i^{(\alpha)} \odot h_i^{(\alpha)} \rangle$$

which implies that

$$X_i^{(\alpha)} = -\beta^{-1} A_i^{(\alpha)}$$
 (4.103)

where  $A_i^{(\alpha)}$  are given by (4.102a)-(4.102d). It is convenient to write the results in the form

$$X_i^{(\alpha)} = -\Phi_i^{(\alpha)}/g_i^{(\alpha)} \tag{4.104}$$

where  $g_i^{(\alpha)}$  can be easily identified from (4.102); their nonrelativistic limits are

$$g_i^{(1)} = 2p_i; \quad g_i^{(2)} = 2p_i/3; \quad g_i^{(3)} = T\hat{C}_{p_i}p_i; \quad g_i^{(4)} = m_i n_i.$$
 (4.105)

Here  $\hat{C}_{pi}$  is the specific heat per mass of species *i* at constant pressure. The results given in (4.105) are already known in the nonrelativistic version of the modified

moment method [20]. This means that the present modified moment method for covariant Boltzmann equation contains the nonrelativistic counterpart as a limiting case. On other hand, the coincidence with the well-known results at the nonrelativistic limit serves as a justification for the extension of the modified moment method for the relativistic Boltzmann equation.

### 4.8 Transport coefficients

In order to evaluate the transport coefficients of relativistic gases in terms of dynamical quantities such as differential cross sections, we first linearize the flux evolution equations (4.39) as follows:

$$\rho D\hat{\Phi}_{i}^{(\alpha)\mu\nu\dots l} = \chi_{i}^{(\alpha)\mu\nu\dots l} - (\beta g)^{-1} g_{i}^{(\alpha)} \sum_{j=1}^{m} \sum_{\gamma \ge 1} \bar{R}_{ij}^{(\alpha\gamma)\mu\nu\dots l} \odot \Phi_{j}^{(\gamma)}$$
(4.106)

where  $\chi_i^{(\alpha)\mu\nu\dots l}$  are the linear parts of the kinematic terms  $Z_i^{(\alpha)\mu\nu\dots l}$ ; they are related to the thermodynamic driving forces by the relations:

$$\chi_{i}^{(1)\mu\nu} = 2p_{i}[\nabla U]^{(2)\mu\nu}; \quad \chi_{i}^{(2)} = -p_{i}Dlnv^{5/3};$$
  
$$\chi_{i}^{(3)\mu} = p_{i}c^{2}(\nabla^{\mu}lnT - \frac{k_{B}T}{h}\nabla^{\mu}lnp); \qquad (4.107)$$

and

$$\bar{R}_{ij}^{(\alpha\gamma)} = (g_i^{(\alpha)})^{-1} R_{ij}^{(\alpha\gamma)} (g_j^{(\gamma)})^{-1}$$
(4.108)

is the collision bracket integrals.

For system in a steady state, the linearized flux evolution equations (4.106) can be reduced to the constitutive equations

$$\chi_{i}^{(\alpha)\mu\nu\dots l} - (\beta g)^{-1} g_{i}^{(\alpha)} \sum_{j=1}^{m} \sum_{\gamma \ge 1} \bar{R}_{ij}^{(\alpha\gamma)\mu\nu\dots l} \odot \Phi_{j}^{(\gamma)} = 0.$$
 (4.109)

This is a set of coupled linear equations. Since the system is isotropic we can expand the various rank tensors  $\bar{R}_{ij}^{(\alpha)\mu\nu...l}$  in terms of isotropic tensors, for instance,

$$\bar{R}_{ij}^{(11)\mu\nu kl} = \bar{\mathcal{R}}_{ij}^{(11)} [\frac{1}{2} (\Delta^{\mu k} \Delta^{\nu l} + \Delta^{\mu l} \Delta^{\nu k}) - \frac{1}{3} \Delta^{\mu \nu} \Delta^{kl}], \qquad (4.110)$$

then,

$$\begin{split} \ddot{\mathcal{R}}_{ij}^{(11)} &= \frac{1}{5} R_{ij}^{(11)\mu\nu kl} [\frac{1}{2} (\Delta^{\mu k} \Delta^{\nu l} + \Delta^{\mu l} \Delta^{\nu k}) - \frac{1}{3} \Delta^{\mu\nu} \Delta^{kl}] \\ &= \frac{1}{10} \beta^2 (g_i^{(1)} g_j^{(1)})^{-1} \sum_{j \neq i} [(h_i^{(1)} - h_j^{(1)*}) : (h_i^{(1)} - h_j^{(1)*})]_{ij}. \end{split}$$
(4.111)

Similarly,

$$\bar{\mathcal{R}}_{ii}^{(11)} = \frac{1}{5} \beta^2 (g_i^{(1)})^{-2} \{ \frac{1}{4} \times [(h_i^{(1)} + h_{i'}^{(1)} - h_i^{(1)*} - h_{i'}^{(1)*}) : (h_i^{(1)} + h_{i'}^{(1)} - h_i^{(1)*} - h_{i'}^{(1)*})]_{ii'} + \frac{1}{2} \sum_{j \neq i} [(h_i^{(1)} - h_i^{(1)*}) : (h_i^{(1)} - h_i^{(1)*})]_{ij} \}.$$

$$(4.111')$$

Here the prime on the subscript *i* means another particles of species *i*. Since  $\Phi_j^{(1)}$  is a traceless symmetric tensor, we find

$$\bar{R}_{ij}^{(11)\mu\nu kl} \Phi_{jkl}^{(1)} = \bar{\mathcal{R}}_{ij}^{(11)} \Phi_j^{(1)\mu\nu}.$$
(4.112)

When  $\alpha = 2$ ,  $\vec{R}_{ij}^{(22)}$  is a scalar, therefore

$$\bar{R}_{ij}^{(22)} = \bar{\mathcal{R}}_{ij}^{(22)} \tag{4.113}$$

where

$$\bar{\mathcal{R}}_{ij}^{(22)} = \beta^2 (g_i^{(2)} g_j^{(2)})^{-1} \frac{1}{2} \sum_{j \neq i} [(h_i^{(2)} - h_j^{(2)*}) \cdot (h_i^{(2)} - h_j^{(2)*})]_{ij}.$$
(4.114)

In case of  $\alpha = 3$ , the tensor  $\bar{R}_{ij}^{(33)\mu\nu}$  is decomposable as follows:

$$\bar{R}_{ij}^{(33)\mu\nu} = \bar{\mathcal{R}}_{ij}^{(33)} \Delta^{\mu\nu} \tag{4.115}$$

where

$$\bar{\mathcal{R}}_{ij}^{(33)} = \frac{1}{3}\beta^2 (g_i^{(3)}g_j^{(3)})^{-1} \frac{1}{2} \sum_{j \neq i} [(h_i^{(3)} - h_j^{(3)*}) \cdot (h_i^{(3)} - h_j^{(3)*})]_{ij}.$$
(4.116)

Therefore, we finally obtain

$$\ddot{R}_{ij}^{(33)\mu\nu}\Phi_{j\nu}^{(3)} = \dot{\mathcal{R}}_{ij}^{(33)}\Phi_{j}^{(3)\mu}.$$
(4.117)

With the help of these properties, we can write (4.109) in the form:

$$\chi_i^{(1)\mu\nu} - (\beta g)^{-1} g_i^{(1)} \sum_{j=1}^m \bar{\mathcal{R}}_{ij}^{(11)} \Phi_j^{(1)\mu\nu} = 0, \qquad (4.118a)$$

$$\chi_i^{(2)} - (\beta g)^{-1} g_i^{(2)} \sum_{j=1}^m \bar{\mathcal{R}}_{ij}^{(22)} \Phi_j^{(2)} = 0, \qquad (4.118b)$$

$$\chi_i^{(3)\mu} - (\beta g)^{-1} g_j^{(3)} \sum_{j=1}^m \bar{\mathcal{R}}_{ij}^{(33)} \Phi_j^{(3)\mu} = 0.$$
(4.118c)

On solving these equations for the fluxes, we obtain the linear constitutive equations from which the transport coefficients may be determined:

$$\Phi_i^{(1)\mu\nu} = \beta g \sum_{j=1}^m (\bar{\mathcal{R}}^{(11)-1})_{ij} \chi_j^{(1)\mu\nu} / g_j^{(1)}, \qquad (4.119a)$$

$$\Phi_i^{(2)} = \beta g \sum_{j=1}^m (\bar{\mathcal{R}}^{(22)-1})_{ij} \chi_j^{(2)} / g_j^{(2)}, \qquad (4.119b)$$

$$\Phi_i^{(3)\mu} = \beta g \sum_{j=1}^m (\bar{\mathcal{R}}^{(33)-1})_{ij} \chi_j^{(3)\mu} / g_j^{(3)}.$$
(4.119c)

Comparing (4.119) with the linear phenomenological constitutive equations, such as, the Newtonian law of viscosity and the Fourier law of heat conduction, we obtain the shear viscousity, bulk viscousity, and heat conductivity in terms of the collision bracket integrals as follows:

shear viscosity:

$$\eta = \sum_{i=1}^{m} \sum_{j=1}^{m} \beta g(p_j/g_j^{(1)})(\bar{\mathcal{R}}^{(11)-1})_{ij}, \qquad (4.120a)$$

bulk viscosity:

$$\zeta = \sum_{i=1}^{m} \sum_{j=1}^{m} \beta g(5p_j/3g_j^{(2)})(\bar{\mathcal{R}}^{(22)-1})_{ij}, \qquad (4.120b)$$

thermal conductivity:

$$\lambda = \sum_{i=1}^{m} \sum_{j=1}^{m} \beta g(p_j c^2 / g_j^{(3)}) (\bar{\mathcal{R}}^{(33)-1})_{ij}.$$
(4.120c)

Once the differential cross sections for particular systems of relativistic gases are given, we are able to compute all these transport coefficients by using the formulas (4.120).

#### 4.9 Discussion and conclusion

We have applied the modified moment method for the covariant Boltzmann equation for a relativistic monatomic gas mixture. The method affords us a rigorous conclusion concerning the entropy differential when the system is away from equilibrium; it is not an exact differential since  $\aleph$ , or equivalently  $\Xi_d$ , is not equal to zero if there exists a nonequilibrium process in the system. This means that the extended Gibbs relation forming the basis of the extended irreversible thermodynamics (EIT) does not hold valid at least from the viewpoint of the covariant Boltzmann equation. However, there is the compensation differential that looks like the extended Gibbs relation used in EIT, but this means a revision of the existing EIT formalism and its logical structure. The entropy balance equation is put into another equivalent form in terms of the Boltzmann function B introduced as a Legendre transformation of the entropy density. However, the differentiation of  $\mathcal{B}$  is not an exact differential, since  $\Xi_d$  is not even a differential form in the nonequilibrium Gibbs space. As a matter of fact, this Boltzmann function  $\mathcal{B}$  is dependent on the initial condition and the history of the process involved, namely,  $\mathcal B$  is path-dependent. This means that  $d\mathcal S$  is not integrable, therefore, not an exact differential, and the extended Gibbs relation simply does not exist. As mentioned earlier, the non-vanishing  $\mathcal{B}$  for irreversible processes has some significant consequences for irreversible thermodynamics and, in particular, for the EIT formalism. The most immediate and obvious consequence is the fact that the extended Gibbs relation for dS cannot be taken for granted and the notion and role of entropy density for nonequilibrium system should be basically revised [33, 57]. In fact, for nonequilibrium systems the entropy density itself is a quantity depending on the path taken in the nonequilibrium thermodynamic phase space (nonequilibrium Gibbs space) by the system when it makes transition from a state to another in the space. Therefore, the notion of equilibrium entropy, which is a state function (an exact differential), does not apply to the nonequilibrium entropy if it is defined by the statistical formula (4.23) or its scalar version.

In the case of the extended Gibbs relation for dS, if the processes are in a steady state so that  $D\varepsilon$ , Dv,  $Dc_i$ ,  $D\hat{\Phi}_i^{(\alpha)}$ , and  $DU_{\mu}$  are equal to zero then the entropy does not change despite the fact that the system is in nonequilibrium. Contrary to this situation, since as long as there are spatial gradients of velocity, temperature, concentrations, etc. so that  $\Xi_d \neq 0$ , the Boltzmann function changes even if the processes are steady, that is, DS does not vanish at the steady state. Therefore, the entropy density evolves on a constant hypersurface:

$$\Psi(\varepsilon, v, c_i, \hat{\Phi}_i^{(\alpha)}, U_\mu) = constant.$$

Figuratively speaking, it winds the surface which may be imagined to be a hypercylinder in the nonequilibrium Gibbs space, owing to the steady production of entropy since the entropy is produced even at a steady state. This difference in the behavior of entropy from the EIT, where the extended Gibbs relation is assumed, makes the present theory suitable to deal with not only systems near equilibrium but also those far away from equilibrium.

The present study also indicates that the compensation differential may be used to investigate the thermodynamics of nonequilibrium systems in a way rather parallel to equilibrium thermodynamics. Nevertheless, such a formalism still requires integration of the relativistic generalized hydrodynamic equations as an integral part of the theory. Since the latter are not trivial to solve, there remains a great deal of work to be done on the subject matter in the future. This formalism in essence puts the statistical mechanics of nonequilibrium thermodynamics on the par with the Gibbs ensemble theory of equilibrium statistical thermodynamics in the sense that all thermodynamic functions and evolution equations are expressed in terms of  $X_i^{(\alpha)}$ , which must be ultimately obtained by solving the generalized hydrodynamics, just as all equilibrium thermodynamic functions and relations are expressed in the Gibbs ensemble theory in terms of a partition function which must be computed for each and every system in the end.

All the macroscopic evolution equations are presented in such forms that they consist of terms which are easily identifiable with the corresponding terms in their nonrelativistic versions and purely relativistic terms which vanish in the nonrelativistic limit. Thus, the relativistic corrections to the classical generalized hydrodynamic equations are clearly exposed and made easy to obtain. Since the full relativistic generalized hydrodynamic equations are much more complicated to solve than their already difficult nonrelativistic counterpart, the first order relativistic corrections to the latter are all one can hope for in practice at present, and the relativistic generalized hydrodynamic equations presented here should be useful for such a study.

### Chapter 5

# Covariant kinetic theory and irreversible thermodynamics of radiation and matter

The nonrelativistic kinetic theory of irreversible processes in a system of radiation and matter presented in the chapter 2 is generalized to the relativistic case. This generalization enables us to remove the awkwardness inherent to the nonrelativistic theory and provide kinetic theory foundations for relativistic irreversible thermodynamics for a system of radiation and matter. The Boltzmann equations, more precisely, a modified form of the Wang Chang-Uhlenbeck equations [58] have been solved by means of the modified moment method which seeks the solution of the kinetic equations in a way consistent with the thermodynamic laws [34]. The motivations to have this covariant kinetic theory are following. Relativity principle requires that governing equations in theory must be Lorentz covariant. As mentioned earlier, treating material particles as nonrelativistic particles and making Doppler shift corrections for photon frequencies makes calculation inconvenient. It is also difficult to make sure that the definitions of statistical formulas for macroscopic variables and the evolution equations are correct limits of relativistic theory. These features can be easily removed if a covariant theory is formulated. Secondly, there are some problems, especially in the study of the early epoch of the universe, where a relativistic formalism is required since particles move at high speeds and interact with radiation. It will be shown that the present covariant kinetic theory recovers all the nonrelativistic evolution equations in correct forms with proper relativistic connections and thus verifies the previous nonrelativistic formulation [17].

First, covariant Boltzmann equations are briefly presented for a system consisting of photons and material particles with internal degrees of freedom. The material gas molecules can make transitions between various internal states in interaction with photons by absorbing, emitting, or scattering the latter. These dynamical processes at the particulate level are described by the Boltzmann collision terms in the covariant Boltzmann equations. Consequently, the generalized hydrodynamic equations are derived from the covariant kinetic equations for radiation and matter which are fully consistent with the thermodynamic laws at any degree of removal from equilibrium.

The consistency between the relativistic Boltzmann distribution and the Planck distribution function has been a point of controversy in the past [59, 60], and present covariant kinetic theory makes it possible to examine it. We show that both distribution functions are consistent with each other within the framework of relativity and their mutual consistency is intimately related to the H theorem and therefore deeply rooted in the second law of thermodynamics. In this connection it is interesting to recall that the original derivation by Planck of the radiation distribution function itself was based on thermodynamics [1].

