

Generalized Thermodynamics

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Generalized Thermodynamics

The Thermodynamics of Irreversible Processes
and Generalized Hydrodynamics

by

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This work is . . .

to the memory of the days of youth

of lavender dreams,

the dreams of light, . . .,

in the sun-woven shade of the lilac

on the old campus in Seoul.

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Preface

Despite a long history of almost 180 years stretching back to the times of Carnot and, later, Clausius and Lord Kelvin, amongst others following him, the subject of thermodynamics has not as yet seen its full maturity, in the sense that the theory of irreversible processes has remained incomplete. The works of L. Onsager, J. Meixner, I. Prigogine on the thermodynamics of linear irreversible processes are, in effect, the early efforts toward the desired goal of giving an adequate description of irreversible processes, but their theory is confined to near-equilibrium phenomena. The works in recent years by various research workers on the extension of the aforementioned thermodynamic theory of linear irreversible processes are further efforts toward the goal mentioned. The present work is another of such efforts and a contribution to the subject of generalizing the thermodynamics of reversible processes, namely, equilibrium thermodynamics, to that of irreversible processes—non-equilibrium thermodynamics, without being restricted to linear irreversible processes. In this context the terms ‘far removed from equilibrium’ is often used in the literature, and such states of macroscopic systems and non-linear irreversible phenomena in them are the objects of interest in this work.

The thermodynamics of processes, either reversible or irreversible, is a continuum mechanical theory of matter and energy and their exchange between different parts of the system, and as such it makes no direct reference to the molecules constituting the substance under consideration. In thermodynamics the nature of molecules composing the continuum matter manifests itself quite indirectly in the constitutive equations for the substance, such as the equation of state, the caloric equation of state, the material functions such as viscosity, thermal conductivity, and diffusion coefficients, and other thermophysical properties. The constitutive equation for a given macroscopic property of a substance contains parameters reflecting the nature of molecules in the substance, but unlike statistical mechanics thermodynamics does not start with individual molecules in its treatment of macroscopic properties. The forms and the values of the parameters in the constitutive equations of different substances for a given property, however, can be classified into different categories according to homologous series of substances, and thermodynamics distinguishes molecular systems in such a sense, but the basic mathematical structure of thermodynamics, either reversible or irreversible, remains generic to continuum matter. In this universality of its mathematical structure conforming to the laws of thermodynamics lies the power, usefulness, and formal beauty of thermodynamics for treating macroscopic phenomena and relating them to each other. Our principal objective is then to acquire a thermodynamic theory of irreversible processes in a form as universal as possible so that it applies to diverse macroscopic phenomena in equally diverse systems

in strict conformity with the laws of thermodynamics. Since often in the literature and everyday life the term thermodynamics refers to the thermodynamics of reversible processes, namely, thermostatics, to avoid confusion we adopt the term ‘generalized thermodynamics’ for the thermodynamic theory of irreversible processes, although in this work we often use simply the term ‘thermodynamics’ in a general sense covering both reversible and irreversible, or equilibrium and non-equilibrium, processes. The term ‘generalized thermodynamics’ was coined by L. Tisza to mean thermodynamics of irreversible processes in my personal interpretation of the term. And I believe it is an appropriate terminology to use for the subject covered in this work, which is the continuum mechanics part of the author’s study of non-equilibrium statistical mechanics and irreversible thermodynamics. For this reason I have consciously tried to avoid any reliance on statistical mechanics or the kinetic theory of matter in this monograph.

My interest in thermodynamics and, in particular, in the thermodynamics of irreversible processes goes back to the late fifties of the last century, when Professor Shoon Kyung Kim of Temple University, then at Seoul National University, gave a few lectures on Prigogine’s work on irreversible processes toward the end of his course on thermodynamics. The subject left a deep and indelible impression on me. Since then, despite my unanticipated but fortunate excursion into the phenomena and theories of molecular scattering in the early part of my research life until I was able to return fully to my initial youthful interest in the mid 1970s, the desire to learn about the subject matter more fully has never left me, but I could only make some intermittent stabs at the subject during the intervening years. The present work is a synthesis of what I have learned and studied on the subject of the thermodynamics of irreversible processes since 1975. I hope that what I have presented in this monograph is perceived as sufficiently coherent in the eyes of the reader and, consequently, reading it gives some benefits to the reader who may have just begun to learn about the subject or may have already acquired a considerable body of knowledge of the subject either along the line presented in this work or in the approaches made by other research workers in the field.

As is well recognized, the subject of thermodynamics is basically founded on the pair of empirical laws known as the first and second laws of thermodynamics, and enunciated by the founders of thermodynamics. In particular, the second law of thermodynamics, being a literal statement based on Sadi Carnot’s deep insights into empirical observations of natural phenomena associated with heat and its transformation into energy, requires a precise mathematical representation so that a mathematical theory of thermodynamic processes in macroscopic systems can be unambiguously formulated in conformity with the laws of thermodynamics. As has been well known, Clausius obtained such a representation only for the reversible process part of the second law of thermodynamics, leaving the representation of the irreversible process part unaccomplished. We have managed

to acquire the desired mathematical representation for the second law of thermodynamics for both reversible and irreversible processes. Such a full mathematical representation gives rise to the notion of calortropy, which extends to irreversible processes the notion of entropy that was discovered by Clausius for reversible processes only and is in the foundations of equilibrium thermodynamics known to us to this day. The notion of calortropy now is in the foundations of the thermodynamics of irreversible processes and the attendant generalized hydrodynamics for flow processes in macroscopic systems that have been presented in this monograph. Of course, the Clausius entropy is recovered from the calortropy in the limit of reversible processes. Interestingly, generalized hydrodynamics is an integral part of thermodynamics of irreversible processes; it reduces to the classical hydrodynamics of Navier, Stokes, and Fourier, as the constitutive equations for stress and heat flow become linear with respect to the thermodynamic forces and the system approaches states near equilibrium. It is significant that hydrodynamics can be framed within the bounds of the laws of thermodynamics even if the hydrodynamic processes are highly non-linear and far removed from equilibrium. Applications of such generalized hydrodynamics are discussed in this monograph.

The generalization of thermodynamics presented in this monograph requires an extension of the thermodynamic space of classical thermodynamics so as to include the non-conserved variables necessary for the description of transport processes in the system. Similar extensions are also made in other approaches recently proposed by various authors under the generic name of ‘extended irreversible thermodynamics’, but in these approaches the non-equilibrium entropy is simply a postulate based on a plausibility argument, but not a quantity deduced from the second law of thermodynamics as originally stated by Clausius and Lord Kelvin. In this respect the present theory and the other theories mentioned earlier differ, and I believe this difference is significant. Nevertheless, there are many features which are similar except for the important constitutive equations for non-conserved variables that turn out to be crucial in validating the theory in comparison with experiment and accounting for the mode of energy and matter dissipation from a useful to a less useful form in a given process. I believe that the success or failure of a theory of irreversible processes can be decided by the capability of the attendant hydrodynamic equations, whose applications to practical problems require laborious and time consuming work. I would like to acknowledge the collaborations with my former graduate students, post-doctoral fellows, and visiting associates who have played indispensable roles in developing, refining, and testing the theories making up the body of this work. I am grateful to all of them for their friendly collaborative companionship and valuable contributions along the journey which otherwise would have been lonely and, perhaps, even not possible by myself alone.

In preparing the camera-ready manuscript of this monograph Dr. Kyunil Rah and my son David have rendered valuable assistance by drawing some of the figures. I would like to thank them for their assistance. I would also like to thank the Natural Sciences and Engineering Research Council of Canada for their continuous financial support throughout the project of non-equilibrium statistical mechanics which I have carried out in the past. Finally, but more than anything else, I would like to express my deepest gratitude to my wife Hui Young for her undiminished patience, which has more than lightened the weight of labor required by research and for her continuous encouragements and devotion throughout all the years spent on my efforts toward this project in the past.

Montreal
December, 2001

B. C. E.

1

Introduction

The thermodynamics of irreversible processes is a continuum theory of macroscopic processes in matter with no reference to its molecular constitution. Since the processes are irreversible they evolve at a finite rate in time and non-uniformly over a region of space if the processes are inhomogeneous in space. In this approach the state of matter is described by a relatively small number of state variables which characterize the matter of interest as a continuous medium. Such variables may evolve in space–time, subject to their initial and boundary conditions. In the currently held natural philosophy of the macroscopic evolution of such processes, which is popularly called the ‘paradigm’ in recent times, it is believed that their evolution is fully subject to the laws of thermodynamics. We take it as our guiding principle in macroscopic physics and, in particular, in this work. The task of the thermodynamics of irreversible processes is then clearly to formulate a theory of macroscopic reversible and irreversible phenomena which is consistent with the laws of thermodynamics, and to explore the limitations of such a theory so that the range of applicability of the theory is as well defined as possible. The present work is a fruit of efforts made towards such a goal over a number of years; it is based on a few mathematical propositions deduced from the laws of thermodynamics originally enunciated by the formulators, such as Clausius [1] and Lord Kelvin [2], of the thermodynamic principles about 150 years ago.

It is now generally accepted by serious students of thermodynamics [3, 4] that the mathematical representation of the second law of thermodynamics was left incompletely delineated by the pioneers of the subject. In the present endeavor we take the position that the first task is to develop a log-

ical structure of mathematical formalism by faithfully remaining within the framework of the original forms of the laws of thermodynamics as phrased by their formulators. It is important to remain within the bounds of the original formulation of the thermodynamic laws, because the science of thermodynamics has not as yet fully developed even on the basis of the original forms of the laws of thermodynamics, and the theory of irreversible processes evidently has not achieved its full potential and maturity. Therefore it would be inappropriate to deviate from their original forms before we see them through to a satisfactory formulation and test the theory so formulated against experiments and observations made in nature to see if it is sufficiently functional.

Since the most difficult and unsettled part of the theory is concerned with the mathematical representation of the second law of thermodynamics, we will devote close attention to it, whereas we will be relatively brief with the representation of the first law of thermodynamics and other conservation laws as well as the zeroth law about the temperature since there is little that is new for us to add to them at present, although there is a need for correcting some important points about the first law in connection with the internal work that were forgotten through the second hand treatments made over numerous decades. Applications of the theory developed for irreversible processes will be taken up in later chapters. We will assume that the substance of interest does not have an intrinsic angular momentum. This assumption is easy to remove if the angular momentum conservation law is added to the set of conservation laws already taken in the present theory. We also assume that the system consists of an r -component mixture where chemical reactions may be present. Since this aspect is easily restored whenever necessary, most of the theoretical development in this work, however, is carried out for the case of no chemical reactions for the simplicity of the theory.

Historically the thermodynamic principles enunciated at the continuum theory level were followed by atomic and molecular theories of matter in the forms of statistical mechanics of Maxwell [5], Boltzmann [6], and Gibbs [7], since the reductionist tradition of natural philosophy inevitably required molecular theoretical foundations of thermodynamics in the form of a particulate theory of matter based on the concept of particles (*e.g.*, atoms and molecules) that was emerging in science at the times of Maxwell, Boltzmann, and others. This molecular theory has sometimes been called the ‘kinetic theory’. Since the times of Maxwell and Boltzmann the kinetic theory of fluids has been primarily developed to provide macroscopic phenomena and thermodynamics of reversible and irreversible processes in continuum matter with molecular theoretical foundations. In such a molecular theory a suitable kinetic equation, which is used for the distribution function of the system in the phase space or the Hilbert space of wave functions, is taken as a mathematical model for macroscopic phenomena, but in practice the solution of the kinetic equation is sought in such a way as to help us

understand at the thermodynamic level of description the macroscopic phenomena which we experience or observe in nature in our everyday life and in the laboratory. Therefore the solution of a kinetic equation is a particular solution corresponding to our thermodynamic level of understanding of the natural phenomena of interest. Here lies a logical circularity in which numerous statistical mechanical efforts in molecular theory foundations of irreversible thermodynamics have been trapped, since statistical mechanics needs thermodynamics to become a physical theory from a mathematical theory of probability; and to break the logical circularity we are inevitably required to examine what is really meant by the thermodynamic level of description, in the first place.

In the course of our scientific training we have been taught thermodynamics of reversible processes, and a great deal of our scientific reasoning and thinking processes is molded and influenced by equilibrium thermodynamics, especially when we are concerned with macroscopic phenomena in continuum matter, but there is a qualitative difference between reversible and irreversible processes that cannot be so simply compromised or removed by using the argument that the latter can be approximated by the former in an asymptotic limit. Therefore the subject of equilibrium thermodynamics turns out to be not very useful for us when we face irreversible macroscopic processes. Consequently our first task in attempting to study the kinetic theory of matter is to establish a theoretical formalism for macroscopic phenomena in continuum matter on the foundations of the laws of thermodynamics as we know them at present in the forms proposed by their original formulators. We then develop a solution procedure for the kinetic equation for the distribution function of matter in the phase space or the Hilbert space depending on whether the classical or quantum mode of description is adopted for development of the theory, in such a way that the thermodynamics of irreversible processes is described from the molecular viewpoint. Such molecular theories are indispensable for understanding natural phenomena at the molecular level, which should evolve also in conformity with the requirements of the thermodynamic laws at the macroscopic level of description. Therefore it may be said that one of the most useful and important applications of the theory, and indeed of the most important tasks, of irreversible processes consistent with the laws of thermodynamics should be in developing molecular theories of matter, namely, non-equilibrium statistical mechanics, consistent with the laws of thermodynamics, and it is one of the principal motivations for the study of irreversible thermodynamics made in the present work.

Of course, a macroscopic theory of irreversible processes is useful on its own for a large class of physical problems we encounter in daily life and natural phenomena in general. It is especially so, since the molecular theory can be too detailed in description for the macroscopic phenomenon of interest. In the macroscopic approach we simply dispense with a molecular theory of material functions, which enable us to distinguish different mate-

rials involved in the processes of interest, and regard the material functions as empirical parameters. The theories developed in various chapters in this work enable us to pursue this line of approach to macroscopic processes in nature. In the present work we present some limited numbers of examples studied so far for application of the theories developed.

In Chapter 2 the notion of temperature, so central to thermal science, is carefully discussed, and especially the meaning of temperature is examined when the system is away from equilibrium. The term temperature is so ingrained in our daily life and scientific activities, and we are so accustomed to the term, that when we use it we hardly think about its precise meaning and the condition under which the notion is quantified for scientific purposes. When a scientific notion falls into such a condition it is liable to be abused, thus lose its precise meanings, and consequently give rise to confusion. It is fair to say that the notion of temperature is in such a state of careless use, especially, when systems are away from equilibrium. It is therefore essential for the notion to receive a careful analysis in the case of non-equilibrium. In Chapter 2 we analyze the meaning of temperature so that it is used unambiguously in the subsequent development of the theory of irreversible processes. The notion of temperature for non-equilibrium carries throughout this work the meanings acquired from the analysis made of temperature in Chapter 2. The notion of local temperature is examined, together with those of local pressure, chemical potentials, and generalized potentials, in Chapter 3 as a preparation for the local theory of irreversible processes formulated subsequently.

The energy conservation law appears as the first law of thermodynamics in Chapter 3, where it is given a mathematical representation for global processes. The corresponding local processes will be given a mathematical representation in Chapter 5. For global processes it appears in the conventional form of the first law known in equilibrium thermodynamics, whereas for local processes it appears in the form of a local balance equation for internal energy, which is well known in continuum mechanics. Although the global form looks mathematically and formally the same in form as in equilibrium thermodynamics, the actual meanings of heat and work involved in the expression are more generalized than those in equilibrium thermodynamics since if the processes are non-equilibrium processes they may have contributions from irreversible effects, such as internal work and non-classical heat transfer. These are notions which attracted Clausius's attention in his long endeavors in thermodynamics, but were lost in the formulations of equilibrium thermodynamics, most importantly, in the work of J.W. Gibbs [7] whose theory has been put into practice by later generations in thermodynamics. The aforementioned notions, of course, are not necessary in equilibrium thermodynamics, and that probably explains the reason why Gibbs did not pay attention to them. In the present work the first law of thermodynamics is formulated with the internal work as well as the work arising from mass transfer and transfers of non-conserved

quantities taken into account in Chapter 3. These quantities are elucidated from the viewpoint of a local field theory in later chapters in the course of this work. In Chapter 5 other conservation laws of the conserved variables, such as mass, mass fractions, and momentum, are also given mathematical representations in local form. Since these local balance equations for the conserved variables are also coupled to those of non-conserved variables such as the pressure tensor, mass diffusion fluxes, and energy flux (heat flux), and so forth, their evolution equations are presented in a generic local form in this chapter. As will be seen later in the development of the theory in this work, the balance equations for the conserved variables and the complete set of evolution equations for the non-conserved variables mentioned earlier form a set of generalized hydrodynamics equations which describes the evolution of macroscopic irreversible processes in continuum matter.

The evolution equations for macroscopic variables forming the aforementioned set of equations are coupled with each other, but are not constrained by the second law of thermodynamics as yet. Under the guiding principle stated earlier regarding macroscopic processes the evolution equations constituting generalized hydrodynamics must be subjected to the constraint of the second law of thermodynamics. This aim is achieved when the second law of thermodynamics is given an appropriate mathematical representation in global form. This topic is discussed in Chapter 4, where the second law of thermodynamics is examined in detail from the historical context beginning with the Carnot theorem which gave rise to the Clausius and Kelvin principles stated for the second law of thermodynamics. The equivalence of the Carnot theorem and the Clausius and Kelvin principles is proved by following Poincaré's exposition [8] of the subject. We then proceed to show the existence of calortropy which extends the notion of Clausius entropy that holds valid only for reversible—that is, equilibrium—processes, to irreversible processes or for systems away from equilibrium. From this line of consideration we acquire mathematical representations of the second law of thermodynamics for global processes, and the formal theory of irreversible processes becomes completed for macroscopic continuous media in systems of a finite size.

When formulated in local form in Chapters 6 and 7, this formal theory lies in the foundations of generalized thermodynamics and thermodynamically consistent generalized hydrodynamics, which basically constitutes application of the former to macroscopic flow processes in fluids presented in the later chapters in this work. In Chapter 4 the relation of the inequality for calortropy to the traditional Clausius–Duhem inequality, which is commonly regarded as an expression of the second law of thermodynamics, is examined in detail. The latter is now seen as a special case of the more general inequality involving the calortropy.

Unlike equilibrium thermodynamics where the thermodynamic properties (*e.g.*, density, concentrations, thermodynamic functions, *etc.*) are uni-

form throughout the system except for the case of phase equilibria, the thermodynamic description of non-equilibrium processes requires a clear distinction between whether they are local or global. In the case of global processes our interest lies in the global behavior of the system properties over the system in the large, but not in the local behavior describing what is happening around points in the system, given some boundary conditions. Since the manners in which the two kinds of processes are described within the thermodynamic formalism are different, they should be treated separately. Since the original version of the second law of thermodynamics is couched in the language of global processes, it is more logical to treat the thermodynamics of global processes first. Thus in Chapter 5 we develop the thermodynamics of global irreversible processes. In particular, we develop a Pfaffian differential form for the global calortropy change and equivalent differential forms for irreversible processes in finite systems, and, furthermore, a theory of irreversible processes in heterogeneous macroscopic systems and their equilibrium conditions. As an application of the theory developed, we study irreversible thermodynamics of chemical neural networks, which are made up of continuously stirred reactor tanks communicating with each other through mass transfer between them according to Hebb's learning rules [9]. This is a topic which is fairly new to neural networks, although the subject of neural networks [10] has been studied for many years up to the present day. The topic of irreversible thermodynamics for the subject is still in the stage of development, but for the interest of stimulating further study of the subject, we discuss the current status of the theory. Although it should eventually deserve to be treated as a topic on its own, in the present work the subject is relegated to a section for an application of the thermodynamics of global irreversible processes.

In the local description of irreversible processes the conservation laws appear as balance equations for mass, momentum, and internal energy, which obey partial differential equations as are the evolution equations for the non-conserved macroscopic variables. Such partial differential equations are field equations for the variables mentioned, and serve as the basic building blocks for the local theory of irreversible processes subjected to the second law of thermodynamics, which also should be expressed in a local form. Derivation of such field equations forms the subject of discussion in Chapter 6.

To complete the set of local evolution equations required for formulating a local theory of irreversible thermodynamics, it is necessary to give the second law of thermodynamics a local form, which is derived from the global form for the second law obtained in Chapter 4. The local form in question appears as the calortropy balance equation and when this balance equation is combined with the balance equations for the conserved variables and the evolution equations for the non-conserved variables, there follows the differential form for the local calortropy density as a non-equilibrium extension of the equilibrium Gibbs relation for the Clausius entropy. The differential

form obtained for non-equilibrium is the extended Gibbs relation on which it is possible to build a formalism of local irreversible thermodynamics that parallels the thermodynamics of equilibrium systems. This extended Gibbs relation for the calortropy density is in a form completely consistent with the second law of thermodynamics originally stated in literal forms by Kelvin and Clausius. This important topic is the subject of Chapter 7.

The local extended Gibbs relation provides a means of conforming the evolution equations for non-conserved variables to the second law of thermodynamics. The mode of the consistency with the laws of thermodynamics for the generalized hydrodynamic equations presented in Chapter 6 and other consequences of the local extended Gibbs relation for the calortropy density are further developed and discussed in Chapter 8. Close attention is paid especially to the integrability conditions for the differential form for the calortropy density, namely, the extended Gibbs relation, because the Pfaffian differential form, for which the extended Gibbs relation is an example, is often thought to be integrable, that is, a total differential, without further conditions imposed on it in the literature. This is far from the truth: the differential one-form (Pfaffian form) must satisfy the integrability conditions before it becomes a total differential or, put in other words, to be an exact differential. This important point is discussed in the chapter. In this chapter some simple examples of application of the theory are also discussed as a way of illustrating the theory developed.

Since the thermodynamic theory developed in the present work is aimed at non-linear irreversible processes occurring far removed from equilibrium beyond the regime of validity of the linear theory of irreversible processes, it is essential to show that the present theory is inclusive of the linear theory and, if so, in what sense. This aspect of the theory is discussed in Chapter 9. Moreover, we show that at the hydrodynamic level of description of macroscopic flows the classical Navier–Stokes–Fourier theory [11] is recovered from the generalized hydrodynamics attendant on the theory of irreversible processes embodied by the generalized thermodynamics and, in particular, by the extended Gibbs relation for the calortropy density. The discussion made to this end requires in essence a linearization of the constitutive (evolution) equations for non-conserved variables. In fact, the linearization method used allows us to be a little more general with regard to time dependence of non-conserved variables than the classical Navier–Stokes–Fourier theory, since the constitutive equations mentioned for the non-conserved variables can be linear differential equations in time and space within the framework of the linear theory, in contrast to the time-independent linear thermodynamic force–flux relations implied by the Navier–Stokes–Fourier theory. In such a linear approximation the differential equations are evidently hyperbolic, and it is possible to examine ultrasonic wave phenomena and viscoelasticity in the regimes in which the classical theory is not capable of describing the phenomena. Such aspects are discussed as examples for the application of the generalized hydrody-

namics within the validity of the aforementioned linear approximation in Chapter 9. For an example of the concurrent application of both the theory of linear irreversible processes and the theory of global irreversible processes we study in this chapter the irreversible thermodynamics of galvanic cells. This topic is taken up in this chapter, not in Chapter 5, because the local forms of the calortropy flux and production necessary for the formulation are unavailable until Chapter 7 as a result of the way this monograph is organized.

Many flow phenomena observed in nature and in the laboratory occur at a steady state of the non-conserved variables such as the stress tensor, heat flux, and so on. Such steady state phenomena superficially seem to require the local equilibrium Gibbs relation for the Clausius entropy at the level of thermodynamics, because the substantial time derivatives of the non-conserved variables do not contribute to the temporal evolution of the calortropy density, which reduces to the Clausius entropy in the case of reversible processes. This gives us the false impression that it is possible to describe them within the framework of the linear theory of irreversible processes, but it can be rather misleading since a linear theory approach to flow problems in the rarefied density regime or the high speed flow regime cannot adequately describe them by means of the classical hydrodynamics, as is well recognized. Studies of such flow phenomena in the past have shown that they can be effectively treated by means of steady state generalized hydrodynamic equations where the non-conserved variables obey steady state evolution equations. We therefore devote a fairly large chapter to the discussion of irreversible thermodynamics of steady state processes and its applications in Chapter 10. The topics of application cover a wide range of flow phenomena including microchannel flows, which should be of considerable interest to those working in the field of microsystems and microelectrical systems. Since all the flow problems studied so far, albeit not as numerous as those by the classical hydrodynamics, cannot possibly be discussed in this monograph for the reason of limitations of space, we have selected some topics of current and fundamental interest. The topics discussed in Chapter 10 demonstrate, within the framework of the generalized thermodynamics formulated in this work, its power and utility for practical problems. Therefore this chapter is where the present theory of irreversible processes makes us relate our work with practical problems that have defied the treatments in good accuracy by the classical hydrodynamics in the past.

In mechanics the Newtonian formulation is given an enormous boost of power and insights by the variational principles, which were formulated, in retrospect, as an alternative to the original Newtonian formulation of mechanics. In analogy with the Newtonian mechanics one can wonder whether a variational formulation of the theory of irreversible phenomena may be formulated. Indeed, Onsager [12] made such a formulation in a restricted sense in the case of linear irreversible processes. It is referred to as On-

sager's restricted variational principle in the literature. Although there are numerous attempts at formulating a variational principle for irreversible phenomena in the literature [13, 14], it is this author's opinion that a well tested and fully satisfactory variational principle that is as capable as the variational principles in mechanics is not in our possession as yet. In Chapter 11 a variational method is examined in the hope that it will induce further study of the subject. This variational method begins with the thermodynamic version [15] of d'Alembert's principle [16] in mechanics and yields a variational functional which gives rise to constitutive equations for the non-conserved variables and differential equations for the variables conjugate to the non-conserved variables. The latter equations collectively may be regarded as a generalized and dynamical form of the zeroth law of thermodynamics for the intensive thermodynamic variables in the extended thermodynamic space.

In Chapter 12 we examine thermodynamics and irreversible thermodynamics from the standpoint of a contact manifold. The materials presented in this chapter require the reader to have some knowledge of the mathematics of vector space and exterior calculus. For irreversible processes the variables considered for the discussion are necessarily those for global processes, because it appears that there are no mathematical tools available at present to study the subject from the viewpoint of local irreversible processes which require generalized hydrodynamic equations for adequate description. The contact manifold approach to thermodynamics or irreversible thermodynamics does not yield practical results, but is interesting from the conceptual and mathematical viewpoints. This topic is intended to be an introduction for those mathematically inclined. Since the results of this chapter do not add to the fundamental structure of the generalized thermodynamics presented in the previous chapters the reader not mathematically inclined may disregard it.

To sum up, the present monograph develops a purely phenomenological thermodynamic theory of irreversible processes that is consistent with the laws of thermodynamics and applies the theory to a number of irreversible phenomena with the help of generalized hydrodynamics attendant on the theory as an integral part of it. Being a macroscopic phenomenological treatment of irreversible processes, there is no reference made to the molecular theories—statistical mechanics—of such processes, but the reader is referred to the previous monographs on the molecular theory approaches by the present author [17, 18]. A thermodynamically consistent phenomenological theory of irreversible processes serves as the guiding light for a thermodynamically consistent theory of non-equilibrium statistical mechanics. Nevertheless, both theories are in a mutually supporting and intimate relationship in the overall mathematical structure of macroscopic physics, and it is difficult to imagine that we will do well without both of them.

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2

The Zeroth Law of Thermodynamics

In thermodynamics, regardless of the nature of the thermal process under consideration, one of the primary state variables of the substance of interest is the measure of hotness or coldness of the body under consideration. Therefore it is important to quantify this measure unambiguously if one aims to formulate properly a theory of thermodynamic processes in the body, and this aim is achieved by the zeroth law of thermodynamics.

2.1 Thermal Equilibrium and Temperature

It is empirically well known that if two bodies of different degrees of hotness are put into contact with each other, they exchange heat and eventually reach thermal equilibrium, at which point there is no longer any heat transfer between the bodies. This phenomenon lies at the root of quantifying the measure of hotness or coldness of bodies (systems). The following statement of the zeroth law of thermodynamics [1, 2] provides a general procedure for quantification of temperature as a measure of hotness of a system in thermal science. It must, however, be noted that this law does not fix the temperature scale, which is acquired universally in thermodynamics by using the ideal gas temperature scale that is identified with the thermodynamic scale with the help of the Carnot cycle, as will be seen in Chapter 4.

The Zeroth Law of Thermodynamics *If two systems A and B are respectively in thermal equilibrium with system C, then the systems A and B are also in thermal equilibrium.*

In other words, if there exists thermal equilibrium between bodies A and C, there is a property called temperature θ such that there holds the equality

$$\theta_a = \theta_c, \quad (2.1)$$

and similarly for bodies B and C which are in equilibrium

$$\theta_b = \theta_c. \quad (2.2)$$

Therefore there follows the equality

$$\theta_a = \theta_b. \quad (2.3)$$

This relation provides a means of devising thermometers and thereby quantifying the temperature of bodies. There are a number of ways of achieving this aim, and the details are to be found in the literature on measurements of temperature [3]. There are also a number of scales in use in our daily life, but the absolute temperature scale is used in scientific work. In this work we will use the absolute temperature scale throughout.

2.2 An Alternative Form of the Law

Although the relations (2.1)–(2.3) are mathematically impeccable and are generally used in thermodynamics textbooks, they are not too useful from the operational standpoint, especially for irreversible thermodynamics, because there is absent the concept of time span in which thermal equilibrium is established between the bodies. A more useful way of saying basically the same thing is to introduce a time interval $\Delta\tau$ in which the establishment of thermal equilibrium is monitored to a sufficient accuracy. Thus we write instead

$$\frac{\Delta_{ac}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{bc}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{ab}\theta}{\Delta\tau} = 0, \quad (2.4)$$

where $\Delta_{ac}\theta = \theta_a - \theta_c$ and so on. These expressions make it possible to deduce more practical means of measuring temperature and the meanings of temperature for systems where non-equilibrium processes may be in progress. For example, if the heat transfer per unit time from body A to body C is Q_{ac} and the heat capacity is denoted by C_{ac} then we may write

$$C_{ac} \frac{\Delta_{ac}\theta}{\Delta\tau} = \lambda_{ac} Q_{ac}, \quad (2.5)$$

where λ_{ac} is the heat transfer coefficient which is, together with the heat capacity, a characteristic of the materials involved. These are non-vanishing

quantities. Therefore, for example, the first condition in Eq. (2.4) means that $Q_{ac} = 0$ at thermal equilibrium of bodies A and C .

Determination of the parameter θ requires thermal equilibrium between a body A and a thermometer B if it is to be quantified as a well defined value, but the term ‘thermal equilibrium’ does not necessarily mean that body A is itself internally in thermodynamic equilibrium. It may, in fact, be a system where a number of irreversible processes are in progress at a value of temperature θ , and thermal equilibrium is between this body and another which is in contact with the former. The important point is that the value of θ remains constant over the time scale $\Delta\tau$ of measurement. This condition can be readily met if the irreversible processes have reached a steady state within $\Delta\tau$. An apt example is an animate body (*e.g.*, a human body) where numerous irreversible processes occur, often in conditions far removed from equilibrium, yet the temperature of the body is a well defined observable and, perhaps more precisely, a local observable, if it meets the condition expressed in Eq. (2.4). Another example is a metallic bar subjected to different temperatures at its two ends. It is well known that the temperature has a distribution between the two endpoints. By this we mean that if infinitesimally thin imaginary slices of the metal are taken perpendicular to the direction of heat flow and each slice is put into thermal equilibrium with a thermometer, the recorded temperature values of the slices along the direction of heat flow will be different depending on the position. Even if this distribution changes in time owing to varying boundary conditions (temperatures), the distribution can be quantified as a function of time by a thermometer of an appropriate resolution power, if the relaxation of a transient temperature distribution is achieved within the time scale $\Delta\tau$ of temperature measurement. The term thermal equilibrium used in stating the zeroth law of thermodynamics therefore must be understood in the sense that equilibrium is between the body and the thermometer over the time span $\Delta\tau$. The consideration made here indicates that the zeroth law of thermodynamics is not limited to bodies in equilibrium, but also to bodies where irreversible processes are in progress as long as the resolution power of the thermometric device permits a meaningful quantification of temperature through the relations in (2.1)—(2.3). This quantification of temperature is often used for a local elementary volume of the body at time t if the body is in a non-equilibrium condition, and temperature becomes a field variable in such a case. If the irreversible process of interest is such that the conditions in Eq. (2.4) are not satisfied within the time interval $\Delta\tau$ achievable experimentally, then it is no longer possible to describe the process by means of a thermodynamic formalism. In other words, thermodynamics has no meaning for such a process. There are other field variables to which laws similar to the zeroth law must be applied for their thermodynamic quantification. The collection of such kindred laws for the aforementioned intensive field variables may be simply called the ‘zeroth law of thermodynamics’ in a generalized sense. They will

be discussed in Chapter 3, where the notions of field variables are properly introduced and defined.

2.3 Absolute Temperature

The notion of temperature given a precise meaning in the previous section can be furnished with a universal scale by means of the ideal gas thermometer. This thermometer enables us to devise the absolute temperature scale used in thermodynamics. Although the absolute temperature scale has no direct basis in the second law of thermodynamics, it is convenient to discuss it here since it is the temperature scale in which the thermodynamic temperature is expressed in thermodynamics and thermal physics in general by virtue of it being a universal temperature scale.

The ideal gas thermometer employs an ideal gas (*e.g.*, helium) as a thermometric material. If volume V is taken for the thermometric property, the temperature θ in the centigrade scale may be expressed in terms of V and the mean expansion coefficient α of the thermometric substance between the two reference points θ_0 and θ_{100} of temperature in the following form

$$\theta = \frac{1}{\alpha} \cdot \frac{(V - V_0)}{V_0}, \quad (2.6)$$

where α is defined by

$$\alpha = \frac{V_{100} - V_0}{100V_0} \quad (2.7)$$

with V_0 and V_{100} denoting the volume at θ_0 and θ_{100} , respectively. The reference points of temperature θ_0 and θ_{100} may be taken, respectively, as the ice point and the boiling point of water at a pressure of 1 atmosphere. The study of behaviors of gases under the influence of heat and pressure traces back to the early stages in the development of modern science and such names as R. Boyle, J. Gay-Lussac, and H.V. Regnault were associated with it. It was found through extensive experiments that gases show certain universal behaviors towards heat and pressure as they become sufficiently diluted so that the pressure is low. The state of such gases is then called ideal. According to the modern molecular theory interpretation of the ideal gas there are no interactions between the molecules in ideal gases.

The mean expansion coefficient α is empirically found that as the gas pressure p decreases it approaches a limit, that is,

$$\lim_{p \rightarrow 0} \alpha = \alpha^*, \quad (2.8)$$

where α^* is a universal constant independent of gases. For example, Gay-Lussac found $\alpha^* = 1/267$ approximately, but Regnault in 1847 obtained $\alpha^* = 1/273$ by using an improved experimental procedure. The best value

of modern experiments gives $\alpha^{*-1} = (273.15 \pm 0.02)$ C. Its value was chosen by the Tenth Conference of the International Committee on Weights and Measures in 1954 which set the triple point of water at 273.16 K so that the value of the ice point becomes 273.15 K precisely. This gives α^* the value

$$\alpha^* = \frac{1}{T_0}, \quad (2.9)$$

where $T_0 = 273.15$ C.

Eq. (2.8) together with Eq. (2.6) implies that

$$\lim_{p \rightarrow 0} \theta = \theta^* \quad (2.10)$$

and thus in the low pressure limit

$$V = V_0(1 + \alpha^* \theta^*). \quad (2.11)$$

Eq. (2.9) therefore implies that there exists a temperature scale which does not depend on the material employed and consequently is *universal*. Such a thermometer is called the ‘ideal gas thermometer’, and the scale of temperature based thereon the ‘ideal gas temperature scale’.

By using Eq. (2.9) we may rewrite Eq. (2.11) in the form

$$T = T_0 \frac{V}{V_0}, \quad (2.12)$$

where

$$T = T_0 + \theta^*. \quad (2.13)$$

This is the absolute temperature scale we use in thermodynamics and in this work.

Let us now consider an immediate implication of the thermodynamic temperature scale devised with an ideal gas. It is empirically established through investigations by Boyle, Gay-Lussac, and others that for ideal gases there holds the relation

$$\lim_{p \rightarrow 0} pV = \beta(\theta), \quad (2.14)$$

where p is the pressure, and at constant pressure

$$\frac{V_{\theta_1}}{V_{\theta_2}} = \frac{\beta(\theta_1)}{\beta(\theta_2)} = C, \quad (2.15)$$

where C is a universal constant independent of gases and β is a function of θ , which is also independent of gases. Since, as $p \rightarrow 0$,

$$V = \frac{\beta(\theta)}{p},$$

it follows from Eqs. (2.12) and (2.14)

$$\frac{T}{T_0} = \frac{\beta(\theta)}{\beta(\theta_0)} = C. \quad (2.16)$$

Since Eq. (2.16) means that

$$T \propto \beta(\theta),$$

we may write

$$\beta(\theta) = nRT, \quad (2.17)$$

where n denotes the number of moles of the gas contained in V and R is a universal constant. It is called the ‘gas constant’ and its value is $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$. Therefore Eq. (2.12) now may be written

$$\lim_{p \rightarrow 0} pV = nRT \quad (2.18)$$

or, more simply,

$$pV = nRT. \quad (2.19)$$

For a mole of an ideal gas it may be written as

$$pv = RT, \quad (2.20)$$

where $v = V/n$ denotes the molar volume. This is the ‘ideal gas equation of state’. When the equation of state is written in the form of Eq. (2.19) it must be understood that it holds only when p is sufficiently low. The formulation of the ideal gas equation of state as in Eq. (2.19) indicates that the ideal gas equation of state is intimately tied up with the ideal gas temperature scale and, as will be seen later, all equations of state and thermodynamic properties for real substances are expressed in terms of the temperature scale devised on the basis of the ideal gas.

Having elucidated the existence of a quantity called temperature and having devised the absolute temperature scale based on the ideal gas, we now come to the inevitable question of whether it is possible to speak of temperature if a system is not in equilibrium internally.

The zeroth law requires that two bodies in thermal contact be in thermal equilibrium for the concept of temperature to be meaningful. This does not mean that the two bodies have to be internally in equilibrium, as was noted earlier. The only condition required for parameter θ to exist is that there is no heat exchange between the two bodies in contact over a characteristic span of observation time. If one of two bodies in contact is a thermometer calibrated against the ideal gas thermometer then the characteristic span of time has to do with the resolution power of the thermometer, which is the measure of how fast the thermometer responds to heat transfer between the body and the thermometer. Even in such a case one still speaks of the

temperature of the body. For example, even if the body is animate like a human body, which is obviously undergoing complex irreversible processes within itself, we still routinely speak of the temperature of the body, and it is recorded as the point of thermal equilibrium between the body and the thermometer at the location of contact with the body. Similarly, one may insert a thermometer in a stream of a liquid, which is obviously not in equilibrium, yet speaks of the temperature of the liquid. Depending on the processes that are going on in the liquid the temperature may be at a constant value over time or may be varying in time and space. The temperature scale devised based on the ideal gas thermometer introduced earlier can be still used to record the thermal state of systems where some irreversible processes are in progress. We remark that, as a matter of fact, the subject of fluid mechanics rests partly on the concept of local temperature and pressure, amongst other local macroscopic quantities which may vary from a point to another.

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3

The First Law of Thermodynamics

The first law of thermodynamics *is* an expression of the energy conservation law, which in the words of Clausius [1] may be stated¹ as ‘The energy of the universe is constant’. This statement, like the companion statement of the second law of thermodynamics made by Clausius, suits the popular understanding of the law, but is rather loose from the rigorous theoretical standpoint. It needs a precise mathematical representation.

Starting from the times of Leibnitz and Huygens, the energy conservation law took a long time before it was formulated as a culmination of the understanding of what is meant by heat and its relation to energy. Joule’s famous experiments on the equivalence of mechanical energy to heat played an important role in the formulation of the first law of thermodynamics among the contributions, including those by Count Rumford (B. Thompson), H. Davy, J.R., Mayer, and H. von Helmholtz. Since there are a number of historical accounts [2, 3, 4, 5], which are quite illuminating on the subject, and we have already discussed the historical evolution of the energy conservation law elsewhere [6], we will not delve into them here, but simply state the first law of thermodynamics. When the first law of thermodynamics is discussed, energy and heat transfer are always involved and signs must be consistently assigned to them. We will therefore find it expedient to establish sign conventions for heat transfer and work performed.

¹ In the original text in German it reads “Die Energie der Welt ist constant”

Sign convention for heat transfer Heat transfer is counted negative if heat is given up by the system to the surroundings and as positive if heat is taken up by the system from the surroundings.

Sign convention for work Work is counted as positive if it is done on the system by the surroundings and as negative if it is done on the surroundings by the system.

These conventions, generally used in the literature on thermodynamics, will be used throughout this work.

3.1 Mechanical Equivalent of Heat

Joule [7] found by his famous experiments that mechanical energy is converted into heat in a universal ratio independent of substance and the processes of conversion. He was thereby able to determine the mechanical equivalent of heat:

$$W = JQ, \quad (3.1)$$

where W is the work, Q is the heat, and J is a constant and called the ‘mechanical equivalent of heat’. Its unit is called the Joule, and $1 \text{ cal} = 4.1840 \text{ Joules}$. Its value may be determined, for example, by measuring the amount of heat generated as a result of the work done when a body (e.g., a ball) of mass M falls a distance h under the influence of the gravitational field:

$$J = \frac{Mgh}{Q},$$

where g is the gravitational acceleration. Joule’s experiment implies that heat must be regarded as a form of energy, and therefore the energy conservation law must be considered with mechanical energy and heat together on an equal footing. If the unit Joule is taken for the unit of energy the constant J in Eq. (3.1) can be set equal to unity, and on using the sign conventions for work and heat Eq. (3.1) may be written in the form

$$Q + W = 0. \quad (3.2)$$

3.2 Energy Conservation Law

The first law of thermodynamics is another way of expressing the mechanical equivalence of heat as summarized by Eq. (3.2). It can be stated in the following two equivalent forms:

The First Law of Thermodynamics

(1) *The energy of an isolated system is constant.*

Equivalently:

(2) *It is impossible to construct a perpetual motion machine of the first kind—a machine that, working in a cycle, expends no heat to produce an equivalent amount of work.*

The first statement was made by Clausius in the paper in which, for the first time, he introduced the notion of entropy [1]. It is a little obtuse and can cause confusion when taken literally. More precisely put, it means that the internal energy of an isolated system is conserved over a cycle of processes restoring the system to its original state. It is significant that the notion of cycle is used here, because in the absence of a precise means of measuring the quantity it is difficult to ascertain that the quantity is conserved over a segment of a process. A cyclic process provides a precise conceptual means for the system to return to its original state and thus to ascertain that the quantity is indeed conserved at the end of the cycle. The second statement in essence is ascribed to Planck [8]. The equivalence of these two statements can be easily shown, as it becomes evident from the following mathematical representation of the law. The equivalence of the first law stated earlier and Eq. (3.2) will be shown presently.

As argued earlier, a conservation law can be best stated by means of a cyclic process, since the state of the system must be exactly restored on completion of the cyclic process, and so must be the value of the internal energy of the system. Vanishing contour (or, alternatively, cyclic) integrals consequently play important roles in formulating the thermodynamics of irreversible processes. For the purpose of obtaining a mathematical representation of the law in the case of an infinitesimal process, let us denote² a differential heat change by dQ and a differential work by dW . The first law of thermodynamics then implies that there exists a quantity E called the internal energy, whose differential dE must be given, under the sign conventions adopted earlier for heat and work, by the differential

$$dE = dQ + dW, \quad (3.3)$$

regardless of whether the process is reversible or irreversible. The reason for this representation is that for a cyclic process

$$\oint dE = 0 \quad (3.4)$$

²In the literature in thermodynamics a slash over the symbol d is used when a non-exact differential is involved as is the case with dW and dQ . We do not use this notational device in this work, first of all, for lack of the symbol in the L^AT_EX typesetting system used here, and secondly, such a device is not necessary.

according to the first law of thermodynamics and this, on substitution of (3.3) into (3.4), yields for the whole cycle the equation

$$Q = \oint dQ = - \oint dW = -W, \quad (3.5)$$

which is precisely Joule's mechanical equivalence of heat and energy, namely, Eq. (3.2). Therefore the differential form (3.3) and Eq. (3.2) are equivalent. On the basis of this result the first law of thermodynamics is traditionally expressed by the vanishing closed contour integral (3.4) for a cyclic process where the contour integral is to be performed over the cycle in the space of macroscopic variables (*i.e.*, thermodynamic space) characterizing the thermodynamic state of the system. Once the differential form (3.3) is obtained from the consideration of a cyclic process and the law is thus given a mathematical representation, it can be applied to finite non-cyclic processes. It must be noted that in Eqs. (3.2) and (3.4) there is nothing said about the nature of the cyclic process involved being reversible or irreversible. The first law of thermodynamics does not distinguish reversible and irreversible processes. That is, energy is conserved regardless of whether the process is reversible or irreversible. We have not defined as yet what is really meant by thermodynamic space, but it will be precisely defined in the next section and used to make discussions more precise. For now it is sufficient to mean a space of macroscopic observables in which the thermodynamic state of the system is described.