### 5.1 Covariant Boltzmann equations for radiation and matter

We assume that the system consists of a gas with internal degrees of freedom (e.g., atoms or diatomic molecules, etc.) which interact with a radiation field (photons) that is not necessarily in equilibrium. The internal quantum states of the material particles will be denoted by i and the particles in different internal quantum states will be regarded as different species. Therefore, the material gas is considered as a mixture of particles with different "colors" distinguished by the value of i. For example, if the particle species is the hydrogen atom, then the index irepresents the  $1s, 2p, \dots$ , states suitably arranged. The mass of the particle species i will be denoted by  $m_i$  and its momentum by  $\mathbf{p}_i$ , the kinetic energy by  $cp_i^0$  with cdenoting the speed of light. It is then convenient to introduce the four-momentum of species i

$$p_i \equiv p_i^{\mu} = (p_i^0, \mathbf{p}_i) \tag{5.1}$$

where

$$p_i^0 = (\mathbf{p}_i \cdot \mathbf{p}_i + m_i^2 c^2)^{1/2}.$$
 (5.2)

This formula looks like the one holding for a structureless particles, but different masses  $m_i$  are assigned to the particles in different internal states. The point can be illustrated in a following way. According to relativistic quantum mechanics, the Dirac equation for the hydrogen atom gives the energy eigenvalues [61] depending on the two quantum numbers n and J

$$E_{nJ} = m_e c^2 [1 + Z_e^2 \alpha^2 / (n - \varepsilon_J)^2]^{-1/2}$$
(5.3a)

where

$$\varepsilon_J = J + \frac{1}{2} - [(J + \frac{1}{2})^2 - Z_e^2 \alpha^2]^{1/2}$$
(5.3b)

 $\alpha$  is the fine structure constant:  $\alpha = e^2/hc \approx 1/137$ ,  $Z_e$  is the electron number in atom and  $m_e$  is the rest mass of the electron. If we set  $E_{nJ} = m_i c^2$  where *i* stands for the set (n, J), (5.3a) suggests that the mass of the excited particles is not same as the rest mass of the ground-state particles. Therefore,  $m_i$  contains the information on the internal state of the particle. It is easy to show by expansion that approximately

$$m_i = m_e + E_i/c^2 \tag{5.4}$$

where  $E_i$  is the energy eigenvalue:  $E_i = -Z_e^2 \alpha^2/2i^2$ . The time component  $p_i^0$  in the four-momentum in (5.1) is understood in the sense of (5.4) or its precursor (5.3a) and will be used accordingly in the calculations made in connection with the two-body dynamics in this work. The singlet distribution function of species *i* will be denoted by  $f_i(x, p_i)$ , the italic subscript *r* being reserved for radiation. We consider the following microscopic collision processes:

$$i+j \rightleftharpoons i^* + j^* \tag{M1}$$

$$i+j \rightleftharpoons k+l \tag{M2}$$

$$i + \hbar \omega \rightleftharpoons i^* + \hbar \omega^* \tag{M3}$$

$$i + \hbar\omega \rightleftharpoons j + \hbar\omega^*$$
 (M4)

where i, j, k and l stand for the species and the asterisk denotes the post-collision quantity. Therefore, for example,  $\omega^*$  means the frequency of radiation after collision. Let subscript a stand for species of particles including photons which will be designated the rth species. We assume that the singlet distribution function  $f_a(x, p_a)$  for species a obeys the covariant Boltzmann equation

$$p_a^{\nu} \partial_{\nu} f_a(x, p_a) = \sum_{b=i}^r \Re_{ba}[f_a f_b] \equiv \Re_a[f_a]$$
(5.5)

where

$$\Re_a[f_a] = \sum_{b=i}^r [C(f_a f_b) + \sum_k \sum_l C_r(f_a f_b | f_k^* f_l^*)].$$
(5.6)

Here the subscript b runs over all species including material particles and photons. The Boltzmann collision integrals  $C(f_a f_b)$  and  $C_r(f_a f_b | f_k^* f_l^*)$  are given by

$$C(f_{a}f_{b}) = G_{a} \int d^{3}\bar{p}_{a}^{*}d^{3}\bar{p}_{b}^{*}d^{3}\bar{p}_{b}W^{(\epsilon)}(p_{a}p_{b}|p_{a}^{*}p_{b}^{*}) \times [f_{a}^{*}f_{b}^{*}(1+\epsilon_{a}f_{a})(1+\epsilon_{b}f_{b}) - f_{a}f_{b}(1+\epsilon_{a}f_{a}^{*})(1+\epsilon_{b}f_{b}^{*})] \\ + \sum_{k}\sum_{l}G_{a} \int d^{3}\bar{p}_{k}^{*}d^{3}\bar{p}_{l}^{*}d^{3}\bar{p}_{b}W^{(n)}(p_{a}p_{b}|p_{k}^{*}p_{l}^{*}) \\ - [f_{k}^{*}f_{l}^{*}(1+\epsilon_{a}f_{a})(1+\epsilon_{b}f_{b}) - f_{a}f_{b}(1+\epsilon_{k}f_{k}^{*})(1+\epsilon_{l}f_{l}^{*})], \quad (5.7)$$

and

$$C_{r}(f_{a}f_{b}|f_{k}^{*}f_{l}^{*}) = G_{r} \int d^{3}\bar{p}_{k}^{*}d^{3}\bar{p}_{l}^{*}d^{3}\bar{p}_{b}W^{(r)}(p_{a}p_{b}|p_{k}^{*}p_{l}^{*}) \times [f_{k}^{*}f_{l}^{*}(1+\epsilon_{a}f_{a})(1+\epsilon_{b}f_{b}) - f_{a}f_{b}(1+\epsilon_{k}f_{k}^{*})(1+\epsilon_{l}f_{l}^{*})].$$
(5.8)

Here  $d^3 \bar{p}_a^* = d^3 \mathbf{p}_a / p_a^0$ , etc. and  $G_a$  and  $G_r$  stand for the statistical weights for the material particles and photons. The  $W^{(c)}, W^{(n)}$  and  $W^{(r)}$  stand for the transition probabilities for elastic, inelastic and "reactive" collisions. The transition probabilities for photon-photon interactions  $W^{(c)}(p_r p_r | p_r^* p_r^*) \equiv 0$ ,  $W^{(n)}(p_r p_r | p_r^* p_r^*) \equiv 0$ , and  $W^{(r)}(p_r p_r | p_r^* p_r^*) \equiv 0$  since the photons do not interact with each other. These transition probabilities can be calculated from the quantum mechanics for a given dynamic mechanism. Therefore, we assume that they are known. Writing the kinetic equations for material particles and photons as in (5.5), we have put both the material gas and photon gas on the equal footing and thereby consider the system of photons and material gas as a dilute gas mixture. We close this section by adding that the transition probabilities have the following symmetry properties

$$W^{(s)}(p_a p_b | p_k^* p_l^*) = W^{(s)}(p_k^* p_l^* | p_a p_b), \quad etc. \quad (s = e, n, r).$$
(5.9)

These relations originate from the microscopic reversibility and are crucial for proving the H theorem.

#### 5.2 Entropy, the H theorem and equilibrium distribution function

In order to formulate irreversible thermodynamics, we must introduce the entropy four-flow for the system of radiation and matter by the formula

$$S^{\mu}(x) = S^{\mu}_{m}(x) + S^{\mu}_{r}(x), \qquad (5.10a)$$

$$S_{in}^{\mu}(x) = -k_B \sum_{i}^{\prime} \langle f_i(x, p_i) [ln f_i(x, p_i) - 1] p_i^{\mu} \rangle_i, \qquad (5.10b)$$

$$S_{r}^{\mu}(x) = -k_{B} \langle \{f_{r}(x, p_{r}) ln f_{r}(x, p_{r}) - [1 + f_{r}(x, p_{r})] ln [1 + f_{r}(x, p_{r})] \} p_{r}^{\mu} \rangle_{r}, \qquad (5.10c)$$

where  $S_m^{\mu}(x)$  and  $S_r^{\mu}(x)$  are the entropy four-flow of matter and radiation, respectively, and the angular brackets abbreviate the integration over momentum space:

$$\langle A_a(x,p_a) \rangle_a = G_a c \int d^3 \bar{p}_a A_a(x,p_a), \quad (a=i,r)$$

The subscript a or r to the angular brackets indicates the particle involved, but they will be omitted whenever no confusion arises because of the omission.

By applying the well-known procedure in the Boltzmann kinetic equation, we obtain the balance equation for the entropy four-flow

$$\partial_{\mu}S^{\mu}(x) = \sigma_{ent}(x) \tag{5.11}$$

where

$$\sigma_{ent}(x) = -k_B \sum_{a=i}^{r} (\{ ln f_a(x, p_a) - ln [1 + \epsilon_a f_a(x, p_a)]\} \Re_a[f_a]).$$
(5.12)

It is easy to show that the entropy production is positive semidefinite and equal to zero, only if the system is at equilibrium:

$$\sigma_{ent}(x) = \frac{1}{4} k_B \sum_{a=i}^{r} \sum_{b=i}^{r} \langle ln \{ f_a^* f_b^* (1 + \epsilon_a f_a) (1 + \epsilon_b f_b) / f_a f_b (1 + \epsilon_a f_a^*) (1 + \epsilon_b f_b^*) \} \Re_{ab} \rangle$$
  

$$\geq 0. \qquad (5.13)$$

This is the H theorem. The equality holds at equilibrium reached in long time.

Owing to the H theorem, the equilibrium distribution functions of material particles and photons can be uniquely determined by the following relations:

$$ln(f_{aeq}^*f_{ieq}^*) = ln(f_{aeq}f_{ieq}) \qquad (a, i \neq r), \tag{5.14a}$$

$$ln[f_{aeq}^*f_{req}^*(1+f_{req})] = ln[f_{aeq}f_{req}(1+f_{req}^*)] \qquad (a \neq r), \tag{5.14b}$$

where  $f_{ieq}$ , etc. are the equilibrium distribution functions. By using the procedure taken for constructing the equilibrium solution of the Boltzmann equation, it is found that

$$f_{ieq} = exp[-\beta_e(p_i^{\nu}U_{\nu} - \mu^0)], \qquad (5.15a)$$

$$exp(-\beta_{\epsilon}\mu^{0}) = \rho^{-1} \sum_{i}^{\prime} \langle exp(-\beta_{\epsilon}p_{i}^{\nu}U_{\nu}) \rangle, \qquad (5.15b)$$

where the total number of material particles  $\rho_t$  is given by

$$\rho_e = \sum_i' \langle f_{ieq}(x, p_i) \rangle.$$
(5.16)

The parameter  $\beta_e$  can be shown to be related to the inverse of the absolute temperature  $T_e$ , if the procedure of the Gibbs ensemble theory described in the chapter 2 is taken, that is,

$$\beta_e = 1/k_B T. \tag{5.17}$$

In the nonrelativistic limit,  $f_{ieq}$  becomes

$$f_{ieq} \to \rho_e (m/2\pi k_B T_e)^{3/2} Z^{-1} exp[-\beta_e (\frac{1}{2}m_e c_i^2 + E_i)],$$
 (5.18a)

where Z is the internal partition function given by

$$Z = \sum_{i}' exp(-\beta_e E_i).$$
 (5.18b)

The equilibrium distribution function of radiation is easily shown to have the form

$$f_{req} = [exp(\beta_e p_r^{\nu} U_{\nu}) - 1]^{-1}, \qquad (5.19)$$

if the photon number is variable [17]. Since  $f_{ieq}$  and  $f_{req}$  both are Lorentz scalars, it is permissible to use the local rest frame

$$U_{\nu} = (c, 0, 0, 0), \tag{5.20}$$

then the covariant forms of the distribution functions are reduced to

$$f_{ieq} = exp[-\beta_e (cp_i^0 - \mu^0)],$$
 (5.21)

$$f_{req} = [exp(\beta_e \hbar \omega) - 1]^{-1}.$$
(5.22)

By using the Stefan-Boltzmann law it is possible to show [8] that the parameter  $\beta_e$  in (5.22) is given by (5.17). Therefore, the two distribution functions  $f_{ieq}$  and

 $f_{req}$  share the same parameter  $\beta_e$ , namely, the same temperature. Furthermore, they are mutually consistent because their mutual consistency is demanded by the H theorem. It is interesting to note that Einstein derived (5.22) from the equilibrium condition between radiation and material particles in his famous paper of 1917 [3]. The present approach elucidates the kinetic theory and dynamic bases which are absent in his theory. In the recent past, Boyer [59] claimed that the Boltzmann distribution function for relativistic material particles and Planck distribution function are not consistent within the framework of quantum theory, and this has been a point of controversy [60]. The derivation of (5.21) and (5.22) presented earlier shows that they are completely consistent with each other. Moreover, it shows that the Planck distribution law is deeply rooted in the H theorem and thus the second law of thermodynamics. It also points out that it is not possible to think of a radiation distribution function without taking into account the corresponding material particle distribution function and the interaction between radiation and matter.

We define the energy-momentum tensor of matter or radiation in equilibrium by the statistical mechanical formula

$$T_{aeq}^{\mu\nu} = \langle p_a^{\mu} p_a^{\nu} f_{aeq}(x, p_a) \rangle, \quad (a = i, r).$$
 (5.23)

With the help of the projector defined by  $\Delta^{\mu\nu} = -g^{\mu\nu} + c^{-2}U^{\mu}U^{\nu}$  the equilibrium energy-momentum tensor can be decomposed into components as follows:

$$T^{\mu\nu}_{aeg} = p^0_a \Delta^{\mu\nu} + c^{-2} E^0_a U^{\mu} U^{\nu}$$
(5.24)

where the energy density  $E_a^0$  is defined by

$$E_a^0 = c^{-2} U_\mu T_{aeq}^{\mu\nu} U_\nu = c^{-2} \langle p_a^\mu p_a^\nu U_\nu U_\mu f_{aeq}(x, p_a) \rangle$$
(5.25a)

and the hydrostatic pressure  $p_a^0$  is given by

$$p_{a}^{0} = \frac{1}{3} \Delta_{\mu\nu} T_{aeq}^{\mu\nu} = \frac{1}{3} \langle p_{a}^{\mu} p_{a}^{\nu} \Delta_{\nu\mu} f_{aeq}(x, p_{a}) \rangle.$$
 (5.25b)

Therefore, the total material internal energy and total material pressure are given, respectively, by the formulas

$$E_m^0 = \sum_i' E_i^0$$
 and  $p_m^0 = \sum_i' p_i^0 = \rho_e k_B T.$  (5.26)

Here the prime on the summation sign means the exclusion of photons. The last equality is easy to show in the local rest frame [33]. The second equation in (5.26) is well known result for gases consisting of structureless particles. It also holds for dilute gases consisting of particles with an internal structure. By using the definition of the projector  $\Delta_{\mu\nu}$  and the identity  $p_r^{\mu}p_{r\mu} = 0$  for photons, we can show from (5.25a) and (5.25b)

$$p_r^0 = \frac{1}{3} E_r^0. \tag{5.27}$$

In fact, this relation is indeed verifiable by using the local rest frame. We also can derive the Stefan-Boltzmann law,

$$E_r^0 = a_{SB} T_e^4 \tag{5.28}$$

where  $a_{SB}$  is the Stefan-Boltzmann constant:

$$a_{SB} = 8\pi^5 k_B^4 / 15h^3 c^3. \tag{5.29}$$

In connection with this, we recall that the parameter  $\beta_e$  in the radiation distribution function is determined such that the equilibrium radiation energy is given by (5.28). The  $\beta_e$  so determined exactly coincides with the one given in (5.17). This coincidence is a result of the demand made by the H theorem that the material gas and radiation be in equilibrium. Other thermodynamic quantities for radiation and matter can be calculated with the equilibrium distribution functions determined.

## 5.3 Modified moment method for the covariant Boltzmann equation
Since the kinetic equations in (5.5) are not solvable in closed, analytical form, approximate solutions must be sought after. In the modified moment method [20] the approximate solutions are constructed such that they are consistent with the second law of thermodynamics. The relativistic extension of this method is presented in chapter 4. In this method the nonequilibrium distribution functions for material species are expressed in an exponential form

$$f_i(x, p_i) = exp[-\beta(p_i^{\nu}U_{\nu} + H_i^{(1)} - \mu)]$$
(5.30a)

where  $\beta$  is a parameter that will be discussed presently,  $\mu$  is the normalization factor defined by

$$exp(-\beta\mu) = \rho^{-1} \sum_{i}^{\prime} \langle exp[-\beta(p_{i}^{\nu}U_{\nu} + H_{i}^{(1)})] \rangle, \qquad (5.30b)$$

and  $H_i^{(1)}$  is the nonequilibrium contribution to the distribution function which may be written in a bilinear form

$$H_i^{(1)} = \sum_{\alpha \ge 1} X_i^{(\alpha)} \odot h_i^{(\alpha)}.$$
(5.31)

Here,  $X_i^{(\alpha)}$  are as yet undetermined functions of macroscopic variables only, which must be determined such that the second law of thermodynamics is satisfied, and  $h_i^{(\alpha)}$  are the molecular expressions for macroscopic moments. They may be chosen to be a set of orthogonal polynomials which are also orthogonal to the conserved moments, namely, the density and the reversible part of the energy-momentum tensor. The symbol  $\odot$  means taking an appropriate scalar product. The leading tensor polynomials  $h_i^{(\alpha)}$  suitably ordered are as follows:

$$h_i^{(1)\mu\nu} = c^2 (U_\lambda p_i^\lambda)^{-1} (\Delta^\mu_\sigma \Delta^\nu_\tau - \frac{1}{3} \Delta_{\sigma\tau} \Delta^{\mu\nu}) p_i^\sigma p_i^\tau, \qquad (5.32a)$$

$$h_{i}^{(2)} = \frac{1}{3}c^{2}(U_{\lambda}p_{i}^{\lambda})^{-1}\Delta_{\mu\nu}p_{i}^{\mu}p_{i}^{\nu} - p_{i}/\rho_{i} + (\vartheta^{-1} - 1)(\bar{E} - E_{i}), \qquad (5.32b)$$

$$h_{i}^{(3)\mu} = -c^{2}(U_{\lambda}p_{i}^{\lambda})^{-1} \{ \Delta^{\mu}_{\sigma} p_{i}^{\sigma} p_{i}^{\tau} U_{\tau} + a_{i}h_{i}[p_{i}^{\mu} - c^{-2}(U_{\lambda}p_{i}^{\lambda})^{-1}U^{\mu}] \}, \quad (5.32c)$$

$$h_i^{(4)\mu} = c^2 (U_\lambda p_i^\lambda)^{-1} [p_i^\mu - c^{-2} (U_\lambda p_i^\lambda)^{-1} U^\mu], \qquad (5.32d)$$

etc.

where  $\rho_i$  and  $h_i$  are the density and the enthalpy of "color" species *i*, respectively, and

$$\bar{E} = \sum_{i}^{\prime} \langle E_{i} f_{icq} \rangle, \qquad (5.33a)$$

$$\vartheta^{-1} = C_{int}/C_{\nu}$$
  $(C_{\nu} = C_{tr} + C_{int})$  (5.33b)

with  $C_{tr}$  and  $C_{int}$  denoting the translational and the internal specific heat per molecule at constant volume, respectively, and  $a_i$  the same as the definition in the previous chapter. In the case of gases without an internal structure the last term in  $h_i^{(2)}$  vanishes and the monatomic gas used previously is recovered [33].

Various balance equations can be derived from the kinetic equations and they contain macroscopic variables such as the stress tensor, heat flux, etc. which require their own evolution equations. They can also be derived from the covariant Boltzmann equation. To this end, we first define a tensor  $\psi_i^{(\alpha)\mu\nu\dots l\sigma}$  as the average of its molecular expression  $p_i^{\sigma} h_i^{(\alpha)\mu\nu\dots l}$ :

$$\psi_i^{(\alpha)\mu\nu\dots l\sigma} = \langle p_i^{\sigma} h_i^{(\alpha)\mu\nu\dots l} f_i(x, p_i) \rangle$$
(5.34)

where  $h_i^{(\alpha)\mu\nu\dots l}$  is the  $\alpha th$  element of the orthogonal tensor polynomial set introduced earlier. We then introduce macroscopic moments  $\Phi_i^{(\alpha)\mu\nu\dots l}$  by taking contraction of  $\psi_i^{(\alpha)\mu\nu\dots l\sigma}$  with  $U_{\sigma}$ 

$$\Phi_m^{(\alpha)\mu\nu\dots l} = \sum_i' c^{-2} U_\sigma \psi_i^{(\alpha)\mu\nu\dots l\sigma} \equiv \rho \hat{\Phi}_m^{(\alpha)\mu\nu\dots l}$$
(5.35)

where  $\rho$  is the total density of material particles. By using the substantial time derivative D defined by  $D = U^{\nu} \partial_{\nu}$ , we easily obtain from the kinetic equation the evolution equation for the material flux  $\hat{\Phi}_m^{(\alpha)\mu\nu...l}$ :

$$\rho D\hat{\Phi}_m^{(\alpha)\mu\nu\dots l} = Z_m^{(\alpha)\mu\nu\dots l} + \Lambda_m^{(\alpha)\mu\nu\dots l}$$
(5.36)

where

$$Z_m^{(\alpha)\mu\nu\dots l} = \sum_i' \langle p_i^{\sigma} \partial_{\sigma} h_i^{(\alpha)\mu\nu\dots l} f_i(x, p_i) \rangle + \sum_i' \partial_{\tau} (\Delta_{\sigma}^{\tau} \psi_i^{(\alpha)\mu\nu\dots l\sigma}), \qquad (5.37)$$

and

$$\Lambda_m^{(\alpha)\mu\nu\dots l} = \sum_i' \langle h_i^{(\alpha)\mu\nu\dots l} \Re_i [f_i(x, p_i)] \rangle.$$
(5.38)

The kinematic terms  $Z_m^{(\alpha)\mu\nu\dots l}$  are the same as those for nonradiative systems given in the chapter 3 and the dissipation terms  $\Lambda_m^{(\alpha)\mu\nu\dots l}$  will be given in a later section where their approximations are discussed.