The vanishing closed contour integral (3.4) in the thermodynamic space mathematically means that dE is an exact differential in the aforementioned space although dQ and dW are not exact differentials in the said space. Derivation of Eq. (3.5) from Eq. (3.4) also may be regarded as proof of equivalence for the two previous statements of the first law of thermodynamics, since work cannot be produced without an equivalent expenditure of heat.

If time is used as a parameter for E then the closed contour integral in (3.4) may be written as an integral over a period τ of the cyclic process

$$\int_0^\tau dt \frac{dE}{dt} = 0. \quad (3.6)$$

The mathematical representation presented here is for the global system comprising the cycle, namely, the working substance in the whole system which goes through the cyclic process in question. The quantities involved are not local field variables appearing in continuum mechanics, but global quantities for the whole system. Henceforth in this work the term 'global variables' pertains to the entire system of interest as opposed to the term 'local variables' which mean thermodynamic variables for matter (*i.e.*, the fluid particle) contained in an elementary volume, and hence depend on their position in the system. Therefore when we say a 'global process' we

mean a process occurring in the global scale encompassing the whole system. Thermodynamic variables for the system may vary with time in a global process if the system is removed from equilibrium.

3.3 Spaces of Macroscopic Variables

3.3.1 Thermodynamic Space

As a preparation of the mathematical description of thermodynamic (irreversible) processes in a macroscopic system envisaged in this work, it is necessary to introduce the notion of thermodynamic space or manifold. It is not a metrised space, but a space spanned by a set of variables appropriate for specifying the thermodynamic state of a given system.

It is reasonable to think that the thermodynamic state of the whole system should be described by its internal energy E , its volume V , the masses M_a of species ($1 \leq a \leq r$). In addition to these variables, in order to describe properly the global irreversible processes of interest it is necessary to specify the volume averages of fluxes of masses, energy, and momentum within the system. They are examples of variables which are not conserved in time, unlike the conserved variables such as the energy, the total momentum, and the mass. They will be generically called ‘non-conserved variables’ and denoted by Γ_{ka} ($k \geq 1; r \geq a \geq 1$) where the subscripts k and a denote the type and species, respectively. We will assume that there is a complete set of non-conserved variables. We define the thermodynamic space (manifold):

Definition *A space spanned by the global variables for the whole system, $\mathfrak{H} = (E, V, M_a, \Gamma_{ka}: k \geq 1; r \geq a \geq 1)$, will be called the thermodynamic space (manifold) for global processes.*

It should be emphasized that this space is not a space with a norm. Therefore there is no concept of distance in the thermodynamic space. If the system is at equilibrium there is no need for the non-conserved variables, and the thermodynamic space will be spanned by the conserved variables only: $\mathfrak{H}_E = (E, V, M_a: r \geq a \geq 1)$.

3.3.2 Space of Conjugate Variables to \mathfrak{H}

A thermodynamic description of a system in general requires variables conjugate to the extensive variables such as the energy, volume, masses of species, and so on. We have already seen in connection with the zeroth law of thermodynamics that a temperature difference is accompanied by heat flow or energy transfer between two bodies as a response to the temperatures being made different between the bodies involved. Similarly, if the pressures of two systems in mechanical equilibrium are made different then

the two systems respond by adjusting their volumes; if the chemical potentials of a species in two systems in equilibrium are varied then the two systems respond by adjusting the masses or concentrations of the species in them, and so on. We denote the pressure by p , the chemical potential per mass of species a by $\hat{\mu}_a$ ($1 \leq a \leq r$), the generalized potential conjugate to the non-conserved variable Γ_{ka} by X_{ka} ($k \geq 1; r \geq a \geq 1$). The space spanned by these variables will be called the conjugate space to the space \mathfrak{H} , or simply the tangent space of \mathfrak{H} . It will be denoted by \mathfrak{F}_h :

Definition *The tangent space of \mathfrak{H} is spanned by intensive variables as follows:*

$$\mathfrak{F}_h = (T^{-1}, p, -\hat{\mu}_a, X_{ka} : k \geq 1; r \geq a \geq 1).$$

We have taken the inverse of T and attached a negative sign to $\hat{\mu}_a$ in anticipation of later results. These are intensive variables as opposed to the variables spanning space \mathfrak{H} , which are extensive, in the sense of the terms used in thermodynamics [9]. Therefore the intensive variables do not change as the mass of the system is altered.

3.3.3 Quantification of the Variables of \mathfrak{F}_h

Just as the zeroth law of thermodynamics provides methods of quantifying temperature, the variables p , $\hat{\mu}_a$, and X_{ka} may be quantified through the relations similar to Eq. (2.5):

$$\begin{aligned} -\kappa \frac{\Delta p}{\Delta \tau} &= \gamma \dot{V}, \\ \vartheta_a \frac{\Delta \hat{\mu}_a}{\Delta \tau} &= \nu_a \dot{M}_a, \\ \omega_{ka} \frac{\Delta X_{ka}}{\Delta \tau} &= \lambda_{ka} \dot{\Gamma}_{ka}, \end{aligned} \quad (3.7)$$

where $\Delta p = p_1 - p_2$, $\Delta \hat{\mu}_a = \hat{\mu}_{a1} - \hat{\mu}_{a2}$, $\Delta X_{ka} = X_{ka1} - X_{ka2}$ with the subscripts 1 and 2 denoting the two systems in contact, and κ , ϑ_a , and ω_{ka} are the susceptibilities of the quantities V , M_a , and Γ_{ka} to the changes Δp , $\Delta \hat{\mu}_a$, and ΔX_{ka} , respectively. The dot over a function denotes its time derivative. The time derivatives \dot{V} , \dot{M}_a , and $\dot{\Gamma}_{ka}$ are functions of the variables in \mathfrak{H} and \mathfrak{F}_h , which may be empirically determined. The γ , ν_a , and λ_{ka} are the associated transfer coefficients. The differential equations in Eq. (3.7) are the zeroth law analogs for pressure, chemical potentials, and generalized potentials. For, as \dot{V} , \dot{M}_a , and $\dot{\Gamma}_{ka} \rightarrow 0$, the derivatives

vanish:

$$\begin{aligned}\frac{\Delta p}{\Delta \tau} &= 0, \\ \frac{\Delta \hat{\mu}_a}{\Delta \tau} &= 0, \\ \frac{\Delta X_{ka}}{\Delta \tau} &= 0,\end{aligned}\tag{3.8}$$

and the systems in contact reach equilibrium with regards to the variables p , $\hat{\mu}_a$, and X_{ka} . They thereby can be quantified experimentally, just as temperature is measured for the system with a thermometer as the other system, since one of the systems in contact may be the instrument of measurement for the intensive variable.

The thermodynamic formalism developed in this work presumes that the conditions (2.4) and (3.8) are satisfied globally in the case of global theory or locally in the case of local theory. Lifting these conditions implies that the theory of macroscopic irreversible processes formulated, for example, with Eqs. (2.5) and (3.7) is outside the range of validity of the thermodynamic theories presented in this work.

It is also useful to remark on the last equation in Eq. (3.8) since it is unfamiliar to eyes accustomed to equilibrium thermodynamics in which non-conserved variables do not appear. Inclusion of non-conserved variables in the set of independent macroscopic variables makes it necessary to take into account the variables conjugate to the non-conserved variables, which are intensive variables, and such intensive variables require a conceptual device akin to the zeroth law of thermodynamics used for quantifying temperature. Thus the last equation in Eq. (3.7) may be regarded as an analog of the other equations in Eq. (3.7) and Eq. (2.5). It suggests that a difference in generalized potentials arises as the non-conserved variable Γ_{ka} is transferred from one system to another over a time span. Eq. (2.4) and Eq. (3.8) will occasionally be referred to as the mathematical representation of the zeroth law of thermodynamics or simply the zeroth law of thermodynamics. We note that equations akin to Eqs. (3.7) and Eq. (2.5) appear among the Euler–Lagrange equations in the variational formulation of irreversible thermodynamics discussed in Chapter 11. We thus come to see the indispensable role played by the zeroth law of thermodynamics in the edifice of irreversible thermodynamics.

3.4 Work

The meaning of work W or its differential form dW will depend on the mechanical task of the cycle in question. It can consist of a number of components, including those attributable to irreversible processes involved. For

example, a pressure–volume work may be performed on the system which changes its volume under an external pressure, or work may be done by the system as it transfers a mass to its surroundings under a material potential (chemical potential) difference between the system and the surroundings. Thus the system generally performs work on its surroundings under the influence of forces that drive changes in the extensive variables of \mathfrak{H} or, more precisely, the densities of extensive variables. In all of these kinds of work there are always conjugate pairs of variables associated, one that drives the process of work, namely, the measure of the force, and the other that is the measure of the response by the system to the driving force. For example, in the case of pressure–volume work the pressure is the force and the volume change is the response by the system. In the case of work associated with a transfer of matter, the driving force is the chemical potential and the response is the change in mass. Similarly, in the case of work associated with non-conserved variables, which is non-classical, it is possible to imagine that the system responds by adjusting the value of Γ_{ka} to the driving force X_{ka} . The driving forces are all in the set of variables \mathfrak{F}_h introduced earlier. If the aforementioned driving forces are in operation, the work done by the system per unit time can be written in the form

$$\frac{dW}{dt} = -p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_e \Gamma_{ka}}{dt} + \frac{d_i W}{dt}. \quad (3.9)$$

The first term on the right represents the pressure–volume work; the second the work of mass transfer; the third the work of ‘transfer’ of Γ_{ka} ; and the last term the internal work which is not accounted for by the first three kinds of work listed. The sign of the mass transfer suggests that it is a work done on the system by the surroundings. This convention is chosen so that the resulting mathematical formalism agrees with the conventional classical theory in the limit of equilibrium. The time derivative d_e/dt denotes the transfer rate of the quantity between the system and the surroundings. Since extensive quantities such as M_a and Γ_{ka} can also change within the system owing to its inherent internal processes, their total rate of change consists of two components, one arising from the transfer of the quantity mentioned earlier, and the other arising from its internal change:

$$\frac{dA}{dt} = \frac{d_e A}{dt} + \frac{d_i A}{dt} \quad (A = M_a, \Gamma_{ka}), \quad (3.10)$$

where $d_i A/dt$ stands for the internal rate of change in A , which contains basically constitutive information on the substance of interest. The time derivatives $d_e A/dt$ and $d_i A/dt$ will be referred to as the transfer time derivative and the internal time derivative of A , respectively. Since there is no physical mechanism for an internal volume change the transfer time derivative $d_e V/dt$ is simply equal to the total time derivative in dV/dt the case

of V . Therefore there is no need to express the volume derivative as in Eq. (3.10).

The heat transfer rate associated with the internal energy conservation law will be denoted by dQ_E/dt by attaching the subscript E to Q because at this point in development, especially if the processes are irreversible, there is no compelling reason that the heat transfer rate in question is necessarily the same as the ‘heat transfer rate’ that will appear in the second law of thermodynamics in the form of compensated heat, which will be denoted by dQ/dt . Since the two quantities are not necessarily the same, we set [10]

$$\frac{dQ}{dt} = \frac{dQ_E}{dt} + \frac{dQ_n}{dt}. \quad (3.11)$$

The difference dQ_n/dt must be elucidated by some means, and it will be done when the second law of thermodynamics is discussed.

With the work made so explicit as in Eq. (3.9) and with the heat transfer rate denoted as indicated, the first law of thermodynamics may be expressed in the form

$$\frac{dE}{dt} = \frac{dQ_E}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_e \Gamma_{ka}}{dt} + \frac{d_i W}{dt}. \quad (3.12)$$

Albeit restricted to within the bounds of the operational meanings of p , $\hat{\mu}_a$, and X_{ka} , the form (3.12) will be useful for developing a generalized form of thermodynamics for global processes in a finite bounded system in later chapters. By use of Eq. (3.11) the differential form (3.12) may be written as

$$\frac{dE}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_e \Gamma_{ka}}{dt} + \left(\frac{d_i W}{dt} - \frac{dQ_n}{dt} \right). \quad (3.13)$$

We close this chapter with the examination of the meaning of ‘work of the task’. A work will be called the ‘work of the task’ if it is the mechanical work designed for a cycle to perform. A particular work of the task is generally accompanied by other kinds of work which are not intended when the cycle of interest is designed. For example, if a pressure–volume work is the work of the task, it is generally unavoidable to have the working fluid heated by the viscous heating effect accompanying the compression or dilatation of the fluid, although it may be made as small as possible by a careful design. We illustrate this point with the example of pressure–volume work for the work of the task. Over a cycle it is given by

$$W_{\text{task}} = - \oint dV p. \quad (3.14)$$

On substitution of the pressure–volume work term from Eq. (3.13) there follows the equation

$$W_{\text{task}} = -Q - W_{\text{ua}}, \quad (3.15)$$

where

$$W_{ua} = \oint (d_i W - dQ_n) + \sum_{a=1}^r \oint \hat{\mu}_a d_e M_a - \sum_{a=1}^r \sum_{k \geq 1} \oint X_{ka} d_e \Gamma_{ka} \quad (3.16)$$

and Q may be expressed in terms of the input Q'_1 and the output Q'_2 of heat

$$Q = Q'_1 - Q'_2. \quad (3.17)$$

Therefore if it is possible to identify Q in Eq. (3.17) with that in Eq. (3.5) we find

$$W = W_{task} + W_{ua}. \quad (3.18)$$

This suggests that caution must be exercised when the first law of thermodynamics is used to calculate the work of the task in terms of heat, if there are irreversible processes involved in the course of a cycle. The expression (3.16) for unavailable work clearly indicates that its precise meaning depends on what W_{task} is. If W_{task} is that of transferring a mass involving the third term on the right hand side of Eq. (3.13), then the second integral on the right hand side of Eq. (3.16) for W_{ua} is replaced by the circular integral

$$- \oint dV p,$$

the pressure-volume work, and hence the meaning of W_{ua} is accordingly altered from that of the unavailable work given in Eq. (3.16). Therefore, the unavailable work to a given task can become the available work to another task. In equilibrium thermodynamics the unavailable work does not appear in the formulation of the theory, because reversible processes considered in equilibrium thermodynamics are precisely the ones that have a vanishing unavailable work.

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4

The Second Law of Thermodynamics

The first law of thermodynamics is simply the law of conservation of energy that must be obeyed by a process regardless of its nature, but it cannot dictate the direction in which a spontaneous irreversible macroscopic process proceeds. In contrast to this nature of the first law, the second law of thermodynamics endows us with criteria to predict whether natural processes will spontaneously progress in only one direction in time or not at all. For this quality the second law of thermodynamics is occasionally associated with the arrow of time in popular science literature [1]. This law is the quintessence of inviolable experimental facts of the unidirectional temporal evolution which spontaneous macroscopic processes in nature possess, and that is presented as a fundamental law of nature in thermodynamics. However, this is a consequence of deduction made from the literally stated original form of the second law of thermodynamics, which has no reference to the unidirectionality of evolution of macroscopic irreversible processes. An important point for us to recognize in the second law of thermodynamics as stated by the original formulators of the law *is* that it is literally stated for cyclic processes in global systems at a gross scale, as is the first law of thermodynamics; it states the impossibility of constructing a certain class of cyclic processes at a gross scale—for example, engines. Therefore it is logically sensible to obtain a mathematical representation of the literal statement of the second law for global cyclic processes and then deduce therefrom its representation for infinitesimal processes. The mathematical representation thus acquired for infinitesimal processes in global systems in the large should then be the basis of the local field theoretic representation of the second law of thermodynamics. This will be done in Chapter 6.

Clausius himself, of course, showed [2] that if the thermodynamic processes are reversible the second law of thermodynamics is mathematically expressible in terms of the quantity he called entropy. However, it should be emphasized that this concept is valid for reversible processes only. He unfortunately did not provide a comparable mathematical representation of the second law for irreversible processes, leaving the crucial part in the mathematical theory of thermodynamic processes in an incomplete form and thereby the science of thermodynamics in a vexed state. The missing part in question will be adequately constituted for the thermodynamics of irreversible processes in this chapter.

Historically the second law of thermodynamics is rooted in the theorem of Carnot [3] which was elucidated a quarter century before the second law of thermodynamics was enunciated by Clausius and Lord Kelvin. Because of its importance to thermodynamics and the utility of the basic notions it provides for the development of thermodynamics, we discuss the Carnot theorem in detail. Then a mathematical representation of the second law of thermodynamics will be given and discussed for global processes.

4.1 Carnot's Theorem

Carnot arrived at this theorem by analyzing the performance of an idealized cycle which captures the essence of real cycles and is now known as the ‘Carnot cycle’. His analysis was based on the caloric theory of heat prevalent at the time of Carnot, but, as is well known, the caloric theory of heat was later shown to be based on an incorrect concept and replaced by the mechanical theory of heat. Despite the incorrect notion of heat used, Carnot was so astute as to use two different notions in connection with heat in his analysis, and they were what he called *chaleur* for heat and *calorique* for something that was not meant to be the same as heat. The latter was something akin to the Clausius entropy in the current terminology and to the calortropy used in this work. It was later found that the Carnot theorem still remained valid, even if it was based on the wrong concept of heat, if the caloric theory of heat was simply replaced by the mechanical theory of heat. With such a modification and a more mathematically precise analysis of his theory by Clapeyron [4] it served as the precursor to the formulation of the second law of thermodynamics by Clausius and Lord Kelvin. The Carnot theorem plays an indispensable role even in the modern thermodynamics. It characterizes in essence the idealized reference process of a real thermodynamic process so that a realizable process in nature is examined relative to the idealized process, namely, the reversible process, corresponding to the real process. In thermodynamics reversible processes are defined as those over the entire course of which the system is in continuous equilibrium with the surroundings. We will find it closer to

their true nature and more definitive as well as more operational to define them as those in which the work of a task is a maximum possible because of the absence of energy dissipation accompanying the process. Under the understanding of reversible processes in the sense as stated, the Carnot theorem is expressed in the following form:

Carnot's Theorem *The efficiency of reversible Carnot cycles is independent of the modes of operation and the materials used, and is maximum. It depends only on the temperatures of the heat reservoirs.*

If the efficiency of a reversible cycle is denoted by η_{rev} and that of an irreversible cycle by η_{irr} , then regardless of the materials used and the modes of operation of the cycle

$$\eta_{\text{rev}} \geq \eta_{\text{irr}} \quad \text{and} \quad \eta_{\text{rev}} = \eta'_{\text{rev}}.$$

The efficiency of a reversible cycle η_{rev} is a function of only the temperatures of the heat reservoirs of the Carnot cycle and the prime denotes another reversible cycle. To appreciate the essence of this theorem we need a little preparation.

4.1.1 Maximum Work

Consider two cycles of the same working material and mode of operation, which operate between two heat reservoirs of different temperatures. Let the temperatures be θ_1 and θ_2 , respectively, and $\theta_2 < \theta_1$. One cycle operates *reversibly* between temperatures θ_1 and θ_2 whereas the other operates *irreversibly* between the same temperatures θ_1 and θ_2 . The reversible cycle performs work W_{rev} whereas the irreversible cycle does work W , both having received the same amount of heat from the higher temperature heat reservoir. The absolute value of work is used in this part of discussion. The Carnot theorem then implies that $W_{\text{rev}} \geq W$. Therefore the following can be concluded [5] as a corollary of the Carnot theorem:

The reversible work is a maximum work, and if a cycle is irreversible the entirety of the work that can be done by the reversible process is not available to the irreversible cycle.

If that amount of unavailable work is denoted by W_{ua} then the reversible work W_{rev} may be decomposable into the form

$$W_{\text{rev}} = W + W_{\text{ua}} \tag{4.1}$$

for the pair of irreversible and reversible cycles under consideration. This unavailable work is intrinsic to irreversible cycles in general and was recognized in essence as the ‘uncompensated heat’ (originally called ‘uncompensated transformation value’) by Clausius [2, 6]. We have bestowed the same symbol on the unavailable work as the complement ($W - W_{\text{task}}$) to

the work of the task W_{task} appearing in connection with the first law of thermodynamics in the previous chapter. Since W_{ua} is positive for any irreversible process, it can be concluded that W_{rev} is a maximum work, that is,

$$W_{\text{rev}} \geq W. \quad (4.2)$$

This is the mathematical content of the corollary mentioned earlier. One of the important objectives in generalized thermodynamics is then to elucidate the nature of unavailable work and learn to deal with it.

4.1.2 Efficiency of Reversible Carnot Cycles

It is possible to verify the Carnot theorem in the case of reversible cycles by using an ideal gas as the working material and to show that the efficiency is indeed a function of the temperatures only of the heat reservoirs. In the literature the efficiency of a cycle is defined by the formula

$$\eta = \frac{-W}{Q_1}, \quad (4.3)$$

where W is the work performed in a cycle of processes on transfer of heat $(Q_1 - Q_2)$ from the heat reservoir to the cycle.

This work W therefore must in general be identified with W_{task} in the present system of notation, and $(Q_1 - Q_2)$ is the heat compensated from the heat reservoir for the task. This heat difference must be distinguished from the heat difference $(Q'_1 - Q'_2)$ given by the first law of thermodynamics in Eq. (3.17), if there is an irreversible process involved. Therefore $(Q_1 - Q_2)$ must be identified with

$$Q_1 - Q_2 = -W_{\text{task}},$$

whereas we must identify $\delta Q \equiv (Q'_1 - Q'_2) - (Q_1 - Q_2)$ with

$$\delta Q = -W_{\text{ua}}.$$

Consequently, it follows that

$$W_{\text{task}} + W_{\text{ua}} = - (Q'_1 - Q'_2)$$

Therefore in the present system of notation the efficiency of a cycle in general must be defined by

$$\eta = \frac{-W_{\text{task}}}{Q_1} = \frac{Q_1 - Q_2}{Q_1}. \quad (4.4)$$

In the case of reversible processes this definition becomes identical with the definition in Eq. (4.3) with W standing for the reversible work, which is a maximum work for the process. This subtle point regarding the definition

of efficiency given in Eq. (4.4) has not been noted in the thermodynamics literature, although it is understandable why it has been so, since reversible cycles are usually the focus of attention in equilibrium thermodynamics. However, if the focus is on irreversible processes it requires caution and an appropriate modification of the kind indicated.

Since calculation of the efficiency of a reversible Carnot cycle is well described in the textbooks of equilibrium thermodynamics, it will be dispensed with in this work, and we simply present the result only. The efficiency of reversible Carnot cycles using an ideal gas for the working substance is given by the well known formula [7]

$$\eta_{\text{rev}} = 1 - \frac{T_2}{T_1}, \quad (4.5)$$

where T_1 and T_2 are the absolute temperatures of hot and cold heat reservoirs, respectively. For ideal gases this formula is very easy to show. However, it is not trivial to show it for a real working fluid. Nevertheless, Eq. (4.5) can be shown [8] to hold valid for a class of real fluids obeying a rather general form of equation of state for a mole of a fluid contained in a volume V and at temperature T

$$p = \frac{RT}{V} + f(V, T), \quad (4.6)$$

where R is the gas constant and $f(V, T)$ is a function of the variables V and T , which is piecewise differentiable at least once, and integrable. Therefore it is possible to take Eq. (4.5) as the general expression for the reversible Carnot cycle efficiency for the class of fluids obeying the equation of state mentioned. It must be emphasized that the efficiency formula (4.5) is essential for deriving the Clausius inequality as a mathematical representation of the second law of thermodynamics, as we will see presently.

4.2 The Second Law of Thermodynamics

Despite the idealization inherent to Carnot's analysis giving rise to his theorem and the incorrect notion of heat used for the analysis it contains the essence of the truth about cycles of macroscopic processes in nature, and this important point was recognized¹ by Clausius [6] and Lord Kelvin (William Thomson) [9] and led them to formulate the second law of thermodynamics as follows²:

¹For a historical account of the formulation of this law, see S.G. Brush, (1976) *The Kind of Motion We Call Heat*, Vol. 1 and 2 (North-Holland: Amsterdam).

²The following statements of the Clausius and Kelvin principles are the modern forms phrased by more recent workers [7, 10, 11, 12] in thermodynamics, which are rephrased slightly differently from the original statements in the papers by Clausius and Kelvin. I believe that the essential meanings remain faithful to the original versions.

Clausius' Principle *It is impossible to transfer heat from a colder to a hotter body without converting at the same time a certain amount of work into heat at the end of a cycle of change.*

Kelvin's Principle *In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work without transferring at the same time a certain amount of heat from a hotter to a colder body.*

It must be recognized that the presence and notion of unavailable work in an irreversible cycle is not as apparent in the Clausius and Kelvin principles as in the Carnot theorem, although the two principles are equivalent [7, 13] to the latter as will be shown shortly. It was this equivalence of the Clausius principle with the Carnot theorem that Clausius exploited to formulate the inequality named after him, which has been used in thermodynamics as a mathematical expression of the second law of thermodynamics. It can be shown that the Clausius and Kelvin principles are equivalent to each other [7] and also to the Carnot theorem [7, 13].

We emphasize that the second law of thermodynamics is phrased in terms of and for cyclic processes only, and for no others. Since even the present form of the second law has not as yet been given a full mathematical representation it must be the goal of the theory of irreversible processes before an alternative or amended form of the second law is proposed or formulated as we occasionally see in the literature in thermodynamics. Such an attempt at amendment is not only premature but also unnecessary at present.

We now prove the equivalence of the Clausius and Kelvin principles to the Carnot theorem. Since the two principles are equivalent, it is sufficient to show that one of them is equivalent to the Carnot theorem. We will use the Kelvin principle for the purpose. The method of proof used here is essentially owed to Poincaré [13].

Proof. In order to prove the first part of the theorem we first consider two reversible engines operating between two heat reservoirs at temperatures θ_1 and θ_2 ($\theta_1 > \theta_2$). One engine En takes heat Q_1 from the hotter reservoir and converts part of it into work³ W and rejects heat Q_2 to the colder reservoir. The other engine En' takes heat Q'_1 from the hotter reservoir and converts part of it into work W and rejects heat Q'_2 to the colder reservoir. The two engines are now coupled in such a way that one engine En is a prime mover and the other engine is a refrigerator operating in reverse to the mode of operation of En' mentioned; see Fig. 4.1. The engine En' therefore operates reversely to the mode by which the engine En operates, pumping heat Q'_2 from the colder reservoir and returning heat Q'_1 to the hotter reservoir at the expense of work W . Now assume, contrary to

³Here W denotes the work of the task W_{task} for the cycle, but for brevity of notation the subscript is omitted from W_{task} .

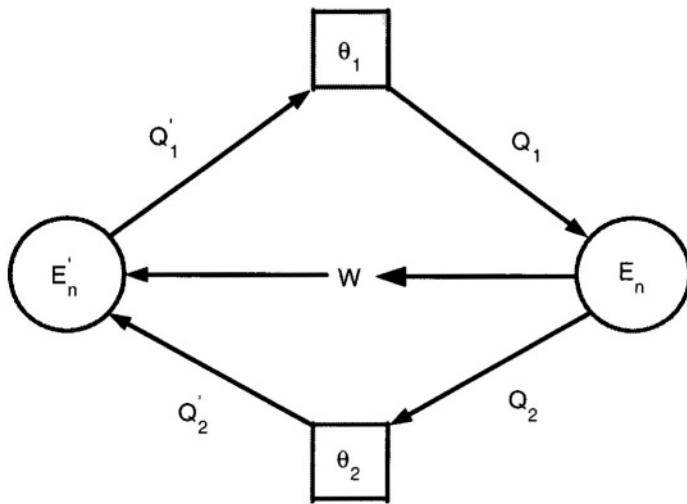


FIGURE 4.1. Coupling of two Carnot cycles to prove the Carnot theorem. $\theta_1 > \theta_2$.

the Carnot theorem, that

$$\eta_{\text{rev}} > \eta'_{\text{rev}}. \quad (4.7)$$

If the efficiency defined in Eq. (4.3) is used in this inequality it then may be equivalently written as

$$\frac{-W}{Q_1} > \frac{-W}{Q'_1}.$$

From this follows the inequality

$$Q'_1 - Q_1 > 0.$$

This inequality implies that at the end of the cycle, heat $\Delta Q = Q'_1 - Q_1$ is transferred from the colder to the hotter reservoir without a compensation. This is against the Kelvin principle, namely, the second law of thermodynamics. Therefore the assumption is false.

Let us then assume that the reverse is true, that is,

$$\eta_{\text{rev}} < \eta'_{\text{rev}}.$$

By reversing the cycle, that is, by regarding En' as a prime mover and En as a refrigerator, we reach the same conclusion as before. Therefore we must conclude that

$$\eta'_{\text{rev}} = \eta_{\text{rev}}. \quad (4.8)$$

Since the same argument can be carried out with another engine En'' instead of En' , the first part of the theorem is proved.

4. The Second Law of Thermodynamics

In order to prove the second part of the theorem we regard En' as an irreversible prime mover and En as a reversible refrigerator. Now suppose, contrary to the Carnot theorem, that

$$\eta_{\text{irr}} > \eta_{\text{rev}}. \quad (4.9)$$

Then, by the definition of efficiency

$$\frac{-W}{Q_1} > \frac{-W}{Q'_1},$$

which means⁴

$$Q'_1 - Q_1 > 0.$$

This again contradicts the Kelvin principle, that is, the second law of thermodynamics, since it implies that heat is transferred from the colder body to the hotter one at the end of a cycle without any compensation. Therefore we must conclude that the assumption is false, and

$$\eta_{\text{rev}} \geq \eta_{\text{irr}}. \quad (4.10)$$

The reverse process is not possible, since it involves an irreversible engine.

We now prove⁵ the last part of the theorem: *that the reversible efficiency depends only on the temperatures of the two heat reservoirs, hot and cold.* We follow Poincaré for this proof.

The reversible Carnot cycle is entirely determined when the adiabatics and isotherms of the cycle are known. If the working substance is specified so that the constitutive relations of the substance are given, the isotherms are determined by the temperatures θ_1 and θ_2 , and the adiabatics by some independent variables, say, v_1 and v_2 , corresponding to the temperatures. The efficiency of the reversible Carnot cycle can then be thought to be a function of θ_1 , θ_2 , v_1 , and v_2 and of the working substance C . Let us therefore assume

$$\frac{-W}{Q_1} = f(\theta_1, \theta_2, v_1, v_2, C). \quad (4.11)$$

This is a continuous function of the variables. The Carnot theorem states that f depends only on θ_1 and θ_2 . Consider two bodies C and C' which transform between the same heat reservoirs and describe cycles En and En' , respectively, the former being a prime mover and the latter working in the reverse sense—a refrigerator.

For this to be possible the temperatures must satisfy certain inequalities. Let θ_1 and θ_2 be the temperatures of two reservoirs, hot and cold; and θ'_1

⁴We remark that the meanings of heat Q_1 and Q'_1 are the same as discussed in Sec. 4.12 in relation to the unavailable work W_{un} or uncompensated heat.

⁵Note that for the proof of this part it is sufficient to consider reversible cycles, because it concerns the efficiencies of reversible cycles only.

and θ'_2 be the temperatures of the isotherms of the cycle En; and θ''_1 and θ''_2 the temperatures of the isotherms of the cycle En'. Denote by W the work produced by the cycle En, Q_1 the heat that is taken from the hot reservoir, and Q_2 the heat that it cedes to the cold reservoir. And W' , Q'_1 , and Q'_2 for similar quantities corresponding to cycle En' (refrigerator). The prime mover En receives on the isotherm at θ'_1 heat Q_1 from the hot reservoir at θ_1 , whereas it cedes on the isotherm at θ'_2 heat Q_2 to the cold reservoir at θ_2 . Therefore the temperatures must satisfy the relation

$$\theta_1 > \theta'_1 > \theta'_2 > \theta_2.$$

On the other hand, the refrigerator En' receives on the isotherm at θ''_1 heat Q'_2 from the cold heat reservoir at θ_2 whereas it cedes on the isotherm at θ''_1 heat Q'_1 to the hot heat reservoir at θ_1 . Therefore these temperatures must satisfy the relation

$$\theta''_1 > \theta_1 > \theta_2 > \theta''_2.$$

Consequently, for the coupled cycles (En + En') to be possible there must hold the inequalities of temperatures

$$\theta''_1 > \theta_1 > \theta'_1 > \theta'_2 > \theta_2 > \theta''_2.$$

Then there must hold the inequality

$$\frac{-W}{Q_1} \leq \frac{-W'}{Q'_1}. \quad (4.12)$$

This is proved as follows.

If m and m' are, respectively, the masses of bodies C and C' which are transformed in the cycles, we have for the heat taken from the high θ (hot) heat reservoir by the combined cycles

$$mQ_1 - m'Q'_1.$$

Since Q_1 and Q'_1 are positive, we can take for m and m' values such that

$$mQ_1 - m'Q'_1 = 0. \quad (4.13)$$

But then the work

$$-mW + m'W'$$

produced by the two cycles cannot be positive because, if so, we will have a production of work with only one source of heat, contrary to the second law of thermodynamics. Therefore

$$-mW + m'W' \leq 0. \quad (4.14)$$

Replacing m and m' with Q_1^{-1} and Q'_1^{-1} we obtain the inequality (4.12).

Consider now two Carnot cycles En and En' which are, respectively, defined by the variables $\theta'_1, \theta'_2, v'_1$, and v'_2 for the former and the variables $\theta''_1, \theta''_2, v''_1$, and v''_2 for the latter. The cycle En runs in the direct sense and the cycle En' in the reverse sense between the two same heat reservoirs of temperatures θ_1 and θ_2 , respectively. For this to be possible we must have the inequalities

$$\theta'_1 < \theta_1, \quad \theta'_2 > \theta_2, \quad \theta''_1 > \theta_1, \quad \theta''_2 < \theta_2.$$

Then it follows from the inequality (4.12) that

$$f(\theta'_1, \theta'_2, v'_1, v'_2, C) \leq f(\theta''_1, \theta''_2, v''_1, v''_2, C'). \quad (4.15)$$

If we suppose

$$\theta'_1 > \theta_1, \quad \theta'_2 < \theta_2, \quad \theta''_1 < \theta_1, \quad \theta''_2 > \theta_2,$$

we can describe the cycle En in the reverse direction and the cycle En' in the direct sense. Then we have the inequality

$$f(\theta'_1, \theta'_2, v'_1, v'_2, C) \geq f(\theta''_1, \theta''_2, v''_1, v''_2, C'). \quad (4.16)$$

Since f is continuous, we can make limits $\theta'_1, \theta''_1 \rightarrow \theta_1$ and $\theta'_2, \theta''_2 \rightarrow \theta_2$ without changing the sign of the inequalities (4.15) and (4.16). We then have

$$f(\theta_1, \theta_2, v'_1, v'_2, C) \leq f(\theta_1, \theta_2, v''_1, v''_2, C'), \quad (4.17)$$

$$f(\theta_1, \theta_2, v'_1, v'_2, C) \geq f(\theta_1, \theta_2, v''_1, v''_2, C'). \quad (4.18)$$

These inequalities cannot be satisfied simultaneously. Therefore we conclude

$$f(\theta_1, \theta_2, v'_1, v'_2, C) = f(\theta_1, \theta_2, v''_1, v''_2, C'),$$

which means that f is independent of variables v_1, v_2 , and C , that is,

$$\eta_{\text{rev}} = f(\theta_1, \theta_2). \quad (4.19)$$

This proves the last part of the Carnot theorem. Therefore the Carnot theorem is completely proved.

The proof presented is, in fact, seen also as the proof of equivalence of the Kelvin principle—the second law of thermodynamics—and the Carnot theorem. The Carnot theorem provides not only a more transparent mathematical representation, but also an important concept, of uncompensated heat that is not transparently seen in the Clausius and Kelvin principles, since it shows that the efficiencies of irreversible cycles cannot exceed the efficiency of the reversible cycles because of the ever present uncompensated heat. Furthermore, we now see that the Clausius and Kelvin principles, which are based on everyday experience and mathematically less transparent than the Carnot theorem, are given a clearer mathematical representation by means of Carnot's theorem. We reiterate that both the second law

of thermodynamics and the Carnot theorem are phrased in terms of cyclic processes, since cyclic processes are the only kind of processes in which the system is assured of returning to the original state without fail, and thus the existence of conserved quantities characteristic of the system is implied without recourse to any other act of measurement to ascertain their conserved nature. And conserved quantities are certainly convenient to use in formulating a theory of macroscopic processes.

4.3 Thermodynamic Temperature

Either one of the aforementioned literally stated forms of the second law of thermodynamics, namely, the Clausius and Kelvin principles, must be represented in a precise mathematical form so that it can be used as the starting point of a thermodynamic theory of macroscopic processes. Because of their equivalence it is sufficient to have a mathematical representation for one of them.

Such a representation was made feasible by a combination of two important ingredients: one is Kelvin's recognition that the Carnot theorem can be the basis of a universal thermodynamic temperature scale; the other is Clausius' representation of the Carnot theorem for a Carnot cycle in the form of his inequality. Here we first discuss the notion of thermodynamic temperature, which is necessary for the Clausius inequality.

One of the most important of the implications of the Carnot theorem is the notion of thermodynamic temperature, which was first deduced from the Carnot theorem by Lord Kelvin [9], since such a temperature is universal inasmuch as the second law of thermodynamics is universal. We consider the gist of it here for completeness.

Since the efficiency of reversible Carnot cycles is independent of materials and the modes of operation, but depends only on the temperatures θ_1 and θ_2 of the heat reservoirs, we see that the ratio of Q_2 to Q_1 is a function of θ_1 and θ_2 only:

$$\frac{Q_2}{Q_1} = f(\theta_2, \theta_1), \quad (4.20)$$

where $f(\theta_2, \theta_1)$ depends on θ_2 and θ_1 only. The properties of this function is elucidated below. Since we may write the left hand side in the form

$$\frac{Q_2}{Q_1} = \frac{Q_2}{Q_0} \cdot \frac{Q_0}{Q_1} = f(\theta_2, \theta_0) f(\theta_0, \theta_1),$$

we conclude that $f(\theta_2, \theta_1)$ is a function with the following property:

$$f(\theta_2, \theta_1) = f(\theta_2, \theta_0) f(\theta_0, \theta_1). \quad (4.21)$$

Let $\theta_2 = \theta_1$. Then

$$f(\theta_1, \theta_0) = \frac{1}{f(\theta_0, \theta_1)}. \quad (4.22)$$

The properties of f described in (4.21) and (4.22) imply that there exists a function $\phi(\theta)$ of θ , such that

$$f(\theta_2, \theta_1) = \frac{\phi(\theta_2)}{\phi(\theta_1)}. \quad (4.23)$$

Consequently it is possible to write

$$\frac{Q_2}{Q_1} = \frac{\phi(\theta_2)}{\phi(\theta_1)}. \quad (4.24)$$

The function $\phi(\theta)$ is a well behaved universal function of θ independent of materials and the modes of operation of the cycle, but otherwise arbitrary. It will be denoted by T :

$$T = \phi(\theta). \quad (4.25)$$

This is called the thermodynamic temperature. The temperature based on the Carnot theorem must be universal since the Carnot theorem is universal owing to reversible efficiencies being independent of the modes of operation and the working substances. In the manner shown the Carnot theorem therefore can serve as the basis of introducing a universal thermodynamic temperature. Since the efficiency calculated for a reversible cycle can be expressed [7, 8] in absolute temperatures in the form

$$\eta_{\text{rev}} = \frac{T_1 - T_2}{T_1},$$

it is appropriate to regard θ here as a temperature in the absolute scale. In this event the efficiency formula for a reversible cycle suggests that $\phi(\theta)$ must be linearly proportional to θ , and the proportionality constant may be taken such that θ coincides with the thermodynamic temperature T :

$$T = \theta. \quad (4.26)$$

In this manner the thermodynamic temperature is made to coincide with the absolute temperature based on the ideal gas temperature, and they now can be interchangeably used.

4.4 Clausius' Inequality

With the preparation made for the temperature scales given in the previous section it is now possible to discuss the mathematical representation of the second law of thermodynamics. For this purpose imagine a pair of irreversible and reversible cycles operating between two heat reservoirs of temperatures T_1 and T_2 , where $T_1 > T_2$. These temperatures are in the absolute scale. The two cycles take the same amount of heat Q_1 from the

higher temperature reservoir and perform work. The irreversible cycle does work W , discharging heat Q_2 to the lower temperature reservoir, whereas the reversible cycle does a maximum work W_{rev} . The efficiency of the reversible cycle is

$$\eta_{\text{rev}} = \frac{-W_{\text{rev}}}{Q_1} = 1 - \frac{T_2}{T_1},$$

whereas the efficiency of the irreversible cycle is

$$\eta_{\text{irr}} = \frac{-W}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

By the Carnot theorem there holds the inequality

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}. \quad (4.27)$$

Clausius [2] rearranges (4.27) to the form⁶

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0 \quad (4.28)$$

and argues that this inequality can be cast in an integral form by imagining a series of infinitesimal Carnot cycles:

$$-\oint \frac{dQ}{T} \geq 0, \quad (4.29)$$

for which the sign convention for heat transfer introduced earlier is used. An infinitesimal Carnot cycle is a cycle that operates between two heat reservoirs an infinitesimally small temperature difference apart. This terminology does not mean that the actual physical size of the device performing the cyclic process is infinitesimal; it refers to the temperature difference of the heat reservoirs involved. Note that the temperature T refers to the heat reservoir at the point in question in the series of infinitesimal cycles making up the cycle under consideration. The dQ is what Clausius called the ‘compensated heat’, which is the heat transfer involved between the system and its surroundings. Clausius also recognized another quantity which is nowadays called the ‘uncompensated heat’ that accompanies a cyclic process when the process is irreversible. This quantity vanishes if the process is reversible. This⁷ is an amount of heat which is intrinsic to

⁶ Kelvin in his 1854 paper on ‘On the dynamical theory of heat. Part VI’ (see Ref. [9]) considered $-Q_1/T_1 + Q_2/T_2 = 0$ in relation to the second law of thermodynamics. Kelvin therefore considered the case of reversible processes from the viewpoint of Clausius who obtained the inequality (4.29) holding for irreversible as well as reversible processes.

⁷ The existence of uncompensated heat was recognized by Carnot when he formulated his theorem. He discussed in what sense he meant *the maximum of motive power* and reasoned that, in the current terminology the *motive power* reaches a maximum when the uncompensated heat vanishes. See pp. 12–13, Ref. [3].

the system when the system undergoes the irreversible cyclic process in question. It is one of the central quantities that must be elucidated in order to formulate a thermodynamic theory of irreversible processes. In this connection it is interesting to quote a passage in an article by Prigogine [14] where it is stated that “150 years after its formulation the second law of thermodynamics still appears to be more a program than a well defined theory in the usual sense, as nothing precise (except the sign) is said about the S production”. Since entropy was not defined for irreversible processes by Clausius, in this passage we may interpret the S production as being meant for production of the uncompensated heat. Incidentally, we use this terminology out of deference to the traditional use of the term, although its dimension is, in fact, $[heat/temperature]$, which is the same as that of entropy.

Following Clausius we denote it by N and express the Clausius inequality (4.27) as

$$N = - \oint \frac{dQ}{T} \geq 0. \quad (4.30)$$

The uncompensated heat N is always positive and vanishes only if the process is reversible, and its positivity can be regarded as an expression of the second law of thermodynamics. Clausius [2] suggested calculating N by using (4.30) where the contour integral of the cycle must be performed along an irreversible path which includes at least one irreversible step. *Here we interpret the Clausius equation (4.30) differently, and recognize the compensated and uncompensated heats as two independent entities that must be elucidated in terms of the system properties for irreversible processes* [8]. It is easy to see that there are such two independent physical entities if the aforementioned corollary of the Carnot theorem is recalled. First, by this corollary the reversible work is larger by W_{ua} than the irreversible work W for the pair of reversible and irreversible cycles in question, and, furthermore, W_{ua} is positive semi-definite, vanishing only if the cycle is reversible. If this unavailable work is taken into account the Carnot theorem may be written as an equation instead of an inequality as follows:

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} - \frac{W_{ua}}{Q_1}. \quad (4.31)$$

This means that there exists a positive semi-definite quantity $N = W_{ua}/T_2$ such that

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1} + N. \quad (4.32)$$

This N vanishes for reversible processes by the Carnot theorem. By using the notion of infinitesimal cycles and the sign convention for heat transfer introduced in Chapter 3 we may cast this equation in the form

$$N = - \left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \right) = - \sum_i \frac{Q_i}{T_i}, \quad (4.33)$$

which gives rise to (4.30) when passage⁸ is made from the sum to the contour integral. This passage requires a little more careful examination. Clearly the uncompensated heat N appears as a quantity related to the work unavailable to the irreversible cycle for the purpose of its task when the work is compared with the work of the reversible cycle. It is evidently intrinsic to the system, namely, the irreversible cycle in hand, and should be treated as a separate entity from the compensated heat. This viewpoint is akin to the recognition taken with regard to heat and energy, which are equivalent to each other so that $Q = -W$, but their physical natures are not the same. The N in inequality (4.30) is equivalent to the closed contour integral on the right, but the two quantities are not of the same physical nature and origin. It is crucial to distinguish their physical meanings if a mathematical representation of the second law of thermodynamics is sought on the basis of the Clausius inequality (4.30).