Let us denote by  $\Pi_m^{\mu\nu}$ ,  $\Delta_m$  and  $Q_m^{\mu}$  the traceless symmetric part of the stress tensor, the excess trace part of the stress tensor, and the heat flux, respectively. They can be introduced in terms of the energy-momentum tensor. Since

$$T_{im}^{\mu\nu} = \sum_{i}^{\prime} T_{i}^{\mu\nu} = \sum_{i}^{\prime} \langle p_{i}^{\mu} p_{i}^{\nu} f_{i}(x, p_{i}) \rangle$$
  
$$= \sum_{i}^{\prime} [c^{-2} E_{i} U^{\mu} U^{\nu} + c^{-2} (Q_{i}^{\mu} U^{\nu} + Q_{i}^{\nu} U^{\mu}) + P_{i}^{\mu\nu}]$$
  
$$= c^{-2} \mathcal{E}_{m} U^{\mu} U^{\nu} + c^{-2} (Q_{m}^{\mu} U^{\nu} + Q_{m}^{\nu} U^{\mu}) + P_{m}^{\mu\nu}, \qquad (5.39a)$$

the aforementioned variables are projections of the energy-momentum tensor:

$$P_m^{\mu\nu} = \sum_i' P_i^{\mu\nu} = \Delta_\sigma^\mu T_m^{\sigma\tau} \Delta_\tau^\nu, \qquad (5.39b)$$

which means that

$$\Delta_m = \frac{1}{3} \Delta_{\mu\nu} P_m^{\mu\nu} - p_m, \qquad (5.39c)$$

$$\Pi_m^{\mu\nu} = P_m^{\mu\nu} - \frac{1}{3} \Delta_{\sigma\tau} T_m^{\sigma\tau} \Delta_{\mu\nu}, \qquad (5.39d)$$

$$Q^{\mu}_{m} = -U_{\nu}T^{\nu\sigma}_{m}\Delta^{\mu}_{\sigma}, \qquad (5.39e)$$

and

$$\mathcal{E}_m = \sum_i' E_i, \tag{5.40}$$

namely, the total internal energy of material gas. Here the diffusion flux is defined by

$$J_i^{\mu} = N_i^{\mu} - c_i N_m^{\mu}, \qquad (5.41a)$$

where

$$N_{m}^{\mu} = \sum_{i}^{\prime} N_{i}^{\mu} = \sum_{i}^{\prime} \langle p_{i}^{\mu} f_{i}(x, p_{i}) \rangle.$$
 (5.41b)

Then, the leading members of the moment set just defined are

$$\Phi_m^{(1)\mu\nu} = \Pi_m^{\mu\nu}; \quad \Phi_m^{(2)} = \Delta_m + [2(\vartheta^{-1} - 1)/3] \Delta E; \quad \Phi_m^{(3)\mu} = Q_m^{\mu}; \quad etc. \quad (5.42)$$

Here

$$\Delta E = \sum_{i}^{\prime} \langle (\tilde{E} - E_i) f_i(x, p_i) \rangle.$$
(5.43)

It is important to note here that the second member of moment set  $\Phi_m^{(2)}$  in (5.42) is different from the one corresponding to monatomic gases [33] since the latter does not have the term arising from the internal energy fluctuation, namely,  $[2(\vartheta^{-1} - 1)/3]\Delta E$ . Since the theory for the matter part is already presented in the previous chapter, here attention will be paid to the radiation part.

The nonequilibrium radiation distribution function is sought after in a form similar to the Planck distribution function. Thus, we take it in the form

$$f_r(x, p_r) = \{ exp[\beta \bar{W}_r(p_r)] - 1 \}^{-1}.$$
(5.44)

Here the function  $\bar{W}_r(p_r)$ , as yet undetermined, will be sought after in such a way that it is thermodynamically consistent as for the distribution function for matter  $f_i(x, p_i)$ . This function also must be dimensionless. Therefore, if we define the wave vector  $\mathbf{k}_r$  of radiation by  $\mathbf{p}_r = \hbar \mathbf{k}_r = \hbar k_r \hat{\mathbf{k}}_r = (\hbar \omega/c) \hat{\mathbf{k}}_r$ , then the unit vector  $\hat{\mathbf{k}}_r$  is dimensionless. It is possible to form a dimensionless variable if  $p_r^{\mu}$  is multiplied by  $c\beta$ :

$$q_r^{\nu} \equiv p_r^{\nu} c\beta. \tag{5.45}$$

Therefore, the space component of the dimensionless four-vector  $q_r^{\nu}$  is given by  $\mathbf{q}_r = \beta \hbar \omega \hat{\mathbf{k}}_r$ . We now look for  $\bar{W}_r$  in terms of  $q_r^{\nu}$ . It is convenient to define

$$W_r(q_r) = \beta \tilde{W}_r(p_r). \tag{5.46}$$

In view of the equilibrium radiation (Planck) distribution function already obtained and the exponential form for  $f_i(x, p_i)$  in (5.30a), it is useful to write  $W_r(q_r)$  in the form

$$W_r(q_r) = \beta p_r^{\mu} U_{\mu} + \beta H_r^{(1)}(q_r) - \beta \mu_r$$
(5.47)

where  $\mu_r$  is the normalization factor and  $H_r^{(1)}(q_r)$  is the nonequilibrium part that can be determined in a way analogous to the one taken for  $f_i$  in (5.30a). That is,

$$H_r^{(1)} = \sum_{\delta \ge 1} X_r^{(\delta)} \odot h_r^{(\delta)}$$
(5.48)

where  $h_r^{(\delta)}$  are orthogonal tensor polynomials of  $p_r^{\nu}$  which are also orthogonal to the conserved moments for radiation, and  $X_r^{(\delta)}$  are the functions of macroscopic variables such as the radiation shear stress tensor, the excess trace part of the radiation stress tensor, radiation heat flux, etc. As mentioned before,  $\beta H_r^{(1)}$  can be expressed as a dimensionless function of the reduced four-vector  $q_r^{\nu}$  and dimensionless variables. The orthogonal tensor polynomials can be constructed by means of the Schmidt orthogonalization method and can be expressible in terms of spherical tensors of  $\hat{q}_r^{\nu}$ , the unit dimensionless four-vector. We show a few leading elements of the set:

$$h_{r}^{(1)\mu\nu} = c^{2} (U_{\lambda} p_{r}^{\lambda})^{-1} (\Delta_{\sigma}^{\mu} \Delta_{r}^{\nu} - \frac{1}{3} \Delta_{\sigma r} \Delta^{\mu\nu}) p_{r}^{\sigma} p_{r}^{\tau}, \qquad (5.49a)$$

$$h_r^{(2)} = \frac{1}{3} c^2 (U_\lambda p_r^\lambda)^{-1} \Delta_{\mu\nu} p_r^\mu p_r^\nu - p_r / \rho_r, \qquad (5.49b)$$

$$h_r^{(3)\mu} = -c^2 (U_\lambda p_r^\lambda)^{-1} \{ \Delta^{\mu}_{\sigma} p_r^{\nu} p_r^{\sigma} U_\nu + a_r h_r [p_r^{\mu} - c^{-2} (U_\lambda p_r^\lambda) U^{\mu}] \}, \quad (5.49c)$$

$$h_r^{(4)\mu} = c^2 (U_\lambda p_r^\lambda)^{-1} [p_r^\mu - c^{-2} (U_\lambda p_r^\lambda) U^\mu], \qquad (5.49d)$$

$$h_r^{(5)\mu\nu l} = c^2 (U_\lambda p_r^\lambda)^{-1} P_3 (\Delta_\tau^\sigma p_r^\tau)^{\mu\nu l}, \qquad (5.49e)$$

etc.

where  $P_3(z)$  is the Legendre polynomial of order 3 and  $a_r$  is defined similarly to (4.34e) that we have defined for the matter species. The higher order terms involve higher order Legendre polynomials. As is the case for the matter parts of the macroscopic fluxes, the radiation parts of the macroscopic fluxes are defined by taking contraction of  $\psi_r^{(\delta)\mu\nu\dots l\sigma}$  whose statistical expression is given by

$$\psi_r^{(\delta)\mu\nu\dots l\sigma} = \langle p_r^{\sigma} h_r^{(\delta)\mu\nu\dots l} f_r(x, p_r) \rangle, \qquad (5.50)$$

then the fluxes are given by

$$\Phi_r^{(\delta)\mu\nu\dots l} = c^{-2} U_\sigma \psi_r^{(\delta)\mu\nu\dots l\sigma}.$$
(5.51)

Let us denote the radiation shear stress tensor, the excess trace part of the radiation shear stress tensor, the heat flux, number flux, and fourth moment corresponding to (5.49e), etc. by  $\Pi_r^{\mu\nu}$ ,  $\Delta_r$ ,  $Q_r^{\mu}$ ,  $J_r^{\mu}$ ,  $\Gamma_r^{\mu\nu l}$ , etc., respectively, then their statistical definitions can be introduced through the energy-momentum tensor of radiation which may be decomposed as follows:

$$T_r^{\mu\nu} = \langle p_r^{\mu} p_r^{\nu} f_r(x, p_r) \rangle$$
  
=  $c^{-2} \mathcal{E}_r U^{\mu} U^{\nu} + c^{-2} (Q_r^{\mu} U^{\nu} + Q_r^{\nu} U^{\mu}) + P_r^{\mu\nu}$  (5.52a)

with the help of the projection operator, we obtain

$$P_r^{\mu\nu} = \Delta^{\mu}_{\sigma} T_r^{\sigma\tau} \Delta^{\nu}_{\tau} \tag{5.52b}$$

which means that

$$\Delta_r = \frac{1}{3} \Delta_{\mu\nu} P_r^{\mu\nu} - p_r \tag{5.52c}$$

$$\Pi_r^{\mu\nu} = P_r^{\mu\nu} - \frac{1}{3} \Delta_{\sigma\tau} T_r^{\sigma\tau} \Delta^{\mu\nu}$$
(5.52d)

and

$$Q_r^{\mu} = -U_{\nu} T_r^{\nu \sigma} \Delta_{\sigma}^{\mu}. \tag{5.52e}$$

Therefore, we can easily identify,

$$\Phi_r^{(1)\mu\nu} = \Pi_r^{\mu\nu}; \quad \Phi_r^{(2)} = \Delta_r; \quad \Phi_r^{(3)\mu} = Q_r^{\mu}; \quad \Phi_r^{(4)\mu} = J_r^{\mu};$$
  
$$\Phi_r^{(5)\mu\nu l} = \Gamma_r^{\mu\nu l}; \quad etc.$$
(5.53)

The evolution equations for  $\Phi_r^{(\delta)}$  can be derived from the covariant Boltzmann equation (5.5) by using the same method as for the matter parts. They may be written in the form

$$D\hat{\Phi}_{r}^{(\delta)\mu\nu...l} = Z_{r}^{(\delta)\mu\nu...l} + \Lambda_{r}^{(\delta)\mu\nu...l},$$
(5.54)

where

$$Z_r^{(\delta)\mu\nu\dots l} = \langle p_r^{\sigma} \partial_{\sigma} h_r^{(\delta)\mu\nu\dots l} f_r(x, p_r) \rangle, \qquad (5.55)$$

$$\Lambda_r^{(\delta)\mu\nu\dots l} = \langle h_r^{(\delta)\mu\nu\dots l} \Re_r[f_r(x, p_r)] \rangle.$$
(5.56)

The explicit forms for the kinematic terms  $Z_r^{(\delta)\mu\nu\dots l}$  are presented in Table 1. The dissipation terms  $\Lambda_r^{(\delta)\mu\nu\dots l}$  will be calculated later when radiative transport processes are examined.

In the case of radiation and matter, since the photons are put on the equal footing as far as the kinetic processes are concerned and the whole system is considered as a mixture of photons and material particles, it is reasonable to define a single temperature for the mixture. Note in this connection that the photons cannot come to equilibrium on their own without a help from the material gas. Therefore, we define the temperature by the statistical mechanical formula

$$\frac{3}{2}\rho_i k_B T = \sum_{a=i}^r \frac{1}{2} \langle [(p_a^{\nu} U_{\nu})^2 - m_a^2 c^4] f_a(x, p_a) \rangle$$
(5.57)

where  $m_r = 0$  in the case of photon species and

$$\rho_t = \rho + (2a_{SB}c^2/k_B)T^3.$$
 (5.58)

This definition of temperature is basically rooted in the equipartition law of energy by Tolman [52] and later discussed by Landsberg [55] and by ter Haar and Wergeland [53]. The second term on the right-hand side in (5.57) arises from the recognition that the photon number density depends on temperature and thus is not conserved, and writing the nonequilibrium photon number density in such a form means that the temperature is determined such that '5.58) holds for nonequilibrium. Eq. (5.57) can be recast into the form

$$3\rho_{t}k_{B}T = \sum_{a=i}^{r} \Delta_{\mu\nu} \langle p_{a}^{\nu} p_{a}^{\mu} f_{a}(x, p_{a}) \rangle = \sum_{a=i}^{r} \Delta_{\mu\nu} T_{a}^{\nu\mu}.$$
 (5.59)

The nonequilibrium canonical forms (5.30a) and (5.44) involve parameters  $\beta, \rho, \rho_r$ , and p which have been defined statistically, but their operational meanings as thermodynamic variables are not as yet fixed. In kinetic theory the nonequilibrium distribution functions are sought after in a form constructed on the basis of the equilibrium distribution function. Since the system of interest is away from equilibrium, it is preferable to endow the parameters such as  $\beta_e, \rho_e, p_e$ , etc. in the equilibrium distribution function the status of nonequilibrium parameters. This aim can be achieved if the nonequilibrium parameters ( $\beta, \rho, p, \epsilon$ ) defined statistically with the nonequilibrium distribution function functions are matched with the equilibrium parameters ( $\beta_e, \rho_e, \rho_e, \epsilon_e$ ):

$$\beta_e \Longrightarrow \beta, \quad \rho_e \Longrightarrow \rho, \quad p_e \Longrightarrow p, \quad \varepsilon \Longrightarrow \varepsilon_e$$

where we have added the internal energy ( $\varepsilon = \mathcal{E}/\rho$ ) matching condition although the distribution functions do not depend on  $\varepsilon$ . The reason is that the internal energy and pressure are independent components of the energy-momentum tensor. In this manner, the local equilibrium distribution functions are constructed with the equilibrium distribution functions and at the same time the statistically defined nonequilibrium quantities are endowed with the thermodynamic, operational meanings. Then, the equilibrium distribution functions are determined around the local equilibrium distribution functions so constructed. When these matching conditions are expressed in their statistical form, they are as follows:

$$\rho = \sum_{i}^{\prime} c^{-2} \langle p_{i}^{\nu} U_{\nu} f_{i} \rangle = \sum_{i}^{\prime} c^{-2} \langle p_{i}^{\nu} U_{\nu} f_{i}^{0} \rangle, \qquad (5.60a)$$

$$N^{j} = \sum_{a}^{r} \langle p_{a}^{j} f_{a} \rangle = \sum_{a}^{r} \langle p_{a}^{j} f_{a}^{0} \rangle, \quad (j = 1, 2, 3)$$
(5.60b)

$$\mathcal{E} = \rho \varepsilon = \sum_{a}^{r} \langle (p_{a}^{\nu} p_{a}^{\mu} U_{\nu} U_{\mu} + E_{a} \delta_{ar}) f_{a} \rangle$$
$$= \sum_{a}^{r} \langle (p_{a}^{\nu} p_{a}^{\mu} U_{\nu} U_{\mu} + E_{a} \delta_{ar}) f_{a}^{o} \rangle, \qquad (5.60c)$$

$$p = \frac{1}{3} \sum_{a}^{r} \Delta_{\mu\nu} \langle p_{a}^{\nu} p_{a}^{\mu} f_{a} \rangle = \frac{1}{3} \sum_{a}^{r} \Delta_{\mu\nu} \langle p_{a}^{\nu} p_{a}^{\mu} f_{a}^{0} \rangle.$$
(5.60*d*)

Here  $f_i^0$  is the local equilibrium distribution function defined by  $f_{ieq}$  where  $\beta_e, \rho_e$ , etc. are replaced by  $\beta$ ,  $\rho$ , etc. according to the matching conditions given earlier. Other symbols are as follows:  $N^{\nu} = N_m^{\nu} + N_r^{\nu}$ ,  $\mathcal{E} = \mathcal{E}_m + \mathcal{E}_r$ , and  $p = p_m + p_r$ , namely, the total number flux, total internal energy and total pressure, respectively. The condition (5.60a) is for the material density only, since the photon density is not conserved and thus should not be included in the condition. In the nonrelativistic theory the fourth condition (5.60d) is not required, but in the relativistic kinetic theory it is necessary as discussed earlier. In view of the definition of the temperature of the system in hand given in (5.57) and its equivalent (5.59), we see that (5.60d) is also a matching condition for temperature. These matching conditions mean that the nonequilibrium part  $(f_a - f_a^0)$  of the distribution function is orthogonal with the equilibrium part  $f_a^0$  with respect to the microscopic variables appearing in the matching conditions. As is shown in the previous chapter in the absence of radiation, these requirements are rigorously satisfied if the molecular moments  $h_a^{(\alpha)}$  are chosen such that they are not only orthogonal with each other but also orthogonal with the conserved moments such as the mass, velocity and reversible parts of the energy-momentum tensor.

By explicitly evaluating the second equality in the matching condition (5.60d), it is easy to find the parameter  $\beta$  appearing in the nonequilibrium distribution functions  $f_i$  and  $f_r$  given in (5.30a) and (5.44):

$$\beta = 1/k_B T. \tag{5.61}$$

The leading tensor polynomials in the sets  $\{h_i^{(\alpha)}\}\$  and  $\{h_r^{(\delta)}\}\$ , chosen earlier for the nonequilibrium parts of the distribution functions, can be shown to satisfy the matching conditions in (5.60a-d). The assumption is that it is possible to choose the sets in such a way as to satisfy (5.60a-d).

In addition to the evolution equations for macroscopic moments  $\Phi_a^{(\alpha)}$  presented earlier, the balance equations for the conserved variables can be derived from the covariant Boltzmann equations (5.5). For the matter part,

$$\partial_{\nu} T_m^{\mu\nu} = \Lambda_m^{\mu}, \qquad (5.62a)$$

$$\partial_{\nu} N_i^{\nu} = \Lambda_i^{(n)}, \qquad (5.62b)$$

where

$$\Lambda_m^{\mu} = \sum_i' \langle p_i^{\mu} \Re_i[f_i] \rangle, \qquad (5.62c)$$

$$\Lambda_i^{(n)} = \langle \Re_i[f_i] \rangle. \tag{5.62d}$$

Since the total number of material particle species is conserved,

$$\sum_{i}^{\prime} \Lambda_{i}^{(n)} = \sum_{i}^{\prime} \langle \Re_{i}[f_{i}] \rangle = 0$$

$$\partial_{\nu} N_{m}^{\nu} = 0 \qquad (5.63)$$

and thus

where

$$N_m^{\nu} = \sum_i' N_i^{\nu}.$$

In order to express the hydrodynamic equations in forms familiar in fluid dynamics we take the Eckart definition [48] of four-velocity of the fluid as was in the previous chapter. Thus the four-velocity of the fluid is defined by

$$N_m^{\nu} = \rho U^{\nu}. \tag{5.64}$$

The balance equations for the matter part are then given by the equations

$$D\rho = -\rho \nabla_{\nu} U^{\nu}, \qquad (5.65a)$$

$$\rho Dc_i = -\partial_\nu J_i^\nu + \Lambda_i^{(n)}, \qquad (5.65b)$$

$$\rho D\varepsilon_m = -\partial_\nu Q_m^\nu + P_m^{\nu\mu} \nabla_\nu U_\mu + c^{-2} Q_m^\nu D U_\nu + U_\nu \Lambda_m^\nu, \qquad (5.66)$$

$$c^{-2}h_m\rho DU^{\mu} = \nabla^{\mu}p_m + \Delta^{\mu}_{\sigma}\partial_{\nu}\Pi^{\sigma\nu}_m + c^{-2}(\Delta^{\mu}_{\nu}DQ^{\nu}_m - Q^{\mu}_m\nabla_{\nu}U^{\nu} - Q^{\nu}_m\nabla_{\nu}U^{\mu}).$$
(5.67)

Here,  $c_i = \rho_i / \rho$  and  $h_m = \epsilon_m + p_m \rho^{-1}$  is the enthalpy of the material gas per particles. The diffusion flux does not vanish provided that the molecules or atoms in different internal states interact according to different force laws. There occurs a source term in the balance equations because of the "reactive" collision terms between photons and material particles.

For the radiation part, with definition

$$c_r = \rho_r / \rho, \tag{5.68}$$

the radiation balance equations can be obtained from the covariant Boltzmann equation:

$$\partial_{\nu} N_r^{\nu} = \Lambda_r^{(n)}, \tag{5.69}$$

$$\partial_{\nu}T_{r}^{\mu\nu} = \Lambda_{r}^{\mu}, \qquad (5.70)$$

where

$$\Lambda_r^{(n)} = \langle \Re_r[f_r] \rangle, \tag{5.71a}$$

$$\Lambda_r^{\mu} = \langle p_r^{\mu} \Re_r[f_r] \rangle. \tag{5.71b}$$

With the help of the relations

$$\partial_{\nu} = c^{-2} U_{\nu} D + \nabla_{\nu} \quad and \quad U_{\nu} \nabla^{\nu} = 0,$$

we obtain from the radiation balance equations presented above

$$\rho D c_r = -\partial_\nu J_r^\nu + \Lambda_r^{(n)},\tag{5.72}$$

$$\rho D\varepsilon_r = -\partial_{\nu}Q_r^{\nu} + P_r^{\mu\nu}\nabla_{\nu}U_{\mu} + c^{-2}Q_r^{\nu}DU_{\nu} + U_{\mu}\Lambda_r^{\mu}$$
(5.73)

where

$$\varepsilon_r = \mathcal{E}_r / \rho.$$
 (5.74)

It is the radiation energy per material particle. We have not listed the radiation momentum equation here, since it is related to the radiation heat flux evolution equation which have been already included in the flux evolution equations. In the nonrelativistic limit of  $u/c \rightarrow 0$ , this radiation energy balance equation reduces to

$$\rho \frac{d}{dt} \varepsilon_r = -\nabla \cdot \mathbf{Q}_r - \mathbf{P}_r : \nabla \mathbf{u} - \mathbf{u} \cdot \nabla \cdot \mathbf{P}_r + \Lambda_r^{(e)}$$
(5.75)

where the last term is the radiation energy term; see Eq. (2.57) in the chapter 2. It is easy to show that other balance equations presented here also reduce to their nonrelativistic counterparts [17].

### 5.4 Entropy differential and the Boltzmann function

The balance equations for conserved variables and the evolution equations for fluxes (moments) for radiation and matter derived in the previous section constitute the set of evolution equations for macroscopic variables of the system. However, these equations must be subjected to the demands of the second law of thermodynamics so that the theory based thereon becomes consistent with the second law. In the modified moment method [20, 40] the theory is developed in a thermodynamically consistent manner in the aforementioned sense. To implement this tenet, the statistical representation of the second law of thermodynamics, namely, the entropy production, must be used. To facilitate the discussion, we define the scalar entropy S(x) by

$$S(x) = c^{-2} U_{\nu} S^{\nu}(x) \tag{5.76}$$

and the entropy flux by

$$J_{s}^{\nu}(x) = S^{\nu}(x) - S(x)U^{\nu}.$$
(5.77)

Then, with the definition of the entropy density S by

$$S(x) = \rho S(x)$$

we obtain, from the balance equation (5.11) for the entropy four-flow, the entropy balance equation

$$\rho DS = -\partial_{\nu} J_{s}^{\nu} + \sigma_{ent}(x) \tag{5.78}$$

where the entropy production  $\sigma_{ent}$  is defined by (5.12). We reiterate that it is positive semidefinite. The modified moment method seeks inevitable approximations for the distribution functions such that the entropy production remains positive semidefinite for the approximations taken. Since approximations to the distribution functions enter the theory through the as-yet-undetermined quantities  $X_a^{(\alpha)}$ appearing in the nonequilibrium contributions  $H_i^{(1)}$  and  $H_r^{(1)}$  in (5.31) and (5.48) respectively, these unknowns must be determined such that the second law is satisfied by the approximately determined unknowns. But, in practice, this second law requirement is easily met if the entropy production is cast into a form that remains positive semidefinite regardless of approximations for  $X_a^{(\alpha)}$ . We will elaborate on this at a more appropriate point. For now it is sufficient to pursue a formal development for the sake of generality.

The entropy production can be formally computed if the nonequilibrium canonical distribution function (5.30a) and the form (5.44) are substituted into the statistical expression for  $\sigma_{ent}$  (5.12) and the definitions of dissipation terms are used along with the collisional invariance of conserved quantities. The entropy production is thereby found to be in the form

$$\sigma_{ent} = T^{-1} \sum_{a=i}^{r} \sum_{\alpha \ge 1} X_a^{(\alpha)} \odot \Lambda_a^{(\alpha)} - T^{-1} \sum_{a=i}^{r} \mu_a \Lambda_a^{(n)}$$
(5.79a)

where we have used the energy-momentum conservation law for the whole system of matter and radiation

$$\sum_{i}^{\prime} \langle p_{i}^{\nu} \Re_{i}[f_{i}] \rangle + \langle p_{r}^{\nu} \Re_{r}[f_{r}] \rangle = 0.$$
(5.79b)

The entropy flux can be calculated with the same forms of matter and radiation distribution functions as for the entropy production. The entropy flux consists of the matter and radiation parts:

$$J_s^{\nu} = J_{sm}^{\nu} + J_{sr}^{\nu}. \tag{5.80}$$

The matter part is easily calculated:

$$J_{sm}^{\nu} = S_m^{\nu} - S_m U^{\nu}$$
  
=  $T^{-1} \sum_i' (Q_i^{\nu} - \mu_i J_i^{\nu}) + T^{-1} \sum_i' \sum_{\alpha \ge 1} X_i^{(\alpha)} \odot \Omega_i^{(\alpha)\nu}$  (5.81)

where

$$\Omega_i^{(\alpha)\nu} = \psi_i^{(\alpha)\nu} - \Phi_i^{(\alpha)}U^{\nu}.$$
 (5.82)

The radiation part of the entropy flux is defined by

$$J_{sr}^{\nu}(x) = S_r^{\nu}(x) - S_r(x)U^{\nu}$$
(5.83)

which can be cast into the statistical mechanical form

$$J_{sr}^{\nu}(x) = k_B \langle [p_r^{\nu} - c^{-2} (U_{\lambda} p_r^{\lambda})^{-1} U^{\nu}] W_r \rangle - k_B \langle [p_r^{\nu} - c^{-2} (U_{\lambda} p_r^{\lambda})^{-1} U^{\nu}] ln [1 - exp(-W_r)] \rangle.$$
(5.84)

On use of (5.47) and (5.48), this expression yields the form

$$J_{sr}^{\nu} = T^{-1} [Q_r^{\nu} - \mu_r J_r^{\nu} + \sum_{\delta \ge 1} X_r^{(\delta)} \odot \Omega_r^{(\delta)\nu}] + J_{sq}^{\nu}$$
(5.85)

where

$$I_{sq}^{\nu} = -k_B \langle [p_r^{\nu} - c^{-2} (U_\lambda p_r^{\lambda})^{-1} U^{\nu}] ln [1 - exp(-W_r)] \rangle$$
(5.86)

and

$$\Omega_r^{(\delta)\nu} = \psi_r^{(\delta)\nu} - \Phi_r^{(\delta)} U^{\nu}, \quad (\delta \ge 1).$$
(5.87)

In the case of photons the quantum contribution  $J_{sq}^{\nu}$  appears in the expression for the entropy flux (5.85) while the matter part does not have such a term since the material gas obeys the Boltzmann statistics.

The entropy balance equation (5.78) can be put into another form which is more explicit with regard to the macroscopic variable dependence. This aim can be achieved by following the same procedure as used in the previous chapter on the relativistic extension of the modified moment method. The basic idea for this is to use the conservation laws to eliminate the divergence terms in the entropy balance equation and also to use the flux evolution equations to eliminate the dissipation terms in the entropy production. Thus, we obtain the equation for DS

$$DS = T^{-1}[D\varepsilon + pDv - \sum_{a=i}^{r} \mu_a Dc_a + \sum_{a=i}^{r} \sum_{\alpha \ge 1} X_a^{(\alpha)} \odot D\hat{\Phi}_a^{(\alpha)}] + \aleph$$
(5.88)

where  $v = \rho^{-1}$  is the specific volume and

$$\aleph = -(\rho T)^{-1} \{ \sum_{a=i}^{r} \sum_{\alpha \ge 1} [X_a^{(\alpha)} \odot Z_a^{(\alpha)} + T \partial_{\nu} (X_a^{(\alpha)} \odot \Omega_a^{(\alpha)\nu})] + T \partial_{\nu} J_{sq}^{\nu} \}$$
$$+ (\rho T)^{-1} [-\Pi^{\sigma\tau} \nabla_{\tau} U_{\sigma} + Q^{\nu} \partial_{\nu} lnT + \sum_{a=i}^{r} J_a^{\nu} \partial_{\nu} (\mu_a/T)].$$
(5.89)

Here

$$Q^{\nu} = Q_m^{\nu} + Q_r^{\nu} \quad and \quad \Pi^{\sigma\tau} = \Pi_m^{\sigma\tau} + \Pi_r^{\sigma\tau}.$$

It is remarkable that (5.88) and (5.89) are in the same forms as those for a material gas mixture in the absence of radiation [33]. This is because the photons and material particles are put on the equal footing in the kinetic equations in the present theory. Since  $\aleph$  does not vanish for systems away from equilibrium, DS is not a Pfaffian differential in contrast to the equilibrium Gibbs relation for DS. We will discuss further on this point later. The conclusion drawn here is the same as for both nonrelativistic and relativistic gases in the absence of radiation. As in the previous cases, the Pfaffian differential part of DS is given a new name, compensation differential, which is defined by

$$D\Psi = T^{-1} [D\varepsilon + pDv - \sum_{a=i}^{r} \mu_a Dc_a + \sum_{a=i}^{r} \sum_{\alpha \ge 1} X_a^{(\alpha)} \odot D\hat{\Phi}_a^{(\alpha)} - c^{-2} \hat{Q}^{\mu} DU_{\mu}].$$
(5.90)

This looks like the extended Gibbs relation for DS commonly used in extended irreversible thermodynamics [21] and its relativistic extension [62]. Then DS in (5.88) takes the form

$$DS = D\Psi + \aleph. \tag{5.91}$$

These results, in fact, show that the extended Gibbs relation for DS does not generally hold if the system is away from equilibrium. If the integrability conditions are satisfied by  $D\Psi$ , then it is an exact differential. Eq. (5.91) may be cast into an equivalent form more insightful in giving the significance of the entropy balance equation for irreversible processes.

To achieve this goal, we first put the covariant kinetic equations in more useful forms:

$$f_i p_i^{\nu} \partial_{\nu} ln(f_i/f_i^0) = \Re_i[f_i], \qquad (5.92a)$$

$$f_r p_r^{\nu} \partial_{\nu} \ln[(1+f_r^{-1})/(1+1/f_r^0)] = -(1+f_r)^{-1} \Re_r[f_r], \qquad (5.92b)$$

where

$$p_a^{\nu} \partial_{\nu} f_a^0 = 0 \qquad (a = i, r). \tag{5.93}$$

The relativistic Gibbs-Duhem relation can be derived from the local equilibrium distribution functions under the matching conditions presented earlier:

$$\sum_{a=i}^{r} c_a D(\mu_a^0/T) = \varepsilon D(1/T) + v D(p/T)$$
(5.94)

where  $\mu_r^0 = 0$ . By using this relation and the statistical mechanical formulas for  $Z_a^{(\alpha)\nu}$  defined earlier, we may rewrite  $\aleph$  in the form

$$\aleph = \sum_{a=i}^{r} \left[ \sum_{\alpha \ge 1} \hat{\Phi}_{a}^{(\alpha)} \odot D\bar{X}_{a}^{(\alpha)} - c_{a}D(\mu_{a}/T) \right] + \varepsilon D(1/T)$$
  
+  $vD(p/T) - \hat{\sigma}_{L} + \aleph_{q}$  (5.95)

where

$$\Re_{q} = \rho^{-1} k_{B} \Big\{ \partial_{\nu} \langle [p_{r}^{\nu} - c^{-2} (p_{r}^{\sigma} U_{\sigma}) U^{\nu}] f_{r} [1 - f^{-1} ln (1 + f_{r})] \rangle - \langle f_{r} (1 + f_{r})^{-1} \Re_{r} [f_{r}] \rangle \Big\},$$
(5.96)

$$\begin{split} \hat{X}_{a}^{(\alpha)} &= X_{a}^{(\alpha)}/T, \\ \hat{\sigma}_{L} &= -(\rho T)^{-1} [-\Pi^{\sigma \tau} \nabla_{\tau} U_{\sigma} + Q^{\nu} \partial_{\nu} lnT + \sum_{a=i}^{r} J_{a}^{\nu} \partial_{\nu} (\mu_{a}/T) \\ &- c^{-2} Q^{\nu} D U_{\nu}]. \end{split}$$
(5.97)

We now define the Boltzmann function  $\mathcal{B}$  by

$$\mathcal{B} = S - T^{-1} [\varepsilon + pv - \sum_{a=i}^{r} \mu_a c_a + \sum_{a=i}^{r} \sum_{\alpha \ge 1} X_a^{(\alpha)} \odot \hat{\Phi}_a^{(\alpha)}].$$
(5.98)

With this function the entropy balance equation (5.78) is transformed into the equivalent form

$$D\mathcal{B} = -\hat{\sigma}_L + \aleph_q. \tag{5.99}$$

This form can be further transformed if a new function  $\Gamma_q$  is defined as follows [42]

$$\Gamma_q = \rho \hat{\Gamma}_q = k_B \langle f_r [1 - f_r^{-1} ln(1 + f_r)] \rangle$$
(5.100)

and its evolution equation derived from the covariant kinetic equation is used:

$$\rho D \hat{\Gamma}_{q} = -\partial_{\nu} k_{B} \langle f_{r} [p_{r}^{\nu} - c^{-2} (p_{r}^{\sigma} U_{\sigma}) U^{\nu}] [1 - f_{r}^{-1} ln (1 + f_{r})] \rangle + k_{B} \langle f_{r} (1 + f_{r})^{-1} \Re_{r} [f_{r}] \rangle.$$
(5.101)

Therefore, we find

$$\aleph_q = -D\hat{\Gamma}_q \tag{5.102}$$

and with the definition of a new Boltzmann function for the quantum system

$$\mathcal{B}_q = \mathcal{B} + \tilde{\Gamma}_q \tag{5.103}$$

we finally obtain an equivalent form for the entropy balance equation for the system of radiation and matter

$$D\mathcal{B}_q = -\hat{\sigma}_L. \tag{5.104}$$

This is in the same form as for the relativistic gas mixture in the absence of radiation [33], but the quantum contribution due to photons is already contained in the expression of  $B_q$ . Since  $\hat{\sigma}_L$  does not vanish in general, if the system is away from equilibrium, the Boltzmann function  $B_q$  is not equal to zero. This means that the entropy differential DS cannot be a Pfaffian differential in general, if the system is not in equilibrium and the extended Gibbs relation for DS is not valid in that case. We have shown that this is the case in the nonrelativistic formalism [17], and it robustly holds up even if the system is relativistic. The equivalent form (5.104) may be looked upon as a local form of the H theorem since there is no approximation made to the distribution function or the unknowns  $X_a^{(\alpha)}$ . Further progress in the theory of transport processes in the system can be made if a suitable approximation is made to the unknowns in a thermodynamically consistent manner. This goal will be achieved in two stages: first, the entropy production will be cast in a form that guarantees its positivity and, second, an approximation for the unknowns will be obtained.

#### 5.5 Cumulant expansion for the dissipation terms

The description of the modified moment method is not as yet complete since the dissipation terms  $\Lambda_a^{(\alpha)}$  in the flux evolution equations are not explicitly calculated. The formal development presented up to this point has not required explicit forms for them, but they are necessary if transport processes are to be studied. Since the dissipation terms are directly related to the entropy production in the system, they must be calculated such that the second law of thermodynamics is rigorously satisfied by the approximate forms taken for them. Such a procedure is established in the modified moment method in which a cumulant expansion method is used [33, 40]. Since the present covariant kinetic equations of radiation and matter are similar in their structure to the covariant kinetic equations for the case of matter alone which is discussed in the previous chapter, the cumulant expansion method is also similar. For this reason we will be brief and present only the final results with necessary definitions not found in the references cited. With the symbol  $g = (mc^2/k_BT)^4/c\lambda^2\rho^2$  which has a dimension of volume × time, the reduced entropy production can be written as

$$\hat{\sigma}_{ent} = \sigma_{ent} g / k_B. \tag{5.105}$$

To the first order cumulant approximation, the reduced entropy production is given by

$$\hat{\sigma}_{ent} = \kappa \sinh \kappa \ge 0 \tag{5.106}$$

which is positive semidefinite for all approximations for the unknowns  $X_a^{(\alpha)}$ . In this expression  $\kappa$  is given by

$$\kappa = \left[\sum_{a=i}^{r} \sum_{b=i}^{r} \sum_{\alpha \ge 1} \sum_{\gamma \ge 1} X_{a}^{(\alpha)} \odot R_{ab}^{(\alpha\gamma)} \odot X_{b}^{(\gamma)}\right]^{1/2}.$$
(5.107)

Here  $R_{ab}^{(\alpha\gamma)}$  are given by the collision bracket integrals appearing in the first order Chapman-Enskog method. Their statistical formulas are as follows. With the notations  $\pi_a = c\beta p_a$  and

$$[A \odot B]_{ab} = G_a G_b \sum_{s} \int d^3 \bar{\pi}_a d^3 \bar{\pi}_b d^3 \bar{\pi}_k^* d^3 \bar{\pi}_l^* \bar{W}_{ab;kl}^{(s)} \bar{f}_a^0 \bar{f}_b^0 \Xi_{abkl}^{(0)} A \odot B, \qquad (5.108a)$$

where

$$\Xi_{abkl}^{(0)} = [(1 + \epsilon_a f_a^0)(1 + \epsilon_b f_b^0)(1 + \epsilon_k f_k^0)(1 + \epsilon_l f_l^0)]^{-1}.$$
(5.108b)

The collision bracket integrals are then given by

$$R_{aa}^{(\alpha\gamma)} = \frac{1}{4}\beta^{2} [(h_{a}^{(\alpha)} + h_{a'}^{(\alpha)} - h_{a}^{(\alpha)*} - h_{a'}^{(\alpha)*})(h_{a}^{(\gamma)} + h_{a'}^{(\gamma)} - h_{a}^{(\gamma)*} - h_{a'}^{(\gamma)*}]_{aa'} + \frac{1}{2}\beta^{2} \sum_{b \neq a} [(h_{a}^{(\alpha)} - h_{a}^{(\alpha)*})(h_{a}^{(\gamma)} - h_{a}^{(\gamma)*})]_{ab}, \qquad (5.109a)$$

$$R_{ab}^{(\alpha\gamma)} = \beta^2 \sum_{b \neq a} [(h_a^{(\alpha)} - h_b^{(\alpha)*})(h_a^{(\gamma)} - h_b^{(\gamma)*})]_{ab}, \qquad (a \neq b)$$
(5.109b)

$$R_{rr}^{(\alpha\gamma)} = \frac{1}{2}\beta^2 \sum_{i}' [(h_r^{(\alpha)} - h_r^{(\alpha)*})(h_r^{(\gamma)} - h_r^{(\gamma)*})]_{ri}, \qquad (5.110a)$$

$$R_{ri}^{(\alpha\gamma)} = \beta^2 \sum_{i} \left[ (h_r^{(\alpha)} - h_i^{(\alpha)*}) (h_r^{(\gamma)} - h_i^{(\gamma)*}) \right]_{ri}.$$
 (5.110b)

When these collision bracket integrals are explicitly evaluated with the differential cross sections or transition probabilities for the collision processes postulated for the covariant Boltzmann equations, the dissipation terms will be known in terms of molecular parameters. This part of calculation is deferred to the next section.