4.5 Clausius Entropy for Reversible Processes

Since a precise mathematical representation for the uncompensated heat was not known at the time of Clausius except that there should exist such a quantity that should vanish if the process was reversible, Clausius restricted the theory to reversible processes for which $N = 0$ and developed the theory of equilibrium thermodynamics [7, 13], namely, thermostatics, with which we are all familiar at present. Reversible processes are traditionally defined as those of quasi-static processes which are in continuous equilibrium with the surroundings. However, it is mathematically and physically more precise to define them as quasi-static processes for which $N = 0$. This will be the definition used throughout in this work; it is also consistent with Carnot

⁸If passage is made as is usually done in the literature, by which the summation over index i is simply replaced with a closed contour integral, it must be taken that there is a contribution which has been absorbed into the factor N . For if the sum is replaced by an integral we obtain

$$\begin{aligned}\frac{Q_1}{T_1} - \frac{Q_n}{T_n} &= \frac{Q_1}{T_1} - \frac{Q_2}{T_2} + \frac{Q_2}{T_2} - \frac{Q_3}{T_3} + \cdots + \frac{Q_{n-1}}{T_{n-1}} - \frac{Q_n}{T_n} \\ &= \sum_{j=1}^{n-1} \int_j^{j+1} d\left(\frac{Q}{T}\right) \\ &= \int_1^n \frac{dQ}{T} + \int_1^n Q d\left(\frac{1}{T}\right),\end{aligned}$$

and the second term on the right of the third line is a kind of uncompensated heat associated with heat transfer. This term is absorbed into the uncompensated heat N in passing from Eq. (4.33) to the Clausius inequality (4.30).

and Clausius to define them by the criterion of $N = 0$. If N is set equal to zero for a reversible cyclic process then there holds the equality

$$\oint \frac{dQ}{T} = 0, \quad (4.34)$$

which implies that there exists a state function S_e which Clausius called the entropy [2] of the system and defined by the differential relation

$$dS_e = \left(\frac{dQ}{T} \right)_{\text{rev}} \quad (4.35)$$

This differential form, on substitution into Eq. (4.34), means that

$$\oint dS_e = 0. \quad (4.36)$$

In other words, dS_e is an exact differential in the thermodynamic (variable) space characteristic of the reversible cyclic process. The differential form combined with the differential form for the first law of thermodynamics for the same cycle

$$dE = dQ + dW$$

is called the equilibrium Gibbs relation

$$dS_e = T^{-1} (dE - dW) \quad (4.37)$$

It is the basis of equilibrium thermodynamics [7, 13]. Keep it in mind that the Clausius entropy is defined for reversible processes only. We will return to this relation later in this work. It must be recalled that for reversible processes the internal work—energy dissipation—vanishes and therefore dW consists of the pressure–volume work or other reversible works only. That is, there is no unavailable work or uncompensated heat involved in dW and dQ in the case of reversible processes.

4.6 Calortropy for Irreversible Processes

The Clausius inequality (4.29) is a deduction made from the literal statement of the second law of thermodynamics by Clausius and Lord Kelvin. However, being an inequality, it is not the most useful mathematical form of representation for the second law of thermodynamics, because it is not possible to formulate with an inequality a theory that allows us to perform quantitative calculations of thermodynamic properties of a system. To proceed in such a direction, it is necessary to give a mathematical representation of the second law of thermodynamics that is not based on an inequality. This goal can be achieved if it is observed that the *uncompensated heat* in Eq. (4.30) is a quantity which is *physically independent of the*

compensated heat. If we recall the analysis made with regard to the Clausius inequality in Sec. 4.4 of this chapter, the aforementioned viewpoint is quite sensible. This observation in fact is crucial for further development of the subject of thermodynamics into the non-equilibrium regime, although it superficially appears to be insignificant as to have escaped the notice of thermodynamicists in the past. In this regard it is useful to recall Meixner's unsuccessful quest [15] for a quantity to replace the Clausius entropy for non-equilibrium systems. The quest is answered by the aforementioned observation, as we will see.

To implement the idea we observe that the uncompensated heat in Eq. (4.30) may be written as a contour integral over the cycle in hand:

$$N = \oint dN \geq 0, \quad (4.38)$$

where dN , or more precisely, dN/dt should be always positive except for reversible processes, in which it vanishes everywhere in the cyclic path in the thermodynamic space. Otherwise it would be possible to devise a cyclic process in such a way that it vanishes or is negative, violating the second law of thermodynamics. Suppose there is a segment of a process where $dN < 0$. Then a simple, albeit somewhat ideal, example for such a case would be a cycle consisting of the irreversible segment where $dN < 0$ and a reversible segment for the remainder of the cycle. This cycle, if possible to construct, would violate the second law of thermodynamics.

4.6.1 Mathematical Representation of the Second Law of Thermodynamics

By combining Eq. (4.38) with Eq. (4.30) and rearranging the terms we obtain the equation [5, 8, 16, 17]

$$\oint \left(\frac{dQ}{T} + dN \right) = 0. \quad (4.39)$$

This vanishing contour integral implies that there exists a state function Ψ in the thermodynamic space such that

$$d\Psi = \frac{dQ}{T} + dN \quad (4.40)$$

and

$$\oint d\Psi = 0. \quad (4.41)$$

Note that the differential form (4.40) and the contour integral (4.41) remain valid regardless of whether the process is reversible or irreversible. Indeed,

if the process is reversible then $dN = 0$, or $dN/dt = 0$, over the differential segment of the process, and we recover the Clausius result: namely,

$$d\Psi|_{\text{rev}} = \frac{dQ}{T} \Big|_{\text{rev}} = dS_e \quad (4.42)$$

and thus within a constant of integration the reversible Ψ coincides with the Clausius entropy S_e :

$$\Psi_{\text{rev}} = S_e. \quad (4.43)$$

This quantity Ψ , which is called the calortropy, is a fundamental variable that holds for irreversible processes and is clearly different from the Clausius entropy defined for reversible processes only. Since the term entropy is used rather indiscriminately in the recent times, to clearly distinguish it from the Clausius entropy holding only for reversible processes the Ψ is given the aforementioned terminology. It is a non-equilibrium extension of the Clausius entropy⁹ and akin to the quantity which Carnot called *calorique*.

4.6.2 Integral and Differential Forms of the Thermodynamic Laws

Having elucidated the relation of the calortropy and the second law of thermodynamics in the case of irreversible processes and having achieved the desired mathematical representations of the thermodynamic laws, it is opportune to summarize the first and second laws of thermodynamics in mathematical forms:

In the case of a cyclic process the first and the second law of thermodynamics can be expressed by a pair of vanishing contour integrals of internal energy and calortropy in thermodynamic space:

$$\oint dE = 0, \quad (4.44)$$

$$\oint d\Psi = 0.$$

⁹In one of the early papers [18] on thermodynamics Clausius conceived the notion of *disgregation* which can be interpreted as being a quantity inclusive of the entropy. Clausius thought, that the disaggregation increases as, for example, a liquid transforms to its vapor. However, this notion was not developed further in terms of a distribution function when he formulated the mean free path theory, unlike Boltzmann who discovered the statistical mechanical H function related to the entropy. Neither did Clausius relate the disaggregation to the notion of entropy when he defined the latter for reversible processes. Boltzmann's H function is not the thermodynamic (Clausius) entropy itself, however. For this point, see Refs. [5] and [8].

The circular integrals are over the cycle performed in thermodynamic space, which was introduced in the previous chapter but is to be specified more precisely as the theory is developed in a mathematically concrete form. This pair of vanishing contour integrals, equivalently, the pair of the corresponding differential forms

$$\begin{aligned} dE &= dQ + dW, \\ Td\Psi &= dQ + dN, \end{aligned} \tag{4.45}$$

provides us with the starting point of a mathematical theory of thermodynamics of irreversible processes developed in this work.

The differential forms for the first and second law of thermodynamics in Eq. (4.45) can be combined to the form

$$d\Psi = T^{-1}(dE - dW) + dN. \tag{4.46}$$

It is convenient to express dN in the form

$$dN = T^{-1}d\mathfrak{N}, \tag{4.47}$$

where by the second law of thermodynamics $d\mathfrak{N}$ is such that

$$\frac{d\mathfrak{N}}{dt} \geq 0. \tag{4.48}$$

If $d\mathfrak{N}$ is suitably represented in terms of global thermodynamic variables the differential form (4.46) can be made the basis of the thermodynamics of irreversible processes in the global scale. However, the precise meaning of the calortropy Ψ will not be known until the meaning of the uncompensated heat, together with that of the compensated heat, is clarified, and vice versa. Therefore the subject of irreversible thermodynamics may be said to be centered around the meanings of compensated and uncompensated heat, or the meaning of Ψ together with that of $d\mathfrak{N}$ in the thermodynamic space. We will address our study to this task later in this chapter.

4.7 Compensated and Uncompensated Heats

The notions of compensated and uncompensated heats, introduced and used in the earlier discussions, have not been precisely elucidated, nor have their mathematical representations been given as yet so that they can be made use of in formulating a theory of global irreversible processes [23]. It is now necessary to investigate them in order to make the thermodynamic principles provide the desired mathematical machineries to describe macroscopic irreversible processes.

To make the discussion more definite we consider a finite system consisting of a mixture of reacting fluids contained in a volume V . The fluid mixture consists of r components which are denoted by \mathcal{C}_a ($a = 1, 2, \dots, r$). There are m chemical reactions of compounds \mathcal{C}_a ($1 \leq a \leq r$), which may be written in the form

$$\sum_{a=1}^r \nu_{al} \mathcal{C}_a = 0 \quad (m \geq l \geq 1). \quad (4.49)$$

Here ν_{al} denotes the stoichiometric coefficients times the mass of species a , which are counted positive for the products and negative for the reactants. Although phrased in the terms of fluids, the formalism presented here is equally applicable to other forms of aggregation of matter.

4.7.1 Variation in Calortropy

The first quantity of interest in the present investigation is the calortropy of the fluid. Since the calortropy Ψ is a state function in the thermodynamic space by virtue of the second law of thermodynamics, some consequences of this property can be deduced. Since it is a property characterizing the thermodynamic state of the system undergoing an irreversible process, the global calortropy Ψ should be described by energy E , volume V , masses M_a of species ($1 \leq a \leq r$), as well as non-conserved variables Γ_{ka} all of which change in time and characterize the irreversible behavior of the system; that is, Ψ should be a function of variables spanning space $\mathfrak{H} = (E, V, M_a, \Gamma_{ka} : k \geq 1, r \geq a \geq 1)$. The presence of non-conserved variables in the set indicates that the process is irreversible. The union of \mathfrak{H} with Ψ will henceforth be called the Gibbs space \mathfrak{H}_G where $\mathfrak{H}_G = \mathfrak{H} \cup \Psi$. Thus in this viewpoint Ψ is a surface in \mathfrak{H}_G .

It should be noted that the dimension of \mathfrak{H} is determined by the nature of the phenomenon and experiment of interest and by our perception of them on phenomenological grounds¹⁰. Thermodynamic principles do not provide guidance in the determination of the dimension of the space \mathfrak{H} . Molecular theories [5, 8] of the phenomenon may provide an idea of the dimension of the Gibbs space, but even there the construction of the thermodynamic branch of the solution for an irreversible kinetic equation must face up to the question of choosing the variables making up space \mathfrak{H} .

¹⁰In this sense the thermodynamics is anthropomorphic and the goal of thermodynamic theory of macroscopic processes is simply to construct a general formalism consistent with the laws of thermodynamics.

By using the chain rule it is then possible to obtain the time derivative of Ψ in the form

$$\begin{aligned}\frac{d\Psi}{dt} &= \left(\frac{\partial\Psi}{\partial E}\right)_{V,M,\Gamma} \frac{dE}{dt} + \left(\frac{\partial\Psi}{\partial V}\right)_{E,M,\Gamma} \frac{dV}{dt} + \sum_{a=1}^r \left(\frac{\partial\Psi}{\partial M_a}\right)_{E,M',\Gamma} \frac{dM_a}{dt} \\ &\quad + \sum_{a=1}^r \sum_{k \geq 1} \left(\frac{\partial\Psi}{\partial \Gamma_{ka}}\right)_{E,M,\Gamma'} \frac{d\Gamma_{ka}}{dt},\end{aligned}\quad (4.50)$$

where the prime on the subscripts M and Γ means the exclusion of the variable of differentiation from the sets $M = (M_a : r \geq a \geq 1)$ and $\Gamma = (\Gamma_{ka} : k \geq 1; r \geq a \geq 1)$. The evolution of Ψ is described by the evolution of the variables spanning space \mathfrak{H} .

4.7.2 Compensated Heat and Changes

Since the system may exchange matter with its surroundings it is necessary to distinguish the mass change within the system that arises from chemical reactions and the mass change incurred by the mass transfer between the body and its surroundings. Transfer of energy may be similarly considered, and it was, in fact, done when the first law was mathematically formulated in Chapter 3. Such exchanges give rise to compensated changes in matter and energy, which can be grouped into compensated heat. Therefore in this work the term compensated heat is used in a more general sense than originally used for it.

The total mass change can thus be written in two parts:

$$\frac{dM_a}{dt} = \frac{d_e M_a}{dt} + \frac{d_i M_a}{dt}, \quad (4.51)$$

where $d_i M_a/dt$ denotes the mass change arising from the chemical reactions within the system and $d_e M_a/dt$ represents the mass change arising from the mass transfer between the system and its surroundings. If the rate of reaction l is denoted by R_l then the rate of mass change arising from the chemical reactions is given by the expression

$$\frac{d_i M_a}{dt} = \int_V d\mathbf{r} \sum_{l=1}^m \nu_{al} R_l. \quad (4.52)$$

The integration over the volume is necessary since we are interested in mass change in the entire volume and the reactions may occur inhomogeneously over the volume. If chemical reactions occur uniformly in V as is the case in the absence of localized reaction sites, this rate may be written as

$$\frac{d_i M_a}{dt} = \sum_{l=1}^m \nu_{al} R_l V. \quad (4.53)$$

The values of non-conserved variables of the system may differ from their values in the surroundings. In such a situation the values of the non-conserved variables may change with time. It is then reasonable to decompose $(d\Gamma_{ka}/dt)$ into the part related to the transfer of Γ_{ka} between the system and the surroundings, and the intrinsic part that has to do with energy dissipation within the system:

$$\frac{d\Gamma_{ka}}{dt} = \frac{d_e\Gamma_{ka}}{dt} + \frac{d_i\Gamma_{ka}}{dt}, \quad (4.54)$$

where the first term on the right hand side represents the transfer part and the second the intrinsic part of the rate of change in Γ_{ka} . These decompositions of dM_a/dt and $d\Gamma_{ka}/dt$ will be presently used in Eq. (4.50). The transfer rates $d_e M_a/dt$ and $d_e\Gamma_{ka}/dt$ and the energy transfer rate dQ_E/dt contribute to the compensated heat.

4.7.3 Uncompensated Heat

Upon making use of Eqs. (3.9) and (4.46) in Eq. (4.50) we obtain

$$\begin{aligned} 0 = & \left[\left(\frac{\partial \Psi}{\partial E} \right)_{V,M,\Gamma} - \frac{1}{T} \right] \frac{dE}{dt} + \left[\left(\frac{\partial \Psi}{\partial V} \right)_{E,M,\Gamma} - \frac{p}{T} \right] \frac{dV}{dt} \\ & + \sum_{a=1}^r \left[\left(\frac{\partial \Psi}{\partial M_a} \right)_{E,V,M',\Gamma} + \frac{\hat{\mu}_a}{T} \right] \frac{d_e M_a}{dt} \\ & + \sum_{a=1}^r \sum_{k \geq 1} \left[\left(\frac{\partial \Psi}{\partial \Gamma_{ka}} \right)_{E,V,M,\Gamma'} - \frac{X_{ka}}{T} \right] \frac{d_e \Gamma_{ka}}{dt} \\ & + \left[\sum_{a=1}^r \left(\frac{\partial \Psi}{\partial M_a} \right)_{E,V,M',\Gamma} \frac{d_i M_a}{dt} + \sum_{a=1}^r \sum_{k \geq 1} \left(\frac{\partial \Psi}{\partial \Gamma_{ka}} \right)_{E,V,M,\Gamma'} \frac{d_i \Gamma_{ka}}{dt} \right. \\ & \left. + \frac{1}{T} \left(\frac{d_i W}{dt} - \frac{dQ_n}{dt} - \frac{d\mathfrak{N}}{dt} \right) \right] \end{aligned} \quad (4.55)$$

Since not only the global variables E , V , M_a , and Γ_{ka} are independent but also their variations are arbitrary, and, moreover, Ψ is a state function in space \mathfrak{H} as a consequence of the second law of thermodynamics, it can be concluded that each term in the square brackets in Eq. (4.55) should be equal to zero. Hence not only the derivatives of Ψ should be given by the

relations

$$\left(\frac{\partial \Psi}{\partial E} \right)_{V,M,\Gamma} = \frac{1}{T}, \quad (4.56)$$

$$\left(\frac{\partial \Psi}{\partial E} \right)_{V,M,\Gamma} = \frac{1}{T}, \quad (4.57)$$

$$\left(\frac{\partial \Psi}{\partial M_a} \right)_{E,V,M',\Gamma} = -\frac{\hat{\mu}_a}{T}, \quad (4.58)$$

$$\left(\frac{\partial \Psi}{\partial \Gamma_{ka}} \right)_{E,V,M',\Gamma} = \frac{X_{ka}}{T}, \quad (4.59)$$

but also the uncompensated heat must be determined by the equation

$$\frac{d\mathfrak{N}}{dt} = \frac{d_i W}{dt} - \frac{dQ_n}{dt} - \sum_{l=1}^m \mathcal{A}_l R_l V + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_i \Gamma_{ka}}{dt} \geq 0, \quad (4.60)$$

where we have used Eq. (4.53) and \mathcal{A}_l is the affinity defined by

$$\mathcal{A}_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (4.61)$$

This form of the rate of change in uncompensated heat generalizes the form by De Donder [24] and Defay [25], who obtained the rate of change in uncompensated heat arising from chemical reactions only. Upon using the relations (4.56)–(4.59) we obtain from Eq. (4.50) the extended Gibbs relation for Ψ

$$d\Psi = T^{-1} \left(dE + pdV - \sum_{a=1}^r \hat{\mu}_a dM_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\Gamma_{ka} \right). \quad (4.62)$$

This fundamental relation is for global irreversible processes, but must be appended by the inequality (4.60) imposing a constraint on $d_i \Gamma_{ka}/dt$, which is a constitutive relation, and other terms therein. It should be noted that the differentials dE , dV , dM_a , and $d\Gamma_{ka}$ in Eq. (4.62) are those corresponding to the transfer time derivatives characterizing the transfers of the quantities between the system and the surroundings.

Detailed consideration is necessary for $d_i \Gamma_{ka}/dt$ and $(d_i W/dt - dQ_n/dt)$ before the uncompensated heat is fully elucidated. On the basis of the knowledge we have gained from the local field theory of irreversible processes, we make a proposition for them in the following. As a preparation for the proposition let us introduce mean (global) thermodynamic forces, namely, volume averages of the local thermodynamic forces, which are conjugate to the non-conserved variables Γ_{ka} , and the fluxes Υ_{ka} of Γ_{ka} . The mean thermodynamic forces for Γ_{ka} will be denoted by ω_{ka} , and those for Υ_{ka} by ϖ_{ka} . These mean thermodynamic forces drive the system of finite volume V to undergo energy dissipating irreversible processes.

4.7.4 Proposition for Uncompensated Heat

If the present theory is a generalization of the linear theory of irreversible processes, it ought to be inclusive of the linear theory form of energy dissipation as a special case. Our experience with the linear theory of irreversible processes [14, 22] suggests that the energy dissipation should be given by a bilinear form of Γ_{ka} and ω_{ka} and also of Υ_{ka} and ϖ_{ka} .

On the basis of the reasoning made earlier we propose the following:

Proposition 1 *The dissipation function $\Sigma_l \equiv T^{-1}(d_i W/dt - dQ_u/dt)$ is a bilinear form of mean fluxes $\bar{\omega}_{ka}$ and $\bar{\Upsilon}_{ka}$ and their mean conjugate thermodynamic forces ω_{ka} and ϖ_{ka} :*

$$\Sigma_l = T^{-1} \sum_{a=1}^r \sum_{k \geq 1} (\Gamma_{ka} \omega_{ka} + \Upsilon_{ka} \varpi_{ka}) \quad (4.63)$$

Therefore the uncompensated heat is given by

$$\frac{d\mathfrak{N}}{dt} = T\Sigma_l - \sum_{l=1}^m \mathcal{A}_l R_l V + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_i \Gamma_{ka}}{dt} \geq 0. \quad (4.64)$$

The irreversible thermodynamics of macroscopic processes in a system contained in a volume V of a finite extension is then described by the extended Gibbs relation (4.62) under the constraint of the second law of thermodynamics (4.64) in which the dissipation function Σ_l is given by Eq. (4.63). The important task of irreversible thermodynamics is in elucidating the physical meanings of dQ/dt and $d\mathfrak{N}/dt$. Therefore their meanings as well as the explicit mathematical formulas of the thermodynamic forces, affinity \mathcal{A}_l , and generalized potential X_{ka} , which are also constitutive quantities appearing in the extended Gibbs relation, will be delineated in the course of development of the theory. Also, a more detailed form for $d_i \Gamma_{ka}/dt$ must be taken such that the inequality (4.64) is satisfied according to the requirement of the second law of thermodynamics. To make this proposition more concrete it is only necessary to take suitable constitutive relations for $d_i \Gamma_{ka}/dt$ and R_l . We will explicitly learn about an example for $d_i \Gamma_{ka}/dt$ in a subsequent section of this chapter and the local continuum field theory foundations of the uncompensated heat presented here in Chapter 5, where some examples are considered for global processes, and in Chapter 6 in particular and also in the subsequent chapters. In fact, the local continuum field theory is indispensable in developing irreversible thermodynamics of fluid dynamics. With regards to the constitutive relations we note that the constitutive quantities \mathcal{A}_l and X_{ka} can be elucidated from the derivatives of Ψ with the help of the extended Gibbs relation (4.62).

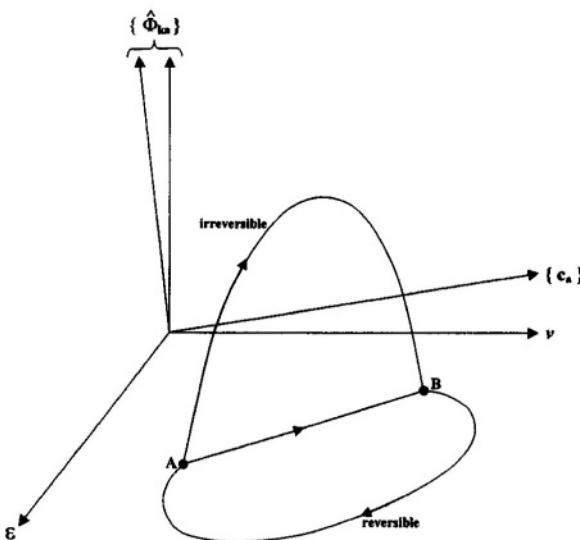


FIGURE 4.2. An irreversible cycle consisting of an irreversible ($A \rightarrow B$) and a reversible segment ($B \rightarrow A$). The states A and B are embedded in the equilibrium part of the space, as is the reversible segment. This figure is a rendering in the thermodynamic space of the irreversible cycle with which Clausius deduced the Clausius—Duhem inequality. In the formulation of Clausius the concept of thermodynamic space is absent. This cycle is a special, if somewhat ideal, case of irreversible cycles because of the presence of a reversible segment. The Clausius entropy is defined over the reversible cycle $A \rightarrow B \rightarrow A$ in the equilibrium thermodynamic space.

4.8 Clausius—Duhem Inequality

Let us now examine the relation of Eq. (4.41) to the Clausius—Duhem inequality. Clausius [2] considered a cyclic process consisting of a segment of irreversible process which starts from state A and ends at state B that are embedded in the equilibrium part of the thermodynamic space, and another segment of reversible process which reversibly restores the system at state B to its original thermodynamic state A ; see Fig. 4.2. For this cycle to be realizable the system must be open. The reason is that whereas the spontaneous irreversible process can proceed from A to B even if the system is isolated, the reversible process from B to A is not possible for an isolated system because the system cannot return on its own to the original state A from the spontaneously reached final state B without leaving an effect on the surroundings. Therefore a closed contour (path) as depicted in Fig. 4.2 is impossible to construct for an isolated system; such a path generally applies to open systems only. A little relaxed case is a cycle in

which the irreversible segment is performed in an isolated system whereas the reversible segment is performed in an open system. However, this cycle represents a physically different situation from the previous case mentioned.

4.8.1 Isolated Systems

We first consider the case of an isolated system for which only the irreversible path $A \xrightarrow{\text{irr}} B$ is realizable. It must be recognized that the process $B \xrightarrow{\text{rev}} A$ is not realizable for an isolated system because the system cannot return to state A from state B on its own if it is isolated. The corresponding calortropy change for the irreversible path indicated is given by the integral

$$\Delta\Psi = \Psi(B) - \Psi(A) = \int_{A(\text{irr})}^B d\Psi, \quad (4.65)$$

since the calortropy is a state function regardless of the nature of the process. Upon use of Eq. (4.40) the integral on the right hand side of Eq. (4.65) can be written as

$$\int_{A(\text{irr})}^B d\Psi = \int_{A(\text{irr})}^B dN, \quad (4.66)$$

because there is no contribution from the compensated heat dQ for the reason that the system is isolated. Therefore

$$\Delta\Psi = \int_{A(\text{irr})}^B dN. \quad (4.67)$$

Since by the second law of thermodynamics

$$\int_{A(\text{irr})}^B dN \geq 0, \quad (4.68)$$

there follows the inequality

$$\Delta\Psi \geq 0, \quad (4.69)$$

where the equality holds only for a reversible process or at equilibrium in which case $\Delta\Psi = \Delta S_e = 0$. Since the system is isolated, ΔS_e clearly vanishes. It is important to recognize that $\Delta\Psi \neq \Delta S_e$ in general, and that they are not equal over the segment in question because the process is irreversible. Therefore this inequality does not imply $\Delta S_e \geq 0$ for the isolated system considered, but *the calortropy increases toward a maximum*, at which the system attains the state of equilibrium and Ψ equals S_e .

4.8.2 Non-isolated Systems

We consider a system which is not isolated, but undergoes the cyclic process depicted in Fig. 4.2. In this case the system can be made to return reversibly from the final state B , which has been reached irreversibly, to the initial state A by compensating the system for the return from the surroundings.

In the sense of the condition imposed on states A and B this cyclic process is rather special, since the system must start from an equilibrium state and end at an equilibrium state but through a non-equilibrium path in the thermodynamic space.

We remark that in his work Clausius [2] made no mention of embedding the states A and B in the equilibrium part of the thermodynamic space. He simply constructed a cycle consisting of an irreversible segment starting from state A and ending at state B , and a reversible segment starting from state B and restoring the system to state A . It is now clear that since states A and B are also part of a reversible process they must be embedded in the equilibrium part of the thermodynamic space. It must also be noted that there was no clear notion of thermodynamic space in the Clausius formulation of his inequality for the second law of thermodynamics.

For the cyclic process in Fig. 4.2 the vanishing contour integral (4.41) can be written as

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{irr})}^B d\Psi, \quad (4.70)$$

where the subscripts attached to the integrals, rev and irr, mean that the integration must be performed along the reversible and the irreversible path, respectively. Note that the integration over the reversible path can be reversed by virtue of the process being reversible. Since $dN = 0$ and hence the calortropy is identified with the Clausius entropy over the reversible segment, we obtain

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{rev})}^B dS_e = S_e(B) - S_e(A) = \Delta S_e. \quad (4.71)$$

By combining Eqs. (4.70) and (4.71) we obtain

$$\Delta S_e = \int_{A(\text{irr})}^B d\Psi, \quad (4.72)$$

but

$$\int_{A(\text{irr})}^B d\Psi = \int_{A(\text{irr})}^B \left(\frac{dQ}{T} + dN \right) \quad (4.73)$$

Because Ineq. (4.68) holds by virtue of the second law of thermodynamics, upon using Eq. (4.73) in Eq. (4.72) we obtain for the non-isolated system

under consideration the inequality

$$\Delta S_e \geq \int_{A(\text{irr})}^B \frac{dQ}{T}. \quad (4.74)$$

This is the Clausius–Duhem inequality. We emphasize that this inequality cannot be used in the case of an isolated system, for which Ineq. (4.69) instead of Ineq. (4.74) holds for the process $A \rightarrow B$; for ΔS_e has no meaning since if the system is isolated it is not definable for the reversible segment, as discussed earlier. This analysis evidently shows that the Clausius–Duhem inequality is contained in the present expression for the second law of thermodynamics (4.41).

At a quick glance the inequality (4.74), together with Eqs. (4.70) and (4.71), may appear to mean that for an isolated system $\Delta S_e \geq 0$, as is generally taken in the thermodynamics literature. However, this inequality for an isolated system can be misleading for the reason given earlier in connection with Fig. 4.2 and further elaborated below.

If the system is isolated during the irreversible process only, but open during the reversible process, which will be called the Clausius irreversible cycle, $dQ = 0$ everywhere in the interval of integration over the irreversible process, and hence $\Delta S_e \geq 0$. If the system is isolated during the entire cycle it is clearly appropriate to think in terms of $\Delta\Psi \geq 0$ instead of $\Delta S_e \geq 0$, since the system cannot reversibly return to state A from state B on its own without a compensation from the surroundings, but there are no surroundings for an isolated system to compensate for the system to return to state A from state B , as pointed out earlier. In this case the inequality $\Delta S_e \geq 0$ is, in fact, inappropriate to use.

Reversible processes are hypothetical processes that are possible only if one can perform the processes in such a way that the system is in continuous equilibrium with its surroundings; consequently the process can be reversed without a cost but takes an infinite duration of time; and the uncompensated heat does not arise. The Clausius–Duhem inequality (4.74) compares the Clausius entropy change accompanying such a hypothetical reversible process with the total amount, namely, the integral, of the compensated heat divided by temperature dQ/T for the irreversible process of interest. In applying this inequality it must be remembered that ΔS_e is, for the reversible segment, complementary to the irreversible step making up the cycle in question; Ineq. (4.74) simply means that ΔS_e computed for the reversible segment with the formula

$$\Delta S_e = \int_{A(\text{rev})}^B dQ/T$$

is always larger than that of the irreversible compensated heat change and becomes equal to the latter, only if the process is reversible. The Clausius–Duhem inequality does not by any means imply that the concept of the

Clausius entropy can be directly extended to a non-equilibrium situation or an irreversible process. In the case of irreversible processes we instead have the calortropy Ψ defined by Eq. (4.40) or Eq. (4.41), which is the properly generalized form for a mathematical representation of the second law of thermodynamics.

Instead of looking for an inequality like Eq. (4.74), by using the fact that $d\Psi$ is an exact differential we may write Eq. (4.70) simply in the form

$$\Delta S_e = \Delta\Psi = \Psi(B) - \Psi(A) \quad (4.75)$$

for the cyclic process considered by Clausius. Therefore for such a special process starting from an equilibrium state and ending at an equilibrium state the calortropy change for an irreversible process can be simply computed in terms of the Clausius entropy change over a complementary reversible process which, with the irreversible segment, makes up the Clausius irreversible cycle. It therefore is useful to consider the Clausius irreversible cycle if we aim to learn about $\Delta\Psi$ of the irreversible segment from the information on the complementary reversible segment, since ΔS_e for the reversible segment is much easier to calculate explicitly than $\Delta\Psi$ for the irreversible segment. Furthermore, Eq. (4.75) implies that there are an infinite number of reversible paths that can produce $\Delta\Psi$ between two states A and B in the case of the particular cycle considered. Note, however, that Eq. (4.75) is for global changes, but not for local changes in a system that is not isolated.

The preceding conclusion drawn for the relation of $\Delta\Psi$ and ΔS_e has considerable significance for understanding and examining from the standpoint of the second law of thermodynamics the thermodynamics of steady irreversible processes and the theory of linear irreversible processes which assumes the local equilibrium hypothesis for the Clausius entropy change, even if there are irreversible processes present in the system. We will return to this aspect later at a more appropriate stage; see Chapters 9 and 10.

Finally, we remark the following: In the case of a local irreversible process it is not possible to transcribe Eq. (4.75) into the equality of the differentials

$$d\Psi = dS_e, \quad (4.76)$$

since

$$\int_{A(\text{irr})}^B (d\Psi - dS_e) \neq \int_{A(\text{irr})}^B d\Psi - \int_{A(\text{rev})}^B dS_e = 0.$$

Pursuing this discussion a little further, we remark that in the linear theory of irreversible processes [19, 20, 21, 22] the entropy density change dS in a system is written as

$$dS = dQ/T + dN$$

in the present notation. In the light of Eq. (4.76) holding for a global process only, this equation for dS cannot be used for local processes if S is meant

for the Clausius entropy. The discussion presented earlier in connection with calortropy suggests that dS in the said equation must, in fact, be interpreted as $d\Psi$. Then the conceptual difficulty inherent in the linear theory of irreversible thermodynamics simply evaporates, and Meixner's qualm mentioned earlier is thus resolved.

We have thus seen that the notion of calortropy clarifies a number of subtle points in equilibrium and non-equilibrium thermodynamics of linear processes, which have not been possible to resolve by means of the Clausius entropy.

4.9 Extended Gibbs Relations

The extended Gibbs relation (4.62) for the calortropy and the inequality (4.64) for the uncompensated heat are a pair of general equations representative of the second law of thermodynamics and, as such, may be used for making some general deductions about non-equilibrium processes in the system.

First of all, from the phenomenological viewpoint the extended Gibbs relation makes it possible to store the macroscopic thermodynamic information of the system in the calortropy of the system, if the constitutive relations are given for the specific heat, equation of state, chemical potentials, and generalized potentials and if the differential form (4.62) can be integrated in the thermodynamic space. If this hierarchical relation between the calortropy and the constitutive relations is reversed it is possible to deduce the constitutive relations from the calortropy if the latter is known from another source such as the molecular model that can provide the calortropy by means of statistical mechanics [5, 8]. In this reversal of the role the derivatives of the calortropy (4.56)–(4.59) give rise to the constitutive relations for the substance under consideration. In this sense the calortropy is an information storage for the system. In the latter approach, in fact, lies the true value of generalized, or irreversible, thermodynamics under study here, if it can be meaningfully implemented for practical problems.

In applications of thermodynamics it is more convenient to use the densities of extensive variables, which are defined by dividing the extensive quantities by the total mass M of the system. These densities are therefore made intensive, but it must be emphasized that their characters are not the same as the intensive variables such as temperature, pressure, chemical potentials, and generalized potentials, which are conjugate to the densities of the extensive variables mentioned. The densities of the extensive variables except for masses will be denoted with a caret; for example, $\widehat{\Psi} = \Psi/M$, $\widehat{\Gamma}_{ka} = \Gamma_{ka}/M$, $\widehat{V} = V/M$, and so on and $m_a = M_a/M$ for masses.

4.9.1 Uncompensated Heat and Constitutive Equations

On use of the derivatives of $\hat{\Psi}$ mentioned, the uncompensated heat can be expressed as a quantity bounded from below in the thermodynamic space:

$$\frac{d\mathfrak{N}}{dt} = F \left(\frac{\partial \hat{\Psi}}{\partial \hat{E}}, \frac{\partial \hat{\Psi}}{\partial \hat{V}}, \frac{\partial \hat{\Psi}}{\partial m_a}, \frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{ka}} : k \geq 1, r \geq a \geq 1 \right) \geq 0, \quad (4.77)$$

where F denotes a positive semi-definite function of the quantities indicated. In the special case where $R_l = 0$ and $\omega_{ka} = 0$ we have for the function F

$$\frac{d\mathfrak{N}}{dt} = T \sum_{a=1}^r \sum_{k \geq 1} \left[\left(\frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{ka}} \right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}'} \frac{d_i \hat{\Gamma}_{ka}}{dt} + \Upsilon_{ka} \varpi_{ka} \right] \geq 0, \quad (4.78)$$

where Υ_{ka} and ϖ_{ka} may be expressed in terms of the derivatives of Ψ .

On the other hand, for example, assume that F is a positive quadratic form of derivatives of $\hat{\Psi}$ with respect to $\hat{\Gamma}_{ka}$, that is, the function F is such that

$$\frac{d\mathfrak{N}}{dt} = T \sum_{a=1}^r \sum_{b=1}^r \sum_{k \geq 1} \sum_{q \geq 1} R_{ab}^{(kq)} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{ka}} \right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}'} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{qb}} \right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}'} \geq 0, \quad (4.79)$$

where $R_{ab}^{(kq)}$ are coefficients independent of $\{\hat{\Gamma}_{ka}\}$. Furthermore, assume that Υ_{ka} is, to an approximation, given by

$$\Upsilon_{ka} = g_{ka} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{ka}} \right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}'}, \quad (4.80)$$

where g_{ka} is a quantity which may depend on T , m_a and others, but not on $\hat{\Gamma}_{ka}$. Then Eqs. (4.78) and (4.79) and the linear independence of the set $\{\hat{\Gamma}_{ka}\}$ imply that there hold the constitutive equations for $\hat{\Gamma}_{ka}$ for all k and a

$$\frac{d_i \hat{\Gamma}_{ka}}{dt} = -g_{ka} \varpi_{ka} + T \sum_{b=1}^r \sum_{k \geq 1} \sum_{q \geq 1} R_{ab}^{(kq)} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Gamma}_{qb}} \right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}'} \quad (4.81)$$

This is an approximate form for the constitutive equation for $\hat{\Gamma}_{ka}$ and an example for the internal rate of change in $\hat{\Gamma}_{ka}$. It is also an example for the role played by the uncompensated heat in providing the constitutive equations for non-conserved variables $\hat{\Gamma}_{ka}$ in the thermodynamics of global irreversible processes in systems of a macroscopic size.

We thus see that if $\widehat{\Psi}$ is quadratic with respect to non-conserved variables $\widehat{\Gamma}_{ka}$ then the constitutive equations for $\widehat{\Gamma}_{ka}$ are linear in $\{\widehat{\Gamma}_{ka}\}$ and the corresponding quadratic form in Eq. (4.79) is the Rayleigh dissipation function for the global processes under consideration. If $\widehat{\Psi}$ is of order higher than quadratic the constitutive equations become non-linear. Therefore we see that study of $d\mathfrak{N}/dt$ for irreversible processes observed in nature and in the laboratory should be of great significance in understanding the energy dissipation mechanisms involved and the evolution of non-conserved macroscopic variables such as $\widehat{\Gamma}_{ka}$. For this reason $d\mathfrak{N}/dt$ should be an important object of attention in irreversible thermodynamics.

It is useful to note that Eq. (4.81) may be written as

$$\frac{d_i \widehat{\Gamma}_{ka}}{dt} = -g_{ka} \varpi_{ka} - \sum_{b=1}^r \sum_{k \geq 1} \sum_{q \geq 1} R_{ab}^{(kq)} \left(\frac{\partial \widehat{E}}{\partial \widehat{\Gamma}_{qb}} \right)_{\widehat{\Psi}, \widehat{V}, m, \widehat{\Gamma}'}, \quad (4.82)$$

which follows since

$$\left(\frac{\partial \widehat{E}}{\partial \widehat{\Gamma}_{qb}} \right)_{\widehat{\Psi}, \widehat{V}, m, \widehat{\Gamma}'} = - \left(\frac{\partial \widehat{\Psi}}{\partial \widehat{\Gamma}_{qb}} \right)_{\widehat{E}, \widehat{V}, m, \widehat{\Gamma}'} \left(\frac{\partial \widehat{\Psi}}{\partial \widehat{E}} \right)_{\widehat{V}, m, \widehat{\Gamma}}^{-1} \quad (4.83)$$

or equivalently there holds the extended Gibbs relation

$$d\widehat{E} = T d\widehat{\Psi} - p d\widehat{V} + \sum_{a=1}^r \widehat{\mu}_a dm_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\widehat{\Gamma}_{ka}. \quad (4.84)$$

Therefore since in the energy representation of the extended Gibbs relation the generalized potentials are given by the relation

$$-X_{qb} = \left(\frac{\partial \widehat{E}}{\partial \widehat{\Gamma}_{qb}} \right)_{\widehat{\Psi}, \widehat{V}, m, \widehat{\Gamma}'}, \quad (4.85)$$

if \widehat{E} is linear with respect to $\widehat{\Gamma}_{pc}$, that is, if there holds the relation

$$\left(\frac{\partial \widehat{E}}{\partial \widehat{\Gamma}_{qb}} \right)_{\widehat{\Psi}, \widehat{V}, m, \widehat{\Gamma}'} = \sum_{c=1}^r \sum_{p \geq 1} E_{bc}^{(qp)} \widehat{\Gamma}_{pc}, \quad (4.86)$$

then with the definition

$$C_{ac}^{(kp)} = \sum_{b=1}^r \sum_{q \geq 1} R_{ab}^{(kq)} E_{bc}^{(qp)} \quad (4.87)$$

the constitutive equation (4.81) can be expressed as

$$\frac{d_i \widehat{\Gamma}_{ka}}{dt} = -g_{ka} \varpi_{ka} - \sum_{c=1}^r \sum_{p \geq 1} C_{ac}^{(kp)} \widehat{\Gamma}_{pc}. \quad (4.88)$$

Here $C_{ac}^{(kp)}$ are phenomenological coefficients to be determined from experiment in the energy representation for the second law of thermodynamics. These constitutive equations or their non-linear generalizations can be applied to study global transport processes occurring in systems of a gross scale.

4.9.2 Non-Equilibrium Thermodynamic Functions

As in equilibrium thermodynamics, the non-equilibrium thermodynamic functions can be transformed into other thermodynamic functions more appropriate for the given condition of the system, if a Legendre transformation is made. For example, we define the non-equilibrium enthalpy density by the Legendre transformation

$$\hat{H} = \hat{E} + p\hat{V}, \quad (4.89)$$

which suggests the differential form for \hat{H}

$$d\hat{H} = Td\hat{\Psi} + \hat{V}dp + \sum_{a=1}^r \hat{\mu}_a dm_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\hat{\Gamma}_{ka}. \quad (4.90)$$

This differential form follows from the differential form for \hat{E} , Eq. (4.84). It means that \hat{H} is a characteristic function of the variable set $\hat{\Psi}$, p , m_a , and $\hat{\Gamma}_{ka}$ where $k \geq 1$ and $r \geq a \geq 1$. Similarly we may define the Helmholtz free energy density \hat{A}

$$\hat{A} = \hat{E} - T\hat{\Psi} \quad (4.91)$$

and the Gibbs free energy density \hat{G}

$$\hat{G} = \hat{H} - T\hat{\Psi}, \quad (4.92)$$

which mean the differential forms

$$d\hat{A} = -\hat{\Psi}dT - pd\hat{V} + \sum_{a=1}^r \hat{\mu}_a dm_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\hat{\Gamma}_{ka}, \quad (4.93)$$

$$d\hat{G} = -\hat{\Psi}dT + \hat{V}dp + \sum_{a=1}^r \hat{\mu}_a dm_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\hat{\Gamma}_{ka}. \quad (4.94)$$

Therefore \hat{A} and \hat{G} are non-equilibrium generalizations of the equilibrium Helmholtz work function and the equilibrium Gibbs free energy. Since these differential forms are exact it is possible to obtain generalized Maxwell relations holding when $\hat{\Gamma}_{ka} \neq 0$ or $X_{ka} \neq 0$. They are easy to derive.

4.9.3 New Thermodynamic Function $\hat{\Omega}$

A more interesting and useful quantity in the context of non-equilibrium, and, especially, for employing the molecular theory approach, is the new function (density) $\hat{\Omega} = \Omega/M$ obtained by the Legendre transformation

$$\begin{aligned}\hat{\Omega} &= \hat{G} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \hat{\Gamma}_{ka} \\ &= \hat{E} + p\hat{V} - T\hat{\Psi} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \hat{\Gamma}_{ka}.\end{aligned}\quad (4.95)$$

This function will be called the thermodynamic potential. With the help of the extended Gibbs relation (4.94) there follows the differential form

$$d\hat{\Omega} = -\hat{\Psi}dT + \hat{V}dp + \sum_{a=1}^r \hat{\mu}_a dm_a + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Gamma}_{ka} dX_{ka}.\quad (4.96)$$

In this scheme of description all the variables involved are intensive, but they consist of two distinctive subsets which are conjugate to each other: one subset consists of densities $(\hat{\Omega}, \hat{\Psi}, \hat{V}, m_a, \hat{\Gamma}_{ka})$; whereas the other consists of fields $(T, p, \hat{\mu}_a, X_{ka})$, which are intensive according to the terminology commonly understood in thermodynamics. The latter subset of variables, which we call the fields, characterizes the nature of equilibrium between global subsystems that make up the entire system in the gross scale and interact with each other across their boundaries. And through the equilibrium conditions between the subsystems the fields are experimentally characterized and given their physical realization. The differential form (4.96) means that $\hat{\Omega}$ is a characteristic function of the variable set $\{T, p, m_a, X_{ka} : k \geq 1; r \geq a \geq 1\}$.

According to the differential form for $\hat{\Omega}$

$$\hat{\mu}_a = \left(\frac{\partial \hat{\Omega}}{\partial m_a} \right)_{T, p, X},\quad (4.97)$$

which suggests that $\hat{\mu}_a$ is a generalized partial molar property of Ω . Furthermore, since it can be concluded from the physical grounds that $\hat{\Omega}$ is a first degree homogeneous function of $\{m_a\}$ it follows that

$$\hat{\Omega} = \sum_{a=1}^r \hat{\mu}_a m_a\quad (4.98)$$

and there consequently holds the equation

$$\sum_{a=1}^r m_a d\hat{\mu}_a = -\hat{\Psi}dT + \hat{V}dp + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Gamma}_{ka} dX_{ka}.\quad (4.99)$$

This is a generalization to non-equilibrium of the equilibrium Gibbs–Duhem equation to which it reduces if $dX_{ka} = 0$ or $\widehat{\Gamma}_{ka} = 0$ for all k and a . This equation can be applied to numerous investigations of irreversible thermodynamics, especially, with regard to the effects of non-conserved variables on conserved and related variables.

4.10 Summary

In this chapter the second law of thermodynamics stated literally by Clausius and Lord Kelvin has been given a mathematical representation valid for global irreversible processes in systems of a finite size. The notion of entropy applicable to reversible processes has been generalized to irreversible processes. In its place the calortropy has appeared as a non-equilibrium extension of the Clausius (equilibrium) entropy in the aforementioned mathematical representation. It also has a Pfaffian differential form in the thermodynamic space spanned by the conserved and non-conserved global macroscopic variables, and the Pfaffian differential (*i.e.*, differential one-form) for $\widehat{\Psi}$ is exact in the aforementioned thermodynamic space, but must be appended with the expression for the rate of uncompensated heat change $d\mathfrak{N}/dt$ that must be positive semi-definite for the second law of thermodynamics to be obeyed by the irreversible processes of interest. This latter inequality is absent in equilibrium thermodynamics because it vanishes if the processes are reversible. It is therefore incomplete to consider equilibrium thermodynamics generalized to non-equilibrium processes, simply because an extended Gibbs relation is obtained for a non-equilibrium extension of the Clausius entropy. The Pfaffian differential form for $\widehat{\Psi}$, or its equivalent forms, and the inequality for $d\mathfrak{N}/dt$ have provided mathematical machineries for investigating the irreversible thermodynamics of macroscopic processes in systems of a finite volume, and the accompanying constitutive equations for the non-conserved variables Γ_{ka} as well as for the intensive variables such as T , p , $\widehat{\mu}_a$, and X_{ka} have enabled us to describe the temporal evolution of the global irreversible processes subject to the laws of thermodynamics. The present chapter has therefore provided in a compact, thermodynamically consistent form the essence of the thermodynamics of global irreversible processes in systems of a finite volume, which is based on and deduced from the Clausius and Kelvin principles literally stated for the second law of thermodynamics. A local continuum theory version of the global theory presented in this chapter follows in the subsequent chapters in this work.

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5

Thermodynamics of Global Irreversible Processes

The second law of thermodynamics is now given a mathematical representation in the form of a calortropy differential accompanied by the rate of uncompensated heat for global irreversible processes [1] in macroscopic systems of a gross scale. We emphasize that the representation is not as yet local but global. Therefore it can only describe irreversible processes globally occurring in a gross system. The local representation of the second law of thermodynamics can be achieved if a local form of the global representation is obtained. This, however, requires some further preparations necessary for developing a local field theory of irreversible processes. It will be the subjects of Chapters 6 and 7.

The global mathematical representation of the second law of thermodynamics that we have achieved in the previous chapter can be further investigated in its global form for some deductions of practical utility, because in practical scientific activities it is often that we are more interested in what is going on in a macroscopic system of a gross scale than the local processes occurring therein, which contain much more detailed information of the system than warranted for the problem in hand. We would then like to learn about what the second law of thermodynamics can say about such macroscopic irreversible processes of a gross scale. This is the aim of the present chapter.

The desired deductions can be most conveniently made by means of the differential form for $\widehat{\Omega}$, which is reproduced here:

$$d\widehat{\Omega} = -\widehat{\Psi}dT + \widehat{V}dp + \sum_{a=1}^r \widehat{\mu}_a dm_a + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Gamma}_{ka} dX_{ka}, \quad (5.1)$$

or equivalently

$$d\hat{\Psi} = T^{-1} \left(d\hat{E} + pd\hat{V} - \sum_{a=1}^r \hat{\mu}_a dm_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d\hat{\Gamma}_{ka} \right) \quad (5.2)$$

It should be emphasized that the extended Gibbs relation (5.1) or (5.2) should be accompanied by the expression for the rate of uncompensated heat change (4.64) or (4.77), without which the extended Gibbs relation incompletely represents the second law of thermodynamics.

Being the differential form directly descending from the second law of thermodynamics and thus the progenitor of all other differential forms, the extended Gibbs relation for the calortropy density $\hat{\Psi}$ is the most natural one to work with, but it is not necessarily the most convenient. Whenever convenient, this differential form can be transformed to another more suitable by using a Legendre transformation, as we have seen in the previous chapter.

5.1 The Convexity of Ω

When constitutive relations are specified for a system, the thermodynamic potential Ω or its density $\hat{\Omega}$ acquires a characteristic mathematical structure that reflects the material properties of the substance. Since it is possible to investigate the mathematical structure with regards to the fields T and p and the mass densities m_a in the same manner as in equilibrium thermodynamics, we will pay attention only to the structure of $\hat{\Omega}$ with regards to the generalized potentials X_{ka} . The result of this investigation will provide us with a new feature absent in the equilibrium thermodynamics of reversible processes.

The differential form (5.1) suggests that if $\hat{\Omega}$ is known, the non-conserved variables $\hat{\Gamma}_{ka}$ can be deduced from the relation

$$\hat{\Gamma}_{ka} = \left(\frac{\partial \hat{\Omega}}{\partial X_{ka}} \right)_{T,p,M,X'} \quad (5.3)$$

From this follows the symmetry relation for non-conserved variables

$$\left(\frac{\partial \hat{\Gamma}_{ka}}{\partial X_{qb}} \right)_{T,p,M,X'} = \left(\frac{\partial \hat{\Gamma}_{qb}}{\partial X_{ka}} \right)_{T,p,M,X'} \quad (5.4)$$

This is in fact a generalized Maxwell relation. Inasmuch as the differential form (5.1) is a part of the mathematical representation of the second law of thermodynamics, the constitutive relations of the non-conserved variable densities are required by the second law to obey this symmetry relation

and also to have the particular geometrical structure of $\widehat{\Omega}$ implied by the symmetry relation; the other important component for the representation of the second law is the positivity of $d\mathfrak{N}/dt$. This point can be better seen if we use approximate linear constitutive relation, for example, Eq. (4.85) for $\widehat{\Gamma}_{ka}$ or Γ_{ka} , or equivalently

$$\widehat{\Gamma}_{ka} = - \sum_{b=1}^r \sum_{q \geq 1} R_{ab}^{(kq)} X_{qb}. \quad (5.5)$$

Here the matrix $(R_{ab}^{(kq)})$ is related to the inverse of the matrix $(E_{ab}^{(kq)})$ introduced in Chapter 4. The generalized Maxwell relation (5.4) then implies the symmetry relation between the material constants in the constitutive equations postulated:

$$R_{ab}^{(kq)} = R_{ba}^{(qk)}. \quad (5.6)$$

This relation in turn suggests that in the linear approximation for the constitutive equations for $\widehat{\Gamma}_{ka}$ the thermodynamic function Ω has a symmetrical quadratic geometric structure, especially, with regard to X_{ka} and X_{qb} in the manifold $\{T, p, m_a, X_{ka} : k \geq 1; r \geq a \geq 1\}$.

As $\Gamma_{ka} \rightarrow 0$ for all k and a , the thermodynamic function $\widehat{\Omega}$ tends to the equilibrium Gibbs free energy density. Furthermore, equilibrium with regard to X_{ka} is defined by the condition

$$\left. \left(\frac{\partial \widehat{\Omega}}{\partial X_{ka}} \right)_{T,p,m} \right|_{X=0} = 0 \quad (5.7)$$

and if

$$\det |R_{ab}^{(kq)}| > 0, \quad (5.8)$$

then at equilibrium

$$\det \left| \left(\frac{\partial^2 \widehat{\Omega}}{\partial X_{ka} \partial X_{qb}} \right)_{T,p,m} \right|_{X=0} > 0. \quad (5.9)$$

On the basis of this consideration we see that there is an intimate relation between the mathematical structure of the constitutive equations for the non-conserved variables $\widehat{\Gamma}_{ka}$ and the geometrical structure of $\widehat{\Omega}$ or the calortropy density $\widehat{\Psi}$. Especially, if the constitutive equations for $\widehat{\Gamma}_{ka}$ are non-linear with regards to the non-conserved variables, the non-linear dynamics of $\widehat{\Gamma}_{ka}$ should inevitably manifest itself in determining the mathematical structure of the thermodynamic function, and vice versa. And here lies an important motivation for studying the mutual relations of, for example, $\widehat{\Omega}$ and $\{\widehat{\Gamma}_{ka}\}$. This section merely serves as a harbinger of what lies ahead in the study of irreversible thermodynamics of global macroscopic processes.

5.2 Thermodynamics of Composite Systems

Suppose a system consisting of ν subsystems, each of which is characterized by the set of fields $(T^{(\alpha)}, p^{(\alpha)}, \hat{\mu}^{(\alpha)}, X_{ka}^{(\alpha)})$ and the conjugate set of densities $(\hat{\Psi}^{(\alpha)}, \hat{V}^{(\alpha)}, m_a^{(\alpha)}, \hat{\Gamma}_{ka}^{(\alpha)})$, where the superscript α denotes the subsystems, $1 \leq \alpha \leq \nu$. The meaning meanings of the subscripts are the same as before.

The subsystems are separated by boundaries which can be *diathermal, mechanically deformable, permeable to matter, and susceptible* to changes in $\hat{\Gamma}_{ka}^{(\alpha)}$. The precise meaning of the term ‘susceptible’ depends on the nature of the non-conserved variable $\hat{\Gamma}_{ka}^{(\alpha)}$. What is generally meant by the term is that a change in $\hat{\Gamma}_{ka}^{(\alpha)}$ in one subsystem is transmitted to another by the boundary in question through some physical mechanism. In connection with this it is useful to recall the discussion regarding the last equation of Eq. (3.7) given in Sec. 3.3.2, where it is indicated how measurement of X_{ka} may be in principle made.

The physical nature of the boundaries can be varied depending on the system we consider, and different circumstances will have different physical properties of the boundaries characteristic of the system of interest. The aforementioned properties of the boundaries are the least restrictive. We assume for simplicity of discussion that there is no chemical reaction in the system. Chemical reactions will be included when we apply the theory developed in this chapter to neural networks.

The thermodynamic potential of each subsystem is then described by the differential form (5.1). Since the densities are additive, the thermodynamic potential $\hat{\Omega}$ for the entire system is described by

$$\begin{aligned} d\hat{\Omega} &= \sum_{\alpha=1}^{\nu} d\hat{\Omega}^{(\alpha)} \\ &= \sum_{\alpha=1}^{\nu} \left(-\hat{\Psi}^{(\alpha)} dT^{(\alpha)} + \hat{V}^{(\alpha)} dp^{(\alpha)} + \sum_{a=1}^r \hat{\mu}_a^{(\alpha)} dm_a^{(\alpha)} \right) \\ &\quad + \sum_{\alpha=1}^{\nu} \sum_{a=1}^r \sum_{k \geq 1} \hat{\Gamma}_{ka}^{(\alpha)} dX_{ka}^{(\alpha)} \end{aligned} \tag{5.10}$$

The equivalent differential for \hat{E} is

$$\begin{aligned} d\hat{E} &= \sum_{\alpha=1}^{\nu} \left(T^{(\alpha)} d\hat{\Psi}^{(\alpha)} - p^{(\alpha)} d\hat{V}^{(\alpha)} + \sum_{a=1}^r \hat{\mu}_a^{(\alpha)} dm_a^{(\alpha)} \right) \\ &\quad + \sum_{\alpha=1}^{\nu} \sum_{a=1}^r \sum_{k \geq 1} X_{ka}^{(\alpha)} d\hat{\Gamma}_{ka}^{(\alpha)}. \end{aligned} \tag{5.11}$$

These differential forms are alternative forms of the extended Gibbs relation (5.2). They can be made the starting point of study in the thermodynamics of the heterogeneous system under consideration.

5.2.1 Thermodynamic Stability of Heterogeneous Systems

Having discovered and defined the notion of entropy for reversible processes, Clausius concluded his famous paper [2] by succinctly stating the second law of thermodynamics in the form¹ “*The entropy of the universe tends toward a maximum*”. This statement was in fact the starting point of another famous paper [3] in thermodynamics by J.W. Gibbs. Nevertheless, it is well known [4] that the statement has caused considerable confusion in the field of thermodynamics, and a little reflection on it should make us draw the conclusion that it is indeed vexing. For if the process is reversible, the system is in continuous equilibrium with the surroundings, and Clausius, in fact, defined the entropy for reversible processes only and thus for a system at equilibrium with its surroundings. Yet a quantity defined only for such a process in a system in continuous equilibrium with its surroundings is now said to increase toward a maximum despite the system having already attained the state of equilibrium with the attendant entropy, which is defined only at equilibrium. Therefore the entropy to which Clausius alludes in the aforementioned statement for the second law of thermodynamics must not be the same quantity as the entropy which he defined for reversible processes only and for systems at equilibrium. However, nowhere in Clausius’s writings on thermodynamics appears the precise mathematical definition of such an extended concept of entropy.

Reading through Clausius’s work on thermodynamics we find that he conceived the notion [5] of *disgregation* which he thought was associated with heat phenomena at the molecular level of description; for example, as a mass of a liquid vaporizes, the value of disaggregation of the matter increases compared with its value for the liquid. Thus it was thought to be a quantity increasing with increasing disorder in the system. It, however, is a quantity that he was not able to fully clarify and develop in a precise mathematical form from a molecular theory viewpoint, for example, with his mean free path theory, which apparently was meant to serve his thermodynamic theory as molecular theory foundations. Nevertheless, it should be inclusive of the entropy defined some ten years later. And it now appears that he meant the disaggregation for the term entropy in the aforementioned statement of the second law of thermodynamics, because with such a replacement of the term the statement becomes quite comprehensible.

¹ The original text in German is “Die Entropie der Welt strebt einem Maximum zu”

In Chapter 4 we have defined the *calortropy* for irreversible processes as a generalization of the entropy defined for reversible processes, and from this perspective, if the term entropy is replaced with the term calortropy in the Clausius statement mentioned, his statement becomes clear and free from the vexing feature. Therefore the original statement of Clausius about the second law of thermodynamics might be revised to the form² “*The calortropy of the universe tends toward a maximum*”. When the maximum is reached and the system is at equilibrium with the surroundings the calortropy has a value identical with the entropy of the system undergoing a reversible process. This is clear from the analysis made in Chapter 4.

In summary, according to the calortropy inequality (4.69) for a finite irreversible process occurring in an isolated system the calortropy increases toward a maximum, and if the system is either closed or open it reaches equilibrium with its surroundings at the maximum, where the value of calortropy becomes identical with the Clausius entropy because $\widehat{\Gamma}_{ka}^{(\alpha)} \rightarrow 0$.

Since for an infinitesimal irreversible process

$$d\Psi = T^{-1}(dQ + d\mathfrak{N}), \quad (5.12)$$

$$d\mathfrak{N} \geq 0 \quad (5.13)$$

with the equality holding for a reversible process or at equilibrium, if a system were irreversibly displaced from the state of equilibrium to neighboring states, the value of the calortropy would be decreased from its maximum value, that is, the equilibrium entropy. This statement also holds true for the calortropy density $\widehat{\Psi}$.

Therefore if the state of the system is varied from that of equilibrium into neighboring states in every possible manner, the equilibrium state of the system is characterized by the inequality

$$\delta\widehat{\Psi} \leq T^{-1}\delta Q, \quad (5.14)$$

where the equality holds at equilibrium and $\widehat{\Gamma}_{ka} = 0$ for all k and a . On use of the first law relation (3.13) and the definition (4.63) of Σ_l in Proposition 1 in Chapter 4 this inequality can be expressed as

$$T\delta\widehat{\Psi} - \delta\widehat{E} - p\delta\widehat{V} + \sum_{a=1}^r \widehat{\mu}_a \delta m_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \delta\widehat{\Gamma}_{ka} \leq -T\delta\mathfrak{N}. \quad (5.15)$$

² This revised statement, just like the original statement of Clausius, is too imprecise to base a scientific theory on it. It is given here to indicate that the original statement might have meant something like the term calortropy instead of entropy.

Because of Ineq. (5.13) it follows that

$$T\delta\hat{\Psi} - \delta\hat{E} - p\delta\hat{V} + \sum_{a=1}^r \hat{\mu}_a \delta m_a - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \delta\hat{\Gamma}_{ka} \leq 0. \quad (5.16)$$

Note that the left hand side of this inequality is for the case where there is no chemical reaction present. Therefore equilibrium at constant \hat{E} , \hat{V} , m_a , and $\hat{\Gamma}_{ka} = 0$ is characterized by the inequality

$$(\delta\hat{\Psi})_{\hat{E}, \hat{V}, m, \Gamma} \leq 0 \quad (5.17)$$

for all conceivable variations from the state of equilibrium. If $\hat{\Psi}$, \hat{V} , m_a , and $\hat{\Gamma}_{ka}$ are kept constant, then equilibrium, where $\hat{\Gamma}_{ka} = 0$, is equivalently characterized by

$$(\delta\hat{E})_{\hat{\Psi}, \hat{V}, m, \Gamma} \geq 0. \quad (5.18)$$

Similar inequalities hold for \hat{H} , \hat{A} , and \hat{G} . In particular, on use of the Legendre transformation (4.95) the inequality (5.17) or (5.18) gives rise to the inequality for $\hat{\Omega}$:

$$(\delta\hat{\Omega})_{T, p, m, X} \geq 0. \quad (5.19)$$

The inequalities developed above can be applied to studying the stability of equilibrium and equilibrium conditions. If $\delta\hat{\Omega} > 0$ equilibrium is said to be stable; if $\delta\hat{\Omega} = 0$ it is marginal; and if $\delta\hat{\Omega} < 0$ it is unstable. Similar criteria of thermodynamic stability of equilibrium apply to other inequalities of \hat{E} , \hat{H} , and so on.

If the first variation of a thermodynamic function from its equilibrium value vanishes, for example, if

$$\delta\hat{\Omega} = 0,$$

the stability of equilibrium is determined by the inequality

$$(\delta^2\hat{\Omega})_{T, p, m, X} \geq 0. \quad (5.20)$$

If the equality holds then the system is said to be thermodynamically marginally stable or of neutral stability; if $\delta^2\hat{\Omega} > 0$ then it is thermodynamically stable and if $\delta^2\hat{\Omega} < 0$ thermodynamically unstable. These thermodynamic stability criteria can be stated similarly in terms of the inequalities of $\delta^2\hat{E}$, $\delta^2\hat{A}$, and so on.

For example, expressed in terms of \hat{E} , if the system is thermodynamically stable with regards to all variations from equilibrium then

$$\Delta\hat{E} > 0; \quad (5.21)$$

if it is marginally stable or neutral then

$$\Delta \hat{E} = 0; \quad (5.22)$$

and if it is unstable then

$$\Delta \hat{E} < 0. \quad (5.23)$$

These stability conditions imply inequalities for some material properties of the substance.

Some examples are given below for equilibrium criteria. Let us consider a system consisting of two subsystems. To make the notation simple we will denote the set of variables in the thermodynamic space for the system by

$$\begin{aligned} \left\{ x_i^{(1)}, x_i^{(2)} \right\} &= \left(v^{(1)}, T^{(1)}, c_1^{(1)}, \dots, c_r^{(1)}, \Gamma_{11}^{(1)}, \dots, \Gamma_{1r}^{(1)}, \dots; \right. \\ &\quad \left. v^{(2)}, T^{(2)}, c_1^{(2)}, \dots, c_r^{(2)}, \Gamma_{11}^{(2)}, \dots, \Gamma_{1r}^{(2)}, \dots \right), \end{aligned}$$

where the superscript denotes the subsystem. Since at equilibrium $\delta \hat{E} = 0$, the second variation should be used for determining the stability criteria of the system. Thus we obtain

$$\delta^2 \hat{E} \left(x_1^{(1)}, \dots, x_l^{(2)} \right) = \frac{1}{2} \sum_{i=1}^l \sum_{j=1}^l \left(\frac{\partial^2 \hat{E}^{(1)}}{\partial x_j^{(1)} \partial x_i^{(1)}} + \frac{\partial^2 \hat{E}^{(2)}}{\partial x_j^{(2)} \partial x_i^{(2)}} \right) \delta x_i^{(1)} \delta x_j^{(1)}, \quad (5.24)$$

since $\hat{E} = \hat{E}^{(1)} + \hat{E}^{(2)}$ and $\delta x_i^{(1)} = -\delta x_i^{(2)}$ owing to the fact that the total variables are kept fixed for the whole system. The heat capacity of a substance is defined by

$$C_v^{(\alpha)} = \left(\frac{\partial \hat{E}^{(\alpha)}}{\partial T} \right)_{\hat{V}, m, \hat{r}} \quad (5.25)$$

and by using the extended Gibbs relation for the internal energy, we obtain from Eq. (5.24) the expression

$$\begin{aligned} \delta^2 \hat{E} &= \frac{T}{2} \left(\frac{1}{C_v^{(1)}} + \frac{1}{C_v^{(2)}} \right) \left(\delta \hat{\Psi}^{(1)} \right)^2 \\ &\quad - \frac{1}{2} \left[\left(\frac{\partial p}{\partial v^{(1)}} \right)_{\xi^{(1)}} + \left(\frac{\partial p}{\partial v^{(2)}} \right)_{\xi^{(2)}} \right] \left(\delta \hat{v}^{(1)} \right)^2 \\ &\quad + \frac{1}{2} \left[\left(\frac{\partial \mu_1}{\partial c_1^{(1)}} \right)_{\xi^{(1)}} + \left(\frac{\partial \mu_1}{\partial c_2^{(2)}} \right)_{\xi^{(2)}} \right] \left(\delta c_1^{(1)} \right)^2 + \dots \\ &\quad - \frac{1}{2} \sum_{k \geq 1} \left[\left(\frac{\partial X_{kr}}{\partial \hat{\Gamma}_{kr}^{(1)}} \right)_{\xi^{(1)}} + \left(\frac{\partial X_{kr}}{\partial \hat{\Gamma}_{kr}^{(2)}} \right)_{\xi^{(2)}} \right] \left(\delta \hat{\Gamma}_{kr}^{(1)} \right)^2, \quad (5.26) \end{aligned}$$

where the subscript $\xi^{(i)}$ ($i = 1, 2$) stands for the variable set excluding the variable used in differentiation. Thus for $\delta^2 \hat{E} > 0$ to hold, that is, for the equilibrium to be stable thermodynamically, it is necessary that

$$\frac{1}{C_v^{(1)}} + \frac{1}{C_v^{(2)}} > 0, \quad (5.27)$$

$$-\left(\frac{\partial p}{\partial v^{(1)}}\right)_{\xi^{(1)}} - \left(\frac{\partial p}{\partial v^{(2)}}\right)_{\xi^{(2)}} > 0, \quad (5.28)$$

$$\left(\frac{\partial \mu_1}{\partial c_1^{(1)}}\right)_{\xi^{(1)}} + \left(\frac{\partial \mu_1}{\partial c_2^{(2)}}\right)_{\xi^{(2)}} > 0, \quad etc., \quad (5.29)$$

$$-\left(\frac{\partial X_{kr}}{\partial \hat{\Gamma}_{kr}^{(1)}}\right)_{\xi^{(1)}} - \left(\frac{\partial X_{kr}}{\partial \hat{\Gamma}_{kr}^{(2)}}\right)_{\xi^{(2)}} > 0, \quad etc. \quad (5.30)$$

Therefore if the system is homogeneous so that there is no distinction between the subsystems then the necessary conditions for the thermodynamic stability are

$$C_v > 0, \quad (5.31)$$

$$-\left(\frac{\partial p}{\partial v}\right)_{\hat{\Psi}, c, \hat{\Gamma}} > 0, \quad (5.32)$$

$$\left(\frac{\partial \mu_1}{\partial c_1}\right)_{\hat{\Psi}, v, c, \hat{\Gamma}} > 0, \quad etc., \quad (5.33)$$

$$-\left(\frac{\partial X_{ki}}{\partial \hat{\Gamma}_{ki}}\right)_{\hat{\Psi}, v, c, \hat{\Gamma}'} > 0, \quad etc. \quad (5.34)$$

The first three conditions in the stability criteria are formally similar to those in the equilibrium thermodynamics except for the conditions of $\hat{\Gamma}_{ki} = \text{constant}$. The last one gives rise to the conditions to be met by the constitutive equations for the generalized potentials. This set of conditions are the constraints imposed by the second law of thermodynamics in constructing the phenomenological constitutive relations for the intensive variables. Here lies one of the important motivations for formulating the thermodynamics of irreversible processes.

The inequalities obtained earlier with regard to thermodynamic stability can be considered to be a part of stability criteria that we can formulate if, for example, the calortropy density $\hat{\Psi}$ is regarded as a Lyapounov function. Thus in the phraseology based on Inequality (5.14) the system is said to be thermodynamically stable if there also holds the inequality for the second variation of $\hat{\Psi}$ which is positive:

$$\left(\delta^2 \hat{\Psi}\right)_{\hat{E}, \hat{V}, m, \hat{\Gamma}} > 0; \quad (5.35)$$

unstable if

$$\left(\delta^2 \widehat{\Psi}\right)_{\widehat{E}, \widehat{V}, m, \widehat{\Gamma}} > 0; \quad (5.36)$$

and neutral if

$$\left(\delta^2 \widehat{\Psi}\right)_{\widehat{E}, \widehat{V}, m, \widehat{\Gamma}} = 0. \quad (5.37)$$

The inequalities (5.14), (5.35)–(5.37) form a set of thermodynamic stability criteria which may be used to examine the implications of the second law of thermodynamics for the evolution of global irreversible processes. Some examples of the thermodynamic stability criteria will be considered in the sections of applications of the present theory.

5.2.2 Equilibrium Conditions

We consider the system consisting of ν subsystems (*e.g.*, phases) introduced at the beginning of the previous section. Since the densities $\widehat{\Psi}$, \widehat{V} , $m = (m_1, m_2, \dots, m_r)$, and $\widehat{\Gamma}_{ka}$ for the entire system must be given by the corresponding densities of the subsystems

$$\begin{aligned} \widehat{\Psi} &= \sum_{\alpha=1}^{\nu} \widehat{\Psi}^{(\alpha)}, \\ \widehat{V} &= \sum_{\alpha=1}^{\nu} \widehat{V}^{(\alpha)}, \\ m_a &= \sum_{\alpha=1}^{\nu} m_a^{(\alpha)} \quad (a = 1, \dots, r), \end{aligned} \quad (5.38)$$

$$\widehat{\Gamma}_{ka} = \sum_{\alpha=1}^{\nu} \widehat{\Gamma}_{ka}^{(\alpha)} \quad (k \geq 1; a = 1, \dots, r),$$

and, moreover, must remain constant if the system is isolated, it follows that

$$\delta\widehat{\Psi} = 0, \quad \delta\widehat{V} = 0, \quad \delta m = 0, \quad \delta\widehat{\Gamma}_{ka} = 0. \quad (5.39)$$

Under these conditions Inequality (5.15) applies. It therefore follows that

$$\begin{aligned} \sum_{\alpha=1}^{\nu} \left(-T^{(\alpha)} \delta\widehat{\Psi}^{(\alpha)} + p^{(\alpha)} \delta\widehat{V}^{(\alpha)} + \sum_{a=1}^r \widehat{\mu}_a^{(\alpha)} \delta m_a^{(\alpha)} \right) \\ + \sum_{\alpha=1}^{\nu} \sum_{a=1}^r \sum_{k \geq 1} X_{ka}^{(\alpha)} \delta\widehat{\Gamma}_{ka}^{(\alpha)} \geq 0. \end{aligned} \quad (5.40)$$

If the subsystems are in internal equilibrium then

$$X_{ka}^{(\alpha)} = 0, \quad \delta\widehat{\Gamma}_{ka}^{(\alpha)} = 0 \quad (5.41)$$

for all k and a , and Inequality (5.40) reduces to the equilibrium theory form

$$\sum_{\alpha=1}^{\nu} \left(-T^{(\alpha)} \delta\widehat{\Psi}^{(\alpha)} + p^{(\alpha)} \delta\widehat{V}^{(\alpha)} + \sum_{a=1}^r \widehat{\mu}_a^{(\alpha)} \delta m_a^{(\alpha)} \right) \geq 0. \quad (5.42)$$

If the conditions (5.39) are used in Inequality (5.40) it follows that

$$\begin{aligned} & \sum_{\alpha=1}^{\nu} (\lambda_{\widehat{\Psi}} - T^{(\alpha)}) \delta\widehat{\Psi}^{(\alpha)} + \sum_{\alpha=1}^{\nu} (p^{(\alpha)} - \lambda_{\widehat{V}}) \delta\widehat{V}^{(\alpha)} \\ & + \sum_{\alpha=1}^{\nu} \sum_{a=1}^r (\widehat{\mu}_a^{(\alpha)} - \lambda_{m_a}) \delta m_a^{(\alpha)} + \sum_{\alpha=1}^{\nu} \sum_{a=1}^r \sum_{k \geq 1} (X_{ka}^{(\alpha)} - \lambda_{X_{ka}}) \delta\widehat{\Gamma}_{ka}^{(\alpha)} \geq 0. \end{aligned} \quad (5.43)$$

Here $\lambda_{\widehat{\Psi}}$, $\lambda_{\widehat{V}}$, λ_{m_a} , and $\lambda_{X_{ka}}$ are Lagrange multipliers for the constraints. Since $\widehat{\Psi}^{(\alpha)}$, $\widehat{V}^{(\alpha)}$, $m_a^{(\alpha)}$, and $\widehat{\Gamma}_{ka}^{(\alpha)}$ are independent and their variations are arbitrary it follows that for the inequality to hold we must have

$$\lambda_{\widehat{\Psi}} = T^{(\alpha)}, \quad \lambda_{\widehat{V}} = p^{(\alpha)}, \quad \lambda_{m_a} = \widehat{\mu}_a^{(\alpha)}, \quad \lambda_{X_{ka}} = X_{ka}^{(\alpha)} \quad (5.44)$$

forall α . That is,

$$\begin{aligned} T^{(1)} &= T^{(2)} = \cdots = T^{(\nu)}, \\ p^{(1)} &= p^{(2)} = \cdots = p^{(\nu)}, \\ \widehat{\mu}_a^{(1)} &= \widehat{\mu}_a^{(2)} = \cdots = \widehat{\mu}_a^{(\nu)} \quad (a = 1, \dots, r), \\ X_{ka}^{(1)} &= X_{ka}^{(2)} = \cdots = X_{ka}^{(\nu)} \quad (k \geq 1; a = 1, \dots, r) \end{aligned} \quad (5.45)$$

for the system to be in mutual equilibrium. If the subsystems are in internal equilibrium in which $X_{ka}^{(\alpha)} = 0$, the equilibrium conditions in Eq. (5.45) reduce to the equilibrium conditions known in the classical thermodynamics, namely, equilibrium thermodynamics. The equilibrium phase rule of Gibbs [3] is therefore implied by the conditions in Eq. (5.45) if $X_{ka}^{(\alpha)} = 0$ for all α , k , and a . It must be recognized that conditions (5.45) are not equilibrium conditions, but stationary state conditions in which the whole system is maintained at an internal non-equilibrium state in which $X_{ka}^{(\alpha)}$ do not vary over the entire set of subsystems. If the conditions in Eq. (5.45) are satisfied, clearly there holds the equation

$$\delta\Omega = 0. \quad (5.46)$$

Therefore the conditions in Eq. (5.45) are necessary and sufficient for Eq. (5.46) to hold.

5.3 Some Examples of Global Processes

5.3.1 Global Thermodynamic Forces

In the previous chapter where the proposition for Σ_l was made, the thermodynamic forces ω_{ka} and ϖ_{ka} were formally introduced. To make them more concrete from the physical standpoint and to facilitate applications to practical problems it is necessary to identify them in a more concrete form and express them in precise mathematical forms. This aim can be fulfilled if the global evolution equations and calortropy balance equation are derived from the local equations arising from the kinetic theory consideration. This approach was taken in Ref. [1]. According to the result of Ref. [1] the leading members of the set of thermodynamic forces, which appear in many of practical applications of the theory, are identified as follows:

$$\omega_{1a} = \chi_u, \quad \omega_{2a} = \chi_v, \quad \omega_{3a} = \chi_{\ln T}, \quad \omega_{4a} = \chi_{\hat{\mu}_{\phi a}},$$

$$\varpi_{ka} = -\chi_{Xa}, \quad (5.47)$$

where the global thermodynamic forces are defined by the volume integrals, and in fact the volume averages, of local thermodynamic forces (*i.e.*, gradients of velocity, temperature, chemical potentials, and generalized potentials)

$$\chi_u = -V^{-1} \int_V d\mathbf{r} \nabla \mathbf{u}, \quad (5.48)$$

$$\chi_v = -V^{-1} \int_V d\mathbf{r} \nabla \cdot \mathbf{u}, \quad (5.49)$$

$$\chi_{\ln T} = -V^{-1} \int_V d\mathbf{r} \nabla \ln T, \quad (5.50)$$

$$\chi_{\hat{\mu}_{\phi a}} = -V^{-1} \int_V d\mathbf{r} \nabla (\hat{\mu}_{\phi a} T^{-1}), \quad (5.51)$$

$$\chi_{Xa} = -V^{-1} \int_V d\mathbf{r} \nabla (X_{ka} T^{-1}). \quad (5.52)$$

The volume averages of the local thermodynamic forces may be explicitly evaluated once the flow configuration is specified. Here they are evaluated for the flow configuration depicted in Fig. 5.1.

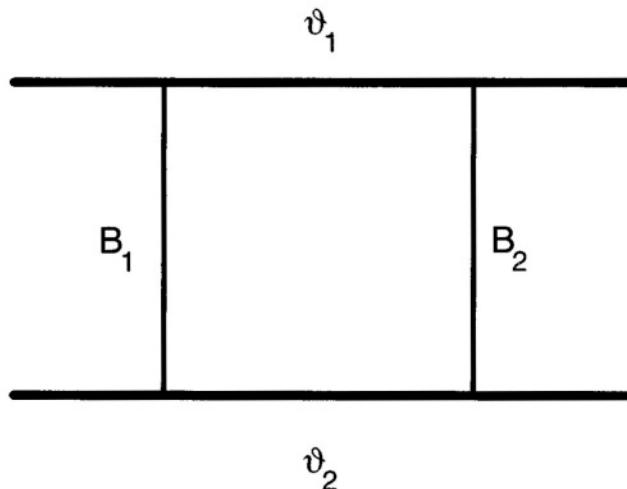


FIGURE 5.1. Schematic representation of a system where flow occurs. The boundaries B_1 and B_2 may be movable, diathermal, and permeable to matter. The boundaries ϑ_1 and ϑ_2 are rigid, adiabatic, and impermeable to matter, but may move in opposite directions in parallel with the channel axis, if the system is sheared in plane Couette flow configuration. The vertical walls ϑ_3 and ϑ_4 of the same nature as ϑ_1 and ϑ_2 are not shown in the figure.

Temperature Gradient

We assume that the temperature distributions are uniform in the boundary surfaces B_1 and B_2 of area B , which are respectively at temperature T_0 and T_L , and boundaries ϑ_1 and ϑ_2 are adiabatic. The axial direction is assumed to be parallel to the x axis. The length of the system is L and the origin of the coordinate system is assumed to be located at the lower left corner of the system. It is then appropriate to express the volume element in the form

$$d\mathbf{r} = dBdx,$$

where dB is the surface element. It is easy to calculate the volume integral for $\chi_{\ln T}$, which takes the form

$$\chi_{\ln T} = -\frac{B}{V} \ln\left(\frac{T_L}{T_0}\right) \delta_x, \quad (5.53)$$

where δ_x is the unit vector in the x direction of the Cartesian coordinate system. If the temperature difference is not too large, $\chi_{\ln T}$ may be written as

$$\chi_{\ln T} = -\frac{\Delta T}{T_0 L} \delta_x + O(\Delta T^2), \quad (5.54)$$

where

$$\Delta T = T_L - T_0. \quad (5.55)$$

This result can be easily generalized to a two- or three-dimensional flow configuration. Similarly to the calculation performed for $\chi_{\ln T}$ we obtain the thermodynamic force defined by

$$\chi_{T^{-1}} = -V^{-1} \int_V d\mathbf{r} \nabla T^{-1}, \quad (5.56)$$

which is easily calculated for the flow configuration under consideration

$$\chi_{T^{-1}} = -\frac{1}{L} \left(\frac{1}{T_L} - \frac{1}{T_0} \right) = -\frac{\Delta T}{T_0^2 L} \left[1 + O\left(\frac{\Delta T}{T_0}\right) \right]. \quad (5.57)$$

Chemical Potential Gradient

We assume the same flow configuration as for the temperature gradient considered earlier. Then we find

$$\chi_{\hat{\mu}_{\phi a}} = -\frac{B}{V} \left[\left(\frac{\hat{\mu}_{\phi a}}{T} \right)_L - \left(\frac{\hat{\mu}_{\phi a}}{T} \right)_0 \right] \delta_x. \quad (5.58)$$

If the chemical potential $\hat{\mu}_{\phi a}$ is decomposed into the material and external force parts as in

$$\hat{\mu}_{\phi a} = \hat{\mu}_a + \phi_a, \quad (5.59)$$

where ϕ_a is the potential energy per mass of a , then $\chi_{\hat{\mu}_{\phi a}}$ can be also split into two parts, material and the external force

$$\chi_{\hat{\mu}_{\phi a}} = -L^{-1} \left[\left(\frac{\hat{\mu}_a}{T} \right)_L - \left(\frac{\hat{\mu}_a}{T} \right)_0 \right] \delta_x - L^{-1} \left[\left(\frac{\phi_a}{T} \right)_L - \left(\frac{\phi_a}{T} \right)_0 \right] \delta_x, \quad (5.60)$$

where the first part gives rise to the material gradient, and the second part to the external force part. If the chemical potential is assumed to be that of an ideal gas or solution the material part of the gradient may be written as

$$\left(\frac{\hat{\mu}_a}{T} \right)_L - \left(\frac{\hat{\mu}_a}{T} \right)_0 = k_B \ln \left(\frac{\xi_a^L}{\xi_a^0} \right) \quad (5.61)$$

$$= k_B \frac{\Delta \xi_a}{\xi_a^0} + O(\Delta \xi_a^2),$$

where $\Delta \xi_a = \xi_a^L - \xi_a^0$ with ξ_a^L and ξ_a^0 denoting the mole fraction of species a at $x = L$ and $x = 0$, respectively. More generally, if activities are used instead of the mole fractions for chemical potentials then

$$\left(\frac{\hat{\mu}_i}{T} \right)_L - \left(\frac{\hat{\mu}_i}{T} \right)_0 = k_B \ln \left(\frac{a_i^L}{a_i^0} \right), \quad (5.62)$$

where a_i^L and a_i^0 are, respectively, the activity of species i at $x = L$ and $x = 0$.

On the other hand, the external force part may be written as

$$\left(\frac{\phi_a}{T}\right)_L - \left(\frac{\phi_a}{T}\right)_0 = \frac{\Delta T}{T_0^2} \phi_a^L + \frac{\Delta \phi_a}{T_0} + O(\Delta T^2),$$

where

$$\Delta \phi_a = \phi_a(L) - \phi_a(0).$$

Insertion of these results into Eq. (5.60) yields the formula for $\chi_{\hat{\mu}_{\phi_a}}$

$$\chi_{\hat{\mu}_{\phi_a}} = - \left(\frac{k_B}{L \xi_a^0} \Delta \xi_a + \frac{\phi_a^L}{T_0^2 L} \Delta T + \frac{1}{T_0 L} \Delta \phi_a \right) \delta_x. \quad (5.63)$$

In the case of an isothermal process we have

$$\chi_{\hat{\mu}_{\phi_a}} = - \left(\frac{k_B}{L \xi_a^0} \Delta \xi_a + \frac{1}{T_0 L} \Delta \phi_a \right) \delta_x. \quad (5.64)$$

It is also straightforward to generalize this formula to the case of two- or three-dimensional flow configurations.

Volume Change

The thermodynamic force associated with the volume change is also readily calculated:

$$\chi_v = - \frac{B}{V} (u_x^L - u_x^0) = - \frac{\Delta u_x}{L}. \quad (5.65)$$

This may be recast into the more conventional form in terms of the rate of volume change:

$$\chi_v = - \frac{d \ln V}{dt}. \quad (5.66)$$

Tensorial Thermodynamic Gradients

The volume averages of tensors such as $\nabla \mathbf{u}$ and ∇X_{ka} yield global tensorial thermodynamic forces associated with shearing, for example, in the case of $\nabla \mathbf{u}$. The calculation of the averages can proceed in the same manner for the vectorial thermodynamic forces already considered. In the flow configuration depicted in Fig. 5.1 the boundaries B_1 and B_2 are absent and consequently the flow system is open in the direction of the x coordinate, but the boundaries ϑ_1 and ϑ_2 perpendicular to the y axis move at velocity $\pm u/2$ in opposite directions parallel to the x axis, while the walls ϑ_3 and ϑ_4 perpendicular to the z axis remain stationary. The gap between the

boundaries ϑ_1 and ϑ_2 is assumed to be D . The volume average of $\nabla \mathbf{u}$ is then evaluated as follows:

$$\begin{aligned}\chi_u &= -\lim_{V \rightarrow \infty} V^{-1} \int_V d\mathbf{r} \left[\delta_x \frac{\partial \mathbf{u}}{\partial x} + \delta_y \frac{\partial \mathbf{u}}{\partial y} + \delta_z \frac{\partial \mathbf{u}}{\partial z} \right] \\ &= -\lim_{V \rightarrow \infty} V^{-1} \left[\int_{B_x} dB_x \delta_x \mathbf{u}(B_x) + \int_{B_y} dB_y \delta_y \mathbf{u}(B_y) \right. \\ &\quad \left. + \int_{B_z} dB_z \delta_z \mathbf{u}(B_z) \right],\end{aligned}\quad (5.67)$$

where B_i ($i = x, y, z$) is the boundary perpendicular to the i -axis and $\mathbf{u}(B_i)$ is the velocity at the boundary B_i . If the flow is laminar in the channel described then the flow velocity \mathbf{u} has no y and z component. Consequently

$$\mathbf{u}(B_i) = u_x(B_i) \delta_x + 0 \times \delta_y + 0 \times \delta_z.$$

Moreover,

$$\int_{B_x} dB_x u_x(B_i) = B [u_x(B_2) - u_x(B_1)] = 0$$

because the flow is translationally symmetric in the case of infinitely long channel under consideration and hence $u_x(B_2) = u_x(B_1)$. Here it must be remembered that the boundaries B_1 and B_2 are located at the $x = \pm\infty$. Similarly,

$$\int_{B_z} dB_z \delta_z \mathbf{u}(B_z) = 0.$$

The remaining contribution to χ_u in Eq. (5.67) is given by the formula

$$\begin{aligned}V^{-1} \int_{B_y} dB_y \mathbf{u}(B_y) &= (BL)^{-1} \int_0^W dz \int_0^L dx [u_x(\vartheta_2) - u_x(\vartheta_1)] \delta_x \\ &= (BL)^{-1} LW [u_x(\vartheta_2) - u_x(\vartheta_1)] \delta_x \\ &= \frac{W}{B} u \delta_x,\end{aligned}$$

where W is the channel width in the z direction, that is, the gap between the boundaries ϑ_3 and ϑ_4 . Here it must be noted that $u_x(\vartheta_2) = -u_x(\vartheta_1) = u/2$. Since $V = LWD = BL$ we finally obtain

$$\chi_u = -\frac{u}{D} \delta_x \delta_y. \quad (5.68)$$

Therefore χ_u is seen to be proportional to the shear rate $\gamma = u/D$ for the channel flow under consideration. For this result it must be remembered that a laminar flow is implicit. If the flow is not laminar or Newtonian then the formula for χ_u will be different.