Comparing (5.79) with (5.107) for  $\kappa$ , we now find the dissipation terms consistent with the second law of thermodynamics

$$\Lambda_a^{(\alpha)} = (\beta g)^{-1} \sum_{b=i}^r \sum_{\gamma \ge 1} R_{ab}^{(\alpha \gamma)} \odot X_b^{(\gamma)}(\sinh \kappa / \kappa).$$
 (5.111)

Higher order cumulant approximations for the dissipation terms may be obtained if the corresponding cumulant approximation is used for the reduced entropy production. It is straightforward to obtain them by following the procedure described in the literature [47]. There now remains the task of determining the unknowns  $X_a^{(\alpha)}$  in order to complete the description of the modified moment method.

# 5.6 The unknowns $X_a^{(\alpha)}$

The nonequilibrium canonical form (5.30a) and (5.44) can be determined by following the procedure described in previous two chapters. Therefore, we will briefly present the formulas to use and the lowest order approximation for the unknowns. The unknowns  $X_a^{(\alpha)}$  are determined by the algebraic equation

$$-\beta X_{a}^{(\alpha)} \odot \langle f_{a}^{0} c^{-2} U_{\mu} p_{a}^{\mu} h_{a}^{(\alpha)} h_{a}^{(\alpha)} \rangle = \langle f_{a}^{0} c^{-2} U_{\mu} p_{a}^{\mu} h_{a}^{(\alpha)} ln (1 + \sum_{\gamma \ge 1} A_{a}^{(\gamma)} \odot h_{a}^{(\gamma)}) \rangle \quad (a = i, r) \quad (5.112)$$

where tensor  $A_a^{(\gamma)}$  is determined as follows:

$$\Phi_a^{(\gamma)} = \langle f_a^0 c^{-2} \mathcal{U}_\mu p_a^\mu h_a^{(\gamma)} h_a^{(\gamma)} \rangle \odot A_a^{(\gamma)}$$
(5.113)

and  $f_a^0$  is the local equilibrium distribution function. The right-hand side of (5.112) can be expanded and evaluated term by term as described in the chapter 4. To the lowest order, the series yields the unknowns in the following form:

$$X_a^{(\alpha)\mu\nu...l} = -\Phi_a^{(\gamma)\mu\nu...l}/g_a^{(\alpha)}$$
(5.114)

where

$$g_a^{(\alpha)} = C_\alpha c^{-2} \beta \langle U_\sigma p_a^\sigma h_a^{(\alpha)} \odot h_a^{(\alpha)} f_a^0 \rangle$$
(5.115)

with  $C_{\alpha}$  defined by  $C_1 = 1/5, C_2 = 1, C_3 = 1/3, C_4 = 1/3$ , etc. This set of solution leaves the first order cumulant approximation for the entropy production positive semidefinite. Therefore, they are thermodynamically consistent. It also satisfies the matching conditions. In this manner, the modified moment method for relativistic Eoltzmann equation is complete. When the approximate solutions are

used in the dissipation terms, the evolution equations are ready for solution and transport properties can be calculated from the solutions of the evolution equations. The evolution equations for the fluxes and the conservation equations, collectively called the generalized hydrodynamic equations, constitute a mathematical structure for irreversible processes in a system of radiation and matter which is consistent with the thermodynamic laws.

# 5.7 Conlusion

We have formulated a covariant kinetic theory for a system consisting of matter and radiation by putting the material particles and photons on an equal footing. This kinetic theory has an attendant theory of irreversible processes in a system of radiation and material gases consistent with the thermodynamic laws. These formulations are achieved by treating the system as a gas mixture of photons and material particles which interact with each other according to the dynamical laws of mechanics. The covariant kinetic equations used are the Boltzmann equations suitablely generalized to accommodate the quantum nature of radiation. By applying the modified moment method, thermodynamically consistent solutions for the kinetic equations are obtained and a theory of irreversible thermodynamics is formulated therewith for the system. As it was the case for nonradiative systems, the entropy differential is found to be nonexact if the system is away from equilibrium, and a differential equation for the Boltzmann function serves as a local H theorem for the system. A theory of radiative transport processes can be developed by the means of the flux evolution equations presented. The present covariant formulation removes the weaknes; inherent to the nonrelativistic kinetic theory as shown in the chapter 2, and the covariant generalized hydrodynamic equations derived from the relativistic Boltzmann equation have better balanced structures, although more difficult to solve in practice. The generalized hydrodynamic equations, namely, the conservation equations and the flux evolution equations, for the system of radiation and matter can be used to describe irreversible thermodynamic and hydrodynamic processes occurring far from equilibrium. The theory of transport processes is developed for the system of radiation and matter in the next chapter. Table 1. Kinetic Terms  $Z_r^{(\alpha)}$  for Radiation

Definitions:

$$\begin{split} [\nabla U]^{(2)\mu\nu} &= \frac{1}{2} (\nabla^{\mu} U^{\nu} + \nabla^{\nu} U^{\mu}) - \frac{1}{3} \Delta^{\mu\nu} \nabla^{\tau} U_{\tau}, \\ [A \cdot B]^{(2)\mu\nu} &= \frac{1}{2} (A^{\mu\sigma} B^{\nu}_{\sigma} + A^{\nu\sigma} B^{\mu}_{\sigma}) - \frac{1}{3} \Delta^{\mu\nu} A^{\sigma\tau} B_{\sigma\tau}. \end{split}$$

Kinetic terms:

$$\begin{split} Z_{r}^{(1)\mu\nu} &= - \nabla_{\sigma} \Omega_{r}^{(1)\mu\nu\sigma} - 2[\Pi_{r} \cdot \nabla U]^{(2)\mu\nu} + 2p_{r}[\nabla U]^{(2)\mu\nu} \\ &+ 2\Delta_{r}[\nabla U]^{(2)\mu\nu} + \Pi_{r}^{\mu\nu} \nabla_{\sigma} U^{\sigma} - 2c^{-2}[Q_{r}DU]^{(2)\mu\nu} \\ &+ \langle f_{r} p_{r}^{\sigma} p_{r}^{r} p_{r}^{l} (p_{r}^{\epsilon} U_{\epsilon})^{-1} \rangle \nabla_{\sigma} U_{r} (\Delta_{l}^{\mu} U^{\nu} + U^{\mu} \Delta_{l}^{\nu}) \\ &- \frac{1}{3} \langle f_{r} p_{r}^{\sigma} p_{r}^{r} p_{r}^{l} p_{r}^{h} c^{2} (p_{\epsilon}^{\epsilon} U_{\epsilon})^{-2} \rangle \nabla_{\sigma} U_{\lambda} (\Delta_{l}^{\mu} \Delta_{r}^{\nu} - \frac{1}{3} \Delta_{lr} \Delta^{\mu\nu}) \\ &- \frac{1}{3} \langle f_{r} p_{r}^{\sigma} p_{r}^{p} p_{r}^{h} p_{r}^{h} c^{2} (p_{\epsilon}^{\epsilon} U_{\epsilon})^{-2} \rangle \nabla_{\sigma} U_{\lambda} (\Delta_{l}^{\mu} \Delta_{r}^{\nu} - \frac{1}{3} \Delta_{lr} \Delta^{\mu\nu}) \\ &- c^{-2} [(P_{r}^{\mu\tau} U^{\nu} + P_{r}^{\nu\tau} U^{\mu}) DU_{\tau} + (p_{r} + \Delta_{r})(U^{\mu} DU^{\nu} + U^{\nu} DU^{\mu})], \\ Z_{r}^{(2)} &= - \nabla_{\mu} \Omega_{r}^{(2)\mu} + \frac{2}{3} \Pi_{r}^{\mu\nu} [\nabla U]_{\mu\nu}^{(2)} - p_{r} Dln(p_{r} v^{5/3}) \\ &+ \frac{2}{3} \Delta_{r} \nabla_{\nu} U^{\nu} - \nabla_{\mu} (J_{r}^{\mu} p_{r} / \rho_{r}) + \frac{2}{3} c^{-2} Q_{r}^{\mu} DU_{\mu} \\ &- \frac{1}{3} \langle f_{r} p_{r}^{\sigma} p_{r}^{\tau} p_{r}^{h} p_{r}^{h} c^{2} (p_{\epsilon}^{\epsilon} U_{\epsilon})^{-2} \rangle \nabla_{\sigma} U_{\lambda} \Delta_{\tau l}, \\ Z_{r}^{(3)\mu} &= - \nabla_{\nu} \Omega_{r}^{(3)\nu\mu} + \Pi_{r}^{\mu\nu} DU_{\nu} - (p_{r} + \Delta_{r}) DU^{\mu} - J_{r}^{\mu} Dh_{r} \\ &- Q_{r}^{\mu} \nabla_{\nu} U^{\mu} + a_{r} J_{r}^{\nu} U^{\mu} \nabla_{\nu} h_{r} + (p_{r} + \Delta_{r}) U^{\mu} \nabla^{\nu} U_{\nu} \\ &- U^{\mu} \Pi_{r}^{\nu\sigma} \nabla_{\nu} U_{\sigma} - c^{-2} U^{\mu} Q_{r}^{\mu} DU_{\nu} \\ &- a_{r} \langle f_{r} p_{r}^{\mu} p_{r}^{h} c^{2} (U_{\epsilon} p_{r}^{\epsilon})^{-1} \rangle \partial_{\nu} h_{r} \\ &+ \langle f_{r} p_{r}^{\mu} p_{r}^{\sigma} c^{2} (U_{\epsilon} p_{r}^{\epsilon})^{-1} \rangle h_{r} \partial_{\sigma} a_{r} + U^{\mu} N_{r}^{\sigma} h_{r} \partial_{\sigma} a_{r}, \\ Z_{r}^{(4)\mu} &= - \nabla_{\nu} \Omega_{r}^{(4)\mu\nu} - J_{r}^{\nu} \nabla_{\nu} U^{\mu} - \rho_{r} DU^{\mu} - c^{-2} U^{\mu} J_{r}^{\nu} DU_{\nu} \\ &- \langle f_{r} p_{r}^{\mu} p_{r}^{\sigma} c^{2} (p_{\epsilon}^{\epsilon} (p_{\epsilon})^{-2}) \nabla_{\sigma} U_{\lambda}, \end{aligned}$$

$$\begin{split} Z_r^{(5)\mu} &= -\nabla_{\nu}\Omega_r^{(5)\mu\nu} + c^{-2}\psi_r^{(5)\mu\nu}DU_{\nu} \\ &- \langle f_r c^2 (p_r^{\epsilon}U_{\epsilon})^{-2} p_r^{\sigma} p_r^{\tau} P_3 (\Delta_{\nu}^{\mu} p_r^{\nu}) \rangle \partial_{\sigma} U_{\tau} \\ &+ \langle c^2 f_r (p_r^{\epsilon}U_{\epsilon})^{-1} p_r^{\sigma} \partial_{\sigma} P_3 (\Delta_{\nu}^{\mu} p_r^{\nu}) \rangle. \end{split}$$

## Chapter 6

#### Radiative transport coefficients and their mutual relations

In the phenomenological theory of radiative energy transfer [6] the radiative transport coefficients are expressed in terms of the Rosseland mean which phenomenologically accounts for radiative absorption by matter interacting with radiation. The radiative transport coefficients so expressed stand in constant ratios independent of material parameters. For example, the ratio of the radiative shear viscosity  $\bar{\eta}_r^0$  to the radiative bulk viscosity  $\bar{\zeta}_r^0$  is  $\bar{\eta}_r^0/\bar{\zeta}_r^0 = 3/5$ , whereas the ratio of the radiative shear viscosity to the radiative thermal conductivity  $\bar{\lambda}_r^0$  is  $\bar{\eta}_r^0/\bar{\lambda}_r^0 = 1/5c^2$  where c is the speed of light. If the thermal conductivity is defined with respect to the temperature gradient  $\nabla T$  instead of  $\nabla lnT$ , the latter ratio must be multiplied by T. In the case of material gas, there exist similar relations and they are Eucken ratios [63]. Such ratios of the radiative transport coefficient from another, but also serve as an internal consistency check for the kinetic theory formulated to study radiative transport processes of interest.

As we have shown in the preceding chapter, a covariant kinetic theory for a nonequilibrium system of radiation and matter is developed [34]. The formalism provides a molecular foundation for the irreversible processes owing to the interaction of radiation and matter. It also furnishes a method of calculating various radiative and material transport coefficients in terms of the transition probabilities of elementary dynamical processes involving the material particles and photons. The formulas obtained allow explicit calculations of the transport coefficients once dynamical quantity, such as differential cross section, is known.

In this chapter, we first present various radiative transport coefficients in terms of the collision bracket integrals reminiscent of the collision bracket integrals appearing in the Chapman-Enskog method of solution for the Boltzmann equation [18] for a material gas. Using the statistical formulas for the radiative transport coefficients and applying them to a photon-electron system, we calculate the radiative transport coefficients and their respective ratios. The ratios thus calculated are found to be in agreement with the phenomenological values mentioned earlier. By assuming that the elementary collision dynamical process is the Compton scattering, we explicitly calculate various radiative transport coefficients [35].

### 6.1 Transport coefficients

To begin the discussion on transport coefficients, we summarize the evolution equations for fluxes  $\Phi_m^{(\alpha)}$  and  $\Phi_r^{(\delta)}$  in one place:

$$\rho D\hat{\Phi}_m^{(\alpha)\mu\nu\ldots l} = Z_m^{(\alpha)\mu\nu\ldots l} + \Lambda_m^{(\alpha)\mu\nu\ldots l}, \qquad (6.1a)$$

$$\rho D\hat{\Phi}_r^{(\delta)\mu\nu\dots l} = Z_r^{(\delta)\mu\nu\dots l} + \Lambda_r^{(\delta)\mu\nu\dots l}.$$
(6.1b)

These equations are coupled to (5.65a)-(5.67) and (5.72)-(5.73) of the previous chapter which are the conservation laws of density, number fractions, internal energy, momentum, etc. for matter and radiation. These sets of conservation equations and flux evolution equations constitute generalized hydrodynamic equations for the system of matter and radiation. The solutions of these equations subject to suitable initial and boundary conditions will describe the relativistic fluid (gas) in interaction with radiation. Our main aim in this section is to obtain the kinetic theory expressions for various transport coefficients.

For this purpose we first linearize the flux evolution equations, namely, the constitutive equations (6.1a) and (6.1b) to obtain the set

$$\rho D\hat{\Phi}_{a}^{(\alpha)\mu\nu\dots l} = \chi_{a}^{(\alpha)\mu\nu\dots l} - (\beta g)^{-1} g_{a}^{(\alpha)} \sum_{b=i}^{r} \sum_{\gamma \ge 1} \bar{R}_{ab}^{(\alpha\gamma)\mu\nu\dots l} \odot \Phi_{b}^{(\gamma)}$$
(6.2)

where a = i, r and  $\chi_a^{(\alpha)\mu\nu\dots l}$  are related to the thermodynamic driving forces as follows:

$$\chi_{a}^{(1)\mu\nu} = 2p_{a}[\nabla U]^{(2)\mu\nu}; \quad \chi_{a}^{(2)} = -p_{a}Dln(p_{a}v^{5/3});$$
  
$$\chi_{a}^{(3)\mu} = p_{a}c^{2}(\nabla^{\mu}lnT - \frac{k_{B}T}{h}\nabla^{\mu}lnp); \qquad (6.3)$$

and

$$\bar{R}_{ab}^{(\alpha\gamma)} = (g_a^{(\alpha)})^{-1} R_{ab}^{(\alpha\gamma)} (g_b^{(\gamma)})^{-1}, \qquad (6.4)$$

the collision bracket integrals  $R_{ab}^{(\alpha\gamma)}$  are defined in (5.109a)-(5.110b). In order to analyze the linear transport processes under a steady state condition, we may neglect the substantial time derivative term in (6.2). Therefore, the constitutive equations become those of linear transport processes

$$\chi_{a}^{(\alpha)\mu\nu\dots l} - (\beta g)^{-1} g_{a}^{(\alpha)} \sum_{b=i}^{r} \sum_{\gamma \ge 1} \bar{R}_{ab}^{(\alpha\gamma)\mu\nu\dots l} \odot \Phi_{b}^{(\gamma)} = 0 \qquad (a=i,r)$$
(6.5)

which is a coupled linear set. Solving these equations for  $\Phi_a^{(\alpha)\mu\nu\ldots l}$  and comparing the result with the linear phenomenological constitutive equations (i.e., the Newtonian law of viscosity, the Fourier law of heat conduction, etc.), we obtain the desired linear transport coefficients in terms of the collision bracket integrals  $R_{ab}^{(\alpha\gamma)\mu\nu\ldots l}$ . The procedure for this is well described in refs. [34, 35]. First, we observe that since the system is isotropic the tensor  $\bar{R}_{ab}^{(\alpha\gamma)\mu\nu\ldots l}$  may be expanded in terms of isotropic tensors. For the case of our interest here, we have

$$\bar{R}_{ab}^{(11)\mu\nu kl} = \bar{\mathcal{R}}_{ab}^{(11)} [\frac{1}{2} (\Delta^{\mu k} \Delta^{\nu l} + \Delta^{\mu l} \Delta^{\nu k}) - \frac{1}{3} \Delta^{\mu \nu} \Delta^{kl}],$$
(6.6)

that is,

$$\bar{\mathcal{R}}_{ab}^{(11)} = \frac{1}{5} \bar{R}_{ab}^{(11)\mu\nu kl} [\frac{1}{2} (\Delta^{\mu k} \Delta^{\nu l} + \Delta^{\mu l} \Delta^{\nu k}) - \frac{1}{3} \Delta^{\mu\nu} \Delta^{kl}] = \frac{1}{10} \beta^2 (g_a^{(1)} g_b^{(1)})^{-1} \sum_{b \neq a} [(h_a^{(1)} - h_b^{(1)*}) : (h_a^{(1)} - h_b^{(1)*})]_{ab}.$$
(6.7)