Tensorial Thermodynamic Gradient in the Presence of Non-Uniform Temperature

It is occasionally necessary to consider the tensorial gradient $\nabla(\mathbf{u}/T)$ or its volume average. Therefore it is useful to evaluate the volume average for the use of later applications of the theory of global processes. We consider the same flow configuration as for the tensorial gradient examined earlier, to which the boundary conditions on temperature must be added. We first consider the case where $T_1 = T(\vartheta_1) > T_2 = T(\vartheta_2)$ whereas the temperature is translationally invariant in the axial direction of the channel. The thermodynamic force associated with the tensorial gradient in question is found to be given by

$$\begin{aligned}\chi_{\bar{\mathbf{u}}} &= - \lim_{V \rightarrow \infty} V^{-1} \int_V d\mathbf{r} \left[\delta_x \frac{\partial}{\partial x} \frac{\mathbf{u}}{T} + \delta_y \frac{\partial}{\partial y} \frac{\mathbf{u}}{T} + \delta_z \frac{\partial}{\partial z} \frac{\mathbf{u}}{T} \right] \\ &= - \lim_{V \rightarrow \infty} V^{-1} \left[\int_{B_x} dB_x \delta_x \frac{\mathbf{u}}{T}(B_x) + \int_{B_y} dB_y \delta_y \frac{\mathbf{u}}{T}(B_y) \right. \\ &\quad \left. + \int_{B_z} dB_z \delta_z \frac{\mathbf{u}}{T}(B_z) \right].\end{aligned}\quad (5.69)$$

Since $u_y = u_z = 0$ we find

$$\begin{aligned}\int_{B_x} dB_x \frac{\mathbf{u}}{T}(B_x) &= \int_0^W dz \int_0^D dy \left[\frac{u_x}{T}(B_2) - \frac{u_x}{T}(B_1) \right] \\ &= W \int_0^D dy \frac{u_x(y)}{T(y)} \\ &= DW \overline{\left(\frac{u_x}{T} \right)},\end{aligned}\quad (5.70)$$

where

$$\overline{\left(\frac{u_x}{T} \right)} = D^{-1} \int_0^D dy \frac{u_x(y)}{T(y)}, \quad (5.71)$$

and

$$\int_{B_z} dB_z \frac{\mathbf{u}}{T}(B_z) = \int_0^L dx \int_0^D dy \left[\frac{u_x}{T}(\vartheta_4) - \frac{u_x}{T}(\vartheta_3) \right] = 0 \quad (5.72)$$

owing to $(u_x/T)(\vartheta_4) = (u_x/T)(\vartheta_3)$. On the other hand, we find

$$\begin{aligned} \int_{B_y} dB_y \frac{\mathbf{u}}{T}(B_y) &= \int_0^L dx \int_0^W dz \left[\frac{u_x}{T}(\vartheta_2) - \frac{u_x}{T}(\vartheta_1) \right] \\ &= \frac{1}{2} LW u \left(\frac{1}{T_1} + \frac{1}{T_2} \right) \\ &= \frac{1}{2} LW u \left[\frac{2}{T_2} - \frac{\Delta T}{T_2^2} + O(\Delta T^2) \right], \end{aligned} \quad (5.73)$$

where

$$\Delta T = T_1 - T_2.$$

Therefore we finally obtain the formula

$$\begin{aligned} \chi_{\bar{u}} &= -\frac{u}{DT_2} \left(1 - \frac{\Delta T}{2T_2} \right) \delta_x \delta_y - \lim_{L \rightarrow \infty} L^{-1} \overline{\left(\frac{u_x}{T} \right)} \delta_x \delta_x \\ &= -\frac{u}{DT_2} \left(1 - \frac{\Delta T}{2T_2} \right) \delta_x \delta_y, \end{aligned} \quad (5.74)$$

since the mean value $\overline{(u_x/T)}$ is a constant independent of L and therefore the limit vanishes. It should be emphasized that the temperature difference is in the y direction.

We now consider the case where the temperature gradient is in the direction of flow. In this case, since $T_L = T(B_2)$ and $T_0 = T(B_1)$, with the definition of mean flow through area B

$$\begin{aligned} \bar{u}_x &= B^{-1} \int_0^W dz \int_0^D dy u_x(y) \\ &= D^{-1} \int_0^D dy u_x(y), \end{aligned} \quad (5.75)$$

we obtain

$$\begin{aligned} V^{-1} \int_{B_x} dB_x \frac{\mathbf{u}}{T}(B_x) &= \frac{1}{2} \bar{u}_x \left(\frac{1}{T_L} + \frac{1}{T_0} \right) \delta_x \\ &= \frac{1}{2} \bar{u}_x \left(\frac{2}{T_0} - \frac{\Delta T}{T_0^2} + O(\Delta T^2) \right) \delta_x \end{aligned} \quad (5.76)$$

with $\Delta T = T_L - T_0$. Since $(u_x/T)(\vartheta_4) = (u_x/T)(\vartheta_3)$ still holds, the integration over surface B_z vanishes. Since $(u_x/T)(\vartheta_1) = -(u_x/T)(\vartheta_2) = u/2T$ at every point in ϑ_1 and ϑ_2 , the integral over the surface B_y is given by

$$\begin{aligned} \int_{B_y} dB_y \frac{\mathbf{u}}{T}(B_y) &= \delta_x \int_0^L dx \int_0^W dz \left[\frac{u_x}{T}(\vartheta_2) - \frac{u_x}{T}(\vartheta_1) \right] \\ &= LWu\overline{T^{-1}}\delta_x, \end{aligned} \quad (5.77)$$

where

$$\overline{T^{-1}} = L^{-1} \int_0^L dx T^{-1}(x). \quad (5.78)$$

It then follows that

$$\chi_{\bar{u}} = -\frac{\bar{u}_x}{T_0} \left(1 - \frac{\Delta T}{2T_0} \right) \delta_x \delta_x - \frac{u}{D} \overline{T^{-1}} \delta_x \delta_y. \quad (5.79)$$

If the temperature profile is linear we find

$$\overline{T^{-1}} = \frac{1}{\Delta T} \ln \left(\frac{T_L}{T_0} \right) = \frac{1}{T_0} \left[1 + O\left(\frac{\Delta T}{T_0}\right) \right] \quad (5.80)$$

and hence

$$\chi_{\bar{u}} = -\frac{\bar{u}_x}{T_0} \left(1 - \frac{\Delta T}{2T_0} \right) \delta_x \delta_x - \frac{u}{DT_0} \delta_x \delta_y \quad (5.81)$$

to the lowest order in $\Delta T/T_0$. Since \bar{u}_x is basically the mean flow rate the diagonal (xx) component of the tensorial thermodynamic force $\chi_{\bar{u}}$ is directly related to the mean flow rate, but this flow rate is effectively diminished by the factor $\Delta T/2T_0$ if there is a positive longitudinal temperature gradient, whereas if $\Delta T < 0$ then the flow rate is effectively enhanced.

The global thermodynamic forces χ_u , χ_v , $\chi_{\ln T}$, $\chi_{\hat{\mu}_{\varphi_a}}$, and $\chi_{\bar{u}}$ calculated in this subsection can be used for formulating a theory of global irreversible processes in the flow configuration specified for their derivation. The calculations performed for them also illustrate how they may be calculated for other flow configurations.

5.3.2 Examples for Global Constitutive Equations

With the thermodynamic forces calculated as in the previous subsection it is now possible to construct some evolution equations for global non-equilibrium variables. We would like to consider them in the case of thermo-viscous phenomena in the flow configuration corresponding to the thermodynamic forces already calculated. For simplicity we consider a single-component fluid near equilibrium. It should be noted that although the evolution equations are assumed on phenomenological grounds, they may be derived from their local forms presented in Chapter 6, which in turn may be derived by resorting to a kinetic theory of fluids [6].

Viscous Phenomena

In the case of the flow configuration depicted in Fig. 5.1 with an axial temperature gradient, if the system is near equilibrium the evolution equation for the global shear stress tensor denoted by Γ may be given in the form

$$\frac{d_i \Gamma_1}{dt} = 2pTV\chi_{\bar{u}} - \frac{p}{\eta_0}\Gamma_1, \quad (5.82)$$

where

$$\chi_{\bar{u}} = -\frac{u}{DT_0}\delta_x\delta_y, \quad (5.83)$$

η_0 is the viscosity of the fluid, p and T are the pressure and temperature which are uniform over the system. Since the non-conserved variables are limited to Γ_1 and Γ_3 and consequently there cannot be higher order non-conserved variables such as the fluxes of Γ_1 and Γ_3 , the transfer time derivatives of Γ_1 and Γ_3 vanish, that is,

$$\frac{d_e \Gamma_j}{dt} = 0 \quad (j = 1, 3), \quad (5.84)$$

and consequently

$$\frac{d\Gamma_j}{dt} = \frac{d_i \Gamma_j}{dt}.$$

Therefore the evolution equation (5.82) finally takes the form

$$\frac{d\Gamma_1}{dt} = 2pTV\chi_{\bar{u}} - \frac{p}{\eta_0}\Gamma_1, \quad (5.85)$$

This equation can be readily solved, provided the temperature, pressure, and η_0 do not change significantly over the time span where the non-conserved variables change. Then it is easy to find

$$\Gamma_1(t) = 2\eta_0 TV \left[1 - \exp\left(-\frac{p}{\eta_0}t\right) \right] \chi_{\bar{u}}, \quad (5.86)$$

for which the initial condition is $\Gamma_1(0) = 0$. The relaxation time for $\Gamma_1(t)$ is readily identified with $\tau_1 = \eta_0/p$. The global non-conserved variable $\Gamma_1(t)$ relaxes to the steady state form

$$\begin{aligned} \Gamma_1(\infty) &= \Gamma_1 \\ &= 2\eta_0 TV \chi_{\bar{u}}. \end{aligned} \quad (5.87)$$

This is the global form of Newton's law of viscosity, which is the steady state solution of the global stress evolution equation (5.85). In fact, Eq. (5.85) may be regarded as the global Maxwell equation for the shear stress tensor.

Thermal Conduction

The evolution equation for the global axial heat flux in the same flow configuration as for the viscous phenomenon described earlier may be given by

$$\frac{d_i \Gamma_3}{dt} = pT\widehat{C}_p V \chi_{T^{-1}} - \frac{pT\widehat{C}_p}{\lambda_0} \Gamma_3, \quad (5.88)$$

which under the condition (5.84) can be written as

$$\frac{d\Gamma_3}{dt} = pT\widehat{C}_p V \chi_{T^{-1}} - \frac{pT\widehat{C}_p}{\lambda_0} \Gamma_3. \quad (5.89)$$

Here \widehat{C}_p is the specific heat per mass of the fluid at constant pressure and λ_0 is the thermal conductivity of the fluid. On integration this equation yields

$$\Gamma_3(t) = \lambda_0 V \left[1 - \exp\left(-\frac{pT\widehat{C}_p}{\lambda_0} t\right) \right] \chi_{T^{-1}}, \quad (5.90)$$

provided that $\Gamma_3(0) = 0$. The relaxation time for this global non-conserved variable (heat flux) is given by

$$\tau_3 = \frac{\lambda_0}{pT\widehat{C}_p}. \quad (5.91)$$

As $t \rightarrow \infty$, the steady state global heat flux follows from Formula (5.90)

$$\begin{aligned} \Gamma_3(\infty) &= \Gamma_3 \\ &= \lambda_0 V \chi_{T^{-1}}. \end{aligned} \quad (5.92)$$

This is the global form of Fourier's law of heat conduction. Eq. (5.89) may be regarded as the Cattaneo–Vernotte equation for the global heat flux.

5.4 Irreversible Thermodynamics of Neural Networks

The subject of neural networks is potentially quite interesting from even the physics and chemistry viewpoints. Since neural networks are assemblies of macroscopic systems—neurons—their dynamic evolution should be subjected to the laws of thermodynamics, and the topic of the irreversible thermodynamics of neural networks should be accorded a treatment worth a chapter, if it was not a relative novelty to physics and chemistry with only a scanty amount of work on the topic reported in the literature. For

this reason we devote a section in this chapter, which seems to be an appropriate place, because global irreversible processes are involved in the neural networks that we will examine. We hope this discussion will induce further studies of the subject in the future.

For the reader unfamiliar with neural networks we briefly discuss their essential aspects so that the relevance of irreversible thermodynamics can be grasped. Neural networks [7] are dynamical structures which are believed to have some of the properties of real biological neurons, and thus provide insights into nervous systems with regard to their logic operations and computational performance. They are an interconnected assembly of logic processing units called neurons, and the information processing ability of the network is stored in the inter-neuronal connection strengths called weights. Weights of their connections are determined by a learning process from a set of training inputs in accordance with the Hebbian learning rules [8]. The subject will be discussed in as simple a form as possible, since I believe that irreversible thermodynamics of more elaborate networks can be formulated in the same manner as for the version presented in this section.

A system of neurons is arranged into layers, and neurons of a layer (*e.g.*, the hidden and output layers) perform a weighted summation of all states of the neurons in the input layer, and the result of the sum is compared with a certain threshold value to decide which will be the new state of the neurons in the next layer receiving the input. Thus there are two states possible, one below and the other above the threshold. These states may be respectively assigned values 0 and 1, the former to the state below the threshold and the latter to the state above the threshold. This model of neuronal activity is called the McCulloch–Pitts neuron model [9]. The two states in this model are akin to the two states identified with the levels of the electric current in a digital computer circuit [10]. There are numerous studies of neural networks made on the basis of this model in recent years [11, 12].

Animate systems function on the basis of numerous intricately coupled chemical reactions involving many chemical species according to the pre-designed rules of biology or biochemistry of the species, and some sorts of computing are involved in the living processes of animate systems. Therefore chemical reactions are evidently involved in them. Indeed, chemical neural networks have been demonstrated as a particular class of the neural networks mentioned earlier. In chemical neural networks the neurons are represented by non-linear chemical systems which are coupled with each other and operate under specified conditions. They have been applied to problems related to the prediction of the dynamics of oscillatory reactions [13], pattern recognition [14, 15], implementation of finite-state machines and Turing machines [16, 17, 18], self-organization [19], chemical computers performing logic operations [20, 21], and simulation of action potentials [22]. Specific applications to computation with chemical logic gates have been made in a number of ways. For example, Ross *et al.* [20] constructed

a chemical neural network where the neurons are represented by a complex cyclic enzyme mechanism which shows bistability and thus essentially two states of activity; a particular state of activity is chosen by the connections between neurons in the network. The logic state of any neuron is determined by the concentration of the catalyst of the biochemical cycle, and if the threshold value is exceeded, the state is assigned the value 1 and otherwise the value 0. Schneider *et al.* [21, 23] made neural networks where the neurons are represented by a chemical oscillator (minimal bromate oscillator) operating in a continuously stirred tank reactor (CSTR). This chemical oscillator exhibits bistability and oscillatory behavior, and they used the bistability to assign the logic states in the neurons, whereas the connections are represented by fluxes that indirectly couple reactors. They gave an experimental and numerical solution of different logic gates for specific inputs, but the weights and the threshold value are needed to be modified for each logic operation.

Regardless of the types of chemical reactions and modes used for constructing chemical neural networks, they are evidently macroscopic systems which are subject to the laws of physics, and as such they must obey, in particular, the laws of thermodynamics according to the currently held viewpoint toward macroscopic phenomena. Therefore it is important to examine chemical neural networks within the framework of the thermodynamic principles. Since the dynamical processes in the chemical neural networks are irreversible, we first formulate a thermodynamic theory of irreversible processes representative of the logical operations accompanying computations performed by chemical neural networks and then apply the theory to typical neural networks and examine the deductions that one can make on the basis of the networks taken as examples. As will be seen, the intended formulation simply requires an adaptation of the formalism already developed in the previous section for finite macroscopic systems undergoing irreversible processes.

In general, the theory developed is applicable to any chemical neural network that performs logic operations. In this section, as an application of the thermodynamic theory we show how the energy and matter dissipation accompanying logical operations may be computed when the chemical neural network [24] performs computation with the logic gates constructed. Here when we say ‘matter dissipation’ we mean that matter transforms from a useful to a less useful form for the given task, chemical or mechanical, of interest. In the thermodynamic theory of irreversible processes the second law of thermodynamics is representable, in the case of irreversible processes, by the quantity called *calortropy* [6], as has been shown. We show that the calortropy provides an integral surface in the thermodynamic space for chemical neural networks on which the system evolves and computation is performed. It turns out that the system evolves on this calortropy surface from one stable minimum to another as computation is performed. The ‘energy integral’ used by Hopfield [11] in his work may be regarded as a special

case of the calortropy for the neural networks performing computations in conformity with the thermodynamic laws.

5.4.1 Neural Networks and Calortropy Production

The formalism developed in Chapter 4 for global systems can be generalized to a system consisting of neurons interacting (*i.e.*, connected) with each other in the sense that they exchange matter and energy through their boundaries. To distinguish the subsystems we affix a superscript s to the global macroscopic variables presented in the previous section. Thus, firstly, the rate of calortropy change is

$$\frac{d\Psi}{dt} = \sum_{s=1}^{\nu} T^{(s)-1} \left(\frac{dQ_c^{(s)}}{dt} + \Xi^{(s)} \right), \quad (5.93)$$

with the condition

$$\sum_{s=1}^{\nu} T^{(s)-1} \Xi^{(s)} \geq 0, \quad (5.94)$$

where the subsystem contributions are given by the equations which have the same meaning for a single finite system considered earlier. The inequality (5.94) is the expression for the second law of thermodynamics. Secondly, the rate of change in compensated heat is given by the equation consisting of two distinct parts

$$\frac{dQ_c^{(s)}}{dt} = \frac{dQ_E^{(s)}}{dt} + \frac{dQ_n^{(s)}}{dt} \quad (5.95)$$

with the definitions

$$\frac{dQ_E^{(s)}}{dt} = - \int_{\mathbf{B}_s} d\mathbf{B}_s \cdot \mathbf{Q}^{(s)}, \quad (5.96)$$

$$\frac{dQ_n^{(s)}}{dt} = - \sum_{a=1}^r \hat{\mu}_a^{(s)} \frac{d_e M_a^{(s)}}{dt} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka}^{(s)} \frac{d_e \Gamma_{ka}^{(s)}}{dt} + \frac{d_i Q^{(s)}}{dt}. \quad (5.97)$$

When the component of the rate of change in uncompensated heat is written out more explicitly for subsystem s , it is given by

$$\begin{aligned} T^{(s)-1} \Xi^{(s)} &= \Sigma_l^{(s)} - T^{(s)-1} \sum_{l=1}^m \mathcal{A}_l^{(s)} R_l^{(s)} V^{(s)} \\ &\quad + T^{(s)-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka}^{(s)} \frac{d_i \Gamma_{ka}^{(s)}}{dt}. \end{aligned} \quad (5.98)$$

Here the superscript s refers to the attributes of phase s ,

$$\mathcal{A}_l^{(s)} = \sum_{a=1}^r \nu_{al} \hat{\mu}_a^{(s)}, \quad (5.99)$$

$$\Sigma_l^{(s)} = T^{(s)-1} \sum_{a=1}^r \sum_{k \geq 1} \left(\Gamma_{ka}^{(s)} \omega_{ka}^{(s)} + Y_{ka}^{(s)} \varpi_{ka}^{(s)} \right), \quad (5.100)$$

$R_l^{(s)}$ is the rate of reaction l , and $\omega_{1a}^{(s)}, \dots, \varpi_{ka}^{(s)}$ stand for the global thermodynamic forces for subsystem s . They have the same meanings as $\omega_{1a}, \dots, \varpi_{ka}$ appearing in Chapter 4 and in the previous section. The rest of the symbols have the usual meanings in this work. The constitutive equations appearing in these equations are given by the evolution equations

$$\frac{d\Gamma_{ka}^{(s)}}{dt} = \frac{d_e \Gamma_{ka}^{(s)}}{dt} + \frac{d_i \Gamma_{ka}^{(s)}}{dt}, \quad (5.101)$$

$$\frac{dM_a^{(s)}}{dt} = \frac{d_e M_a^{(s)}}{dt} + \frac{d_i M_a^{(s)}}{dt}. \quad (5.102)$$

If the system is at a uniform temperature, free from stress, and of uniform composition then the structure of the aforementioned formalism becomes simpler, and we obtain

$$\frac{dQ_c^{(s)}}{dt} = \frac{dQ_n^{(s)}}{dt} \quad (5.103)$$

with the contribution to the right hand side coming from mass changes only

$$\frac{dQ_n^{(s)}}{dt} = - \sum_{a=1}^r \hat{\mu}_a^{(s)} \frac{d_e M_a^{(s)}}{dt}, \quad (5.104)$$

whereas the calortropy production is given by

$$\Xi^{(s)} = - \sum_{l=1}^m \mathcal{A}_l^{(s)} R_l^{(s)} V, \quad (5.105)$$

since the species are uniformly distributed within the subsystems and hence there is no chemical potential gradients within the subsystems (neurons). Therefore under the assumption made earlier regarding the stress and other processes the calortropy change in the entire neural network is simply given by the expression

$$\frac{d\Psi}{dt} = - T^{-1} \sum_{s=1}^{\nu} \sum_{a=1}^r \hat{\mu}_a^{(s)} \frac{d_e M_a^{(s)}}{dt} - T^{-1} \sum_{s=1}^{\nu} \sum_{l=1}^m \mathcal{A}_l^{(s)} R_l^{(s)} V. \quad (5.106)$$

In this form the rate of calortropy change coincides with the rate of entropy change for a system in local equilibrium, which appears in the theory

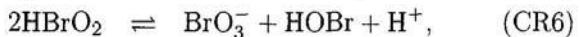
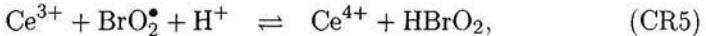
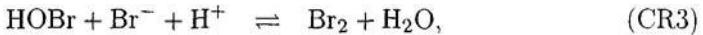
of linear irreversible processes. However, it should be noted that because of the ongoing chemical reactions the system is not in thermodynamic equilibrium and the notion of entropy does not really apply in such circumstances. Therefore we will continue to use the notion of calortropy in this section.

If we assume that some of the subsystems which are fed with, and drained of, matter at a fixed rate by reservoirs, while the rest of subsystems is not connected with the reservoirs, then the part of the compensated heat corresponding to the interaction with the reservoirs can be separated out from the first term on the right hand side of Eq. (5.106) and the remainder may be regarded as the calortropy production. We will assume that this separation has been already made in the first term on the right hand side of Eq. (5.106) and regard it as part of the calortropy production for the whole system. Thus the first term on the right hand side of Eq. (5.106) is the calortropy production arising from the inter-subsystem (*e.g.*, inter-neuron) interactions which give rise to exchange of matter between the subsystems (*e.g.*, neurons), and the second term is the calortropy production arising from the chemical reactions within each subsystem (*e.g.*, a neuron). Eq. (5.106) thus provides a thermodynamic theory of the neural network under consideration, if the mass transfer rates and the reaction rates are suitably specified as constitutive equations.

5.4.2 Network of Bromate Oscillators

Coupled Chemical Reactions

Application [24] of the theory described in the previous subsection was made to neural networks based on the minimal bromate oscillator. It will be described in this subsection. The reactions for the minimum bromate oscillator [25, 26, 27] are as follows:



where BrO_2^\bullet denotes the free radical. When conducted in a continuously stirred tank reactor (CSTR) the reaction system exhibits bistability with hysteresis between two steady states, and oscillations in a small region of values for the flow rate (k_f), which is used as a control parameter; this parameter typically ranges from $3.87 \times 10^{-3} \text{ s}^{-1}$ to $5.43 \times 10^{-3} \text{ s}^{-1}$; see Fig. 1 of Ref. [24] for the details of this aspect.

If the value of k_f is smaller than $3.87 \times 10^{-3} \text{ s}^{-1}$ the steady state is characterized by high concentrations in the Ce^{4+} ion, while if the value of

k_f is larger than $5.43 \times 10^{-3} \text{ s}^{-1}$ the steady state is characterized by low concentrations in the Ce^{4+} ion. Therefore in the case of the former flow rate the oxidized state of cerium ion is predominant, whereas in the case of the latter flow rate the reduced state of cerium ion is predominant. Thus the two concentrations of cerium ions characterize the two states of the neuron. The values of the forward and reverse rate constants k_i and k_{-i} for this system of reactions are given in Ref. [24].

To cast the evolution equations for the chemical species of the minimal bromate oscillator in a general form it is convenient to use a unified system of notations. Let us denote the concentrations by x_i and order them in the following manner: $x_1 = \text{Ce}^{4+}$, $x_2 = \text{Ce}^{3+}$, $x_3 = \text{Br}^-$, $x_4 = \text{BrO}_3^-$, $x_5 = \text{H}^+$, $x_6 = \text{HBrO}_2$, $x_7 = \text{BrO}_2$, $x_8 = \text{HOBr}$, $x_9 = \text{Br}_2$.

Evolution Equations for the Neural Network

Then the mass action laws for the forward and reverse reactions are given by:

$$\begin{aligned}\Lambda_1 &= k_1 x_3 x_4 x_5^2, & \Lambda_{-1} &= k_{-1} x_6 x_8, \\ \Lambda_2 &= k_2 x_3 x_5 x_6, & \Lambda_{-2} &= k_{-2} x_8^2, \\ \Lambda_3 &= k_3 x_3 x_5 x_8, & \Lambda_{-3} &= k_{-3} x_9, \\ \Lambda_4 &= k_4 x_4 x_5 x_6, & \Lambda_{-4} &= k_{-4} x_7^2, \\ \Lambda_5 &= k_5 x_2 x_5 x_7, & \Lambda_{-5} &= k_{-5} x_1 x_6, \\ \Lambda_6 &= k_6 x_6^2, & \Lambda_{-6} &= k_{-6} x_4 x_5 x_8.\end{aligned}\quad (5.107)$$

In this notation the reaction rates for various species are given by the formulas

$$\begin{aligned}R_1 &= \Lambda_5 - \Lambda_{-5} - (\Lambda_6 - \Lambda_6) \equiv \Lambda_1^+ - \Lambda_1^-, \\ R_2 &= -(\Lambda_5 - \Lambda_{-5}) + \Lambda_6 - \Lambda_{-6} \equiv \Lambda_2^+ - \Lambda_2^-, \\ R_3 &= -\sum_{j=1}^3 (\Lambda_j - \Lambda_{-j}) \equiv \Lambda_3^+ - \Lambda_3^-, \\ R_4 &= -(\Lambda_1 - \Lambda_{-1}) - (\Lambda_4 - \Lambda_{-4}) + \Lambda_6 - \Lambda_{-6} \equiv \Lambda_4^+ - \Lambda_4^-, \quad (5.108)\end{aligned}$$

$$\begin{aligned}R_5 &= -2(\Lambda_1 - \Lambda_{-1}) - \sum_{j=2}^5 (\Lambda_j - \Lambda_{-j}) + \Lambda_6 - \Lambda_{-6} \equiv \Lambda_5^+ - \Lambda_5^-, \\ R_6 &= \Lambda_1 - \Lambda_{-1} - (\Lambda_2 - \Lambda_{-2}) - (\Lambda_4 - \Lambda_{-4}) + \Lambda_5 - \Lambda_{-5} \equiv \Lambda_6^+ - \Lambda_6^-, \\ R_7 &= 2(\Lambda_4 - \Lambda_{-4}) - (\Lambda_5 - \Lambda_{-5}) - (\Lambda_6 - \Lambda_{-6}) \equiv \Lambda_7^+ - \Lambda_7^-, \\ R_8 &= \Lambda_1 - \Lambda_{-1} + 2(\Lambda_2 - \Lambda_{-2}) - (\Lambda_3 - \Lambda_{-3}) \equiv \Lambda_8^+ - \Lambda_8^-, \\ R_9 &= \Lambda_3 - \Lambda_{-3} \equiv \Lambda_9^+ - \Lambda_9^-. \quad (5.109)\end{aligned}$$

The evolution of species is then described by the ordinary differential equations

$$\frac{dx_i}{dt} = k_f(x_i^0 - x_i) + R_i \quad (i = 1, \dots, 9), \quad (5.110)$$

where $x_i^0 = 0$ for $i = 1, 6, 7, 8, 9$ and $x_i^0 \neq 0$ for $i = 2, 3, 4, 5$ are the concentrations of inflowing reactants, and k_f is the flow rate. This is the set of concentration evolution equations for a neuron in the network. To distinguish the neurons we affix a superscript (s) on various quantities. Thus for the whole neural network we have the evolution equations

$$\frac{dx_i^{(s)}}{dt} = k_f(x_i^{0(s)} - x_i^{(s)}) + R_i^{(s)} \quad (i = 1, \dots, 9; s = 1, 2, \dots), \quad (5.111)$$

where $x_i^{0(s)}$ have the same meanings as for x_i^0 for a single neuron.

5.4.3 Hebbian Learning Rules

To illustrate explicitly a neural network and apply the formalism presented in the previous section, an architecture of a neural network similar to that used by Schneider *et al.* [21, 23] may be used. The chemical neural networks considered by them are 2–1 and 2–2–1 feedforward networks through which the information flows in just one direction. These networks have a computational capability of performing logic operations. The input layer of neurons consists of two neurons which do not directly transfer mass to the output neurons, but triggers mass transfer from the reservoir into the output neurons through a circuit (*e.g.*, an interface consisting of a PC monitoring the input). The flow rate into the output neuron is determined according to the Hebbian rules of learning [8]: *The network is trained by using different inputs until it has learned to perform desired logic operations, and the computational capability of the trained network is tested by using random inputs to ensure that the network is trained as desired.* Each neuron in the network is represented by a CSTR tank containing the aforementioned minimal bromate system, and the connections between the neurons are realized by means of their flow rates in such a way that the flow rate in the output neuron is ‘controlled’ according to the output signal (x_1) in the input layer of neurons through the ‘circuit’ (*e.g.*, the interface). Therefore mass exchange between the neurons of the input and output layers of the network is not directly made, but through the interface, and the total input into the output neuron is determined by the transfer function

$$\Gamma_j = \sum_{i=1}^2 w_{ij} x_1^{(i)} + \Theta_j, \quad (5.112)$$

where Θ_j (normally called ‘bias’) is related to a threshold that has to be exceeded by the net input

$$\sum_{i=1}^2 w_{ij}x_1^{(i)}.$$

In the particular case considered here the magnitude of the transfer function determines the mass transfer from the reservoir according to the rule

$$\begin{cases} k_f \leq 3.86 \times 10^{-3} \text{ s}^{-1}, & \text{if } \Gamma_j < 0, \\ k_f \geq 5.44 \times 10^{-3} \text{ s}^{-1}, & \text{if } \Gamma_j > 0. \end{cases} \quad (5.113)$$

If the threshold value is exceeded in this network the output neuron is said to have fired with the value of the state variable ‘1’ or ‘true’ assigned to it; otherwise the output neuron is said to have been inhibited with the value of the state variable ‘0’ or ‘false’ assigned to it. We exploit the bistable behavior of the minimal bromate oscillator by assigning the logic value ‘1’ or ‘0’ to the high ($k_f \leq 3.86 \times 10^{-3} \text{ s}^{-1}$) or low ($k_f \geq 5.44 \times 10^{-3} \text{ s}^{-1}$) steady state values of the output signal (x_1), respectively. The value of the bias Θ_j is fixed at a value, as is generally required in theory of neural networks.

5.4.4 Calortropy Production

Irreversible processes in the neural network evolve on the calortropy surface spanned by species concentrations. In the sense that the calortropy surface is a mathematical realization of the second law of thermodynamics they are consistent with it, which, in particular, demands that the calortropy production [28, 29] be positive and vanish at equilibrium only. Since the processes evolve in the calortropy surface it obviously is interesting to understand the consequences for the calortropy production of the global system, which also indicates a measure of energy and matter dissipation. In the case of chemical neural networks matter is transformed from a useful to a less useful form. The calortropy production is calculated by using the formula presented in the previous section under the assumption that the solutions of chemical species are ideal, that is, the chemical potentials for the species in the neurons are given by the formula

$$\hat{\mu}_a(T, p, x_a) = \hat{\mu}_a^0(T, p) + \mathcal{R}T \ln x_a, \quad (5.114)$$

where $\hat{\mu}_a^0(T, p)$ is the reference chemical potential of species a , x_a is the mole fraction of a (the total mole number is set equal to unity in this manner of writing the chemical potentials), and \mathcal{R} is the gas constant. The reference chemical potentials are defined such that the change of Gibbs free energy for an isolated neuron is equal to zero at chemical equilibrium. With

Eq. (5.114) for $\hat{\mu}_a$ the calortropy production for the neural network is given by the formula

$$\begin{aligned} (\Xi)_{\text{nn}} &= -VT^{-1} \sum_{s=1}^{\nu} \sum_{l=1}^m A_l^{(s)} R_l^{(s)} \\ &= V\mathcal{R} \sum_{s=1}^{\nu} \left[\sum_{l=1}^m (\Lambda_l^+ - \Lambda_l^-) \ln \left(\frac{\Lambda_l^+}{\Lambda_l^-} \right) \right]_s, \end{aligned} \quad (5.115)$$

where the quantity in the square brackets on the right hand side represents the calortropy production in neuron s . The second line of this equation is derived by using the relation between the chemical equilibrium constants, which is equal to the ratio of the forward and reverse rate constants of the reaction. On summing the neuronal contributions over the neural network the total calortropy production arising from the system of chemical reactions is obtained. In the case of the neural network in which neurons interact by exchanging matter there are also contributions to the calortropy production of the neural network that arises from the compensated heat of the interacting neurons. This contribution is given by

$$\left(\frac{dQ_c}{dt} \right)_{\text{nn}} = -T^{-1} \sum_{s=1}^{\nu} \sum_{a=1}^r \hat{\mu}_a^{(s)} \frac{d_e M_a^{(s)}}{dt}. \quad (5.116)$$

It accounts for the calortropy change arising from inter-neuron mass exchanges. Since at chemical equilibrium

$$\sum_{s=1}^{\nu} \sum_{a=1}^r \hat{\mu}_a^{0(s)} \frac{d_e M_a^{(s)}}{dt} = 0, \quad (5.117)$$

we obtain

$$\left(\frac{dQ_c}{dt} \right)_{\text{nn}} = -\mathcal{R} \sum_{s=1}^{\nu} \left[\sum_{a=1}^r k_f (x_a^0 - x_a) \ln x_a \right]_s. \quad (5.118)$$

Finally the total rate of calortropy change in the neural network is given by

$$\begin{aligned} \sigma_{\text{net}} &\equiv \left(\frac{d\Psi}{dt} \right)_{\text{nn}} \\ &= -\mathcal{R} \sum_{s=1}^{\nu} \left[\sum_{a=1}^r k_f (x_a^0 - x_a) \ln x_a \right]_s \\ &\quad + V\mathcal{R} \sum_{s=1}^{\nu} \left[\sum_{l=1}^m (\Lambda_l^+ - \Lambda_l^-) \ln \left(\frac{\Lambda_l^+}{\Lambda_l^-} \right) \right]_s. \end{aligned} \quad (5.119)$$

TABLE 5.1. Logic table for computing the output in the logic gates

Input1	Input2	AND	NAND	OR	NOR	XOR	XNOR
1	1	1	0	1	0	0	1
1	0	0	1	1	0	1	0
0	1	0	1	1	0	1	0
0	0	0	1	0	1	0	1

If the concentrations oscillate with a period τ then it is useful to define the mean value of σ_{net} by the time average over the period of oscillation

$$\sigma_{\text{osc}} = \frac{1}{\tau} \int_0^\tau d\tau \sigma_{\text{net}}. \quad (5.120)$$

This formula is used for the oscillatory states of the neural network. The calortropy production has features characteristic to the logic operations performed by the neural network.

5.4.5 Logic Operations and Calortropy Production

The neural network based on the bromate system is capable of performing logic operations AND, NAND, OR, NOR, XOR, and XNOR. The logic table is given in Table 5.1 in which relations between the inputs and the logic functions are summarized³. The 2–1 feedforward network is capable of logic operations AND, NAND, OR, and NOR, whereas to perform logic operations XOR and XNOR in addition to the AND, NAND, OR, and NOR logic operations it is necessary to have the 2–2–1 feedforward network.

³For the reader unfamiliar with logic operations and their algebraic representations we add the following: Each logic operation (gate) has one or two binary input variables (*i.e.*, 0 or 1) denoted by y and z and one binary output denoted by x . The logic gates (operations), AND, NAND, OR, NOR, XOR, and XNOR, listed in Table 5.1, have the algebraic functions associated with them. In addition to these gates it is necessary to have an inverter which has only one input and produces the complement of the input as an output; for example, if the input is ‘0’ then the output of the inverter is ‘1’, which is the complement of the binary set (0,1). The inversion will be denoted by an asterisk. Thus its algebraic representation is, for example, $x = y^*$ if the input is y . In this notation the aforementioned logic operations are, respectively, represented by an algebraic function as follows: AND, $x = yz$; OR, $x = y + z$; NAND, $x = (yz)^*$; NOR, $x = (y + z)^*$; XOR, $x = y^*z + yz^*$; XNOR, $x = A^*B^* + AB$. Incidentally, the algebraic representation of the buffer (a gate) is $x = y$ if the input is y . Therefore the output is the same as the input. With the aforementioned algebraic representations for the logic operations the logic operation table or the truth table given in Table 5.1 can be easily constructed.

The 2-1 Feedforward Network

The architecture of a 2-1 feedforward network is depicted in Fig. 5.2a. This neural network is capable of computing the logic functions AND, NAND, OR, and NOR. The two squares on the left within the broken lined box in Fig. 5.2a denote input neurons. These neurons receive only one constant input from the exterior world. The square on the right in the box is for the

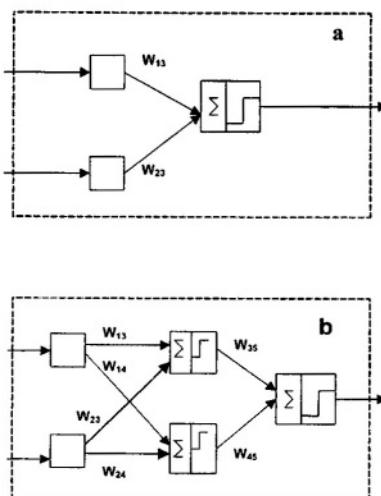


FIGURE 5.2. Architectures of the chemical networks: (a) a 2-1 feedforward network to compute the logic operations AND, NAND, OR, and NOR; (b) a 2-2-1 feedforward network to compute the logic operations XOR and XNOR. [Reproduced with permission from (2001) J. Phys. Chem., 105, 7104. © 2001 American Chemical Society.]

output neuron, and its left half comprises the interface made up of a PC monitoring the total input, which is represented by

$$\sum_{i=1}^2 w_{ij} x_1^{(j)}.$$

This input will have to exceed the Θ_j threshold value (*i.e.*, the bias) to give an output of value 1, or an output ‘true’, or it will give no output, that is, a value 0 or ‘false’. Depending on the value of the input relative to the threshold value the output neuron (*i.e.*, the right half of the square on the right) puts out a ‘true’ (upper line) output or a ‘false’ (lower line) output. The training of the network consists of determining the weights w_{ij} , which allow to compute the correct output by the network according to the logic operation intended. For a single threshold value for Θ_j there

TABLE 5.2. Weights

logic operation	w_{13}	w_{23}	w_{14}	w_{24}	w_{35}	w_{45}
AND	0.61	0.61	-	-	-	-
NAND	-0.61	-0.61	-	-	-	-
OR	0.97	0.97	-	-	-	-
NOR	-0.97	-0.97	-	-	-	-
XOR	0.61	0.61	-0.97	-0.97	-0.97	-0.97
XNOR	0.61	0.61	-0.97	-0.97	0.97	0.97

can be different weights w_{ij} that allow us to compute the different logic operations AND, NAND, OR, NOR, XOR and XNOR as shown in Table 5.2. The network is now trained to performed the desired logic operations.

The 2–2–1 Feedforward Network

If the 2–2–1 feedforward network depicted in Fig. 5.2b is used, logic operations XOR and XNOR can be performed. In the figure the squares on the left in the broken lined box represent the input neurons and the other squares represent two layers of output neurons with the meanings of the symbols in the squares being the same as for Fig. 5.2a. Since this network is more complex, in order to compute one output it is necessary to compute two additional logic operations internally: $\text{XOR} = [(\text{AND}, \text{NOR}), \text{NOR}]$ and $\text{XNOR} = [(\text{AND}, \text{OR}), \text{NOR}]$. By this notation the following is meant: for XOR the inputs from the neurons (layer 1) on the left are integrated (or summed) to yield ‘true’ for the output by the first neuron and ‘false’ by the second neuron in layer 2. These outputs are integrated and the output neuron in layer 3 yields NOR. The output for different logic operations is summarized in Table 5.2. It must be noted that the logic state of a neuron is not given by a single definite value of the Ce^{+4} concentration but by a range of values which is set to value ‘1’ or ‘0’. Therefore, different concentrations for inputs can be representing the same logic output. The values of weights in Table 5.2 are for Figs. 5.2a and 5.2b. Since the threshold value is fixed at a value for a network and consequently the weights are different from those chosen by Schneider et al. [21, 23], the present neural networks have different neural dynamics despite the same architectures as those of Refs. [21, 23].

5.4.6 Numerical Simulations

In Ref. [24] the systems (5.111) of ordinary differential equations corresponding to the 2–1 and 2–2–1 neural networks described earlier were numerically solved with Gear’s method [30] for stiff ordinary differential equa-

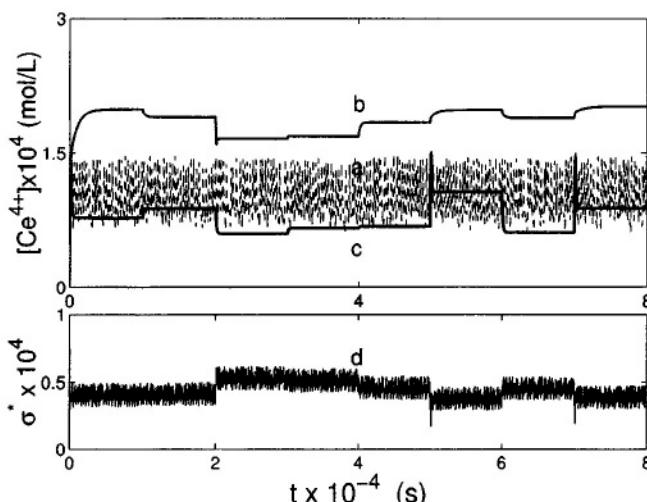


FIGURE 5.3. Logic operation $(1,0)\text{AND} = 0$ and the calorropy production: (a) logic state '0' for the output neuron; (b) logic state '1' for one input neuron; (c) logic states '0' for the other input neuron; (d) dissipation in the network. [Reproduced with permission from (2001) J. Phys. Chem., **105**, 7104. © 2001 American Chemical Society.]

tions. The following initial conditions were taken for the concentrations of chemical species: $x_4 = 0.1$, $x_5 = 0.75$, $x_2 = 3 \times 10^{-4}$, $x_3 = 3 \times 10^{-4}$. These values taken were the same as the concentrations of the inflowing reactants.

Since the global behavior of a network is determined by the dynamics of neurons and their outputs, once the network has been trained, the capability to process information and to produce the output desired must be independent of the inputs provided from the external world.

In Ref. [24] the dynamics of the network is investigated in the following manner: Initially each one of the input neurons is provided with a random value for the control parameter k_f . If $k_f \leq 3.86 \times 10^{-3} \text{ s}^{-1}$ the system evolves to a steady state where the logic state of the neuron is interpreted as '1' or 'true'; if $k_f \geq 5.44 \times 10^{-3} \text{ s}^{-1}$ the system evolves to a steady state where the logic state of the neuron is interpreted as '0' or 'false'. After this and every 10,000 seconds the input neurons are provided with new random values for the control parameter k_f , whereas the output neuron continuously processes the information and the output is assessed for assignment to the 'true' or 'false' value. Even when a new random control parameter k_f is given every 10,000 seconds which changes the state values, the output level remains virtually constant independently of the input levels.

Fig. 5.3 shows the capability of the network (Fig. 5.2a and Table 5.2) when the logic operation AND is computed, more specifically, when $(1,0)\text{AND}$ with output equal to '0' is computed. The curve *a* shows that the

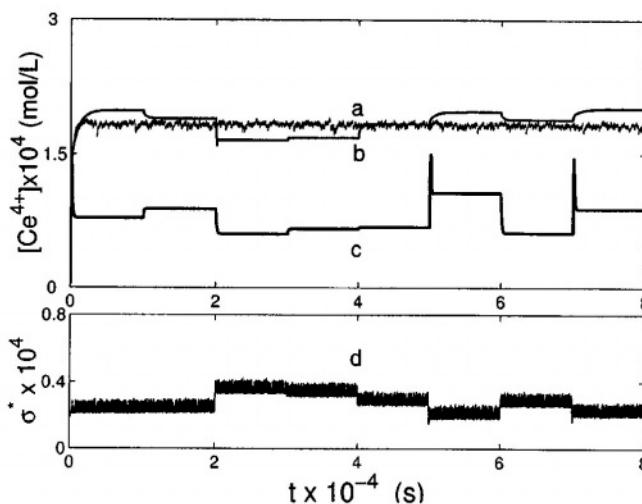


FIGURE 5.4. Logic operation $(1, 0)\text{OR} = 1$ and the calorropy production: (a) logic state "1" for the output neuron; (b) logic states "0" for one input neuron; (c) logic states "1" for the other input neuron; (d) dissipation in the network. [Reproduced with permission from J. Phys. Chem., **105**, 7104 (2001). Copyright © American Chemical Society.]

logic state of the output neuron is at all times below value 1.5×10^{-4} for the output signal (x_1). This logic state is interpreted as '0', whereas curves *b* and *c* show that the input neurons are at all times firing values in the output signal (x_1) that are interpreted as '1' and '0', respectively. The curve *d* shows the profile of dissipation in the network, which is approximately constant for a logic state of the output neuron. The scale for the curve (d) is given in units of \mathcal{R} according to the definition $\sigma^* = \sigma_{\text{net}}/\mathcal{R}$. The observed discontinuous changes in the matter dissipation are associated with the changes that occur in the input neurons.

Fig. 5.4 shows the network computing the logic operation OR, specifically, the state '1' or '0' with the output equal to T. The explanation for curves *a*, *b*, *c*, and *d* is similar to that given for Fig. 5.4. In this logic state the output neuron is continuously firing a value greater than 1.6×10^{-4} in the signal output (x_1), namely, curve *a*, which is interpreted as '1'.

Fig. 5.5 shows the network computing the logic operation $(0,0)\text{NAND}$ with the output equal to '1', and Fig. 5.6 shows the network in Fig. 5.2b computing the logic operation $(1,1)\text{XOR}$ with the output equal to '0'.

To analyze the dissipation of matter in the networks in detail each one of the networks was tested with 30 different random values for the control parameter k_f in the input neurons (300,000 seconds for running time). By analyzing the output data, correlations between the values in the input

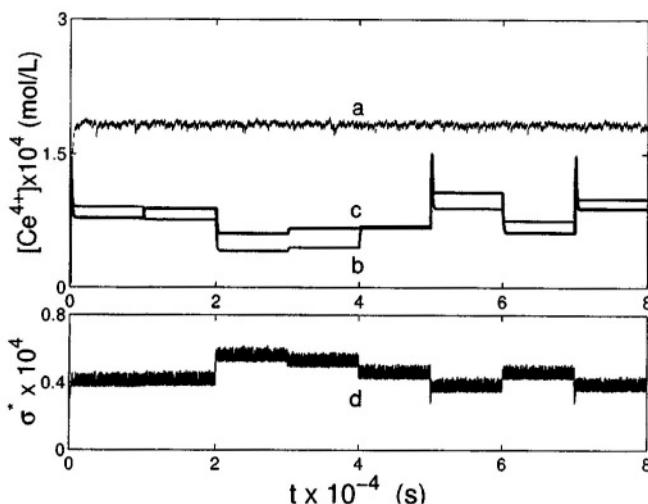


FIGURE 5.5. Logic operation $(0,0)\text{NAND} = 0$ and the calorropy production: (a) logic state '1' for the output neuron; (b) logic states '0' for one input neuron; (c) logic states '0' for the other input neuron; (d) dissipation in the network. The scale for the curve (d) is given by the secondary y-axis. [Reproduced with permission from J. Phys. Chem., 105, 7104 (2001). © 2001 American Chemical Society.]

neurons and the dissipation of matter were made to indicate the tendency in the behavior of the dissipation of matter from a useful to a less useful form.

Fig. 5.7 shows as the dissipation levels are increased as the network in Fig. 5.2a computes for the logic operation AND with different inputs, namely, (1,1), (0,0), and (1,0), the highest level being when the network computes the logic state AND with '0' and '0' for the inputs, whereas the lowest level of dissipation is attained when it computes the logic operation AND with inputs '1' and '1'. The level of dissipation for the logic state '1' AND '0' is in the middle. In the case of logic operation NAND the levels of dissipation in the network are similar those of AND so that the level of dissipation decreases in the order of (0,0)NAND, (1,0)NAND, and (1,1)NAND. To learn about the effect of oscillation the dissipation was computed when in one or both input neurons the state was oscillatory, whereas the output neuron was in the steady state all the time; in this situation the network does not compute for any logic operation. The curve a in the figure shows the level of dissipation in the network when the output neuron is in a steady state at $k_f = 7 \times 10^{-3} \text{ s}^{-1}$ with logic function value '0' and one input neuron is in a steady state at $k_f = 7 \times 10^{-3} \text{ s}^{-1}$ with logic function value '0' whereas the other input neuron is in an oscillatory state at $k_f = 5.4 \times 10^{-3} \text{ s}^{-1}$. The curve b shows the level of dissipation

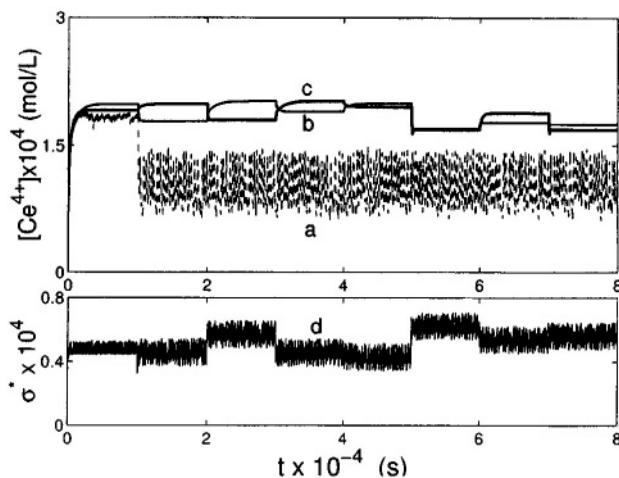


FIGURE 5.6. *Logic operation (1,1)XOR=0 and the calortropy production: (a) logic state '0' for the output neuron; (b) logic states '1' for one input neuron; (c) logic states '1' for the other input neuron; (d) dissipation in the network. σ^* is in the units of \mathcal{R} .* [Reproduced with permission from (2001) J. Phys. Chem., **105**, 7104. © 2001 American Chemical Society.]

when both input neurons are in oscillatory state at the control parameter value $k_f = 4.2 \times 10^{-3} \text{ s}^{-1}$ and $k_f = 4.8 \times 10^{-3} \text{ s}^{-1}$, respectively. The curve c is for the level of dissipation in the network when one input neuron is in steady state with logic function value '1' at $k_f = 1.5 \times 10^{-3} \text{ s}^{-1}$ whereas the other input neuron is in oscillatory state at the control parameter value $k_f = 5.4 \times 10^{-3} \text{ s}^{-1}$. It is evident that the lowest dissipation is given when both input neurons are in an oscillatory state. But then, no computation is performed by the network in an oscillatory state. Fig. 5.8 shows that in the case of logic operation OR the highest level of dissipation is obtained when the network computes for the logic state (0,0)OR, whereas in the case of logic operation NOR the highest levels of dissipation are obtained when the network computes for the logic states (0,0)NOR and (1,0)NOR.

When the network in Fig. 5.2b is computing for the logic operation XOR or XNOR, the behavior of the levels of dissipation is more complex, but some tendencies can be shown as in Fig. 5.8. For the logic operation XOR the highest level of dissipation in the network was obtained when it computed for the logic state (0,0)XOR, whereas for the logic operation XNOR the highest levels of dissipation were obtained when the network computes for the logic states (0,0)XNOR and (1,0)XNOR. It is not clear whether this trend is general or not, but further work appears to be necessary to elucidate it.

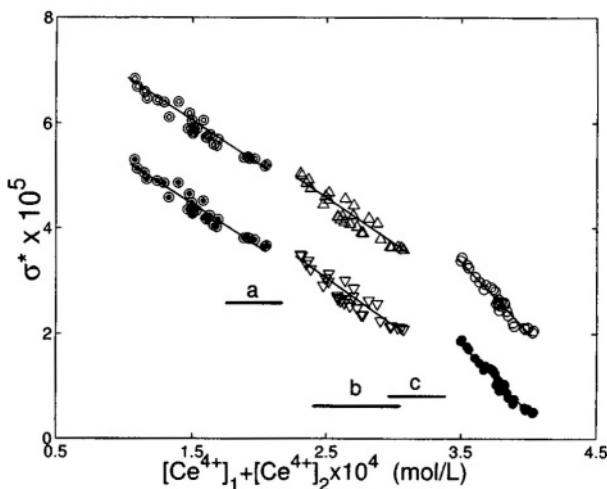


FIGURE 5.7. Levels of dissipation for the logic operations AND and NAND (\bullet : (1, 1)AND = 1; \circ : (1, 1)NAND = 0; ∇ : (1, 0)NAND = 1; Δ : (1, 0)AND = 0; @: (0, 0)AND = 0; @: (0, 0)NAND = 1). (a) dissipation for the case of one input neuron in oscillatory state; the other input neuron in steady state '0'; and the output neuron in steady state '0'. (b) dissipation for the case of both input neurons in oscillatory state. (c) dissipation for the case of one input neuron in steady state '1' and the other input neuron in oscillatory state. [Reproduced with permission from (2001) J. Phys. Chem., 105, 7104. © 2001 American Chemical Society.]

The notable feature of the calculations made for the dissipation associated with various logic operations appears to be not in their magnitudes but in that the neurons have characteristic steady states corresponding to logic operations and evolve toward a particular steady state which not only has what seems to be a characteristic level of dissipation on the calortropy production surface, but also appears to be a local minimum in the surface. This minimum, however, is not sharply defined for a given logic operation, because the true or false states do not have a constant but a varying dissipation within a limit, as is clear from the figures shown. In the sense that the calortropy production is not equal to zero at the steady states the system is removed from equilibrium, and consequently logic operations in the neural networks are energy-dissipating irreversible processes in systems removed from equilibrium. The level of energy and matter dissipation by neurons and by the whole neural network is important if it is the aim to design an energetically and materially efficient neural network, although it is quite conceivable that since the primary aim of a neural network is to perform desired logic operations and computation, the neural network, especially the biological (animate) ones, may appropriate to itself whatever amount of energy and matter required to achieve the aim. Nevertheless,

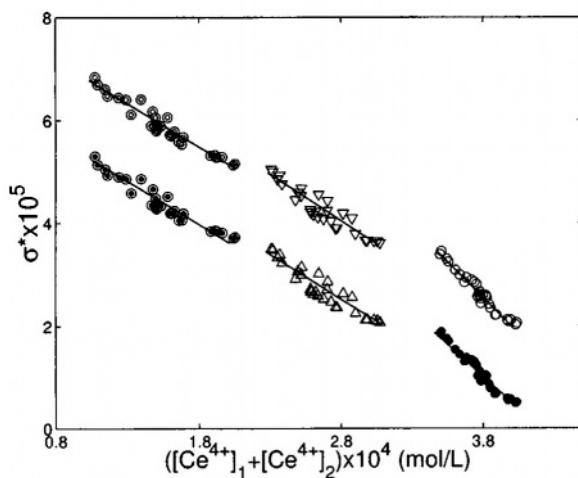


FIGURE 5.8. Levels of dissipation for the logic operations OR and NOR (●: (1,1)OR = 1; ○: (1,1)NOR = 0; ▽: (1,0)NOR = 0; △: (1,0)OR = 1; ⊙: (0,0)OR = 0; ⊖: (0,0)NOR = 1). [Reproduced with permission from (2001) J. Phys. Chem., **105**, 7104. © 2001 American Chemical Society.]

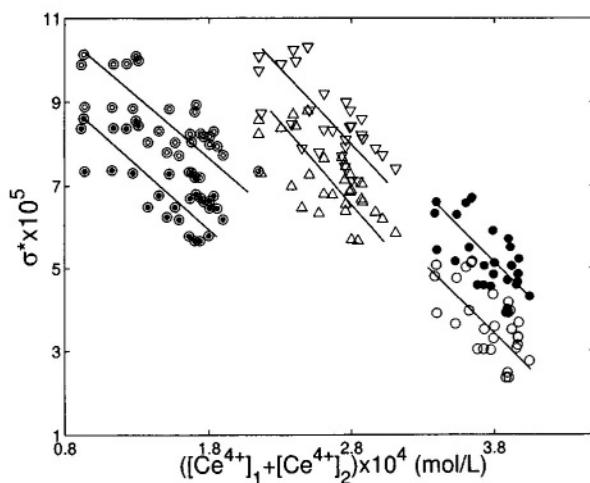


FIGURE 5.9. Levels of dissipation for the logic operations XOR and XNOR (●: (1,1)XOR = 0; ○: (1,1)XNOR = 1; ▽: (1,0)XNOR = 0; △: (1,0)XOR = 1; ⊙: (0,0)XOR = 0; ⊖: (0,0)XNOR = 1). [Reproduced with permission from (2001) J. Phys. Chem., **105**, 7104. © 2001 American Chemical Society.]

the irreversible thermodynamic formalism presented will enable us to investigate in the future the question of efficiency of neural networks, mutual relations of various processes, and the efficiency of information processing and transfer in the networks. In these questions seems to lie the usefulness of irreversible thermodynamics for neural networks formulated in this section.

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6

Conservation Laws and Evolution Equations

Since the first and second laws of thermodynamics presented in the previous two chapters are phrased for a finite macroscopic system as a whole (*i.e.*, a cycle of a gross scale) and no reference is made to what is happening locally within the system, they are applicable to macroscopic processes occurring globally over the entire system. Our fundamental viewpoint taken for macroscopic thermal physics is that these laws applicable to processes in a finite system as a whole can be also applied to local processes occurring in an elementary volume around every position within the system. For if these laws do not apply locally and if there indeed exists a local domain where they are in fact broken, then it is possible to construct a small cycle which breaks the laws of thermodynamics and by continuity there will be other domains where such cycles exist. If so, by suitably stringing such cycles together up, it is possible to construct a cycle of macroscopic size which also breaks the laws of thermodynamics. This is not acceptable from the basic tenet of thermal physics which is upheld in science and in this work.

The local densities of global macroscopic variables obey balance equations. Thus the local densities of such global variables can be regarded as field variables described by partial differential equations in space-time. In this chapter we develop such local balance equations of macroscopic variables associated with the first and second laws of thermodynamics. They must be accompanied by the conservation laws of mass and momentum. They also must include the angular momentum conservation law if the fluid molecules have an intrinsic angular momentum. The mass and momentum conservation laws do not explicitly appear in equilibrium thermodynamics,

but they must be considered together with the energy conservation law in generalized thermodynamics—that is, irreversible thermodynamics.

6.1 Local Field Variables

For a system consisting of an r species components we define the densities \mathcal{E} , v , c_a , and $\hat{\Phi}_{ka}$ of various global variables spanning the thermodynamic space \mathfrak{H} as follows:

$$\begin{aligned} E &= \int_V d\mathbf{r} \rho \mathcal{E}(\mathbf{r}, t), \\ V &= \int_V d\mathbf{r} \rho v(\mathbf{r}, t), \\ M_a &= \int_V d\mathbf{r} \rho c_a(\mathbf{r}, t), \\ \Gamma_{ka} &= \int_V d\mathbf{r} \rho \hat{\Phi}_{ka}(\mathbf{r}, t), \end{aligned} \tag{6.1}$$

where ρ is the mass density, $v = \rho^{-1}$ is the specific volume, and $c_a = \rho_a \rho^{-1}$ is the mass fraction of species a with ρ_a denoting the mass density of species a . We thus define the local variable space as follows:

Definition *The space $\mathfrak{P} = (\mathcal{E}, v, c_a, \hat{\Phi}_{ka} : k \geq 1; r \geq a \geq 1)$ spans the local field variable space corresponding to the global variable (thermodynamic) space \mathfrak{H} . This space¹ will be called the local thermodynamic space or simply the thermodynamic space.*

We will find that non-conserved variables Φ_{ka} ($1 \leq a \leq r$ and $k \geq 1$), defined by $\Phi_{ka} = \rho \hat{\Phi}_{ka}$, are sometimes more convenient to use instead of their densities $\hat{\Phi}_{ka}$. Here the index k , running over a complete set, is used to designate the type of non-conserved variables and a is for the species. This set includes the stress (pressure) tensors, heat fluxes, and mass diffusion fluxes of various species as the leading members of the set. Other non-conserved variables are often not used in interpreting experimental data since they are rarely measured, although they should be included in formulating a complete theory of irreversible processes. Therefore it is convenient to make the stress tensors, heat fluxes, and mass diffusion fluxes

¹ In a more precise mathematical terminology it should be called a manifold, but we will use this term because it is generally used in the subject field.

the leading members of a complete set of non-conserved variables. The set of non-conserved variables thus is suitably ordered as follows:

$$\Phi_{1a} \equiv \boldsymbol{\Pi}_a = \frac{1}{2}(\mathbf{P}_a + \mathbf{P}_a^t) - \frac{1}{3}\delta\text{Tr}\mathbf{P}_a = [\mathbf{P}_a]^{(2)}.$$

$$\Phi_{2a} \equiv \Delta_a = \frac{1}{3}\text{Tr}\mathbf{P}_a - p_a,$$

$$\Phi_{3a} \equiv \mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a,$$

$$\Phi_{4a} \equiv \mathbf{J}_a, \quad \text{etc.} \quad (1 \leq a \leq r),$$

where the superscript t denotes the transpose of the tensor, the boldface $\boldsymbol{\delta}$ the unit second rank tensor, p_a the hydrostatic pressure of species a , and \hat{h}_a the enthalpy per unit mass of species a . The rest of the symbols are:

$$\mathbf{J}_a = \rho_a(\mathbf{u}_a - \mathbf{u}) \quad (6.2)$$

is the mass diffusion flux of species a where \mathbf{u}_a is the mean velocity of species a ; \mathbf{P}_a is the pressure tensor (stress tensor) of species a , which is a part of the total pressure tensors \mathbf{P}

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a; \quad (6.3)$$

\mathbf{F}_a is the external force density per unit mass of a in terms of which the total external force density at position r can be expressed as

$$\mathbf{F} = \sum_{a=1}^r c_a \mathbf{F}_a; \quad (6.4)$$

and \mathbf{Q}_a is the heat flux of species a in terms of which the total heat flux can be decomposed as follows:

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a. \quad (6.5)$$

Since the barycentric velocity, which we often refer to as the fluid velocity, is defined by the formula

$$\rho\mathbf{u} = \sum_{a=1}^r \rho_a(\mathbf{u}_a - \mathbf{u}), \quad (6.6)$$

the diffusion fluxes, by definition, has the property

$$\sum_{a=1}^r \mathbf{J}_a = 0. \quad (6.7)$$

This implies that there are only $(r - 1)$ independent diffusion fluxes.

In addition to the local variables presented there will also appear the fluid velocity \mathbf{u} as an important field variable although it does not explicitly appear in the extended Gibbs relation in the local non-relativistic thermodynamic theory of irreversible processes. The global calortropy can be also expressed in terms of its density $\widehat{\Psi}(\mathbf{r}, t)$ through the volume integral

$$\Psi(t) = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t) \quad (6.8)$$

The union of the space \mathfrak{P} and $\widehat{\Psi}$ will be called the local Gibbs space \mathfrak{P}_G or simply the Gibbs space: $\mathfrak{P}_G = \mathfrak{P} \cup \widehat{\Psi}$. As in the case of the global calortropy Ψ the local calortropy density is a surface in the local Gibbs space \mathfrak{P}_G .

6.2 Local Intensive Variables

Since the thermodynamics of irreversible processes is intimately connected with fluid dynamics, which is a local field theory, it is preferable to carry over the global differential forms for dE and $d\Psi$, (4.62), (4.40), and (4.46), to local forms. This localization of various evolution equations, however, requires the concept of local temperature, pressure, and so forth for intensive variables such as temperature, pressure, chemical potentials, and generalized potentials. We will first deal with these latter quantities before formulating the desired local theory. The same consideration as made here can be found in Ref. [1].

6.2.1 Local Temperature

The temperature appearing in the global differential form (4.40) for Ψ is the temperature in the absolute scale of the heat reservoir of the infinitesimal Carnot cycle at the point of interest in the contour integral (4.41) for the cyclic process. Therefore it is appropriate, although not mandatory, to consider a Carnot cycle. This Carnot cycle operates between two heat reservoirs of infinitesimally different temperatures, $T + \epsilon$ and T , where $\epsilon > 0$. Let us imagine a cylinder which is fitted with a frictionless piston and contains a gaseous working substance. It is connected to the heat reservoirs of temperatures $T + \epsilon$ and T ; see Fig. 6.1. The substance in this cylinder goes through a Carnot cycle as the piston moves in and out in the cylinder. The system is macroscopic in size and the process spans over the entire length of the cylinder. We now imagine that this cylinder consists of a sequence of infinitesimally small cylinders with a piston which are in thermal contact with hypothetical heat reservoirs of temperatures $T_0, T_1, T_2, \dots, T_{n-1}, T_n$ where $T_0 = T + \epsilon$, $T_n = T$, and T_1, T_2, \dots, T_{n-1} are the temperatures of the heat reservoirs at positions x_1, x_2, \dots, x_{n-1} . For example, if the

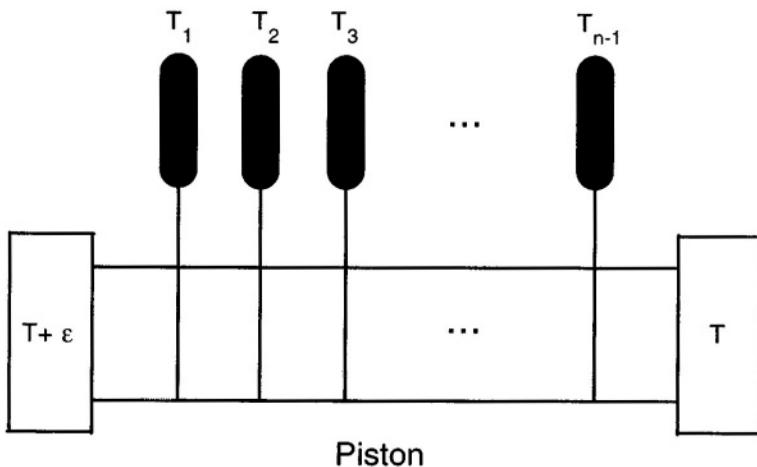


FIGURE 6.1. Division of a cylinder with a piston operating between two heat reservoirs of temperatures $T + \epsilon$ and T , where ϵ is infinitesimally small. The temperatures of the intermediate heat reservoirs are T_1, T_2, \dots, T_{n-1} at positions x_1, x_2, \dots, x_{n-1} . The intervals between these positions do not have to be equal. If the temperature profile is linear then it is convenient to make the intervals equal. The temperatures of the intermediate heat reservoirs define the local temperature in the cylinder.

temperature distribution is linear and an equal interval δ is taken, then $T_0 = T + \epsilon$, $T_1 = T + \epsilon - \delta$, $T_2 = T + \epsilon - 2\delta, \dots, T_i = T + \epsilon - i\delta, \dots, T_{n-1} = T + \epsilon - (n-1)\delta$, $T_n = T$ where $\delta = \epsilon/n$ and n can be as large as necessary. Here the term ‘infinitesimally small cylinder’ means a cylinder infinitesimally small in physical size, but still large enough for a continuum mechanical treatment to be valid for the assembly of particles contained therein. The word ‘infinitesimal’ used in connection with the cylinder means a small size, whereas its use in connection with the Carnot cycle means an infinitesimally small temperature difference between the heat reservoirs involved, even though the physical size of the cylinder may be large. In view of δ being sufficiently small, the temperature of the working substance in the i th cylinder may be taken as the mean temperature $T(i) \equiv \frac{1}{2}(T_{i-1} + T_i)$, and, for example, $T(i) = T + \frac{1}{n}(n-i+\frac{1}{2})\epsilon$ in the case of equal intervals taken earlier. This is the local temperature of the substance in the ‘undivided’ cylinder of the global scale. This local temperature can be quantified by the following means. A thermometer is inserted in the heat reservoirs in contact with the i th cylinder and let into thermal equilibrium with them so that the temperature T_{i-1} or T_i is registered on the thermometer. These temperatures of the heat reservoirs with which the infinitesimal piston is in thermal contact define the local temperature $T(i)$ of the system.

Now, the index i in $T(i)$ may be replaced with the position vector \mathbf{r} and time t in a suitable coordinate system in space-time so that $T(i)$ may be replaced by $T(\mathbf{r}, t)$. The local temperature used in the discussion below has the operational meaning as described above. It must be emphasized that the thermometer inserted is in thermal equilibrium with the hypothetical heat reservoirs of the infinitesimal piston that is undergoing a step of the irreversible Carnot cycle apportioned to the i th cylinder at time t . It is important to remember that the working substance in the cylinder is still undergoing an irreversible process², and this local temperature characterizes the thermal state of the non-equilibrium system at position i or \mathbf{r} and time t .

For a typical example for the kind of temperature measurement discussed here we may take measurement of the temperature of an animate body with a thermometer. The animate body undergoes various energy-matter dissipating³ irreversible processes to sustain it as an open living system. Nevertheless, it is possible to quantify its temperature and even establish the temperature distribution over the body. The temperature of the animate body also depends on what is going on inside the body, namely, the inevitable irreversible processes occurring in it. For example, the body may be locally inflamed and the temperature of the part or the whole body may be higher than the normal average value. Therefore the body temperature is a function of the (irreversible) processes associated with the inflammation and spatially non-uniform. We also recognize on empirical grounds that if there is a spatial inhomogeneity in temperature, that is, if there is a difference in temperatures between two points in space, there is flow of heat or an exchange of energy induced between the two points in question. Yet it is possible to quantify the temperature distribution between the two points. Such a temperature distribution is a set of local temperatures at a given time. We mean by local temperature such temperature as meant in the discussion presented here.

6.2.2 ***Local Pressure***

The pressure of a system can be gauged by means of a manometer, for example. For this purpose a pressure gauge at the same temperature as the local temperature of an infinitesimal cylinder is inserted into the aforementioned infinitesimal cylinder fitted with a piston and its value is read off the gauge when the system comes into mechanical equilibrium with the gauge.

² By an irreversible process we mean a thermodynamic process in which the uncompensated heat does not vanish. Therefore it has the same meaning as used for formulating the global expression for the second law of thermodynamics in Chapter 4.

³ By the term ‘dissipating’ we do not mean destruction or vanishing of energy and matter. The term implies that energy and matter are transformed from a useful to a less useful form for the given task of the process by the system in question.

This procedure can be applied in principle to all the infinitesimal cylinders considered in connection with the measurement of local temperature in Subsection 6.2.1. The mechanical equilibrium between the system and the gauge, however, does not mean that the system itself as a whole is mechanically in equilibrium, but that it is possible to define a mean local pressure in the infinitesimal cylinder which is in mechanical equilibrium with the pressure gauge. Therefore if the pressure gauge is sufficiently small and of sufficiently good resolution the pressure distribution can be experimentally established in the system in the sense compatible with notions of field variables in continuum mechanics. The notion of local pressure has this kind of operational meaning in the local theory presented below. A pressure difference between two points in the system induces a volume change in the local elementary volumes involving the said points.

6.2.3 *Local Chemical Potentials*

In the same manner as for temperature and pressure, local chemical potentials can be measured by means of a gauge which is fitted with a semi-permeable membrane through which only one species is allowed to pass. The temperature and pressure of the gauge can be maintained at the same values as those of the temperature and pressure gauges used earlier to measure local temperature and pressure of an infinitesimal cylinder. Such measurements can, in principle, be made throughout the series of infinitesimal cylinders in Fig. 6.1 and for all species in the system, and a distribution of chemical potentials can be established over all positions in the system at time t even if there are irreversible processes in progress in the system. In this manner the operational meaning of a local chemical potential can be given. A difference in chemical potentials for a species at two spatial points induces a change in the composition of matter in the elementary volumes around the said points in the system.

It is helpful to remark that the aforementioned notions of local intensive variables such as temperature, pressure, and chemical potentials appear in the classical hydrodynamics without their thermodynamic basis and operational meanings sufficiently well discussed and elucidated. The discussions presented in this and previous subsections have enabled us to see what they really mean from the standpoint of generalized thermodynamics.

6.2.4 *Local Generalized Potentials*

The aforementioned local quantities we have considered in the previous three subsections are intimately related to the conserved variables of the system, namely, energy, volume, and mass fractions or concentrations of species. However, as we have seen in earlier chapters, these are not the only macroscopic variables possible that are considered in the generalized

theory. There are non-conserved variables to consider as local field variables which are necessary for the description of irreversible processes in a system, and they may be induced by spatial inhomogeneities in certain potentials akin to the chemical potentials considered earlier. These potentials have been given the name ‘generalized potentials’. We will denote by X_{ka} the local generalized potential conjugate to the non-conserved variable Φ_{ka} . Therefore there are as many generalized potentials as there are non-conserved variables taken in the theory. This plurality of generalized potentials is akin to that of chemical potentials, which are conjugate to concentration variables c_a . Unlike the case of the global theory these generalized potentials are functions of position and time in general. How are the generalized potentials quantified, at least, in principle?

To devise a scheme to make them operational let us recall how chemical potentials are quantified. It is done by putting two bodies in material equilibrium across a semi-permeable contact boundary (membrane), and the state at which there is no longer a mass flow is characterized by a common chemical potential of the two bodies; see Eq. (3.8). Pressure is similarly made operational by putting two bodies in mechanical equilibrium across a deformable contact boundary and by the state where the volume change ceases to occur in the two bodies involved. Therefore a local generalized potential can be determined in principle if the system of a given local temperature, pressure, and chemical potentials in the infinitesimal piston at the point of interest is locally balanced with the measuring device with respect to the non-conserved variable Φ_{ka} that is transferred across the contact boundary. The term transfer is used in the sense that the terms diathermal, deformable, and semi-permeable are used in connection with temperature, pressure, and chemical potentials. It means that the contact boundary lets the system and the measuring device adjust themselves with regard to a difference in Φ_{ka} across the boundary and X_{ka} is defined by the state of the system where the flux of Φ_{ka} vanishes across the contact boundary. Operationally, if the spatial gradient of the flux of Φ_{ka} vanishes across the boundaries of the system and the surroundings, then the values of generalized potentials X_{ka} should be equal to each other across the aforementioned boundaries.

Operationally feasible methods of determining them will be realizable when a thermodynamic theory of irreversible processes is properly formulated in a way consistent with the laws of thermodynamics. We recall that such is the case for chemical potentials which are defined by the state where the fluxes of the species vanish across the contact boundary. However, in the case of equilibrium systems they are not directly measured in practice, but determined in terms of other observables which depend on chemical potentials such as osmotic pressure, freezing point changes, and so forth. Here our task is to define quantities in a logically and thermodynamically self-consistent manner so that they can be measured at least in principle. The present definition of generalized potentials should do for formulating a

thermodynamic theory of irreversible processes, and they are local variables since they may have different values depending on position and time.

6.2.5 The Set of Local Intensive Variables

We have seen through the discussions presented in the previous four subsections that there are intensive variables conjugate to extensive variables of a macroscopic system undergoing a thermodynamic process and how they may be locally measured in principle. As a general remark we note that it is not possible to formulate a local theory of irreversible thermodynamics in the extreme limit where the local intensive variables cannot be defined in the elementary volumes in the system, because they are not uniform in each elementary volume. If this situation occurs then either it is necessary to reduce the scale of the elementary volume to the extent that there are uniform intensive variables properly defined or the description of the phenomenon is beyond the realm of thermodynamics. This latter case is excluded in the present work.

As a summary for the discussions on measurements of temperature, pressure, chemical potentials, and generalized potentials in the previous four subsections, we make the following proposition.

Proposition 2 *There exists a set of measurable local intensive variables, namely, temperature T , pressure p , chemical potentials $\hat{\mu}_a$ ($1 \leq a \leq r$) of species a , and generalized potentials X_{ka} , which are conjugate to the internal energy \mathcal{E} , specific volume v , mass fractions c_a ($1 \leq a \leq r$), and non-conserved variables $\hat{\Phi}_{ka}$ ($k \geq 1, 1 \leq a \leq r$), respectively, for a system consisting of r species. These intensive local variables are amenable to measurements, at least, in principle.*

The set of these local intensive variables will be denoted by \mathfrak{F} , that is, $\mathfrak{F} = (T, p, -\hat{\mu}_a, X_{ka} : k \geq 1, 1 \leq a \leq r)$.

The thermodynamics of irreversible processes developed below will provide theories of measurements for $\hat{\mu}_a$ and X_{ka} as well as other intensive variables just as equilibrium thermodynamics gives theories of measurements of equilibrium pressure, chemical potentials, and so on. These intensive variables are basically the constitutive parameters which must be determined as functions of the conjugate variables. Their determination is therefore a major task of the phenomenological thermodynamics of irreversible processes that emerges in this work.

The simplest example for an approximate X_{ka} which can be used for studies of experimental data is $X_{ka} = -\rho g_{ka} \hat{\Phi}_{ka}$ where g_{ka} is independent of $\hat{\Phi}_{ka}$ but depends on ρ , T , and p . More generally, g_{ka} should be nonlinear functions of $\{\hat{\Phi}_{ka}\}$ as well as ρ , T , and p , which must be empirically

determined with the help of experiment⁴. The examples for the leading members of the set $\{\widehat{\Phi}_{ka}\}$ are:

$$\begin{aligned} X_{1a} &= -\frac{\Pi_a}{2p_a}, \\ X_{2a} &= -\frac{3\Delta_a}{2p_a}, \\ X_{3a} &= -\frac{\mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a}{\widehat{C}_p T p_a} \equiv -\frac{\mathbf{Q}'_a}{\widehat{C}_p T p_a}, \\ X_{4a} &= -\frac{\mathbf{J}_a}{\rho_a}, \end{aligned} \tag{6.9}$$

where \widehat{h}_a is the enthalpy per mass of species a , p_a is the partial pressure of species a , and \widehat{C}_p is the specific heat per unit mass of species a at constant pressure. These in fact are approximate thermodynamic constitutive relations for the generalized potentials, which are valid near equilibrium and on the same footing as the equation of state and the equations for chemical potentials. These approximations for the generalized potentials will find some applications in later chapters, where the local theory of irreversible processes formulated here will be used to study some typical hydrodynamic flow phenomena. The approximation X_{ka} in Eq. (6.9) is, in fact, equivalent to a quadratic approximation for the calortropy in the space \mathfrak{P} .

6.3 Local Forms of the Conservation Laws

Many macroscopic processes in nature are described from the local theory viewpoint. Typical examples are various flow processes in fluid dynamics where local field variables of fluids are assumed to obey partial differential equations for variables such as velocity, mass, and internal energy, for example. Since flow phenomena in fluids must obviously be subjected to the laws of thermodynamics as any macroscopic phenomena should be, it is necessary to cast the internal energy conservation law, namely, the first law of thermodynamics together with the mass and momentum conserva-

⁴ The generalized potentials X_{ka} can be calculated if the non-equilibrium partition function is calculated by using a non-equilibrium ensemble distribution function appropriate for the system. See Farhat, H. and Eu, B.C. (1998) J. Chem. Phys., **109**, 10169 and Al-Ghoul, M. and Eu, B.C. (2001) J. Chem. Phys., **115**, 8481.

tion laws, in local form. This is easily done by following the method of continuum mechanics [2].

6.3.1 Time Derivative of Global Variables

In addition to the first law of thermodynamics the system must obey the mass conservation law and the momentum conservation law as a continuum theory extension of Newton's law of motion. We would first like to obtain a general formula for the relation between the time derivative of a global variable \mathfrak{M} and its local form so that local field equations can be readily written down. As we have already seen in Section 6.1, the global variable \mathfrak{M} of a fluid contained in volume V can be expressed in terms of its local density m and the mass density ρ as follows:

$$\mathfrak{M}(t) = \int_V d\mathbf{r} \rho m(\mathbf{r}, t), \quad (6.10)$$

where the integration is over the whole volume. The time derivative of this quantity is given by [1]

$$\frac{d\mathfrak{M}(t)}{dt} = \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho m(\mathbf{r}, t) + \int_{\mathcal{B}} d\mathcal{B} \cdot \mathbf{u}_B \rho m(\mathbf{r}, t), \quad (6.11)$$

where \mathbf{u}_B is the velocity of the moving boundary and \mathcal{B} stands for the boundary of the system. The direction of the outward normal vector of the boundary is taken for the positive direction of the boundary surface. If the fluid sticks with the boundary then the boundary velocity \mathbf{u}_B is equal to the fluid velocity \mathbf{u} , namely, $\mathbf{u}_B = \mathbf{u}$. Furthermore, if there is a flow \mathfrak{J}_m of the quantity $m(\mathbf{r}, t)$ across the boundary and there is a source Λ_m of $m(\mathbf{r}, t)$ within the volume, the time rate of change in Eq. (6.11) must be balanced by the flow \mathfrak{J}_m and the contribution from the source. Since the outward normal direction of the boundary surface is taken positive, there must hold the relation

$$\frac{d\mathfrak{M}(t)}{dt} = - \int_{\mathcal{B}} d\mathcal{B} \cdot \mathfrak{J}_m + \int_V d\mathbf{r} \Lambda_m(\mathbf{r}, t). \quad (6.12)$$

Equating Eqs. (6.11) and (6.12) yields the global equation

$$\int_V d\mathbf{r} \left[\frac{\partial}{\partial t} \rho m(\mathbf{r}, t) + \nabla \cdot \mathbf{u} \rho m(\mathbf{r}, t) + \nabla \cdot \mathfrak{J}_m - \Lambda_m(\mathbf{r}, t) \right] = 0,$$

which by virtue of continuity implies the local balance equation for $m(\mathbf{r}, t)$

$$\frac{\partial}{\partial t} \rho m(\mathbf{r}, t) + \nabla \cdot [\mathfrak{J}_m + \mathbf{u} \rho m(\mathbf{r}, t)] - \Lambda_m(\mathbf{r}, t) = 0. \quad (6.13)$$

We have used the Gauss theorem for the divergence of \mathfrak{J}_m in these equations. By using the substantial time derivative defined by

$$d_t = \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \quad (6.14)$$

and the mass balance equation presented below, it is possible to cast Eq. (6.13) in the following form

$$\rho d_t \mathfrak{m}(\mathbf{r}, t) = -\nabla \cdot \mathfrak{J}_m + \Lambda_m(\mathbf{r}, t). \quad (6.15)$$

The symbol d_t is reserved for the ‘substantial time derivative’ throughout this work unless stated otherwise. The ‘substantial time derivative’ is the time derivative in the coordinate system moving with the fluid particle of velocity \mathbf{u} . We remark that by the fluid particle we mean a packet of particles (*e.g.*, atoms or molecules) contained in a small elementary volume in the terminology of continuum mechanics. Therefore from the molecular standpoint there are a sufficiently large number of molecules contained in a fluid particle to justify the use of statistical mechanics if one elects to use it.

We have seen that when a fluid system is globally described, it is often convenient to use the global time derivative of a variable as given in Eq. (6.12), which can be split into transfer and dissipation parts as in

$$\frac{d\mathfrak{m}(t)}{dt} = \frac{d_e \mathfrak{m}}{dt} + \frac{d_i \mathfrak{m}}{dt}. \quad (6.16)$$

Comparing it with Eq. (6.12), we identify the transfer and dissipation (or source) parts

$$\frac{d_e \mathfrak{m}}{dt} = - \int_{\mathcal{B}} d\mathcal{B} \cdot \mathfrak{J}_m, \quad (6.17)$$

$$\frac{d_i \mathfrak{m}}{dt} = \int_V d\mathbf{r} \Lambda_m(\mathbf{r}, t). \quad (6.18)$$

Here $d_e \mathfrak{m}/dt$ clearly is the change in $\mathfrak{m}(t)$ per unit time which arises from the exchange of $\mathfrak{m}(\mathbf{r}, t)$ between the system and its surroundings, and $d_i \mathfrak{m}/dt$ is the intrinsic change in $\mathfrak{m}(t)$ per unit time which arises from either the intermolecular force or some other effects of interactions, such as chemical reactions or other irreversible processes, within the system. The former is the transfer part and the latter the source part, which usually provides the mechanism for energy-matter dissipation. These are the transfer and internal time derivative, which were introduced in the previous chapters. The definitions of time derivatives in Eqs. (6.17) and (6.18) are consistent with the rates of change in extensive variables, such as Eqs. (3.10), (4.51), and (4.54), considered in Chapters 3 and 4. The aforementioned two time

derivatives of $\mathfrak{M}(t)$ are inherently, and also evidently, different in their nature and therefore must be regarded as independent contributions to the overall rate of change in $\mathfrak{M}(t)$.

6.3.2 Conservation Laws and Balance Equations

The general balance equation (6.13) presented can be used to obtain the balance equations for mass, momentum, and internal energy if appropriate expressions are chosen for $\mathfrak{M}(t)$. We find it easier to grasp the structure of the theory presented if their derivations are summarized as a proposition and then discuss their derivations afterward.

Proposition 3 *For reacting fluids without a rotational angular momentum the local conservation laws hold for the conserved variables in the forms:*

mass:

$$\rho d_t v = \nabla \cdot \mathbf{u} \quad \text{or} \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}, \quad (6.19)$$

mass fractions:

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l \quad (1 \leq a \leq r), \quad (6.20)$$

momentum:

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (6.21)$$

internal energy:

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{F}_a \cdot \mathbf{J}_a. \quad (6.22)$$

In Eq. (6.20) R_l is the rate of reaction l and ν_{al} is the mass-weighted stoichiometric coefficient of species a in reaction l ; see Eq. (4.49). If the fluid is non-reactive then $R_l = 0$ in the mass fraction balance equations (6.20).

If $\mathfrak{M}(t) = M = \sum_{a=1}^r M_a$ is the total mass of the fluid in volume V then $\mathfrak{m}(\mathbf{r}, t) = \rho(\mathbf{r}, t)$, $\mathfrak{J}_m = \rho \mathbf{u}$, and the source term is absent because the mass is conserved whether there is a chemical reaction or not. Therefore the local equation of continuity follows easily from Eq. (6.13).

If $\mathfrak{M}(t) = M_a$ in the presence of chemical reactions then $\mathfrak{m}(\mathbf{r}, t) = \rho_a(\mathbf{r}, t)$, $\mathfrak{J}_m = \rho_a \mathbf{u}_a$, and the source term is made up of chemical reaction rates R_l :

$$\Lambda_a = \sum_{l=1}^m \nu_{al} R_l, \quad (6.23)$$

which is related to the intrinsic rate of change in mass, as was defined in Eq. (6.18). Note that

$$\sum_{a=1}^r \Lambda_a = \sum_{a=1}^r \sum_{l=1}^m \nu_{al} R_l = 0,$$

which easily follows from Eq. (6.20).

If $\mathbf{M}(t)$ is the momentum of the fluid then $\mathbf{m}(\mathbf{r}, t) = \mathbf{u}$, \mathfrak{J}_m is found to be the stress tensor \mathbf{P} , and the source term Λ_m turns out to be the external force $\rho\mathbf{F}$. Putting these elements together into Eq. (6.13) yields the momentum balance equation, namely, the local momentum conservation law. The mass and momentum balance equations are more mechanical than the internal energy balance equation, which requires a non-mechanical (*i.e.*, thermal) component, namely, \mathbf{Q} , to complete it.

The internal energy balance equation does not manifestly show that the total energy of the system is conserved nor can its relation to the total energy balance equation be obviously seen. To obtain this relation in a manifest form it is necessary to consider the total energy or its density \mathcal{E}_t . For this purpose we first define the potential energy density

$$\rho\mathcal{E}_{\text{pot}} = \sum_{a=1}^r \rho_a \phi_a, \quad (6.24)$$

where ϕ_a is the potential energy per mass defined by

$$\begin{aligned} \mathbf{F}_a &= -\nabla \phi_a, \\ \frac{\partial \phi_a}{\partial t} &= 0. \end{aligned} \quad (6.25)$$

Eq. (6.25) implies that the external force is conservative. The potential energy balance equation for a non-reacting fluid is then obtained by making use of the definition for $\rho\mathcal{E}_{\text{pot}}$ and the mass balance equation already derived:

$$\rho d_t \mathcal{E}_{\text{pot}} = -\nabla \cdot \sum_{a=1}^r \mathbf{J}_a \phi_a - \sum_{a=1}^r \rho_a \mathbf{u}_a \cdot \mathbf{F}_a. \quad (6.26)$$

If there are chemical reactions present in the system the potential energy balance equation is modified owing to the reactive contribution. It can be written in the form

$$\rho d_t \mathcal{E}_{\text{pot}} = -\nabla \cdot \sum_{a=1}^r \mathbf{J}_a \phi_a - \sum_{a=1}^r \rho_a \mathbf{u}_a \cdot \mathbf{F}_a + \sum_{a=1}^r \sum_{l=1}^m \phi_a \nu_{al} R_l. \quad (6.27)$$

If the potential energies do not change before and after chemical reactions the reactive contribution vanishes and the potential energy balance

equation becomes identical with Eq. (6.26) even if there are chemical reactions. This assumption can be often justified because chemical reactions involve rearrangements of chemical bonds over distances comparable to the intermolecular forces or less, and the external forces remain practically unchanged over such distances.

With the definition of the kinetic energy \mathcal{E}_{kin} of the fluid particle associated with convective flow of the fluid

$$\mathcal{E}_{\text{kin}} = \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \quad (6.28)$$

the kinetic energy balance equation is easily derived from the momentum balance equation (6.21)

$$\rho d_t \mathcal{E}_{\text{kin}} = -\nabla \cdot (\mathbf{P} \cdot \mathbf{u}) + \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \rho_a \mathbf{F}_a \cdot \mathbf{u}. \quad (6.29)$$

Finally, we assert that the total energy density is made up of the kinetic energy density \mathcal{E}_{kin} , the potential energy density \mathcal{E}_{pot} , and the internal energy density which is denoted by \mathcal{E} , that is,

$$\mathcal{E}_t = \mathcal{E} + \mathcal{E}_{\text{kin}} + \mathcal{E}_{\text{pot}}. \quad (6.30)$$

This in fact may be regarded as the definition of internal energy. It is further asserted that the total energy of the fluid in a volume V is conserved. This conservation law of total energy has the local form

$$\rho d_t \mathcal{E}_t = -\nabla \cdot \mathbf{J}_E, \quad (6.31)$$

which arises from the generic equation (6.13) because the source term is absent owing to the fact that the total energy is conserved. The total energy flux \mathbf{J}_E here is defined by

$$\mathbf{J}_E = \mathbf{Q} + \mathbf{P} \cdot \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \phi_a. \quad (6.32)$$

The last two terms on the right hand side of Eq. (6.32) is mechanical in origin since they stem from Eqs. (6.27) and (6.29), whereas the quantity \mathbf{Q} called the heat flux is not mechanical, but thermal. The precise physical meaning of \mathbf{Q} is elucidated in such a manner that the energy conservation law (6.31) is satisfied upon definition of \mathbf{J}_E as in Eq. (6.32). Therefore one may interpret that Eq. (6.32) defines \mathbf{Q} . Incorporation of a quantity of thermal origin, namely, \mathbf{Q} , into other forms of mechanical energy fluxes recognizes the fact that heat is a form of energy, and the internal energy is a natural outcome of such recognition; it is intimately tied up with heat, and the total energy balance equation (6.31) provides the necessary connection between them.