Similarly,

$$\hat{\mathcal{R}}_{aa}^{(11)} = \frac{1}{5} \beta^2 (g_a^{(1)})^{-2} \{ \frac{1}{4} \times [(h_a^{(1)} + h_{a'}^{(1)} - h_a^{(1)*} - h_{a'}^{(1)*}) : (h_a^{(1)} + h_{a'}^{(1)} - h_{a'}^{(1)*} - h_{a'}^{(1)*})]_{aa'} + \frac{1}{2} \sum_{b \neq a} [(h_a^{(1)} - h_a^{(1)*}) : (h_a^{(1)} - h_{a}^{(1)*})]_{ab} \}.$$
(6.7)

Here the prime on the subscript *a* means another particles of species *a*. Since  $\Phi_b^{(1)}$  is already traceless symmetric, we find

$$\bar{R}_{ab}^{(11)\mu\nu kl} \Phi_{bkl}^{(1)} = \bar{\mathcal{R}}_{ab}^{(11)} \Phi_{b}^{(1)\mu\nu}.$$
(6.8)

In case of  $\alpha = 3$ , the tensor  $\ddot{R}^{(33)\mu\nu}_{ab}$  is decomposable as follows:

$$\bar{R}^{(33)\mu\nu}_{ab} = \bar{\mathcal{R}}^{(33)}_{ab} \Delta^{\mu\nu} \tag{6.9}$$

where

$$\bar{\mathcal{R}}_{ab}^{(33)} = \frac{1}{3}\beta^2 (g_a^{(3)}g_b^{(3)})^{-1} \frac{1}{2} \sum_{b \neq a} [(h_a^{(3)} - h_b^{(3)*}) \cdot (h_a^{(3)} - h_b^{(3)*})]_{ab}.$$
(6.10)

Therefore, we finally obtain

$$\bar{R}^{(33)\mu\nu}_{ab}\Phi^{(3)}_{b\nu} = \bar{\mathcal{R}}^{(33)}_{ab}\Phi^{(3)\mu}_{b}.$$
(6.11)

In case of  $\alpha = 2$ , we write

$$\bar{R}_{ab}^{(22)} = \bar{\mathcal{R}}_{ab}^{(22)} \tag{6.12}$$

where

$$\bar{\mathcal{R}}_{ab}^{(22)} = \beta^2 (g_a^{(2)} g_b^{(2)})^{-1} \frac{1}{2} \sum_{b \neq a} [(h_a^{(2)} - h_b^{(2)*}) \cdot (h_a^{(2)} - h_b^{(2)*})]_{ab}.$$
(6.13)

Therefore, the linear set (6.5) may be written as

$$\chi_{a}^{(1)\mu\nu} - (\beta g)^{-1} g_{a}^{(1)} \sum_{b=i}^{r} \bar{\mathcal{R}}_{ab}^{(11)} \Phi_{b}^{(1)\mu\nu} = 0, \qquad (6.14a)$$

$$\chi_{a}^{(2)} - (\beta g)^{-1} g_{a}^{(2)} \sum_{b=i}^{r} \bar{\mathcal{R}}_{ab}^{(22)} \Phi_{b}^{(2)} = 0, \qquad (6.14b)$$

$$\chi_{a}^{(3)\mu} - (\beta g)^{-1} g_{a}^{(3)} \sum_{b=i}^{r} \bar{\mathcal{R}}_{ab}^{(33)} \Phi_{b}^{(3)\mu} = 0.$$
 (6.14c)

On solving these equations for the fluxes, we obtain the linear constitutive equations from which the transport coefficients may be determined:

$$\Phi_{a}^{(1)\mu\nu} = \beta g \sum_{b=i}^{r} (\hat{\mathcal{R}}^{(11)-1})_{ab} \chi_{b}^{(1)\mu\nu} / g_{b}^{(1)}, \qquad (6.15a)$$

$$\Phi_a^{(2)} = \beta g \sum_{b=i}^r (\hat{\mathcal{R}}^{(22)-1})_{ab} \chi_b^{(2)} / g_b^{(2)}, \qquad (6.15b)$$

$$\Phi_a^{(3)\mu} = \beta g \sum_{b=i}^r (\bar{\mathcal{R}}^{(33)-1})_{ab} \chi_b^{(3)\mu} / g_b^{(3)}.$$
(6.15c)

Here the subscript a is for either the matter or radiation. The transport coefficients may then be defined as follows:

shear viscosity:

$$\eta_{ab}^{0} = \beta g(p_b/g_b^{(1)})(\bar{\mathcal{R}}^{(11)-1})_{ab}, \qquad (6.16a)$$

bulk viscosity:

$$\zeta_{ab}^{0} = \beta g(5p_a/3g_b^{(2)})(\bar{\mathcal{R}}^{(22)-1})_{ab}, \qquad (6.16b)$$

thermal conductivity:

$$\lambda_{ab}^{0} = \beta g(c^{2} p_{b} / g_{b}^{(3)}) (\tilde{\mathcal{R}}^{(22)-1})_{ab}.$$
(6.16c)

In practice, since the component transport coefficients are generally not measured, perhaps, except for the photon species, the transport coefficients defined in (6.16) must be summed over species to obtain the corresponding coefficients measured for matter in the laboratory. Therefore, the transport coefficients for matter are given by the formulas

$$\eta_m^0 = \sum_{i,j}' \eta_{ij}^0, \tag{6.17a}$$

$$\zeta_m^0 = \sum_{i,j}' \zeta_{ij}^0, \tag{6.17b}$$

$$\lambda_m^0 = \sum_{i,j}' \lambda_{ij}^0. \tag{6.17c}$$

Here the prime on the summation sign means that the summation is over the matter species only. In the case of radiation, if the coupling terms  $(\mathcal{R}^{(11)-1})_{rb}$ , etc. are neglected, then the radiative transport coefficients are given by the formulas

shear viscosity:

$$\eta_r^0 = \beta g(p_r/g_r^{(1)})(\bar{\mathcal{R}}^{(11)-1})_{rr}, \qquad (6.18a)$$

bulk viscosity:

$$\zeta_r^0 = \beta g(5p_r/3g_r^{(2)})(\bar{\mathcal{R}}^{(22)-1})_{rr}, \qquad (6.18b)$$

thermal conductivity:

$$\lambda_r^0 = \beta g(c^2 p_r / g_r^{(3)})(\bar{\mathcal{R}}^{(33)-1})_{rr}.$$
(6.18c)

Especially, in connection with (6.18) we note that

$$g_r^{(1)} = \frac{4}{15} \beta c^{-2} \langle (U_\mu p_r^\mu)^3 f_r^0 \rangle = 2.96 p_r, \qquad (6.19a)$$

$$g_r^{(2)} = \frac{1}{9}\beta c^{-2} \langle (U_\mu p_r^\mu)^3 f_r^0 \rangle = 1.23p_r, \qquad (6.19b)$$

$$g_r^{(3)} = \frac{1}{3}\beta c^{-2} [\langle (U_\mu p_r^\mu)^3 f_r^0 \rangle - 2a_r \bar{h}_r \langle (U_\mu p_r^\mu)^2 f_r^0 \rangle + (a_r \bar{h}_r)^2 \langle U_\mu p_r^\mu f_r^0 \rangle]$$
  
= 18.81c<sup>2</sup>p<sub>r</sub>, (6.19c)

where

$$a_r = \Delta^{\mu}_{\sigma} \Delta^{\nu}_{\tau} \langle p^{\sigma}_r p^{\tau}_r f^0_r \rangle g_{\mu\nu} [\beta \Delta^{\mu}_{\sigma} \Delta^{\nu}_{\tau} \langle p^{\sigma}_r p^{\tau}_r (p^{\lambda}_r U^{\lambda})^{-1} f^0_r \rangle g_{\mu\nu}]^{-1}, \qquad (6.20a)$$

$$\bar{h}_r = 4\pi^4 k_B T / 90\zeta(3), \tag{6.20b}$$

$$\langle (U_{\mu}p_{r}^{\mu})^{n}f_{r}^{0}\rangle = (2c/\hbar^{3})\int \frac{d^{3}p_{r}}{p_{r}^{0}}(U_{\mu}p_{r}^{\mu})^{n}f_{r}^{0}.$$
(6.20c)

The rest of notations is the same as that in the previous chapter.

Since the collision bracket integrals are appeared in the transport coefficients, we will write them out explicitly:

$$\bar{\mathcal{R}}_{rr}^{\alpha\gamma} = (cg/h^6)[g_r^{(\alpha)}g_r^{(\gamma)}]^{-1} \sum_{i,j}' \sum_s G_r \int d^3\bar{p}_r d^3\bar{p}_i d^3\bar{p}_r^* d^3\bar{p}_j^* f_r^0 f_i^0 \Xi_{rir^*j^*}^{(0)}$$

$$\times W_{ri;r^{*}j^{*}}^{(s)}(p_{r}p_{i}|p_{r}^{*}p_{j}^{*})\frac{1}{2}\beta^{2}(h_{r}^{(\alpha)}-h_{r}^{(\alpha)*}) \odot (h_{r}^{(\gamma)}-h_{r}^{(\gamma)*}),$$
(6.21a)  
$$\bar{\mathcal{R}}_{ri}^{\alpha\gamma} = (cg/h^{6})[g_{r}^{(\alpha)}g_{i}^{(\gamma)}]^{-1} \sum_{j}^{\prime} \sum_{s} G_{r} \int d^{3}\bar{p}_{r}d^{3}\bar{p}_{i}d^{3}\bar{p}_{r}^{*}d^{3}\bar{p}_{j}^{*}f_{r}^{0}f_{i}^{0}\Xi_{rir^{*}j^{*}}^{(0)}$$
$$\times W_{ri;r^{*}j^{*}}^{(s)}(p_{r}p_{i}|p_{r}^{*}p_{j}^{*})\beta^{2}(h_{r}^{(\alpha)}-h_{r}^{(\alpha)*}) \odot (h_{r}^{(\gamma)}-h_{r}^{(\gamma)*}).$$
(6.21b)

Here

$$f_i^0 = exp[-\beta(p_i^{\mu}U_{\mu} - \mu^0)]; \qquad f_r^0 = [exp(\beta p_r^{\mu}U_{\mu}) - 1]^{-1}$$
(6.21c)

where the chemical potential  $\mu^0$  is given by

$$exp(-\beta\mu^0) = \sum_{i}' 4\pi m_i^2 K_2(m_i c^2 \beta) k_B T/\rho.$$
 (6.21d)

The prime on the summation sign means the exclusion of the photon species. The collision bracket integral  $\bar{\mathcal{R}}_{rr}^{(\alpha\gamma)}$  given in (6.21a) requires a comment. In (6.21a), the first collision bracket integral involving r and r' in (6.7') is absent because photons do not directly interact with each other and therefore there is no collision event corresponding to the collision bracket integral  $[\ldots]_{rr'}$ . The collision bracket integrals can be reduced if a more specific form is assumed for the transition probability  $W_{ri;r^*j^*}^{(s)}$ . In this chapter we will take into account only the Compton scattering. Therefore, the sum over the collision processes denoted by the index s will be reduced to a term and the corresponding transition probability will be denoted by the elastic scattering component  $W_{ri;r^*j^*}^{(e)}$  related to the Compton scattering cross section of the electron. Evaluation of the collision bracket integrals for such a scattering process is described in the next section.

In the phenomenological theory the radiative transport coefficients are given in terms of the phenomenological Rosseland coefficient  $\bar{\kappa}$  as follows [6]:

$$\tilde{\eta}_r^0 = 4aT^4/15c\bar{\kappa},\tag{6.22a}$$

$$\bar{\zeta}_r^0 = 4aT^4/9c\bar{\kappa},\tag{6.22b}$$

$$\bar{\lambda}_r^0 = 4acT^4/3\bar{\kappa},\tag{6.22c}$$

where  $a = 8\pi^5 k_B^4/15h^3c^3$  is the so-called radiation constant. Therefore, these radiative transport coefficients are related to each other by a proportionality constant. For example, we have

$$\bar{\eta}_r^0/\bar{\zeta}_r^0 = 3/5, \qquad \bar{\eta}_r^0/\bar{\lambda}_r^0 = 1/5c^2.$$
(6.23)

Comparison of  $\bar{\eta}_r^0$  and  $\eta_r^0$  yields the Rosseland coefficient in terms of the collision bracket integral  $\tilde{\mathcal{R}}_{rr}^{(11)}$ :

$$\bar{\kappa} = \frac{4k_B T g_r^{(1)}}{5cg} \bar{\mathcal{R}}_{rr}^{(11)}.$$
(6.24)

Similar identifications can be made by means of  $\bar{\zeta}_r^0$  and  $\bar{\lambda}_r^0$ , but they give the equivalent forms since different collision bracket integrals appearing in the transport coefficients are related to each other.

## 6.2 Evaluation of the collision bracket integrals

In order to be specific, we shall consider a photon-electron system where the electron is treated as a relativistic classical particle and only the electron-photon elastic scattering is taken into consideration. Therefore, the question of divergence associated with the long-range Coulomb scattering does not arise and thus the Coulomb logarithm is not present in the collision integrals. Although the present treatment is specific to the photon-electron system, the method used is basically the same as for other plasmas and relativistic particles. Therefore, the system considered is a physically realistic example covered by the present kinetic theory. The procedure used for computing the collision bracket integrals is similar to the work of de Groot et al. [8].

There are only two sets of four-momenta for the present system, namely, those of the photon and electron. They will be distinguished by the subscripts r and e, respectively. For the collision process

$$\hbar\omega(r) + e \rightarrow \hbar\omega^*(r^*) + e^*$$

we first introduce the transformation of four-momenta

$$P^{\mu} = p_r^{\mu} + p_e^{\mu} = p_r^{*\mu} + p_e^{*\mu}, \qquad (6.25a)$$

$$Q^{\mu} = \tilde{\Delta}^{\mu\nu} (p_{r\nu} - p_{e\nu}), \qquad Q^{*\mu} = \tilde{\Delta}^{\mu\nu} (p^*_{r\nu} - p^*_{e\nu}), \qquad (6.25b)$$

where

$$\bar{\Delta}^{\mu\nu} = g^{\mu\nu} - P^{\mu}P^{\nu}/P^2 \tag{6.26}$$

with  $P^2 = P^{\mu}P_{\mu}$ . We will also denote by  $Q^2$  the length of the four-relative momentum:  $Q^2 = Q^{\mu}Q_{\mu}$ . From (6.25a), (6.25b) and (6.26) we can show the following relations:

$$P^{\mu}Q_{\mu} = 0, \qquad \bar{\Delta}^{\mu\nu}P_{\nu} = 0, \qquad \bar{\Delta}^{\mu\nu}Q_{\nu} = Q^{\mu}.$$
 (6.27)

Therefore, the total four-momentum  $P^{\mu}$  is perpendicular to the the relative fourmomentum  $Q^{\mu}$ . The four-momenta  $p_{r}^{\mu}$ , etc. can be decomposed into the orthogonal components  $P^{\mu}$  and  $Q^{\mu}$  as follows:

$$p_r^{\mu} = \frac{1}{2}(1+d_{re})P^{\mu} + \frac{1}{2}Q^{\mu}, \qquad (6.28a)$$

$$p_e^{\mu} = \frac{1}{2}(1 - d_{re})P^{\mu} - \frac{1}{2}Q^{\mu}, \qquad (6.28b)$$

$$p_e^{*\mu} = \frac{1}{2}(1+d_{re})P^{\mu} + \frac{1}{2}Q^{*\mu}, \qquad (6.28c)$$

$$p_{e}^{*\mu} = \frac{1}{2}(1 - d_{re})P^{\mu} - \frac{1}{2}Q^{*\mu}, \qquad (6.28d)$$

where

$$d_{re} = (m_r^2 - m_e^2)c^2/P^2 = -m_e^2 c^2/P^2$$
(6.29)

in view of the fact that the photon mass is equal to zero. Since the collision process under consideration is elastic, the electron masses are the same before and after the collision and hence

$$Q^{2} = -(1 + m_{e}^{4}c^{4}/P^{4})P^{2} + 2m_{e}^{2}c^{2} = Q^{*2}.$$
 (6.30)

In order to make the integration in the collision bracket integrals easily, we will change the variables from  $p_r^{\mu}, p_e^{\mu}$  etc. to  $P^{\mu}, Q^{\mu}$  etc. The Jacobian of this transformation is

$$\frac{\partial(P,Q)}{\partial(p_r,p_e)} = \frac{\partial(P^\bullet,Q^\bullet)}{\partial(p_e^\bullet,p_e^\bullet)} = 16.$$

The transition probability  $W^{(e)}$  can be written in terms of the cross section  $\sigma(P, \Theta)$ as follows:

$$W^{(e)} = P^2 \sigma(P, \Theta) \delta^{(4)}(P^{\mu} - P^{*\mu})$$
(6.31)

where  $\sigma(P, \Theta)$  is a differential cross section. For the Compton scattering it is given by the formulas [8]:

$$\sigma(P,x) = \frac{1}{2}r_0^2(1-\xi)\left\{1 + \frac{\xi^2(1-x)^2}{4[1-\xi(1-x)/2]} + \frac{1+(1-\xi/2)(1-x)}{1-\xi(1-x)/2}\right\}$$
(6.32)

where

$$\xi = (P^2 - m_e^2 c^2)/P^2, \qquad r_0 = e^2/m_e c^2, \qquad x = \cos\Theta,$$

 $\Theta$  being the scattering angle defined by  $\cos\Theta = \mathbf{Q} \cdot \mathbf{Q}^*/Q^2$ . The cross section is expanded in  $\xi$  and only up to the quadratic term in  $\xi$  will be retained in the subsequent calculations:

$$\sigma(P,\Theta) = \frac{1}{2}r_0^2[1+x^2+C_1(x)\xi+C_2(x)\xi^2+\cdots]$$
(6.32')

where

$$C_1(x) = x(1-x^2) - (1+x^2),$$
  

$$C_2(x) = \frac{1}{4}(1-x)\{(1-x)[1+(1+x)(1+3x)] - 4x(1+x)\}, \quad etc.$$

The volume element of the the space may be written as

$$d^{3}\bar{p}_{e}d^{3}\bar{p}_{e}d^{3}\bar{p}_{e}^{*}d^{3}\bar{p}_{e}^{*} = dM(P)dM(P^{*})dM(Q)dM(Q^{*})$$
(6.33)

where

$$dM(P) = d^4 P \theta(P^0) \theta(P^2 - m_e^2 c^2), \qquad (6.34a)$$

$$dM(Q) = d^4Q\delta(P \cdot Q)\delta[Q^2 + (1 + m_e^4c^4/P^4)P^2 - 2m_e^2c^2], \qquad (6.34b)$$

here  $\theta(y)$  denoting the Heaviside step function of y. The volume elements  $dM(P^*)$ and  $dM(Q^*)$  have similar forms.