The total energy balance equation (6.31) means that the total energy E_t is conserved since

$$\begin{aligned} \frac{dE_t}{dt} &= \frac{d}{dt} \int_V d\mathbf{r} \rho \mathcal{E}_t \\ &= \int_V d\mathbf{r} \left(\frac{\partial}{\partial t} \rho \mathcal{E}_t + \nabla \cdot \mathbf{u} \rho \mathcal{E}_t + \nabla \cdot \mathbf{J}_E \right) \\ &= 0. \end{aligned} \quad (6.33)$$

The internal energy balance equation can be obtained by starting from Eq. (6.33) and reversing the process of calculation leading to Eq. (6.33) with the help of the definitions for \mathcal{E}_t and \mathbf{J}_E as well as the balance equations for \mathcal{E}_{kin} and \mathcal{E}_{pot} .

The absence of a rotational angular momentum implies that the angular momentum conservation law is expressed by the symmetry of the stress tensor : $\mathbf{P} = \mathbf{P}^t$. Eqs. (6.19)–(6.22) are the desired local forms for the mass, mass fractions, momentum, and internal energy conservation laws, respectively, for fluids without an angular momentum.

If there is an internal angular momentum present then the internal angular momentum balance equation should be added to the balance equations mentioned. If the internal angular momentum tensor is denoted by $S_{\alpha\beta}$ and its flux by $Q_{\alpha\beta\gamma}$ ($\alpha, \beta, \gamma = x, y, z$, Cartesian coordinates) the internal angular momentum balance equation is given by [6]

$$\rho d_t S_{\alpha\beta} + \sum_{\gamma} \nabla_{\gamma} Q_{\alpha\beta\gamma} = P_{\alpha\beta} - P_{\beta\alpha}, \quad (6.34)$$

if the angular momentum is not coupled to the external fields. This balance equation implies that if $P_{\alpha\beta} = P_{\beta\alpha}$ the internal angular momentum is conserved as mentioned earlier.

6.3.3 Local Internal Energy Differential

The global energy differential (3.3) is a mathematical representation of the first law of thermodynamics for a global infinitesimal process, and it can be expressed in a differential form for a local infinitesimal process. For the aim in mind we define the change in heat density q by the relation

$$\rho d_t q = -\nabla \cdot \mathbf{Q}. \quad (6.35)$$

In addition to this we also define

$$\mathbf{J}_a = \rho \hat{\mathbf{J}}_a, \quad (6.36)$$

$$[\nabla \mathbf{u}]^{(2)} = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^t] - \frac{1}{3} \delta \nabla \cdot \mathbf{u}, \quad (6.37)$$

$$\boldsymbol{\Pi} = \rho \hat{\boldsymbol{\Pi}} = \frac{1}{2} (\mathbf{P} + \mathbf{P}^t) - \frac{1}{3} \delta \text{Tr} \mathbf{P}, \quad (6.38)$$

$$\Delta = \rho \hat{\Delta} = \frac{1}{3} \text{Tr} \mathbf{P} - p, \quad (6.39)$$

so that the stress tensor is decomposable into hydrostatic pressure (p), excess normal stress (Δ), shear stress ($\boldsymbol{\Pi}$) contributions:

$$\mathbf{P} = p \boldsymbol{\delta} + \Delta \boldsymbol{\delta} + \boldsymbol{\Pi}. \quad (6.40)$$

We note that the stress tensor \mathbf{P} and the heat flux \mathbf{Q} can be further decomposed into species components. Then the internal energy balance equation can be written in the form

$$d_t \mathcal{E} = d_t q + d_t w, \quad (6.41)$$

where $d_t w$ is decomposable into two parts:

$$d_t w = -p d_t v + d_t w_{\text{int}}, \quad (6.42)$$

$$d_t w_{\text{int}} = -\hat{\Delta} \nabla \cdot \mathbf{u} - \hat{\boldsymbol{\Pi}} : [\nabla \mathbf{u}]^{(2)} + \sum_{a=1}^r \hat{\mathbf{J}}_a \cdot \mathbf{F}_a. \quad (6.43)$$

The differential form in Eq. (6.41) is the local form of the global differential form for the first law of thermodynamics, which has been presented in Chapter 3 and 4. In Sect. 6.5 below we will show how and under what condition such global forms may arise from the local internal energy balance equation. It will not only demonstrate their mutual connection but also indicate the subtlety of irreversible thermodynamics in local theory.

6.4 Evolution Equations for Non-Conserved Variables

The balance equations for mass, momentum, and internal energy are the field equations for local macroscopic field variables v or ρ , c_a , \mathbf{u} , and \mathcal{E} , which are called the conserved variables since they obey the conservation laws. We notice that these field equations contain the variables \mathbf{J}_a , \mathbf{P} ,

and \mathbf{Q} in addition to the aforementioned conserved variables. These additional variables \mathbf{J}_a , \mathbf{P} , and \mathbf{Q} are examples of non-conserved variables as already noted, and in the theory of linear irreversible processes [3] or in the conventional classical hydrodynamics [4] they are specified by means of constitutive relations characterizing the substance of interest. These traditionally used constitutive relations, namely, Newton's law of viscosity for the stress tensor, Fourier's law of heat conduction for the heat flux, and Fick's law of diffusion for the diffusion flux, are not necessarily the most general forms of constitutive relations which properly describe the evolution of the non-conserved variables in question. There is a considerable body of experimental and kinetic theory evidence that they require suitable generalizations. Examples for such necessity can be found in rarefied gas dynamics [5], heat transport [6], rheology [7], and non-linear phenomena in semiconductor physics [8], and so on. The non-conserved variables, such as the pressure tensor, heat flux, and diffusion fluxes evolve in space-time. Since they may, in fact, obey their own field equations it is appropriate to present them together with the balance equation for the conserved variables.

To put the theory we have in mind into a form as general as possible we have already introduced a new set of symbols for the non-conserved variables. The set of non-conserved variables can include as many non-conserved variables as necessary for proper description of the process in hand. They are field variables, as are the conserved variables. In some cases, the non-conserved variables may be changing on different, usually faster, time scales and shorter spatial scales than the conserved variables, but, in some other cases, they may be changing on time and spatial scales comparable to those for the conserved variables. Since we are looking for a general formalism for macroscopic phenomena in this work, the conserved and non-conserved variables will be provisionally put on an equal footing with regard to the time and spatial scales of variation. In actual applications of the theory thus formulated we may take into consideration the relative magnitudes of time and spatial scales of variation for the two classes of field variables and develop approximate theories. This will usually turn out to be the case in practice. In the phenomenological irreversible thermodynamics these evolution equations for non-conserved variables are constitutive equations that must be elucidated in comparison with experiment. Having formed this viewpoint we now are able to see the direction to take and make the following proposition for the evolution equations for non-conserved variables Φ_{ka} .

Since the non-conserved variables are field variables they obey partial differential equations. These equations take the form of a balance equation with a source term because they are not conserved in time. It will be found convenient to assume a general form for the evolution equations for the non-conserved variables as below.

Proposition 4 *The non-conserved variable densities $\hat{\Phi}_{ka}$ ($k \geq 1$; $1 \leq a \leq r$) obey the evolution equation*

$$\rho d_t \hat{\Phi}_{ka} = -\nabla \cdot \psi_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka}, \quad (6.44)$$

where ψ_{ka} is the flux of $\Phi_{ka} = \rho \hat{\Phi}_{ka}$, \mathcal{Z}_{ka} is called the kinematic term, which contains a term driving the process Φ_{ka} among other terms non-linearly depending on non-conserved variables and gradients of the conserved variables, and Λ_{ka} is called the dissipation term, which is responsible for energy dissipation arising from the process Φ_{ka} .

The evolution equations (6.19)-(6.22) and (6.44) for macroscopic variables of the space \mathfrak{P} will be called the generalized hydrodynamic equations. The constraint on Eq. (6.44) by the second law of thermodynamics will be the subject of discussion in Chapter 7.

The evolution equation for the non-conserved variable Φ_{ka} is cast in terms of its density $\hat{\Phi}_{ka}$ since the balance equations for the conserved variables are cast in terms of their densities which are members of the variable set spanning the manifold \mathfrak{P} of thermodynamic states. In that way the evolution equations for the conserved and non-conserved variables are put on an equal footing and thus become formally compatible. The dissipation terms are generally algebraic functions of conserved and non-conserved variables. They also depend on material parameters such as transport coefficients and variables such as density, pressure, and so on. Since the kinematic and dissipation terms have different physical origins and characteristics, we have put them as separate terms in the evolution equation (6.44). However, they could have been combined as a single term.

It is possible to give statistical mechanical definitions for the kinematic and dissipation terms, as shown in the work [1, 6] on kinetic theory, and their examples are given in Table 6.1 in the case of dilute monatomic gases. However, their explicit forms in terms of conserved and non-conserved variables are not necessary for the formal theory of irreversible processes we have in mind in the formulation part of this work. As will be seen, they will be subjected to the constraint of the second law of thermodynamics, and in this sense the theory developed here is fully consistent with the second law of thermodynamics.

It is remarked that the linearized versions of the evolution equations for the stress tensor and heat flux were known to Maxwell [9] as the transfer equations, on which he based his calculation of transport coefficients under the steady state assumption, and Chapman [10] later used them in his theory of linear transport processes in gases. Finally, although the examples for \mathcal{Z}_{ka} presented in Table 6.1 are for dilute monatomic gases they are not too different from those for dense simple fluids as far as their mathematical forms are concerned. The additional terms appearing in \mathcal{Z}_{ka} in the case of dense fluids stem from the intermolecular and intramolecular forces [6], but they are usually higher order moments than Φ_{ka} . Therefore they may

be neglected in a lower order theory. Consequently the examples for Z_{ka} presented in Table 6.1 have a fairly wide range of utility in the theory of irreversible processes in simple fluids. We emphasize that the constitutive equations (6.44) are empirical in the present theory and, as such, must be determined empirically. Irreversible thermodynamics is a theory by which constitutive equations can be determined in a manner consistent with the laws of thermodynamics.

6.5 Global Form of the First Law Revisited

Having introduced various conservation laws and the evolution equations for the non-conserved variables, it is important to see if the global form of the first law of thermodynamics presented in Chapter 3 follows from the internal energy balance equation, and under what condition if it does. This derivation is useful because the internal energy balance equation can be derived from suitable molecular models which provide kinetic equations of matter in non-equilibrium. The investigation carried out in the following therefore will enable us to learn about the local theory details of the internal work, which we have presented as a proposition in Chapter 4. and the non-classical contribution to heat transfer dQ . The investigation of the recovery of the global form for the first law of thermodynamics is particularly valuable, because the internal energy balance equation is deduced from the total energy conservation law with the help of the mass and momentum conservation laws and it is possible to see thereby the connection of the so obtained internal energy balance equation with the global form for the first law. The byproduct of this investigation is the clarification of the internal work, or the power d_iW/dt , in the global formulation, which is usually ignored in the conventional theory of thermodynamic processes in the literature.

On multiplying $T^{-1}\rho$ with Eq. (6.41), integrating over V , introducing a new heat flux \mathbf{Q}^c defined by

$$\mathbf{Q}^c = \mathbf{Q} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \psi_{ka}, \quad (6.45)$$

and rearranging the terms, we obtain the equation

$$\int_V d\mathbf{r} T^{-1} \rho \frac{d\mathcal{E}}{dt} = - \int_V d\mathbf{r} \nabla \cdot \left(\frac{\mathbf{Q}^c}{T} \right) + T^{-1} \frac{dW_{ex}}{dt} + T^{-1} \frac{dW_{int}}{dt}. \quad (6.46)$$

Here

$$\frac{dW_{\text{ex}}}{dt} = T \int_V d\mathbf{r} \left[\frac{p}{T} \nabla \cdot \mathbf{u} - \sum_{a=1}^r \frac{\hat{\mu}_a}{T} \nabla \cdot \mathbf{J}_a + \sum_{a=1}^r \sum_{k \geq 1} \frac{X_{ka}}{T} \nabla \cdot \psi_{ka} \right], \quad (6.47)$$

$$\begin{aligned} \frac{dW_{\text{int}}}{dt} = & -T \int_V d\mathbf{r} T^{-1} \left[\Delta \nabla \cdot \mathbf{u} + \boldsymbol{\Pi} : [\nabla \mathbf{u}]^{(2)} + \mathbf{Q}^c \cdot \nabla \ln T \right] \\ & - T \int_V d\mathbf{r} T^{-1} \sum_{a=1}^r \left[\mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a) - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka} \right] \end{aligned} \quad (6.48)$$

Before proceeding further in the discussion, it is useful to note that the new heat flux \mathbf{Q}^c in fact is intimately related to the local calortropy flux, as will be found in Chapter 7.

If the temperature is uniform on the surface \mathcal{B} then the first term on the right hand side of Eq. (6.46) can be written as

$$\begin{aligned} - \int_V d\mathbf{r} \nabla \cdot \left(\frac{\mathbf{Q}^c}{T} \right) &= -T^{-1} \int_{\mathcal{B}} d\mathcal{B} \mathbf{Q}^c \\ &\equiv T^{-1} \frac{dQ}{dt}. \end{aligned} \quad (6.49)$$

The second line of Eq. (6.49) amounts to the assertion of the meaning for the heat transfer rate dQ/dt from the local theory viewpoint. Furthermore, since \mathbf{Q}^c consists of components associated with the internal energy transfer and others, it is appropriate to decompose the surface integral into two components attributed to the two distinct quantities below:

$$- \int_{\mathcal{B}} d\mathcal{B} \mathbf{Q}^c = \frac{dQ_E}{dt} + \frac{dQ_n}{dt}, \quad (6.50)$$

where the first term on the right hand side is the transfer rate of internal energy whereas the second consists of a heat transfer rate arising from a mass transfer and a heat transfer rate arising from a transfer of non-conserved quantities:

$$\frac{dQ_E}{dt} = - \int_{\mathcal{B}} d\mathcal{B} \mathbf{Q}, \quad (6.51)$$

$$\frac{dQ_n}{dt} = - \int_{\mathcal{B}} d\mathcal{B} \left[- \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \psi_{ka} \right]. \quad (6.52)$$

Thus we see that

$$\frac{dQ}{dt} = \frac{dQ_E}{dt} + \frac{dQ_n}{dt}. \quad (6.53)$$

The heat transfer rate arising from the non-conserved quantities, namely, the second term on the right hand side, in Eq. (6.52) is a non-classical contribution, which is not present in the theory of linear irreversible thermodynamics. When the global form of the first law of thermodynamics was formulated in Sec. 3.4, Chapter 3, heat transfer dQ was split into two parts as in Eq. (6.53). The derivation of Eq. (6.53) presented here provides the local theory foundation of the viewpoint represented by the equation regarding the meaning of dQ for the heat change in the first law of thermodynamics.

We now examine Eq. (6.47). It is convenient to define the following mean values (volume averages) of the intensive variables:

$$\begin{aligned} \left\langle \frac{p}{T} \right\rangle &= V^{-1} \int_V d\mathbf{r} \frac{p}{T}, \\ \left\langle \frac{\hat{\mu}_a}{T} \right\rangle &= V^{-1} \int_V d\mathbf{r} \frac{\hat{\mu}_a}{T}, \\ \left\langle \frac{X_{ka}}{T} \right\rangle &= V^{-1} \int_V d\mathbf{r} \frac{X_{ka}}{T}. \end{aligned} \quad (6.54)$$

If fluctuations of intensive variables from their averages, $p/T - \langle p/T \rangle$, and so on are negligible then Eq. (6.47) can be replaced with their volume averages, and Eq. (6.47) can be written as

$$\frac{dW_{ex}}{dt} = T \left[- \left\langle \frac{p}{T} \right\rangle \frac{dV}{dt} + \sum_{a=1}^r \left\langle \frac{\hat{\mu}_a}{T} \right\rangle \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} \left\langle \frac{X_{ka}}{T} \right\rangle \frac{d_e \Gamma_{ka}}{dt} \right], \quad (6.55)$$

where the transfer time derivatives are defined by

$$\begin{aligned} \frac{d_e M_a}{dt} &= - \int_B d\mathcal{B} \mathbf{J}_a, \\ \frac{d_e \Gamma_{ka}}{dt} &= - \int_B d\mathcal{B} \psi_{ka}. \end{aligned} \quad (6.56)$$

These are the rate of mass transfer and the transfer rate of non-conserved quantity, respectively. If the volume is reduced to such an extent that the

intensive variables T , p , $\hat{\mu}_a$, and X_{ka} are uniform over the volume then Eq. (6.55) can be written in the form

$$\frac{dW_{ex}}{dt} = -p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_e \Gamma_{ka}}{dt}. \quad (6.57)$$

Recall that this is the work done by the system which appears in the expression for work in Eq. (3.9) in Chapter 3. Thus the meanings of the intensive variables appearing in this expression and the manner in which it is derived from the local formula for work clarify the limitations of Eq. (3.9) from the local theory viewpoint: that is, p , $\hat{\mu}_a$, and X_{ka} must be uniform over V for Eq. (3.9) to be meaningful. This derivation therefore indicates the range of validity of the global form of irreversible thermodynamics based on the global differential form for the internal energy.

We consider Eq. (6.48). Let us define the following volume averages:

$$\langle T^{-1} A \rangle = V^{-1} \int_V d\mathbf{r} T^{-1} A,$$

where $A = \Delta$, $\mathbf{\Pi}$, \mathbf{Q}^c , and ψ_{ka} . Also define the mean thermodynamic forces

$$\chi_v = - \langle \nabla \cdot \mathbf{u} \rangle,$$

$$\chi_s = - \langle [\nabla \mathbf{u}]^{(2)} \rangle,$$

$$\chi_t = - \langle \nabla \ln T \rangle,$$

$$\chi_{X_{ka}} = - \langle \nabla X_{ka} \rangle,$$

$$\chi_a = - \langle (\nabla \hat{\mu}_a - \mathbf{F}_a) \rangle = - \langle \nabla \hat{\mu}_{\phi a} \rangle,$$

where

$$\hat{\mu}_{\phi a} = \hat{\mu}_a + \phi_a, \quad (6.59)$$

if there exists a potential for \mathbf{F}_a . An example of $\hat{\mu}_{\phi a}$ is the electrochemical potential of charged species if the external potential is electric. If the volume is reduced sufficiently small so that the temperature is uniform within the volume then the volume average can be written as

$$\langle T^{-1} A \rangle = T^{-1} \langle A \rangle \equiv T^{-1} V^{-1} \langle A \rangle_V, \quad (6.60)$$

where

$$\langle A \rangle_V = \int_V d\mathbf{r} A.$$

If fluctuations of A/T from $\langle T^{-1}A \rangle$ are negligible then Eq. (6.48) can be written in the form

$$\begin{aligned} \frac{dW_{\text{int}}}{dt} &= \langle \Delta \rangle_V \chi_v + \langle \Pi \rangle_V : \chi_s + \langle Q^c \rangle_V \cdot \chi_t + \sum_{a=1}^r \langle J_a \rangle_V \cdot \chi_a \\ &\quad + \sum_{a=1}^r \sum_{k \geq 1} \langle \psi_{ka} \rangle_V \odot \chi_{Xka} \\ &\equiv \frac{d_i W}{dt}, \end{aligned} \quad (6.61)$$

where the symbol \odot denotes contraction of the tensors to a scalar. On combining the results obtained earlier, the first law of thermodynamics for global processes is deduced from the local internal energy balance equation in the following form

$$\frac{dE}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \frac{d_e \Gamma_{ka}}{dt} + \frac{d_i W}{dt}. \quad (6.62)$$

Since this equation is formally identical with Eq. (3.12), we are now able to identify Σ_l in Proposition 1 in Sec. 4.7.4 with Eq. (6.61) and thus the thermodynamic forces ω_{ka} and ϖ_{ka} in the proposition. Since

$$\begin{aligned} \langle \Pi_a \rangle_V &= \Gamma_{1a}, \quad \langle \Delta_a \rangle_V = \Gamma_{2a}, \quad \langle Q'_a \rangle_V = \Gamma_{3a}, \\ \langle J_a \rangle_V &= \Gamma_{4a}, \quad \langle \psi_{ka} \rangle_V = \Upsilon_{ka}, \end{aligned} \quad (6.63)$$

where $k \geq 1$ and $1 \leq a \leq r$, it follows that

$$\begin{aligned} \omega_{1a} &= \chi_s, \quad \omega_{2a} = \chi_v, \quad \omega_{3a} = \chi_{\ln T}, \\ \omega_{4a} &= \chi_a + (\hat{h}_a - \hat{\mu}_a) \chi_{\ln T}, \quad \varpi_{ka} = \chi_{Xka} + X_{ka} \chi_{\ln T}. \end{aligned} \quad (6.64)$$

This derivation not only enables us to identify $d_i W/dt$ and dQ_n/dt in terms of thermodynamic forces and volume averages of local field variables, but also clarifies the underlying assumptions and approximations from the viewpoint of the local field theory of macroscopic irreversible processes when the first law is written in the form of Eq. (6.62). It also verifies the consistency with the first law of thermodynamics of the local balance equations presented earlier for the conserved variables. Moreover, the aforementioned assumptions and approximations regarding Eq. (6.62) and, in particular, the intensive variables imply the limitations to which the thermodynamics of irreversible processes in systems of a finite volume is subjected.

It is helpful for deeper insight into the mathematical structure of irreversible thermodynamics to examine the term $\langle Q^c \rangle_V \cdot \chi_{\ln T}$ in the internal work. When $\langle Q^c \rangle_V$ is identified with Q in the Clausius inequality, this is

TABLE 6.1. Examples for Z_{ka} and Λ_{qa} for Dilute Gases

$Z_{1a} = -2[\mathbf{J}_a(d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u}]^{(2)}$
$- 2\Delta_a [\nabla \mathbf{u}]^{(2)} - 2p_a [\nabla \mathbf{u}]^{(2)}$
$Z_{2a} = -\frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \frac{2}{3}\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u}$
$- p_a d_t \ln(p_a v^{5/3}) - \nabla \cdot (\mathbf{J}_a p_a / \rho_a)$
$Z_{3a} = -(d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \delta) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \boldsymbol{\varphi}_a^{(3)} : \nabla \mathbf{u}$
$- \mathbf{J}_a d_t \hat{h}_a - \mathbf{P}_a \cdot \nabla \hat{h}_a$
$Z_{4a} = -\rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u} = c_a \nabla \cdot \mathbf{P} - (\mathbf{F} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}$
$\Lambda_{qa} = (\beta g)^{-1} \sum_{b=1}^r \sum_{k \geq 1} R_{ab}^{(qk)} X_{kb} q(X)$

a term that accounts for the energy dissipation accompanying the heat transfer between the system and the surroundings at the boundaries of two different temperatures. It appears in Eq. (6.61) because the local internal energy balance equation (6.46) is multiplied by T^{-1} ; see Footnote 6 below Eq. (4.33). The reader will recall that this particular term appeared when the Clausius inequality (4.30) was derived from the Carnot theorem or Eq. (4.33) and when the derivation of Ineq. (4.30) was carefully analyzed, but to preserve the original form of the Clausius inequality the term was absorbed into the uncompensated heat N . Therefore, if the uncompensated heat were written as

$$N = N' - \langle \mathbf{Q}^c \rangle_V \cdot \chi_{\ln T},$$

then it would not have been necessary to multiply T^{-1} to the local internal energy balance equation and consequently the term $\langle \mathbf{Q}^c \rangle_V \cdot \chi_{\ln T}$ would have appeared in $d_i W/dt$ in Eq. (6.61). Either way, Proposition 1 remains the same for the uncompensated heat, as will be readily seen in the next chapter. To give a more concrete idea of the kinematic and dissipation terms in Eq. (6.44) for Proposition 4, examples for them are presented for dilute gases in Table 6.1. These examples, derivable from the Boltzmann equation as shown in Refs. [1] and [6], are not only thermodynamically

consistent but also quite well tested in comparison with experimental data on flow characteristics of gases.

The symbols in Table 6.1 are as follows: $\varphi_a^{(3)}$ is a moment of rank three, namely, a rank three tensor,

$$\mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a, \quad (6.65)$$

$$g = (m/2k_B T)^{1/2} n^{-2} d^{-2}, \quad (6.66)$$

with n being the number density, d the mean size parameter of the molecule, m the mean mass; and $q(X)$ is a positive non-linear function of $\{X_{qa}\}$, which, for example, has the form

$$q(X) = \frac{\sinh \kappa(X)}{\kappa(X)}, \quad (6.67)$$

where $\kappa(X)$ denotes a non-dimensional dissipation function

$$\kappa(X) = \left(\sum_{a=1}^r \sum_{b=1}^r \sum_{q \geq 1} \sum_{k \geq 1} X_{qa} R_{ab}^{(qk)} X_{kb} \right)^{1/2} \quad (6.68)$$

and $R_{ab}^{(qk)}$ are phenomenological coefficients which obey the Onsager reciprocal relations [11]. See Chapters 7 and 9 of Ref. [1] for the kinetic theory expressions for these quantities. In fact, $q(X)$ is the first order cumulant approximation for the Boltzmann collision integral. There are higher order cumulant expressions for the dissipation terms Λ_{qa} in Refs. [1] and [6]. They may be more appropriate for some irreversible processes far removed from equilibrium, but are more mathematically complicated than $\Lambda_{qa}(X)$ given in Table 6.1. The function $\kappa^2(X)$ is a generalization of the Rayleigh dissipation function [12] to which it reduces in the lowest order approximation for X_{qa} , because X_{qa} are generally non-linear with regards to $\Pi_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a$, and so on, as was indicated in the previous chapter. In the aforementioned approximation $\kappa^2(X)$ becomes quadratic with respect to the fluxes $\Pi_a, \Delta_a, \mathbf{Q}'_a$, and \mathbf{J}_a and thus the Rayleigh dissipation function. In the case of dense fluids and liquids there appear terms related to intermolecular potentials in the kinematic terms Z_{ka} , but the dilute gas forms for Z_{ka} are still capable of describing the flow properties quite well according to the studies carried out up to now.

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Local Form of the Second Law of Thermodynamics

The mathematical representation of the second law of thermodynamics was given for global reversible and irreversible processes in Chapter 4. In the case of reversible processes such a global representation is sufficient for describing the thermodynamics of a system because the thermodynamic variables involved are spatially uniform over the system. Distinction between global and local processes does not occur in equilibrium thermodynamics. However, if the processes are irreversible the thermodynamic variables generally are no longer uniform in space except for some special cases where they are dependent on time only or the processes of interest are global. Therefore it is generally necessary to develop a local theory of irreversible processes. To initiate such a development a local representation is required for the second law of thermodynamics. The formalism developed in Chapter 4 then must be given a local form in terms of field variables. The aim of the present chapter is to deduce a local field theory from the global form of the second law of thermodynamics.

In applying irreversible thermodynamics one may find that a global description of irreversible processes is sufficient, or it is sometimes a practical necessity because the local description may be too detailed for the given phenomenon of interest and thus can be dispensed with. Nevertheless, a local formulation of the second law of thermodynamics is important because the local evolution equation of calortropy serves as a guide in developing a molecular theory of irreversible processes which often gives rise to a local field theory and thus can provide non-equilibrium statistical mechanics with phenomenological foundations of macroscopic irreversible processes. Furthermore, hydrodynamics, which encompasses diverse flow phenomena

in fluids, is a local field theory of irreversible processes. It thus gives another reason for studying the local formulation of the second law of thermodynamics.

Once a thermodynamically consistent molecular model is constructed, the local field theory deduced from the model can be taken advantage of to derive a global theory of irreversible processes by taking volume averages of the local variables and their local evolution equations, as was demonstrated in the last section of Chapter 6. This latter line of approach to the description of global processes is, in fact, very advantageous since the local variables and their evolution equations can often be easily derived from the molecular model for them, whereas it is hard to deduce their global counterparts from the thermodynamic laws alone, especially, if the processes are non-linear, as we have already seen in Chapters 3 and 4.

7.1 Local Differential Form for Calortropy

With the preparations made in Chapters 4 and 6 regarding the mathematical representation of the second law of thermodynamics and operational definitions of local temperature, pressure, and so forth for the intensive quantities conjugate to various thermodynamic variables, we now formulate a thermodynamic theory of irreversible processes in local form.

7.1.1 Calortropy Balance Equation

We have shown that the second law of thermodynamics expressed by the Clausius inequality can be represented by the differential form of Calortropy Ψ , which extends to irreversible processes the notion of the Clausius entropy introduced for reversible processes only. The local calortropy density $\hat{\Psi}$ is related to the global calortropy Ψ through the volume integral

$$\Psi = \int_V d\mathbf{r} \rho \hat{\Psi}(\mathbf{r}, t), \quad (7.1)$$

as was briefly indicated together with other local variables in the previous chapter. The vanishing contour integral (4.41), a form similar to the vanishing contour integral (3.3) used for the first law of thermodynamics in the case of a cyclic process, can be written in the form of time integral similar to Eq. (3.6)

$$\int_0^\tau dt \frac{d\Psi}{dt} = 0, \quad (7.2)$$

where τ is the period of the cyclic process. The differential form (4.40) can be cast into a time derivative form

$$\frac{d\Psi}{dt} = T^{-1} \frac{dQ}{dt} + \frac{dN}{dt}. \quad (7.3)$$

Since this is a formal relation between three physical quantities which do not render themselves in explicit forms in the space \mathfrak{P} , the first and major task of irreversible thermodynamics is in elucidating their physical meanings, and we have done that for global processes in Chapter 4 and partly in Chapter 6. Their physical meanings will be elucidated in local form in the following.

For the goal we aim at in this chapter we will first cast Eq. (7.3) into a local form. Since the time derivatives in Eq. (7.3) are the global rates of change, it is possible to express them as volume integrals of the following forms by using the procedure discussed in Chapter 6 and particularly the formula developed in Subsec. 6.3.1. First of all, $d\Psi/dt$ may be written in the form

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \left[\frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right], \quad (7.4)$$

where \mathbf{u} is the fluid velocity. It is assumed in the derivation of Eq. (7.4) that the fluid sticks with the boundaries, as was in Chapter 6. Otherwise \mathbf{u} must be replaced by the velocity of the boundary movement \mathbf{u} .

On the other hand, since dQ/dt represents a measure of the compensated heat transferred between the system and the surroundings, it should be identified with the heat transfer rate in the global form of the first law of thermodynamics presented in Chapter 3. We shall provisionally assume that there exists a local heat flux \mathcal{Q} which gives rise to the aforementioned heat transfer rate:

$$T^{-1} \frac{dQ}{dt} = - T^{-1} \int_{\mathcal{B}} d\mathcal{B} \cdot \mathcal{Q}. \quad (7.5)$$

The subscript \mathcal{B} to the integral in Eq. (7.5) stands for the surface of the enclosing volume whose outward normal direction is counted positive.

The equality in Eq. (7.5) can be achieved in the following way: let us observe that since $T^{-1}dQ$ is the differential form for $[(Q/T)_i - (Q/T)_{i-1}]$, the term $T^{-1}dQ/dt$ may be written as the sum over the infinitesimal cylinders:

$$T^{-1} \frac{dQ}{dt} = \sum_i \left(T^{-1} \frac{dQ}{dt} \right)_i,$$

which then can be written as

$$\sum_i \left(T^{-1} \frac{dQ}{dt} \right)_i = - \sum_i \int_{\mathcal{B}_i} d\mathcal{B}_i \cdot \frac{\mathcal{Q}(\mathcal{B}_i)}{T(\mathcal{B}_i)} = - \int_{\mathcal{B}} d\mathcal{B} \cdot \frac{\mathcal{Q}}{T},$$

where $\mathcal{B} = \cup_i \mathcal{B}_i$. Eq. (7.5) then follows easily if T is uniform over \mathcal{B} . In this connection the reader should recall the argument used for the meaning of local temperature in Sec. 6.2. The same argument underlies the discussion on the meaning of T as given earlier. The vector \mathcal{Q} is the net heat flux at the surface; it is the compensated heat flux.

If the temperature is uniform on the surface \mathcal{B} , with the help of the Gauss theorem the surface integral in this equation may be written in the form

$$T^{-1} \frac{dQ}{dt} = - \int_V d\mathbf{r} \cdot \nabla \left[\frac{\mathcal{Q}}{T(\mathbf{r}, t)} \right] \quad (7.6)$$

It must be recalled that the differential form (7.3) pertains to one of infinitesimal Carnot cycles that operate between two heat reservoirs at a minute difference of temperature and comprise the original Carnot cycle for which Eq. (4.33) or Inequality (4.28) holds. It is assumed that the temperature is uniform over the surface \mathcal{B} of the volume of the infinitesimal Carnot cycle which is in contact with the heat reservoir of temperature T . Except for the terminal infinitesimal Carnot cycles this heat reservoir of temperature T is not one of the heat reservoirs of the original finite Carnot cycle, which operates between temperatures T_1 and T_2 and is imagined to consist of infinitesimal Carnot cycles that Clausius used in his derivation of Inequality (4.29). The precise meaning of \mathcal{Q} in Eq. (7.6) is not as yet elucidated, but it is clearly related to the heat and matter transfer between the system and its surroundings. This vector \mathcal{Q} is counted positive in the direction normal to the surface. We recall that the heat transfer rate dQ/dt was related to the vector \mathbf{Q}^c in Chapter 6, and indeed \mathcal{Q} will be identified with \mathbf{Q}^c , but at the moment we have no particular reason to jump to the conclusion that the former must be identical with the latter before further analysis is made.

Since the last term dN/dt on the right of Eq. (7.3) is a quantity—more precisely, an uncompensated heat change per unit time—inherent to the system itself, it is reasonable to decompose it into local contributions within the system and thus to write it in terms of density $\widehat{\Xi}_c$:

$$\frac{dN}{dt} = \int_V d\mathbf{r} \rho \widehat{\Xi}_c(\mathbf{r}, t). \quad (7.7)$$

By the second law of thermodynamics and by continuity

$$\widehat{\Xi}_c(\mathbf{r}, t) \geq 0 \quad (7.8)$$

everywhere in V . The equality holds for reversible processes or at equilibrium only. The quantity $\rho \widehat{\Xi}_c(\mathbf{r}, t)$ is the local rate of uncompensated heat per volume and Inequality (7.8) therefore is the local form of the second law of thermodynamics.

Use of Eqs. (7.4)–(7.7) in Eq. (7.3) implies, by virtue of continuity, the balance equation for the calortropy density [2]:

$$\rho \frac{d\widehat{\Psi}}{dt} = - \nabla \cdot \left[\frac{\mathcal{Q}}{T(\mathbf{r}, t)} \right] + \rho \widehat{\Xi}_c(\mathbf{r}, t). \quad (7.9)$$

We will call $\mathbf{J}_c \equiv \mathcal{Q}/T$ and $\rho \widehat{\Xi}_c$ the calortropy flux and the calortropy production, respectively. Except that $\rho \widehat{\Xi}_c$ must be always positive and vanishes

for reversible processes by virtue of $dN/dt \geq 0$, at this point we do not as yet have the precise forms for these quantities \mathcal{Q} and $\widehat{\Xi}_c$ that would permit deductions on the properties of calortropy. The basic aim of the theory of irreversible processes is to elucidate these quantities in a manner consistent with the second law of thermodynamics.

To learn about \mathcal{Q} and $\widehat{\Xi}_c$ and deduce their mathematical forms we make the following reasoning. First of all, since a macroscopic system clearly must evolve in conformity with the conservation laws of mass, momentum, and energy according to the basic tenet held in this work, the relevant variables for characterizing the macroscopic state of the system should include the conserved variables obeying the balance equations put forward in Proposition 3. Since these balance equations require constitutive equations for the stress tensor, heat flux, and diffusion fluxes, it is necessary to append the set of the former with the evolution equations for non-conserved variables presented in Proposition 4. Furthermore, the constitutive equations for non-conserved variables must be subjected to the constraints of the thermodynamic laws. Therefore it is evident that the space (or manifold) of local macroscopic variables necessary to describe the calortropy is the thermodynamic space \mathfrak{P} . The desired deduction of the properties of calortropy will be possible if the calortropy flux and the calortropy production are also elucidated in the space \mathfrak{P} . These quantities, however, do not suggest themselves in an obvious mathematical form nor are their forms suggested by the second law of thermodynamics except that $\widehat{\Xi}_c$ must be positive semi-definite everywhere in V so as to satisfy the second law of thermodynamics. Nevertheless, for the thermodynamic constraints to be made as explicitly and clearly as possible it is reasonable to have the mathematical forms for $\widehat{\Psi}$, \mathcal{Q} , and $\widehat{\Xi}_c$ as parallel to their global theory counterparts as possible. Given the consideration made here just now, it is reasonable, and will be found consistent with the global theory presented in the earlier chapters, to set $\mathcal{Q} \equiv \mathbf{Q}^c$ and to have a form $f o \widehat{\Xi}_c t h a t$ can be readily related¹ to $(d_i W/dt - dQ_n/dt)$. On the basis of the consideration just given now, to facilitate further progress we make the following proposition for them [2].

Proposition 5 *The calortropy flux $\mathbf{J}_c \equiv \mathcal{Q}/T \equiv \mathbf{Q}^c/T$ is given by the bilinear form of the intensive variables T^{-1} , $\widehat{\mu}_a T^{-1}$, and $X_{ka} T^{-1}$ ($k \geq 1$, $1 \leq a \leq r$) paired, respectively, with \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} (flux of Φ_{ka}) as follows:*

$$\mathcal{Q}_a \equiv \mathbf{Q}_a^c = \mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \quad (7.10)$$

¹ An important input is made for \mathcal{Q} and $\widehat{\Xi}_c$ from the kinetic theory of matter [1] which yields molecular representations of \mathcal{Q} and $\widehat{\Xi}_c$. The kinetic theory of matter, in fact, is indispensable in elucidating these quantities, especially, if the processes are non-linear as often is the case in practice.

so that

$$\begin{aligned}\mathcal{Q} &= \sum_{a=1}^r \mathcal{Q}_a, \\ \mathbf{J}_c &= \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \right),\end{aligned}\quad (7.11)$$

and the calortropy production $\Xi_c = \rho \hat{\Xi}_c$ is given by the bilinear form

$$\Xi_c \equiv \rho \hat{\Xi}_c \quad (7.12)$$

$$\begin{aligned}&= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a) \\ &\quad - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka}] + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}).\end{aligned}$$

By the second law of thermodynamics there always holds the inequality $\Xi_c \geq 0$, the equality holding for reversible processes only.

The inequality for the calortropy production Ξ_c imposes the positivity condition that the kinematic and dissipation terms \mathcal{Z}_{ka} and Λ_{ka} in the evolution equation for $\hat{\Phi}_{ka}$ must satisfy, and thus dictates the acceptable forms for them as parts of constitutive relations for the material of interest. Therefore the evolution equations for non-conserved variables are not free but must have certain mathematical forms in order for the theory of irreversible processes in hand to conform to the second law of thermodynamics, represented by $\Xi_c \geq 0$ in local theory. In the sense that $\Xi_c \geq 0$ the evolution equations for Φ_{ka} ($k \geq 1$) presented in Proposition 4 are consistent with the second law of thermodynamics and so are the evolution equations made up of Eqs. (6.19)–(6.22) and (6.44) which are coupled to each other and constitute the equations of generalized hydrodynamics or, simply, *generalized hydrodynamic equations*. The theory of irreversible processes is then said to be thermodynamically consistent.

It must be noted that $(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u}$ may be split into two parts as

$$(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} = \boldsymbol{\Pi} : [\nabla \mathbf{u}]^{(2)} + \Delta \nabla \cdot \mathbf{u}$$

and the terms in the square brackets in Eq. (7.12) except for the last term involving ∇X_{ka} are those making up the entropy production in the theory of linear irreversible processes [3, 4, 5, 6]. The last term mentioned is a bilinear product of the gradient of the generalized potential and the flux ψ_{ka} of the non-conserved variable $\hat{\Phi}_{ka}$ just as the other terms are bilinear products of the velocity gradient and the momentum flux (*i.e.*, the stress

tensor), of the temperature gradient and the compensated heat flux, and so on.

Therefore it may be said that the gradient ∇X_{ka} induces the flux ψ_{ka} of non-conserved variable $\hat{\Phi}_{ka}$ just as $\nabla \hat{\mu}_a$ induces diffusion flows of species. The occurrence of such a flux gives rise to an uncompensated heat just as do the stress, compensated heat flux, and so on. In addition to the aforementioned contribution from ψ_{ka} , there are contributions to the uncompensated heat from the kinematic and dissipation terms—the last group of terms in Eq. (7.12)—in the evolution equations for the non-conserved variables in the present generalized theory. The calortropy production Ξ_c presented here generalizes the Rayleigh dissipation function [7] holding for linear irreversible processes. Recall that the Rayleigh dissipation function is quadratic with respect to fluxes or thermodynamic forces, or is bilinear with regard to fluxes and conjugate thermodynamic forces. In the case of linear irreversible processes the three modes of expressing the Rayleigh dissipation function are equivalent, but the bilinear form is not the same as the quadratic form for it if the processes are non-linear, as is usually the case for systems far removed from equilibrium.

The calortropy flux proposed is also seen to include the classical terms as well as non-classical terms—the last group of terms in Eq. (7.11)—attributable to the non-conserved variables. The calortropy flux and the calortropy production proposed in Proposition 5 are mutually compatible in the sense that they give rise to a differential form for $d_t \hat{\Psi}$, as will be shown. Although Eqs. (7.11) and (7.12) are sufficient for \mathbf{J}_c and Ξ_c to yield a one-form for $d_t \hat{\Psi}$, it is not unique. For example, a vector \mathbf{A} and its divergence $\nabla \cdot \mathbf{A}$ can be added to \mathbf{J}_c and Ξ_c , respectively, with no effect at all on the one-form that can be obtained from the balance equation for the calortropy. In fact, the vector \mathbf{A} can be taken with $\sum_{a=1}^r \mathbf{J}_a / m_a$, for example. The formulas for \mathbf{J}_c and Ξ_c proposed in Proposition 5 therefore are minimal in the sense that they are sufficient to produce a one-form for $d_t \hat{\Psi}$, which will be shown in the next subsection, and to account adequately for experiments on thermophysical phenomena in matter.

7.1.2 Calortropy Differential

Use of Eqs. (7.11) and (7.12) in the calortropy balance equation (7.9) makes it possible to determine $\hat{\Psi}$ in the space \mathfrak{P} if the conservation laws in Proposition 1 and the evolution equations in Proposition 3 are used. In particular, if the fluxes \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} are either eliminated or rearranged by means of generalized hydrodynamics equations (6.19)–(6.22) and (6.44), then it is possible to put the balance equation for $\hat{\Psi}$ in a Pfaffian differential form

(one-form):

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right). \quad (7.13)$$

We now describe how this differential form is obtained from the calortropy balance equation.

To derive this differential form it is necessary to transform the calortropy balance equation by using the balance equations for c_a , \mathcal{E} , and $\hat{\Phi}_{ka}$. First substitute Eq. (7.11) for \mathbf{J}_c in the divergence term of the calortropy balance equation. It yields the expression

$$\begin{aligned} \nabla \cdot \mathbf{J}_c &= T^{-1} \nabla \cdot \mathbf{Q} + \sum_{a=1}^r \mathbf{Q}_a^c \cdot \nabla T^{-1} - T^{-1} \sum_{a=1}^r \hat{\mu}_a \nabla \cdot \mathbf{J}_a \\ &\quad - T^{-1} \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \hat{\mu}_a + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \nabla \cdot \psi_{ka} \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka}. \end{aligned}$$

Eliminate the divergence terms $\nabla \cdot \mathbf{Q}$, $\nabla \cdot \mathbf{J}_a$, and $\nabla \cdot \psi_{ka}$ by using the internal energy balance equation, the mass fraction balance equation, and the evolution equation for $\hat{\Phi}_{ka}$. Then on substitution of the resulting expression into the calortropy balance equation and use of Ξ_c in Eq. (7.12) we obtain the calortropy differential form (7.13) presented earlier.