With the help of the previous preparation, we are capable of writing the collision bracket integrals in more useful forms. We begin with  $\bar{\mathcal{R}}_{rr}^{(11)}$ . It may be written in the form

$$\begin{split} \bar{\mathcal{R}}_{rr}^{(11)} &= (2gc\beta^2 G_r/15h^6 g_r^{(1)2})exp(\bar{\mu}^0) \int dM(P)dM(P^*)dM(Q)dM(Q^*) \\ &\times exp(-\beta P^{\mu}U_{\mu})\Gamma(P,Q)W^{(e)}[U_{\mu}(p_r^{\mu}-p_r^{*\mu})]^2 \\ &= (gc\beta^2 G_r/30h^6 g_r^{(1)2})exp(\bar{\mu}^0) \int dM(P)dM(P^*)dM(Q)dM(Q^*) \\ &\times exp(-\beta P^{\mu}U_{\mu})\Gamma(P,Q)W^{(e)}[U_{\mu}(Q^{\mu}-Q^{*\mu})]^2 \end{split}$$
(6.35)

where

$$\bar{\mu}^{0} = \beta(\mu_{r}^{0} + \mu_{e}^{0}) = \beta\mu_{e}^{0}, \qquad (6.36a)$$

$$\Gamma(P,Q) = [1 - exp(-\beta p_r^{\mu} U_{\mu})]^{-2}.$$
(6.36b)

Substitution of the expression for  $W^{(e)}$  into (6.35), the collision bracket integral  $\bar{\mathcal{R}}_{rr}^{(11)}$  can be written in the form

$$\bar{\mathcal{R}}_{rr}^{(11)} = (gc\beta^2 G_r/30h^6 g_r^{(1)2})exp(\bar{\mu}^0)[\mathcal{R}_r^{(1)} + \mathcal{R}_r^{(2)} + 2\mathcal{R}_r^{(3)}]$$
(6.37)

where

$$\mathcal{R}_{r}^{(1)} = \int dM(P) dM(P^{*}) dM(Q) dM(Q^{*}) exp(-\beta P^{\mu} U_{\mu})$$
$$\times \Gamma(P,Q) P^{2} \sigma(P,\Theta) (U_{\mu} Q^{\mu})^{2} \delta^{(4)} (P^{\mu} - P^{*\mu}), \qquad (6.38a)$$
$$\mathcal{R}_{r}^{(2)} = \int dM(P)dM(P^{*})dM(Q)dM(Q^{*})exp(-\beta P^{\mu}U_{\mu}) \times \Gamma(P,Q)P^{2}\sigma(P,\Theta)(U_{\mu}Q^{*\mu})^{2}\delta^{(4)}(P^{\mu} - P^{*\mu}), \qquad (6.38b) \mathcal{R}_{r}^{(3)} = -\int dM(P)dM(P^{*})dM(Q)dM(Q^{*})exp(-\beta P^{\mu}U_{\mu}) \times \Gamma(P,Q)P^{2}\sigma(P,\Theta)U_{\mu}U_{\nu}Q^{\mu}Q^{*\nu}\delta^{(4)}(P^{\mu} - P^{*\mu}). \qquad (6.38c)$$

In the subsequent calculation we will put  $\Gamma(P, Q)$  equal to unity to an approximation. This approximation is tantamount to the condition that  $\beta$  is such that  $\beta P^{\mu}U_{\mu} \gg 1$ . The correction terms can be calculated in the same manner as for the case of  $\Gamma = 1$ .

It is convenient to define the integral I(a, b, c|P) by

$$I(a, b, c|P) = (\beta P c)^2 \int dM(Q) dM(Q^*) \sigma(P, \Theta) (\beta U_{\mu} Q^{\mu})^a \times (\beta U_{\mu} Q^{*\mu})^b (-\beta^2 c^2 Q^{\mu} Q^*_{\mu})^c.$$
(6.39)

In the center-of-momentum frame the four-momentum  $P^{\mu}$  is time-like whereas the relative momentum  $Q^{\mu}$  is space-like:

$$P^{\mu}=(P^0,0),$$

and

$$Q^{\mu} = (0, \mathbf{Q}), \qquad Q^{*\mu} = (0, \mathbf{Q}^*).$$

We assume that the center-of-momentum frame is oriented in such a way that the space component of  $U^{\mu} = (U^0, \mathbf{U})$  is parallel to the z axis. Then, since  $c^2 = (U^0)^2 - (U^z)^2$  and  $U^0$  and  $U^z$  may be written as

$$U^0 = U \cdot P/P,$$

and

$$U^{z} = [(U \cdot P)^{2}/P^{2} - c^{2}]^{1/2}.$$

Furthermore, if the spherical coordinate angles are denoted by  $(\theta, \phi)$  for  $\hat{\mathbf{Q}} = \mathbf{Q}/|\mathbf{Q}|$ and  $(\theta^*, \phi^*)$  for  $\hat{\mathbf{Q}}^* = \mathbf{Q}^*/|\mathbf{Q}^*|$ , respectively, then

$$\hat{\mathbf{Q}} \cdot \mathbf{U} = U^2 \cos\theta, \qquad \hat{\mathbf{Q}}^* \cdot \mathbf{U} = U^2 \cos\theta^*$$
 (6.40a)

and

$$x = \hat{\mathbf{Q}} \cdot \hat{\mathbf{Q}}^* = \cos\Theta = \cos\theta \cos\theta^* + \sin\theta \sin\theta^* \cos(\phi - \phi^*). \tag{6.40b}$$

In such frame, the collision cross section may be expanded in Legendre polynomials  $P_l(\cos\Theta)$ :

$$(\hat{\mathbf{Q}} \cdot \hat{\mathbf{Q}}^{*})^{c} \sigma(P, \hat{\mathbf{Q}} \cdot \hat{\mathbf{Q}}^{*}) = \sum_{l=0}^{\infty} (2l+1)\sigma(c, l|\beta Pc)P_{l}(cos\Theta)$$
(6.41)

where

$$\sigma(c, l|\beta Pc) = \frac{1}{2} \int_{-1}^{1} dx x^{c} P_{l}(x) \sigma(P, x).$$
 (6.42)

With the definition of

$$d\Omega = sin\theta d\theta d\phi, \qquad d\Omega^* = sin\theta^* d\theta^* d\phi^*,$$

and the abbreviation

$$K(a,b,l) = (4\pi)^{-2} \int d\Omega d\Omega^* (-\cos\theta)^a (-\cos\theta^*)^b P_l(x)$$
(6.43)

the integral I(a, b, c|P) may be written as

$$I(a,b,c|P) = 4\pi^{2}(i\beta cQ)^{(a+b+1)}(i\beta cQ^{*})^{(b+c+1)}[(P \cdot U)^{2}/c^{2}P^{2} - 1]^{(a+b)/2} \times \sum_{l=0}^{\infty} (2l+1)\sigma(c,l|\beta Pc)K(a,b,l).$$
(6.44)

It is now straightforward to obtain  $\mathcal{R}_r^{(1)}$  in terms of I(a, b, c|P):

$$\mathcal{R}_{r}^{(1)} = \beta^{-4} c^{-2} \int dM(P) I(2,0,0|P) exp(-\beta p_{r}^{\mu} U_{\mu})$$
  
$$= \frac{8}{9} \pi^{2} c^{2} r_{0}^{2} \int dM(P) Q^{2} Q^{*2} (1-\xi) [(P \cdot U)^{2} / c^{2} P^{2} - 1]$$
  
$$\times exp(-\beta p_{r}^{\mu} U_{\mu}). \qquad (6.45)$$

To evaluate this integral, we define the reduced variables

$$\tau = \beta p_r^{\mu} U_{\mu}, \qquad v = \beta P c. \tag{6.46}$$

Then, when the hydrodynamic four-velocity  $U^{\mu}$  is taken purely time-like, the dimensionless four-vector may be written as

$$\beta p_r^{\mu} c = (\tau, \mathbf{1}(\tau^2 - v^2)^{1/2}) \tag{6.47}$$

and the volume element dM(P) may be written in the spherical coordinates as

$$(\beta c)^4 d^4 P = (\beta c)^4 v (\tau^2 - v^2)^{1/2} d\tau dv d\Omega.$$
(6.48)

Furthermore,

$$Q^{2}Q^{*2} = (\beta c)^{-4}v^{-4}(v^{2} - z^{2})^{4},$$
  
$$1 - \xi = 1 - (P^{2} - m_{e}^{2}c^{2})/P^{2} = z^{2}v^{-2},$$

here z being defined by  $z = m_e c^2/k_B T$ . In terms of these variables the integral may be written in the form

$$\mathcal{R}_{r}^{(1)} = \frac{8}{9}\pi^{2}c^{2}r_{0}^{2}z^{2}(\beta c)^{-8}\int_{z}^{\infty}\int_{v}^{\infty}d\tau\int d\Omega v^{-7}(v^{2}-z^{2})^{4}(\tau^{2}-v^{2})^{3/2}e^{-\tau}.$$
 (6.49)

By using the integral representation of the modified Bessel function  $K_n(z)$  [8], we may write (6.49) in the form

$$\mathcal{R}_r^{(1)} = \frac{32}{3} \pi^3 c^2 r_0^2 z^2 (\beta c)^{-8} \int_z^\infty dv v^{-5} (v^2 - z^2)^4 K_2(v).$$
(6.50)

With the help of the asymptotic expansion of  $K_2(v)$  in the limit of large z, we obtain

$$\mathcal{R}_r^{(1)} \approx \frac{2048}{3\sqrt{2}} (4\pi)^2 \sqrt{\pi} c^2 \sigma_T c^2 z^{1/2} (\beta c)^{-8} e^{-z}$$
(6.51)

where  $\sigma_T$  is the Thomson cross section of the electron:

$$\sigma_T = \frac{8}{3}\pi r_0^2.$$

Owing to the symmetry of the integral, it is easy to show

$$\mathcal{R}_r^{(2)} = \mathcal{R}_r^{(1)}.\tag{6.52}$$

Taking the same procedure as for  $\mathcal{R}_r^{(1)}$ , we obtain

$$\mathcal{R}_r^{(3)} = \frac{6344}{9\sqrt{2}} (4\pi)^2 \sqrt{\pi} c^2 z^{-1/2} (\beta c)^{-8} e^{-z}.$$
 (6.53)

From (6.51) and (6.53), we have the following relation

$$\mathcal{R}_r^{(3)}/\mathcal{R}_r^{(1)} = 1.03/z.$$
 (6.54)

With these equations we finally obtain the collision bracket integral in the form

$$\bar{\mathcal{R}}_{rr}^{(11)} = (gc\beta^2 G_r/15h^6 g_r^{(1)2})exp(\beta\mu_e)\mathcal{R}_r^{(1)}(1+1.03/z).$$
(6.55)

The shear viscosity of the photon gas then given by

$$\eta_r^0 = 0.0305(k_B T / c\sigma_T) \tag{6.56}$$

for which the term of order  $z^{-1}$  is neglected as will be for other transport coefficients.

The collision bracket integral  $\bar{\mathcal{R}}_{rr}^{(22)}$  can be evaluated in a manner similar to the procedure used for  $\bar{\mathcal{R}}_{rr}^{(11)}$ . Here we omit the details. The final expression for  $\bar{\mathcal{R}}_{rr}^{(22)}$  is given by

$$\bar{\mathcal{R}}_{rr}^{(22)} = \frac{15}{36} (2gc\beta^2/30h^6 g_r^{(2)2}) exp(\bar{\mu}^0) \int dM(P) dM(P^*) dM(Q) dM(Q^*) \times exp(-\beta P^{\mu} U_{\mu}) \Gamma(P,Q) W^{(\epsilon)} [U_{\mu}(Q^{\mu} - Q^{*\mu})]^2 = \frac{15}{36} (g_r^{(1)}/g_r^{(2)})^2 \bar{\mathcal{R}}_{rr}^{(11)}.$$
(6.57)

Therefore, if the approximate value for  $\mathcal{R}_{rr}^{(11)}$  given by (6.55) is used, the bulk viscosity of nonequilibrium photon gas can be computed by the formula

$$\zeta_r^0 = 0.0508(k_B T / c\sigma_T). \tag{6.58}$$

The collision bracket integral  $\bar{\mathcal{R}}_{rr}^{(33)}$  can be also calculated similarly. In fact, it is related to  $\bar{\mathcal{R}}_{rr}^{(11)}$  as follows:

$$\bar{\mathcal{R}}_{rr}^{(33)} = \frac{5}{4} c^2 (2gc\beta^2/30h^6 g_r^{(3)2}) exp(\bar{\mu}^0) \int dM(P) dM(P^*) dM(Q) dM(Q^*) \times exp(-\beta P^{\mu} U_{\mu}) \Gamma(P,Q) W^{(e)} [U_{\mu}(Q^{\mu} - Q^{*\mu})]^2 = \frac{5}{4} c^2 (g_r^{(1)}/g_r^{(3)})^2 \bar{\mathcal{R}}_{rr}^{(11)}.$$
(6.59)

Thus the thermal conductivity of the photon gas to the same approximation as for the viscosity is given by the formula

$$\lambda_r^0 = 0.154 (ck_B T / \sigma_T). \tag{6.60}$$

It is useful to remark that the radiative transport coefficients given in (6.56), (6.58) and (6.60) are independent of the photon and electron densities as are the gas transport coefficients in the Chapman-Enskog approximation, namely, the linear transport coefficients of dilute gases.

We obtain the ratios of the transport coefficients as follows:

$$\eta_r^0 / \zeta_r^0 = \frac{3}{5} (g_r^{(2)} \bar{\mathcal{R}}_{rr}^{(22)} / g_r^{(1)} \bar{\mathcal{R}}_{rr}^{(11)}), \tag{6.61}$$

$$\eta_r^0 / \lambda_r^0 = \frac{1}{c^2} (g_r^{(3)} \bar{\mathcal{R}}_{rr}^{(33)} / g_r^{(1)} \bar{\mathcal{R}}_{rr}^{(11)}).$$
(6.62)

In view of the relations (6.57) and (6.59), we easily find the following universal relations:

$$\eta_r^0 / \zeta_r^0 = \frac{3}{5},\tag{6.63}$$

$$\eta_r^0 / \lambda_r^0 = \frac{1}{5c^2} (1 - 0.0165).$$
 (6.64)

Eq. (6.63) is the same as the phenomenological theory value whereas the ratio (6.64) is less than 2% off the phenomenological theory value. This difference is attributed to the approximate values obtained for the various integrals in the expression for  $g_r^{(3)}$  presented earlier. For all practical purposes the ratio may be said to be in agreement with the phenomenological value.

In conclusion, we have computed the radiative transport coefficients [35] for the photon-electron system by treating the electron as a relativistic classical particle in the limit of large z. We have also computed the ratios of radiative transport coefficients which are in agreement with the phenomenological theory values. The kinetic theory values of the ratios support the kinetic theory model presented for the system of photons and material gases which are displaced from equilibrium and interact with each other. The present theory provides a well defined molecular theory method of computing the parameters in the phenomenological theory and, especially, macroscopic observables for nonequilibrium radiation and the phenomenological coefficients such as the Rosseland coefficient.

#### Chapter 7

### Conclusion

The objective of this thesis is to develop a kinetic theory for irreversible processes in a system of radiation and matter. Instead of using the usual equation of radiation energy transfer we have postulated a semiclassical Boltzmann equation for photons which is coupled to the Boltzmann equations for material particles. This way, the system of radiation and matter is viewed as a mixture of photons and material particles which interact with each other according to the laws of mechanics for the system. The major motivation for this approach is in the desire to formulate irreversible thermodynamics of radiation and matter on equal footing and in a unified manner. This allows us to prove the H theorem for the system of radiation and matter, which is the cornerstone of irreversible thermodynamics. In addition, we show that the Planck distribution for equilibrium radiation and the Maxwell distribution for equilibrium material particles are the natural consequences of the H theorem (the second law of thermodynamics). Since the kinetic theory establishes a bridge which links the macroscopic measurable quantities of a system and the dynamic mechanism of constituent particles (atoms or molecules), we are able to evaluate the transport coefficients of nonequilibrium photon and material gases in terms of differential cross sections. Furthermore, the hydrodynamic description for a system of radiation and matter has been derived from the kinetic theory. This is the so-called generalized hydrodynamic equations for radiation and matter. The present thesis includes the nonrelativistic kinetic theory and the covariant kinetic theory of radiation and matter and some applications.

We first develop a nonrelativistic kinetic theory for a system of radiation and matter. The H theorem for such a system is proved. This allows us to establish irreversible thermodynamics for the system consisting of photons and material particles. The analysis leads to the conclusion that the entropy differential is not an exact differential form. Therefore the extended Gibbs relation does not hold for the entropy differential when the system is away from equilibrium. The reformulation of irreversible thermodynamics has been done by using the compensation differential which is an exact differential form. The new local H theorem is proposed in terms of the Boltzmann function. A coupled set of the generalized hydrodynamic equations is derived from the proposed semiclassical Boltzmann equations for photons and material particles. Its application to the light-induced viscous flow has shown that the radiative generalized hydrodynamic equations can account for nonlinear flow problems for which the conventional hydrodynamic equations fail. It has also been applied to the light-induced kinetic effects and laser-cooling [30]. Therefore, the validity of the generalized hydrodynamic equations for radiation and matter is confirmed by these experiments. This way, we provide a statistical mechanical foundat<sup>1</sup> on for nonequilibrium phenomena occurring in the system of radiation and matter.

We have applied the modified moment method to solve the covariant Boltzmann equation for a relativistic gas mixture. The advantages of our method are as follows. It is capable of dealing with nonlinear processes in nonequilibrium systems of relativistic gases. The Chapman-Enskog method and the Grad moment method give rise to thermodynamically consistent solutions only in the linear regime. This extension of the modified moment method also affords us a rigorous conclusion concerning the entropy differential of a nonequilibrium system: The relativistic form of the extended Gibbs relation which forms the basis of extended irreversible thermodynamics (EIT) does not hold valid at least from the viewpoint of the covariant Boltzman equation. However, there is the compensation differential that looks like the extended Gibbs relation used in EIT, but this requires a revision of the existing EIT formalism and its logical structure. The compensation differential can be used to investigate the thermodynamics of nonequilibrium systems in a way parallel to equilibrium thermodynamics. All the evolution equations for the macroscopic variables which are necessary to describe physical systems are presented in such forms that they consist of terms which are easily identified as the corresponding terms in their nonrelativistic versions and those of purely relativistic terms.

With the help of the relativistic Boltzmann equation, a covariant kinetic theory for a system consisting of matter and radiation has been formulated by putting the material particles and photons on an equal footing. This kinetic theory has an attendant theory of irreversible processes in a system of radiation and relativistic gases consistent with the thermodynamic laws. These formulations are achieved by treating the system as a mixture of photons and relativistic diluted gases which interact with each other according to the microscopic dynamical laws of mechanics. The covariant kinetic equations used are the Boltzmann equations suitably generalized to accommodate the quantum nature of photons. By applying the modified moment method, thermodynamically consistent solutions for the covariant kinetic equations are obtained and a theory of irreversible thermodynamics is formulated therewith for the system. The covariant formulation removes the awkwardness inherent in the nonrelativistic theory, and the covariant generalized hydrodynamic equations have better balanced structures.

A theory of radiative transport processes can be developed by means of the flux evolution equations. In chapter 6 we have computed the radiative transport coefficients for the photon-electron system by treating the electron as a relativistic classical particle. We have also computed the ratios of radiative transport coefficients which are in agreement with the phenomenological theory values. The correct values of the ratios support the kinetic theory model for the system of radiation and matter which are displaced from equilibrium and interact with each other. The theory provides a well defined molecular theory method of evaluating the parameters in the phenomenological theory and, especially, macroscopic observables for nonequilibrium radiation and the phenomenological coefficients such as the Rosseland coefficient.

On the whole, this thesis demonstrates the importance of the kinetic theory of radiation and matter as a basis for explaining irreversible processes for systems consisting of photons and material particles. In essence, the present formalism puts the statistical mechanics of nonequilibrium thermodynamics on the par with the Gibbs ensemble theory of equilibrium statistical thermodynamics in the sense that all thermodynamic functions and evolution equations are expressed in terms of  $X_i^{(\alpha)}$  and  $X_r^{(\alpha)}$ , which must be ultimately obtained by solving the generalized hydrodynamic equations of radiation and matter, just as all equilibrium thermodynamic functions and relations are expressed in the Gibbs ensemble theory in terms of a partition function which must be computed for each and every system in the end. The generalized hydrodynamic equations, namely, the conservation equations and the flux evolution equations, presented for the system of radiation and matter can be used to describe irreversible and hydrodynamic processes occurring far from equilibrium.

Finally, we provide some discussions on the validity of kinetic theory for describing irreversible processes of radiation and matter. In particular, we may ask what approximations, in the underlying physics, are contained in the kinetic equation for photons?

The most important approximation as far as the photon kinetic equation is concerned is that we consider photons basically as point particles which satisfy Bose-Einstein statistics. However, according to quantum mechanics photon has

dual character (particle-like and wave-like), therefore, photons also exhibit wave behavior. In other words, a photon in reality is a wave packet. For the point particle picture of a photon to be valid, it is necessary that the spread of the wave packet in phase space (momentum and coordinate) be small [43]. This means that the spread must be small compared to the resolution of interest in the coordinate space (x) and momentum space  $(\mathbf{p}_r)$  or  $(\nu, \mathbf{n})$ . Since the photon distribution function is written as a function of variables  $\mathbf{x}$ ,  $\nu$  and  $\mathbf{n}$ , it is sufficient to specify the phase space coordinates of the center of wave packet and any information concerning the distribution about this center is irrelevant. Owing to the Heisenberg uncertainty principle the wave packet spreads in spatial and momentum space cannot both be made arbitrarily small at the same time. These considerations impose a maximum possible resolution on the spatial and momentum coordinates. In fact, a kinetic equation for photons cannot describe the strong wave behavior manifested in diffraction and reflection since it does not take into account the wave behavior of photons. These phenomena depend on interference among the waves arising from different scattering centers which scatter the same photon.

The kinetic equation of photons also neglects the effects of refraction and dispersion. It is known that a photon will move at less than the vacuum speed of light in matter with a refraction index other than unity. In particular, if the refractive index is a function of position, the photon will not stream in straight lines between collisions but will undergo (continuous) refraction. In addition, if the refractive index is time dependent, a photon will continuously change its frequency as it streams between collisions. The origin of these effects are due to an interference phenomenon of the scattering of photons which is discussed by Feynman et al. [64]. A discussion on the validity of Boltzmann equation for material particles can be found in the book of Smith and Jensen [65]. Nevertheless, the present kinetic theory of radiation and matter is essential to understand some macroscopic phenomena of nonequilibrium systems consisting of photons and material particles. Note that the Maxwell equations are dynamical theory for radiation like Newton's law for classical particles whereas kinetic theory for photons provides a statistical description for photons in which irreversible processes are involved. The role of kinetic theory for photons is similar to that of Boltzmann equations for classical particles. Maxwell's theory and kinetic theory represent different levels of description of physical systems.

#### Appendix

# Nonrelativistic limits of the relativistic generalized hydrodynamic equations

In this appendix we examine the nonrelativistic limit of the kinematic terms  $Z_i^{(\alpha)\mu\nu...l}$  and the dissipation terms  $\Lambda_i^{(\alpha)\mu\nu...l}$ . It can be shown that in the limit of  $u/c \to 0$ ,  $Z_i^{(\alpha)\mu\nu...l}$  and  $\Lambda_i^{(\alpha)\mu\nu...l}$  are reduced to their nonrelativistic counterparts. Therefore the relativistic generalized hydrodynamic equations have the correct non-relativistic limit which has been confirmed by the experiments in various fields.

As mentioned earlier, the time-component of four-momentum is given by

$$p_{i}^{0} = m_{i}c(1 + p_{i}^{2}/m_{i}^{2}c^{2})^{1/2}$$

$$= m_{i}c(1 + p_{i}^{2}/2m_{i}^{2}c^{2}) + O(1/c^{3})$$

$$= m_{i}c + p_{i}^{2}/2m_{i}c + O(1/c^{3})$$

$$\approx m_{i}c, \quad c \to \infty.$$
(A.1)

Since the hydrodynamic velocity  $U^{\mu}$  may be written as

$$U^{\mu} = \gamma_{u}(c, \mathbf{u}) \tag{A.2}$$

where

$$\gamma_u = (1 - u^2/c^2)^{-1/2}. \tag{A.3}$$

It is clear that the space-components of  $U^{\mu}$  is reduced to the nonrelativistic hydrodynamic velocity in the limit of  $u/c \rightarrow 0$ . Therefore,

$$p_{i}^{\mu}U_{\mu} = \gamma_{u}(cp_{i}^{0} - \mathbf{p}_{i} \cdot \mathbf{u})$$

$$= (1 + u^{2}/2c^{2})(m_{i}c^{2} + p_{i}^{2}/2m_{i} - \mathbf{p}_{i} \cdot \mathbf{u}) + O(1/c^{2})$$

$$= \frac{1}{2}m_{i}v_{i}^{2} - m_{i}\mathbf{v}_{i} \cdot \mathbf{u} + \frac{1}{2}m_{i}u^{2} + m_{i}c^{2} + O(1/c^{2})$$

$$= \frac{1}{2}m_{i}(\mathbf{v}_{i} - \mathbf{u})^{2} + m_{i}c^{2} + O(1/c^{2})$$

$$\equiv \frac{1}{2}m_{i}c_{i}^{2} + m_{i}c^{2} + O(1/c^{2}) \qquad (A.4)$$

where  $\mathbf{c}_i = \mathbf{v}_i - \mathbf{u}$  is the nonrelativistic peculiar velocity of species *i* and  $m_i c^2$  term will be neglected in the nonrelativistic theory. This means that the Jüttner function has the following limit

$$f_{i} = exp[-\beta(p_{i}^{\mu}U_{\mu} - \mu_{i})]$$
  

$$\rightarrow exp[-\beta(\frac{1}{2}m_{i}c_{i}^{2} - \mu_{i})], \quad c \rightarrow \infty.$$
(A.5)

Therefore the Maxwell-Boltzmann distribution function is the nonrelativistic limit of the Jüttner distribution function.

We will show that the macroscopic variables and the operators in the relativistic generalized hydrodynamic equations approach to their nonrelativistic counterparts in the limit of  $c \to \infty$ .

The number density

$$\rho_{i} = c^{-2} U_{\mu} N_{i}^{\mu} = c^{-1} \int \frac{d^{3} p_{i}}{p_{i}^{0}} U_{\mu} p_{i}^{\mu} f_{i}$$

$$= \int d^{3} p_{i} f_{i} + O(1/c)$$

$$= n_{i}^{(n)} + O(1/c) \qquad (A.6)$$

here  $n_i^{(n)}$  denotes the number density in the nonrelativistic kinetic theory.

The covariant operators D and  $\nabla^{\mu}$  have the nonrelativistic limit as follows:

$$D = U^{\mu}\partial_{\mu} = U^{0}\partial_{0} + U^{k}\partial_{k}$$
$$= \partial_{t} + \mathbf{u} \cdot \nabla + O(1/c)$$
$$\equiv \frac{d}{dt} + O(1/c). \qquad (A.7)$$

The nonrelativistic counterpart of operator D is the substantial time derivative d/dt which is widely used in fluid mechanics. The space-component of operator  $\nabla^{\mu}$  is given by

$$\nabla^{j} = -\Delta^{jk}\partial_{k} - \Delta^{j0}\partial_{0}$$
  
=  $\partial/\partial x_{j} + O(1/c), \qquad (k, j = 1, 2, 3).$  (A.8)

Obviously,  $\nabla^{\mu}$  is reduced to the spatial derivative in the limit of  $c \to \infty$ .

Let us analyze the nonrelativistic limit of the entropy four-flow. According to the definitions in the relativistic kinetic theory [33]:

$$S^{\mu}(x) = -k_{B}c \sum_{i} \int \frac{d^{3}p_{i}}{p_{i}^{0}} p_{i}^{\mu} f_{i}(lnf_{i}-1)$$
(A.9)

and

$$S \equiv \rho S = c^{-2} U_{\mu} S^{\mu}(x)$$
  
=  $-k_B c^{-1} \sum_i \int \frac{d^3 p_i}{p_i^0} U_{\mu} p_i^{\mu} f_i(ln f_i - 1)$   
=  $-k_B \sum_i \int d^3 p_i f_i(ln f_i - 1) + O(1/c)$   
=  $S^{(n)} + O(1/c)$  (A.10)

where  $S^{(n)}$  is the entropy of a nonrelativistic gas-mixture. The space-component of entropy flux  $J_s^{\mu} = S^{\mu} - SU^{\mu}$  is given by

$$J_{s}^{k} = S^{k} - SU^{k}$$
  
=  $-k_{B} \sum_{i} \int d^{3}p_{i}c_{i}^{k}f_{i}(lnf_{i}-1) + O(1/c)$   
=  $J_{s}^{(n)k} + O(1/c).$  (A.11)

The entropy production has the limit

$$\sigma = -k_B c \sum_i \sum_j \int \frac{d^3 p_i}{p_i^0} ln f_i C(f_i, f_j)$$
$$= -k_B \sum_i \sum_j \int d^3 v_i ln f_i C(f_i, f_j) + O(1/c)$$
$$= \sigma^{(n)} + O(1/c)$$
(A.12)

where  $\sigma^{(n)}$  is the entropy production of nonrelativistic gas. The dissipative terms are given by

$$\Lambda_{i}^{(\alpha)\mu\nu...l} = c \sum_{j} \int \frac{d^{3}p_{i}}{p_{i}^{0}} h_{i}^{(\alpha)\mu\nu...l} C(f_{i}, f_{j})$$
$$= \sum_{j} \int d^{3}v_{i} h_{i}^{(\alpha)\mu\nu...l} C(f_{i}, f_{j}) + O(1/c).$$
(A.13)

In order to show the nonrelativistic limit of the relativistic generalized hydrodynamic equations, it is necessary to analyze the energy-momentum tensor and other macroscopic variables. Since

$$T^{\mu\nu} = c \sum_{i} \int \frac{d^3 p_i}{p_i^0} p_i^{\mu} p_i^{\nu} f_i(x, p_i), \qquad (A.14)$$

then

$$T^{00} = c \sum_{i} \int \frac{d^{3} p_{i}}{p_{i}^{0}} p_{i}^{0} p_{i}^{0} f_{i}(x, p_{i})$$
  
=  $nmc^{2} + \epsilon_{k} + O(1/c).$  (A.15)

On ignoring the rest energy part, it becomes the kinetic energy density. Let us consider the components  $T^{0k}$ , k = 1, 2, 3

$$T^{0k} = T^{k0} = c \sum_{i} \int \frac{d^{3}p_{i}}{p_{i}^{0}} p_{i}^{0} p_{i}^{k} f_{i}$$
  
=  $c \sum_{i} \int d^{3}p_{i} p_{i}^{k} f_{i}$  (A.16)

that is,  $T^{0k}/c$  becomes the momentum density of nonrelativistic gas when  $c \to \infty$ . Moreover,

$$T^{kj} = c \sum_{i} \int \frac{d^3 p_i}{p_i^0} p_i^k p_j^j f_i$$
  
=  $T^{(n)kj} + O(1/c), \quad k, j = 1, 2, 3$  (A.17)

where  $T^{(n)kj}$  denotes the nonrelativistic energy-momentum tensor.

With the help of these properties it is easy to show that the kinematic terms  $Z_i^{(\alpha)\mu\nu\dots l}$  have the following nonrelativistic limit:

$$Z_{i}^{(\alpha)\mu\nu\dots l} = \langle p_{i}^{\sigma}\partial_{\sigma}h_{i}^{(\alpha)\mu\nu\dots l}f_{i}(x,p_{i})\rangle + \partial_{\tau}(\Delta_{\sigma}^{\tau}\psi_{i}^{(\alpha)\mu\nu\dots l\sigma})$$

$$= \int \frac{d^{3}p_{i}}{p_{i}^{0}}p_{i}^{\sigma}f_{i}(x,p_{i})\partial_{\sigma}h_{i}^{(\alpha)\mu\nu\dots l}$$

$$+ \partial_{\tau}\Big(\int \frac{d^{3}p_{i}}{p_{i}^{0}}\Delta_{\sigma}^{\tau}p_{i}^{\sigma}h_{i}^{(\alpha)\mu\nu\dots l}\Big). \qquad (A.18)$$

Since

$$\Delta^{0}_{\mu}p^{\mu}_{i} = (c^{-2}U^{0}U_{\mu} - g^{0}_{\mu})p^{\mu}_{i}$$
  
=  $c^{-1}\mathbf{u} \cdot \mathbf{p}_{i} + O(1/c^{2}),$  (A.19)

and

$$\Delta^{k}_{\mu}p^{\mu}_{i} = (c^{-2}U^{k}U_{\mu} - g^{k}_{\mu})p^{\mu}_{i}$$
$$= -m_{i}c^{k}_{i} + O(1/c), \qquad (A.20)$$

then

$$\Delta_{\mu\nu} p_i^{\mu} p_i^{\nu} = m_i^2 c_i^2 + O(1/c). \tag{A.21}$$

Therefore,

$$Z_{i}^{(\alpha)} = \int d^{3}p_{i}f_{i}(d_{t} + \mathbf{c}_{i} \cdot \nabla)h_{i}^{(\alpha)} - \nabla \cdot \int d^{3}p_{i}\mathbf{c}_{i}h_{i}^{(\alpha)}f_{i} + O(1/c)$$
  
$$= \langle f_{i}(d_{t} + \mathbf{c}_{i} \cdot \nabla)h_{i}^{(\alpha)} \rangle - \nabla \cdot \langle \mathbf{c}_{i}h_{i}^{(\alpha)}f_{i} \rangle + O(1/c)$$
  
$$= \langle f_{i}(d_{t} + \mathbf{c}_{i} \cdot \nabla)h_{i}^{(\alpha)} \rangle - \nabla \cdot \psi_{i}^{(\alpha)} + O(1/c). \qquad (A.22)$$

This means that in the limit  $c \to \infty$  (the last term vanishing) the kinematic terms are reduced to their nonrelativistic counterparts which are given in the ref. 40:

$$Z_{i}^{(1)} = -\nabla \cdot \psi_{i}^{(1)} - 2[\mathbf{J}_{i}d_{t}\mathbf{u}]^{(2)} + 2[\mathbf{\Pi}_{i} \cdot \underline{\gamma}]^{(2)} - [\underline{\omega}, \mathbf{\Pi}_{i}] - \frac{2}{3}\mathbf{\Pi}_{i}\nabla \cdot \mathbf{u} + 2\Delta_{i}\underline{\gamma} + 2p_{i}\underline{\gamma}, \qquad (A.23)$$

$$Z_i^{(2)} = -\nabla \cdot \psi_i^{(2)} - \frac{2}{3} d_t \mathbf{u} \cdot \mathbf{J}_i + \frac{2}{3} \mathbf{\Pi}_i : \underline{\gamma} - \frac{2}{3} \Delta_i \nabla \cdot \mathbf{u} - p_i d_t ln(p_i v^{5/3}) - \nabla \cdot (\mathbf{J}_i p_i / \rho_i), \qquad (A.24)$$

$$Z_{i}^{(3)} = -\nabla \cdot \psi_{i}^{(3)} - d_{t}\mathbf{u} \cdot (\mathbf{P}_{i} - p_{i}\mathbf{U}) + \mathbf{Q}_{i}' \cdot (\underline{\gamma} + \underline{\omega} - \frac{1}{3}\mathbf{U}\nabla \cdot \mathbf{u}) + \varphi_{i}^{(3)} : (\underline{\gamma} + \underline{\omega} - \frac{1}{3}\mathbf{U}\nabla \cdot \mathbf{u}) - \mathbf{J}_{i}d_{t}\hat{h}_{i} - \mathbf{P}_{i} \cdot \nabla\hat{h}_{i}, \qquad (A.25)$$

$$Z_i^{(4)} = -\nabla \cdot \mathbf{P}_i - \rho_i d_t \mathbf{u} + \mathbf{J}_i \cdot (\underline{\gamma} - \frac{1}{3}\mathbf{U}\nabla \cdot \mathbf{u}) + \mathbf{J}_i \cdot \underline{\omega}, \qquad (A.26)$$

etc.

where

$$\underline{\omega} = \frac{1}{2} [\nabla \mathbf{u} - (\nabla \mathbf{u})^t], \qquad (A.27)$$

$$\varphi_i^{(3)} = \langle m_i \mathbf{c}_i \mathbf{c}_i \mathbf{c}_i f_i \rangle, \qquad (A.28)$$

$$[\underline{\omega}, \Pi_i] = \underline{\omega} \cdot \Pi_i - \Pi_i \cdot \underline{\omega}. \tag{A.29}$$

In this sense, the relativistic generalized hydrodynamic equations are reduced to their nonrelativistic counterparts under the condition  $c \rightarrow \infty$ 

$$\frac{\partial}{\partial t}\rho = -\nabla \cdot \rho \mathbf{u},\tag{A.30}$$

$$\rho \frac{d}{dt} \mathbf{u} = -\nabla \cdot \mathbf{P}, \tag{A.31}$$

$$\rho \frac{d}{dt} \varepsilon = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \mathbf{u}, \qquad (A.32)$$

$$\rho \frac{d}{dt} \hat{\Phi}_i^{(\alpha)} = Z_i^{(\alpha)} + \Lambda_i^{(\alpha)}. \tag{A.33}$$

These are well known results in the scheme of the modified moment method for nonrelativistic gases [20]. The discussion on the nonrelativistic limit of the generalized hydrodynamic equations for radiation can also be carried out by using the aforementioned method. Since the procedure is similar, we do not repeat here. In conclusion, the present relativistic kinetic theory has the correct nonrelativistic limit which has been confirmed by various experiments.

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