Inasmuch as the calortropy balance equation (7.9) is the local equivalent of the second law of thermodynamics, the Pfaffian differential form (7.13) is an equivalent of the second law in the thermodynamic space \mathfrak{P} under Proposition 5. In this connection we would like to make the remark that a Pfaffian differential form is not necessarily an exact differential unless it satisfies a set of integrability conditions. This remark is called for since in the recent literature on extended irreversible thermodynamics a Pfaffian form is simply regarded as an exact differential in the space \mathfrak{P} , and this kind of indiscriminate use of the term can give rise to an incorrect reasoning with regard to the second law of thermodynamics and its local representation. In the case of (non-equilibrium) thermodynamics, because of the vanishing contour integral of $d\Psi$ given in Eq. (4.41) the second law of thermodynamics preempts the integrability conditions for the Pfaffian form, which are partial differential equations not easy to solve in general. Therefore it is not appropriate to state that $d\hat{\Psi}$ is an exact differential until Eq. (4.41) is established for the second law of thermodynamics. It is also important to recognize that the differential form (7.13) by itself is not synonymous with the second law of thermodynamics, since it must be necessarily accompanied by the condition $\hat{\Xi}_c \geq 0$, which puts restrictions on the differentials

on the right hand side of Eq. (7.13). The misconception that the extended Gibbs relation alone is the mathematical representation of the second law of thermodynamics seems to have originated from equilibrium thermodynamics where since $\widehat{\Xi}_c = 0$ identically, the second law of thermodynamics gives rise to the equilibrium Gibbs relation with no additional condition attached to it.

The differential form $d_t \widehat{\Psi}$ is exact in the space \mathfrak{P} by virtue of the vanishing contour integral (4.41). This can be shown as follows. From Eqs. (7.2) and (7.4) we obtain

$$\begin{aligned} \int_0^\tau dt \frac{d\Psi}{dt} &= \int_0^\tau dt \int_V dr \left(\frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot \mathbf{u} \rho \widehat{\Psi} \right) \\ &= \int_V dr \int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0, \end{aligned} \quad (7.14)$$

from which, by continuity, follows the vanishing local integral

$$\int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0. \quad (7.15)$$

This implies that $d_t \widehat{\Psi}$ is an exact differential in the space \mathfrak{P} since $\rho(d\widehat{\Psi}/dt)$ may be replaced by $(d\rho\widehat{\Psi}/dt)$, provided that

$$\widehat{\Psi} = T^{-1} \left(\mathcal{E} + pv - \sum_{a=1}^r \widehat{\mu}_a c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \widehat{\Phi}_{ka} \right), \quad (7.16)$$

which is an integral of the differential form for $d_t \widehat{\Psi}$ in Eq. (7.13). This is brought about, because it is possible to express [8] the integrability condition of differential form (7.13) in the space \mathfrak{P} as the generalized Gibbs—Duhem equation

$$\mathcal{E} d_t \left(\frac{1}{T} \right) + v d_t \left(\frac{p}{T} \right) - \sum_{a=1}^r c_a d_t \left(\frac{\widehat{\mu}_a}{T} \right) + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Phi}_{ka} d_t \left(\frac{X_{ka}}{T} \right) = 0, \quad (7.17)$$

which, when added to Eq. (7.13), yields $\widehat{\Psi}$ in Eq. (7.16). Eq. (7.17) is a generalized form of the equilibrium Gibbs—Duhem equation [9].

It is not simple to prove the exactness of a differential form like Eq. (7.13) if a purely mathematical approach is taken for the proof, but in the present case the differential form $d_t \widehat{\Psi}$ is exact by the requirement of the second law of thermodynamics, and there exists a hypersurface in the Gibbs space $\mathfrak{P}_G = \mathfrak{P} \cup \widehat{\Psi}$. Furthermore, when the calortropy flux and the calortropy production are suitably elucidated in terms of variables in the space \mathfrak{P}

and their spatial derivatives the second law assures, from another angle, the integrability of the differential form $d_t \hat{\Psi}$ together with the positivity condition on the calortropy production. These results are collected in a theorem.

Theorem 1 *Under Propositions 2-5 the second law of thermodynamics is expressible, for local irreversible processes in space-time, in the Pfaffian differential form in the space \mathfrak{P}*

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + pd_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right), \quad (7.18)$$

with the condition $\hat{\Xi}_c \geq 0$, as the local expression of the second law of thermodynamics, on the evolution equations for the non-conserved variables $\hat{\Phi}_{ka}$. This differential form is integrable and there exists a state function $\hat{\Psi}$ in the space \mathfrak{P} . This function may be regarded as a hypersurface in the Gibbs space \mathfrak{P}_G as a consequence of the second law of thermodynamics. The integrability condition for this differential form is the Gibbs–Duhem equation.

This theorem provides the foundation for the thermodynamics of local irreversible processes in a fairly general form which we will later develop with it. The generalized hydrodynamic equations (6.19)–(6.22) and (6.44) presented in Chapter 6 are now made fully consistent with the laws of thermodynamics. Therefore it may be said that the present version of generalized hydrodynamics is consistent with the laws of thermodynamics.

7.2 Chemically Reacting Fluids

We now would like to take chemical reactions into consideration. Let us denote by R_l the rate of reaction l and by ν_{al} the associated stoichiometric coefficient times the mass of species a . As in the previous chapter the chemical reactions are written in the form

$$\sum_{a=1}^r \nu_{al} c_a = 0,$$

where c_a denotes chemical species a .

Except for the source term appearing in the mass fraction balance equation the macroscopic evolution equations retain the same forms as Eqs. (6.19), (6.21), (6.22), and (6.44) although the dissipation terms in the evolution equations for the non-conserved variables may contain reactive contributions, but they do not have to be written out explicitly for our purpose

here. The calortropy balance equation remains formally invariant regardless of whether there are chemical reactions present in the system or not. Nevertheless, the calortropy production gets contribution from chemical reactions, and the presence of chemical reactions requires the following modification of Proposition 5:

Proposition 5c *For a system where there are m chemical reactions $\sum_{a=1}^r \nu_{al} \mathcal{C}_a = 0$ ($m \geq l \geq 1$) the calortropy flux $\mathbf{J}_c \equiv \mathbf{Q}^c/T$ is given by the bilinear form of the intensive variables T^{-1} , $\hat{\mu}_a T^{-1}$, and $X_{ka} T^{-1}$ ($k \geq 1$, $1 \leq a \leq r$) paired, respectively, with \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} (flux of Φ_{ka}) as follows:*

$$\mathbf{J}_c \equiv \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \right), \quad (7.19)$$

and the calortropy production $\Xi_c \equiv \rho \hat{\Xi}_c$ is given by the bilinear form

$$\begin{aligned} \Xi_c &\equiv \rho \hat{\Xi}_c \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\ &\quad - T^{-1} \sum_{a=1}^r \left[\sum_{l=1}^m \nu_{al} \hat{\mu}_a R_l - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka} \right] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}). \end{aligned} \quad (7.20)$$

By the second law of thermodynamics the inequality $\Xi_c \geq 0$ always holds as the constraint on the evolution equations for non-conserved variables, with the equality holding for reversible processes only.

Therefore the calortropy flux remains the same as for non-reactive systems, but the calortropy production is modified since there is an energy dissipation term which arises from chemical reactions present:

$$\Xi_c^{\text{chem}} = -T^{-1} \sum_{l=1}^m \mathcal{A}_l R_l, \quad (7.21)$$

where \mathcal{A}_l is the chemical affinity of reaction l defined by

$$\mathcal{A}_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (7.22)$$

This is the familiar looking form used for the reactive contribution to the entropy production in the linear theory of irreversible processes [5, 6]. We emphasize that this additional term is not arbitrary but a consequence of the modification of the mass fraction balance equations which is necessitated by the chemical reactions. When used in the calortropy balance equation, Proposition 5c gives rise to the same differential form for $d_t \hat{\Psi}$ as in Eq. (7.18) of Theorem 1. Therefore the differential form for $d_t \hat{\Psi}$ remains invariant in its formal structure but the meaning of chemical potentials changes since they now get contributions from the chemical reactions and the mass fractions become non-conserved variables joining the ranks of $\Phi_{ak}(k \geq 1)$ whose evolution equations are also modified in the dissipation terms, which get a contribution from chemical reactions. Thus the hydrodynamic equations are modified, but the basic mathematical structure of thermodynamics remains the same whether the fluid is reactive or not.

If other irreversible processes, such as shearing, heat flow, and so on, are absent and chemical reactions are the only irreversible process in the system, then $d_t \hat{\Psi}$ becomes the local equilibrium formula for $d_t S_e$. Chemical reactions, in fact, stand out as the only example of non-steady dissipative irreversible processes which can be described within the framework of the local equilibrium hypothesis. The local equilibrium formula for the entropy appears superficially to be sufficient if the non-conserved variables are in the steady state in the moving frame of reference. It should, however, be noted that it does not mean that the calortropy production assumes a form [5, 6] appearing in the theory of linear irreversible processes. This point will be elaborated upon in a later chapter in which steady state processes are discussed.

7.3 Connection with Equilibrium Thermodynamics

Since the present theory is a generalization of equilibrium thermodynamics it is necessary to examine the condition under which equilibrium thermodynamics is recovered from the present theory. First of all, we see that as the X_{ka} vanish for all k and a equilibrium thermodynamics is recovered from Eq. (7.18), since $\hat{\Psi}$ tends to its equilibrium limit $\hat{\Psi}_e$, which coincides with the Clausius entropy density S_e . In other words, we recover the equilibrium Gibbs relation [9]

$$\begin{aligned} d\hat{\Psi}_e &= T_e^{-1} \left(dE + p_e dv - \sum_{a=1}^r \hat{\mu}_a^e dc_a \right) \\ &= dS_e, \end{aligned} \tag{7.23}$$

where

$$T_e = \lim_{X \rightarrow 0} T = \lim_{\Phi \rightarrow 0} T,$$

$$p_e = \lim_{X \rightarrow 0} p = \lim_{\Phi \rightarrow 0} p,$$

$$\hat{\mu}_a^e = \lim_{X \rightarrow 0} \hat{\mu}_a = \lim_{\Phi \rightarrow 0} \hat{\mu}_a.$$

It must be noted that $\Xi_e = 0$ in the same limit as indicated above. Equilibrium thermodynamics is developed with the differential form in Eq. (7.23). The Gibbs—Duhem equation corresponding to the differential form (7.23) is

$$\mathcal{E}d\left(\frac{1}{T_e}\right) + vd\left(\frac{p_e}{T_e}\right) - \sum_{a=1}^r c_a d\left(\frac{\hat{\mu}_a^e}{T_e}\right) = 0. \quad (7.24)$$

Since our main interest lies in non-equilibrium thermodynamics we will not dwell on equilibrium thermodynamics in this work.

7.4 Legendre Transformations for Local Variables

As in equilibrium thermodynamics, other thermodynamic functions can be defined by using the calortropy in the place of the entropy. For example, by using Legendre transformations we may define the local generalized work function \mathcal{A} and the local generalized Gibbs free energy \mathcal{G}

$$\mathcal{A} = \mathcal{E} - T\hat{\Psi}, \quad (7.25)$$

$$\mathcal{G} = \mathcal{H} - T\hat{\Psi}, \quad (7.26)$$

where \mathcal{H} is the local enthalpy density

$$\mathcal{H} = \mathcal{E} + pv. \quad (7.27)$$

We remark that \mathcal{H} is basically a mechanical quantity because \mathcal{E} and p are mechanically calculable from their molecular expressions. In this sense \mathcal{H} is different from \mathcal{A} and \mathcal{G} . The properties of the functions \mathcal{A} and \mathcal{G} can be discussed in complete parallel with equilibrium thermodynamics by using the fundamental equation (7.13), but we will not dwell on them further in this section. The local functions \mathcal{A} and \mathcal{G} have the same forms as their equilibrium thermodynamics counterparts except that the calortropy is used in the place of the Clausius entropy and the extended Gibbs relations

for \mathcal{A} and \mathcal{G} of course must be accompanied by Inequality (7.20) for Ξ_c . The presence of $\widehat{\Psi}$ in \mathcal{A} and \mathcal{G} instead of the Clausius entropy has a significant effect when the free energies are considered in the case of systems removed from equilibrium.

Taking an additional Legendre transform of \mathcal{G} we may define a function $\widehat{\Omega}$ by the relation

$$\begin{aligned}\widehat{\Omega} &= \mathcal{G} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \widehat{\Phi}_{ka} \\ &= \mathcal{E} + pv - T\widehat{\Psi} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \widehat{\Phi}_{ka},\end{aligned}\tag{7.28}$$

The new function $\widehat{\Omega}$ is a non-equilibrium thermodynamic potential in local form, which also may be written as

$$\widehat{\Omega} = \sum_{a=1}^r \widehat{\mu}_a c_a.\tag{7.29}$$

The Legendre transform (7.28) gives rise to the extended Gibbs relation for $d_t \widehat{\Omega}$:

$$d_t \widehat{\Omega} = -\widehat{\Psi} d_t T + v d_t p + \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Phi}_{ka} d_t X_{ka}.\tag{7.30}$$

This form is defined in the space $\mathfrak{P}^\Omega = (\widehat{\Psi}, p, c_a, X_{ka} : 1 \leq a \leq r; k \geq 1)$. It should be compared with its global process counterpart, Eq. (4.96). Since Eq. (7.30) can be obtained by using a molecular model [1] it is possible to learn the limitations of the differential form (4.96) for global processes from the standpoint of the local field theory underlying Eq. (7.30), if the procedure is reversed to obtain the differential form from the local differential form (7.30).

The differential form (7.30) was found useful in connection with the non-equilibrium ensemble method in non-equilibrium statistical mechanics [1]. The function $\widehat{\Omega}$ also gives rise to the integrability condition [8] for the differential form for $d_t \widehat{\Psi}$:

$$\sum_{a=1}^r c_a d_t \left(\frac{\widehat{\mu}_a}{T} \right) = \mathcal{E} d_t \left(\frac{1}{T} \right) + v d_t \left(\frac{p}{T} \right) + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Phi}_{ka} d_t \left(\frac{X_{ka}}{T} \right).\tag{7.31}$$

This integrability condition is, as mentioned earlier, a generalization of the Gibbs—Duhem equation appearing in equilibrium thermodynamics [9]. It will be found useful for applying the present theory to non-equilibrium phenomena.

7.5 Other Versions of Irreversible Thermodynamics

There are kindred versions of irreversible thermodynamics in which the equilibrium thermodynamic space is extended to include non-conserved variables. They are generically called extended irreversible thermodynamics. This terminology itself needs examination, since if irreversible thermodynamics is already an extension of thermodynamics (*i.e.*, thermostatics) and extended irreversible thermodynamics aims to study irreversible processes, the term ‘extended’ is redundant. In any case, in the versions² of extended irreversible thermodynamics proposed in Refs. [11, 12, 13, 14, 16, 17] and Refs. [18, 19] it is assumed that there exists a non-equilibrium entropy which is a state function in the space \mathfrak{P} . Consequently it has a differential form similar to that for $\hat{\Psi}$ in Eq. (7.13). The common characteristic of the aforementioned theories is that the non-equilibrium entropy used in them has not been established on the basis of the second law of thermodynamics as stated by Kelvin and Clausius, but is a postulate made as an extension of the equilibrium entropy obtained by Clausius for reversible processes. The postulate of non-equilibrium entropy, however, detaches the theory based thereon from the very second law of thermodynamics, under the guidance of which the theory aims to work. This point needs an elaboration, which will be made presently.

The non-equilibrium entropy used in the versions mentioned has usually been justified by using an approximation of the distribution function obey-

² There are basically two different versions of extended irreversible thermodynamics: one class of versions can be found in [11, 12, 13, 14]; and the other in [15] and this work. In the former it is assumed that there exists a non-equilibrium entropy which is a state function in the thermodynamic space, and the non-equilibrium entropy is statistically represented by approximations of the Boltzmann entropy or its dense fluid generalization, for example, the information entropy for dynamical systems. In the latter class (*i.e.*, in [15]) it is shown from the second law of thermodynamics that there exists a quantity called the compensation function (renamed calortropy in this work and in [20]), arid its differential is an exact differential in the thermodynamics space by virtue of the second law. The compensation function, however, is not the same as the Boltzmann entropy appearing in the kinetic theory of dilute gases by Boltzmann. Since the thermodynamics of irreversible processes must be securely founded on the laws of thermodynamics, it is crucial to show that the basic equations are consistent with the laws of thermodynamics and, for example, the extended Gibbs relation is equivalent to the second law of thermodynamics. An assumption for such a basic equation is not acceptable if the resulting theory will have anything to do with the laws of thermodynamics in accounting for macroscopic processes in nature. Neither can the laws of thermodynamics afford approximate representations. The basic thermodynamic equation in the formulation made in [1, 20] and in this work is a rigorous consequence of the second law of thermodynamics which mathematically extends equilibrium thermodynamics that is certainly endowed with a physical basis supported by the second law; it is not an assumption as in [11, 12, 13, 14].

ing the Boltzmann equation which provides an information entropy—the negative of the Boltzmann H function—in the kinetic theory for dynamical processes. The assumption of such a non-equilibrium entropy in the space \mathfrak{P} has no foundation in the laws of thermodynamics, firstly, because the second law of thermodynamics is not used to deduce that there exists such a quantity when the system is away from equilibrium, and, secondly, because the local differential form for the non-equilibrium entropy itself is a derivative quantity from the global differential form that mathematically represents the second law of thermodynamics, which in the first place has not been established in the aforementioned approaches. Moreover, the assumption made in the aforementioned approaches that the phenomenological ‘non-equilibrium entropy’ is given by the Boltzmann entropy in the Boltzmann kinetic theory of gases is groundless, since the calortropy $\hat{\Psi}$ is the quantity deduced from the Kelvin—Clausius principle, but it is not the same as the Boltzmann entropy, as has been shown [1] in the kinetic theory foundations of the phenomenological theory described here and as will be elaborated on shortly. The versions of extended irreversible thermodynamics in [11, 12, 13, 14, 16, 17] and [18, 19], which are based on the assumption on a non-equilibrium entropy and its differential form, are therefore not founded on the second law of thermodynamics; they are just mathematical formalisms³ based on an extended space analogous to that of equilibrium thermodynamics. Furthermore, the Pfaffian differential form for the non-equilibrium entropy is not sufficient for a thermodynamically consistent theory of irreversible processes, because it by itself is not a representation of the second law of thermodynamics, but must be supplemented by another postulate of dissipation inequality.

Notwithstanding, the aforementioned theories can be given thermodynamic foundations, only if the non-equilibrium entropy postulated therein is replaced by $\hat{\Psi}$ and the tacit assumption of equivalence of the non-equilibrium entropy with the Boltzmann entropy (*i.e.*, information entropy) is abandoned.

Another feature peculiar to the version in Ref. [17] is the appearance of a differential form for the non-equilibrium entropy flux, which from the manner of its treatment appears to be tacitly acknowledged that it is inte-

³It is important to realize that kinetic equation for matter, for example, the Boltzmann kinetic equation, is a mathematical model for a collection of particles, and statistically uncorrelated particles in the case of the Boltzmann kinetic theory, which is made physical upon connection with the phenomenological thermodynamics—thermodynamic correspondence. Therefore, until this thermodynamic correspondence is made between the mathematical model and the phenomenology, any result of the kinetic theory remains detached from physical reality; just a probability theory result. Consequently, if one is not able to extract a mathematical structure of thermodynamics from the kinetic theory that can be compared with the structure of the phenomenological thermodynamics consistent with the thermodynamic laws, the kinetic theory is not useful for the thermodynamics of the physical system under consideration.

grable in the space of the macroscopic variables chosen, namely, the space \mathfrak{P} .

However, such a differential form is not necessarily integrable in the space \mathfrak{P} , and since the compensated heat generally does not have a vanishing contour integral if the process is irreversible; in other words, since for an irreversible process there holds

$$\oint T^{-1} \frac{dQ}{dt} \neq 0, \quad (7.32)$$

it seems unlikely that it will give rise to a local differential form integrable in the space \mathfrak{P} so that the desired mathematical structure emerges for irreversible thermodynamics in a way consistent with the laws of thermodynamics. As a matter of fact, if the compensated heat or the calortropy flux differential were integrable in the space \mathfrak{P} then it would follow that

$$\oint T^{-1} \frac{dQ}{dt} = 0 \quad (7.33)$$

and, since

$$\oint d\Psi = 0, \quad (7.34)$$

the cyclic integral of the uncompensated heat would vanish, namely, $N = 0$, in the space \mathfrak{P} . This means that the vanishing contour integral of dQ/dt as in Eq. (7.33) violates the second law of thermodynamics if the process is irreversible. Therefore it is possible to conclude that the differential form for the ‘entropy flux’ in Ref. [17] is not integrable in the space \mathfrak{P} ; in other words, the local differential form corresponding to dQ/dt in Ref. [17] is not exact.

The aforementioned pitfalls are avoided in the theory of irreversible processes presented in this chapter and the chapters preceding it. And we have a formalism consistent with the Kelvin—Clausius principle for the second law of thermodynamics.

We now return to the question of the relation between the Boltzmann H theorem and the mathematical representation of the second law of thermodynamics. It was mentioned that some efforts [16, 17, 18, 19] have been made to put the extended Gibbs relation on the foundation of the H theorem of Boltzmann. However, Boltzmann’s H theorem itself should not simply be taken as an equivalent of the second law of thermodynamics although it is often and uncritically done in kinetic theory and irreversible thermodynamics. In a recent series of work [2, 20, 21] the present author has shown that the Boltzmann H theorem indeed is not the same as the second law of thermodynamics and neither does the kinetic equation formally projected from the Liouville equation for a many-particle distribution function provide foundations for irreversible thermodynamics [22, 23], unless the thermodynamic branch of solution is constructed from the distribution

function obeying the kinetic equation. Besides these points just mentioned, the extended Gibbs relation for the non-equilibrium entropy raises various subtle questions as to what we really mean by the non-equilibrium entropy; if it really does exist, as is assumed in extended irreversible thermodynamics; whether its differential form is indeed exact in the thermodynamic space taken for description of irreversible processes in hand and on what grounds it is exact; what we really mean by the intensive variables appearing in the differential form and their operational thermodynamic significance. Unless these questions are satisfactorily answered and settled, the theory thus formulated is merely a mathematical formalism that has little to do with thermodynamic laws and the macroscopic reality. The theory presented up to this point in the present work has been addressed to these questions and, as a result of resolving the questions, put the thermodynamic theory of irreversible processes on firmer foundations of the laws of thermodynamics.

Some authors in the literature tried to modify the second law of thermodynamics to resolve some of sticking issues arising from the second law of thermodynamics as stated by the founders of thermodynamics. However, it is the opinion of the present author that it is not advisable to tamper with the Clausius principle or the Kelvin principle until they are given a complete and adequate mathematical representation, or until such a representation is proved inadequate upon having applied it to irreversible processes in nature. It is also the opinion of the author that an adequate mathematical representation can be and has been given for the second law of thermodynamics, as has been shown in the previous chapters. The theory of irreversible processes constructed therewith is applied to various problems in macroscopic physics described in this work and in the literature [24–40]. The results of such applications attest to the adequacy of the mathematical representation of the second law of thermodynamics presented earlier and the theory of irreversible processes based thereon.

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8

Local Irreversible Thermodynamics

We have seen that the local form of the second law of thermodynamics is given by the calortropy balance equation with a positive semi-definite source term (calortropy production) as demanded by the second law of thermodynamics. On taking bilinear representations of the calortropy flux and the calortropy production and using the balance equations for mass, momentum, and internal energy as well as the evolution equations for non-conserved variables, the calortropy balance equation can be transformed into a local differential form in the space \mathfrak{P} . Furthermore, the calortropy production in turn puts on the dissipation terms of the evolution equations for non-conserved variables the positivity restriction, which is demanded by the second law of thermodynamics. Therefore the extended Gibbs relation on the support of the evolution equations for the conserved and non-conserved variables, which are subjected to the restriction of the second law of thermodynamics, constitutes a theory of irreversible processes in the space \mathfrak{P} that is consistent with the thermodynamic principles. The aim of the present chapter is to show that thermodynamics of irreversible processes in the extended thermodynamic space \mathfrak{P} can indeed be developed on the basis of the extended Gibbs relation for calortropy (7.13).

8.1 Generalized Thermodynamics

For the purpose stated in the introduction to this chapter it is useful to have all the necessary evolution equations for the conserved and non-conserved

variables collected in one place:

$$\rho d_t v = \nabla \cdot \mathbf{u}, \quad (8.1)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \Lambda_{0a}, \quad (8.2)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (8.3)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (8.4)$$

$$\rho d_t \hat{\Phi}_{ka} = -\nabla \cdot \psi_{ka} + Z_{ka} + \Lambda_{ka} \quad (k \geq 1), \quad (8.5)$$

where $r \geq a \geq 1$ for the species. In accordance with the modification made with regard to chemical reactions, which might be present in the system, the reaction rate Λ_{0a} is added to the mass fraction evolution equation (8.2); it is given in terms of reaction rates R_l by the formula

$$\Lambda_{0a} = \sum_{l=1}^m \nu_{al} R_l. \quad (8.6)$$

The evolution equations in the set presented here are called *the generalized hydrodynamics equations*. The reason for this terminology is as follows: if suitable approximations are made to the constitutive equations (8.5) for the stress tensors, heat fluxes, and diffusion fluxes such that there arise linear thermodynamic force–flux relations for them and if other non-conserved variables than those just mentioned are neglected, the differential equations (8.1)–(8.4) with the thermodynamic force–flux relations thus obtained become the classical hydrodynamic equations—namely, the Navier–Stokes, Fourier, and Fick’s equations.

The generalized hydrodynamic equations also describe the evolution of calortropy in the thermodynamic space \mathfrak{P} through the extended Gibbs relation

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + \rho d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d_t \hat{\Phi}_{ka} \right) \quad (8.7)$$

irrespective of whether there is a chemical reaction in progress within the system or not. Since hydrodynamic processes must obey the second law of thermodynamics, the generalized hydrodynamic equations are subjected to

the second law of thermodynamics through the local inequality

$$\begin{aligned}\Xi_c = & -T^{-1} \sum_{a=1}^r [\Pi_a : \nabla \mathbf{u} + \Delta_a \nabla \cdot \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\ & - T^{-1} \sum_{a=1}^r \left(\hat{\mu}_a \Lambda_{0a} - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka} \right) \\ & + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}) \\ \geq & 0.\end{aligned}\tag{8.8}$$

The kinematic and dissipation terms \mathcal{Z}_{ka} and Λ_{ka} in the constitutive equations must be chosen such that this inequality is satisfied. The calortropy flux compatible with this form of calortropy production is given by

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \mathbf{J}_a \hat{\mu}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \right).\tag{8.9}$$

We note that $X_{ka} \psi_{ka}$ is a tensor product which contracts to a vector. Our aim in this chapter is to develop a thermodynamic theory of irreversible processes on the basis of Eqs. (8.1)–(8.9), which, being local field equations for local variables, constitute a local thermodynamic theory of irreversible processes in the space \mathfrak{P} . We begin the study of the theory by examining some mathematical aspects of the extended Gibbs relation (8.7). Before proceeding to such a study, we make the following remark regarding the calortropy flux and the calortropy production which is of general interest and, I believe, useful for deeper understanding of thermodynamics of irreversible processes.

The extended Gibbs relation (8.7) may be used to express the calortropy flux and the calortropy production in terms of calortropy derivatives characterizing tangents to the calortropy surface in Gibbs space \mathfrak{P}_G . We thus find for the calortropy flux the formula

$$\mathbf{J}_c = \sum_{a=1}^r \left[\left(\frac{\partial \hat{\Psi}}{\partial \mathcal{E}} \right)_\xi \mathbf{Q}_a + \sum_{a=1}^r \left(\frac{\partial \hat{\Psi}}{\partial c_a} \right)_\xi \mathbf{J}_a + \sum_{a=1}^r \sum_{k \geq 1} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Phi}_{ka}} \right)_\xi \psi_{ka} \right],\tag{8.10}$$

where the subscript ξ on the derivatives denotes variables of \mathfrak{P} other than the one used for the derivative. If the external force is conservative so that

$\mathbf{F}_a = -\nabla\phi_a$ and if we define the intrinsic substantial time derivatives by

$$\frac{d_i \mathcal{E}}{dt} = - \sum_{a=1}^r [\mathbf{\Pi}_a : \nabla \mathbf{u} + \Delta_a \nabla \cdot \mathbf{u} + \mathbf{J}_a \cdot \nabla \phi_a], \quad (8.11)$$

$$\frac{d_i c_a}{dt} = \Lambda_{0a}, \quad (8.12)$$

$$\frac{d_i \hat{\Phi}_{ka}}{dt} = (\mathcal{Z}_{ka} + \Lambda_{ka}), \quad (8.13)$$

then the calortropy production may be written in the form

$$\begin{aligned} \Xi_c &= \mathbf{Q} \cdot \nabla \left(\frac{\partial \hat{\Psi}}{\partial \mathcal{E}} \right)_{\xi} + \sum_{a=1}^r \left[\mathbf{J}_a \cdot \nabla \left(\frac{\partial \hat{\Psi}}{\partial c_a} \right)_{\xi} + \sum_{k \geq 1} \dot{\psi}_{ka} \cdot \nabla \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Phi}_{ka}} \right)_{\xi} \right] \\ &\quad + \frac{d_i \mathcal{E}}{dt} \left(\frac{\partial \hat{\Psi}}{\partial \mathcal{E}} \right)_{\xi} + \sum_{a=1}^r \left[\frac{d_i c_a}{dt} \left(\frac{\partial \hat{\Psi}}{\partial c_a} \right)_{\xi} + \sum_{k \geq 1} \frac{d_i \hat{\Phi}_{ka}}{dt} \left(\frac{\partial \hat{\Psi}}{\partial \hat{\Phi}_{ka}} \right)_{\xi} \right]. \end{aligned} \quad (8.14)$$

The expression obtained here for the calortropy flux in terms of the calortropy derivatives allows the interpretation of \mathbf{J}_c as being a directional derivative of surface $\hat{\Psi}$ in the \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} directions of the tangent vectors to the calortropy surface. On the other hand, the calortropy production consists of two distinctive parts, one made up of spatial derivatives of the tangents to the calortropy surface projected onto the \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} directions conjugate to \mathcal{E} , c_a , and $\hat{\Phi}_{ka}$, and the other made up of the intrinsic substantial time derivatives of the calortropy with regards to \mathcal{E} , c_a , and $\hat{\Phi}_{ka}$. The form of Ξ_c in Eq. (8.14) suggests that the calortropy production arises when the calortropy derivatives vary in the configuration space and the calortropy itself also varies intrinsically in time. This latter part of Ξ_c arises because of the stress, chemical reactions, and various non-conservative processes that dissipate energy from a useful to a less useful form. Written in the forms of Eqs. (8.10) and (8.14), the physical origins of the calortropy flux and the calortropy production are quite transparent.

In the discussions presented below in this chapter substantial time derivatives $d_t x$ of variable x will be simply denoted by dx with the subscript t omitted for notational brevity. The differential dx therefore stands for an infinitesimal change in x in the frame of reference moving at velocity \mathbf{u} of the fluid particle; they should not be confused with the similar symbol used for the differentials in the theory of global irreversible processes. Consequently the extended Gibbs relations merely furnish relations between variables in the space \mathfrak{P} , but not their modes of evolution in space-time. The latter are provided by the generalized hydrodynamic equations, which

must be solved subject to the initial and boundary conditions suitable for the system of interest. On interpreting the differential dx in the space \mathfrak{P} as the substantial time derivative and using the generalized hydrodynamic equations for x , a local description of $\hat{\Psi}$ is made possible. This point is usually not made explicit in the theory of irreversible processes, but we should bear it in mind in using the theory developed here. Since the extended Gibbs relations provide various relations between the variables necessary for the description of evolution of the system, the value of irreversible thermodynamics then is seen in the economy of information necessary for the description of the processes involved.

8.2 Integrating Factor

A differential one-form (a Pfaffian differential form) is said to be integrable if it has an integral in the space in which the differential form is defined. From the mathematical viewpoint the extended Gibbs relation is a Pfaffian differential form in the space \mathfrak{P} . Pfaffian differential forms are not generally integrable unless they satisfy integrability conditions [1]. However, the extended Gibbs relation (8.7) is integrable, just as the equilibrium Gibbs relation is, thanks to the second law of thermodynamics, which demands that the calortropy exists. We should, especially, note that the inverse temperature factor appearing in the extended Gibbs relation for calortropy (8.7) has a special meaning, as has the inverse temperature in the equilibrium Gibbs relation in the equilibrium theory [2, 3].

When (8.7) is considered from the viewpoint of differential forms, the inverse temperature emerges as an integrating factor for the differential form

$$\omega = d\mathcal{E} + pdv - \sum_{a=1}^r \hat{\mu}_a dc_a + \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka}. \quad (8.15)$$

For the sake of definiteness, the set of non-conserved variables is made finite; there are m non-conserved variables. Therefore the dimension of the space \mathfrak{P} is $l = (m+1)r + 2$. The differential form (8.15) will be written as

$$\omega = \sum_{i=1}^l \omega_i dx_i, \quad (8.16)$$

where $(\omega_i: 1 \leq i \leq l) \equiv (1, p, -\hat{\mu}_a, X_{ka}: 1 \leq a \leq r; 1 \leq k \leq m)$ and $x = (x_i: 1 \leq i \leq l) \in \mathfrak{P} = (\mathcal{E}, v, c_a, \hat{\Phi}_{ka}: 1 \leq a \leq r; 1 \leq k \leq m)$.

According to the second law of thermodynamics the differential form $\omega = 0$ is integrable and there exists a function $\hat{\Psi}$ such that $\omega = f(x)d\hat{\Psi}$, where $f(x)$ is an integrating factor. Comparison of this result with (8.7) implies that $f(x) = T(x)$. That is, the inverse temperature T^{-1} is an

integrating factor for ω . This shows that although T^{-1} may be regarded as an intensive variable, it has a special status among the intensive variables ω_i .

Starting from the integrability [1, 5, 6, 7, 8] of ω it is possible to show that the integrating factor can, indeed, be chosen to be the inverse absolute temperature of the system. The details of this analysis can be found in the literature [9].

8.3 Integrability Conditions and Maxwell's Relations

Since $d\hat{\Psi}$ is exact in the space \mathfrak{P} , generalized forms of the Maxwell relations are expected of the differential form (8.7). Thus we obtain the relations

$$\frac{\partial}{\partial x_j} \varpi_i = \frac{\partial}{\partial x_i} \varpi_j \quad (i, j = 1, 2, \dots, l), \quad (8.17)$$

where $\varpi = (\varpi_i : 1 \leq i \leq l)$ with $\varpi_i = T^{-1}\omega_i$. Since the integrability condition [1, 5, 7, 8] for ω is

$$\omega \wedge d\omega = 0, \quad (8.18)$$

where the symbol \wedge denotes the exterior product [5, 7], and for a function $h \neq 0$ in open domain $\subset \mathfrak{P}$ there also holds the condition

$$(h\omega) \wedge d(h\omega) = 0, \quad (8.19)$$

the integrability condition may be written as

$$\varpi \wedge d\varpi = 0, \quad (8.20)$$

if we choose $h = T^{-1}$. By using the rules of exterior calculus [5, 7, 8], this condition can be explicitly written out:

$$\begin{aligned} \varpi \wedge d\varpi &= \frac{1}{6} \sum_{ijk} [\varpi_i(\partial_j \varpi_k - \partial_k \varpi_j) + \varpi_j(\partial_k \varpi_i - \partial_i \varpi_k) \\ &\quad + \varpi_k(\partial_i \varpi_j - \partial_j \varpi_i)] dx_i \wedge dx_j \wedge dx_k \\ &= 0, \end{aligned} \quad (8.21)$$

where $\partial_i = \partial/\partial x_i$. From this follow the necessary and sufficient conditions for the integrability of ϖ

$$\varpi_i(\partial_j \varpi_k - \partial_k \varpi_j) + \varpi_j(\partial_k \varpi_i - \partial_i \varpi_k) + \varpi_k(\partial_i \varpi_j - \partial_j \varpi_i) = 0 \quad (8.22)$$

for $i, j, k = 1, 2, \dots, l$. These conditions are satisfied by the generalized Maxwell relations (8.17). It shows the intimate relation of the integrating factor to the generalized Maxwell relations for ϖ .

The generalized Maxwell relations make it possible to deduce information on the behavior of a variable from that of another because they give mutual relations between the variables necessary for a consistent description of processes mentioned, and an economy of description is thus made possible for a given system. And in such an economy lie the power and utility of thermodynamics and, in the present more general case, irreversible thermodynamics. It is important to recognize that the necessity of using the integrability conditions (8.22) is obviated by the second law of thermodynamics that provides a state function $\hat{\Psi}$ in the space \mathfrak{P} .

By using the notion of homotopy [7] it is possible to express the integrability conditions in a single differential form which in the case of thermodynamics takes the form of the Gibbs–Duhem equation. The Gibbs–Duhem equation corresponding to the extended Gibbs relation (8.7) is found to be [9]

$$\sum_{a=1}^r c_a d\left(\frac{\hat{\mu}_a}{T}\right) = \mathcal{E} d\left(\frac{1}{T}\right) + v d\left(\frac{p}{T}\right) + \sum_{a=1}^r \sum_{k \geq 1}^m \hat{\Phi}_{ka} d\left(\frac{X_{ka}}{T}\right). \quad (8.23)$$

If this equation is added to the extended Gibbs equation (8.7) it is easily seen that there exists an integral in the Gibbs space:

$$\hat{\Psi} = T^{-1} \left[\mathcal{E} + pv - \sum_{a=1}^r \hat{\mu}_a c_a + \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} \hat{\Phi}_{ka} \right], \quad (8.24)$$

apart from a constant which is set equal to zero. This result verifies the integral (7.16) in the Gibbs space \mathfrak{P}_G which was mentioned in the previous chapter.

Now that we know that there exists a state function $\hat{\Psi}$ in the space \mathfrak{P} we may treat it as a primitive independent variable while treating \mathcal{E} as the dependent variable. In other words, we may use the internal energy as the dependent variable and write the differential form in the space of $\mathfrak{P}^E \equiv (\hat{\Psi}, v, c_a, \hat{\Phi}_{ka} : m \geq k \geq 1; r \geq a \geq 1)$

$$\begin{aligned} d\mathcal{E} &= T d\hat{\Psi} - pdv + \sum_{a=1}^r \hat{\mu}_a dc_a - \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka} \\ &= \sum_{i=1}^l W_i dy_i, \end{aligned} \quad (8.25)$$

where $(W_i : 1 \leq i \leq l) = (T, -p, \hat{\mu}_a, -X_{ka} : 1 \leq a \leq r; 1 \leq k \leq m)$ and $y = (y_i : 1 \leq i \leq l) \in \mathfrak{P}^E$.

This is known as the energy representation in the literature [10]. This energy representation gives the impression that there is an exact differential form in the Gibbs space even if the system is in non-equilibrium. However, it masks the fact that there is a non-mechanical variable, namely, $\hat{\Psi}$ in the present notation, or ‘the entropy density’ in the notation of Ref. [10], among the variables, and this non-mechanical variable must be deduced from the second law of thermodynamics. Therefore the energy representation must be used with this point clearly understood. It does not free us from facing up to the question of existence of $\hat{\Psi}$ and its thermodynamic nature.

The generalized Maxwell relations for the differential form (8.25) are then given by

$$\frac{\partial}{\partial y_j} W_i = \frac{\partial}{\partial y_i} W_j \quad (i, j = 1, 2, \dots, l). \quad (8.26)$$

These generalized Maxwell relations, especially those involving the generalized potentials X_{ka} , provide symmetry relations for phenomenological coupling constants appearing in the representations of X_{ka} in the space \mathfrak{P} . Such relations have already been considered in connection with global irreversible processes in Chapters 4 and 5. The symmetry relations hold in both linear and non-linear regimes, where various non-conserved variables of different symmetry groups can couple non-linearly. This subject will be further investigated in a later section because of its practical importance.

8.4 Applications of Maxwell’s Relations

We would now like to examine implications of the generalized Maxwell relations obtained earlier, especially, with regards to some constitutive properties. The generalized Maxwell relations associated with the differential forms $d\mathcal{E}$, $d\mathcal{A}$, and $d\mathcal{G}$ give rise to relations of derivatives similar to those in equilibrium thermodynamics except for those involving the non-conserved variables; the relations constitute a non-equilibrium generalization of the equilibrium Maxwell relations. Note that these differential forms are the local versions of the global differential forms considered in Chapter 5, just as the local extended Gibbs relation for $d\hat{\Psi}$ used in this chapter corresponds to the global extended Gibbs relation considered in Chapters 4 and 5. Before proceeding further on the aforementioned topics it must be reiterated that the extended Gibbs relations and the derivatives arising them are in the substantial frame of reference moving at the fluid particle velocity \mathbf{u} unlike those in the case of global extended Gibbs relations considered in Chapters 4 and 5.

Since the non-equilibrium thermodynamic potential $\hat{\Omega}$ defined by Eq. (7.28) is most convenient in irreversible thermodynamics, we will consider the generalized Maxwell relations related to $\hat{\Omega}$. Since its differential form

is given by

$$d\widehat{\Omega} = -\widehat{\Psi}dT + vdp + \sum_{a=1}^r \widehat{\mu}_a dc_a + \sum_{a=1}^r \sum_{k \geq 1}^m \widehat{\Phi}_{ka} dX_{ka}, \quad (8.27)$$

the Maxwell relations reminiscent of those in equilibrium thermodynamics are found to be in the forms

$$\begin{aligned} \left(\frac{\partial \widehat{\Psi}}{\partial p} \right)_{T,\xi} &= - \left(\frac{\partial v}{\partial T} \right)_{p,\xi}, \\ \left(\frac{\partial \widehat{\Psi}}{\partial c_a} \right)_{T,\xi} &= - \left(\frac{\partial \widehat{\mu}_a}{\partial T} \right)_{c,\xi}, \\ \left(\frac{\partial v}{\partial c_a} \right)_{p,\xi} &= \left(\frac{\partial \widehat{\mu}_a}{\partial p} \right)_{c,\xi}, \\ \left(\frac{\partial \widehat{\mu}_b}{\partial c_a} \right)_{c,\xi} &= \left(\frac{\partial \widehat{\mu}_a}{\partial c_b} \right)_{c,\xi}, \end{aligned} \quad (8.28)$$

whereas those involving non-conserved variables or generalized potentials are given by the forms

$$\begin{aligned} \left(\frac{\partial \widehat{\Psi}}{\partial X_{ka}} \right)_{T,\xi} &= - \left(\frac{\partial \widehat{\Phi}_{ka}}{\partial T} \right)_{X_{ka},\xi}, \\ \left(\frac{\partial v}{\partial X_{ka}} \right)_{p,\xi} &= \left(\frac{\partial \widehat{\Phi}_{ka}}{\partial p} \right)_{X_{ka},\xi}, \\ \left(\frac{\partial \widehat{\mu}_a}{\partial X_{kb}} \right)_{c,\xi} &= \left(\frac{\partial \widehat{\Phi}_{kb}}{\partial c_a} \right)_{X_{kb},\xi}, \\ \left(\frac{\partial \widehat{\Phi}_{kb}}{\partial X_{ka}} \right)_{X_{kb},\xi} &= \left(\frac{\partial \widehat{\Phi}_{ka}}{\partial X_{kb}} \right)_{X_{ka},\xi}. \end{aligned} \quad (8.29)$$

In the partial derivatives in the preceding relations the subscript ξ stands for the variables other than those involved in differentiation. The Maxwell relations in Eq. (8.28) are similar to those in equilibrium thermodynamics except that there still appear non-equilibrium variables as the variables fixed, whereas those in Eq. (8.29) do not have equilibrium analogs because they are derivatives with respect to non-equilibrium variables X_{ka} . These relations of derivatives are useful for constructing formulas for the tangents to the $\widehat{\Omega}$ surface in the space \mathfrak{P} in terms of data on derivatives such as $(\partial v / \partial T)_{p,\xi}$, $(\partial \widehat{\mu}_a / \partial T)_{c_a,\xi}$, $(\partial \widehat{\Phi}_{ka} / \partial T)_{\widehat{\Phi}_{ka},\xi}$, and so on.

Since $\hat{\mu}_a$ is found to be a partial molar property of $\hat{\Omega}$ according to the definition given in Chapter 6 and thus $\hat{\Omega}$ is given by

$$\hat{\Omega} = \sum_{a=1}^r \hat{\mu}_a c_a,$$

it follows from Eq. (8.27) that there holds the relation

$$\sum_{a=1}^r c_a d\hat{\mu}_a = -\hat{\Psi} dT + vdp + \sum_{a=1}^r \sum_{k \geq 1}^m \hat{\Phi}_{ka} dX_{ka}. \quad (8.30)$$

This is a form of the generalized Gibbs–Duhem equation which can be put into the equivalent form (8.23) since $\hat{\Psi}$ is an integral of the extended Gibbs relation as given in Eq. (8.7). This relation therefore implies that $\hat{\Omega}$ is a more proper non-equilibrium generalization in \mathfrak{P}^Ω of the equilibrium Gibbs free energy than \mathcal{G} defined by the Legendre transform (7.26).

Generalized Maxwell relations similar to those in Eq. (8.28) can be obtained from the differential forms for $d\mathcal{A}$ and $d\mathcal{G}$, which take the forms

$$d\mathcal{A} = -\hat{\Psi} dT - pdv + \sum_{a=1}^r \hat{\mu}_a dc_a - \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka}, \quad (8.31)$$

$$d\mathcal{G} = -\hat{\Psi} dT + vdp + \sum_{a=1}^r \hat{\mu}_a dc_a - \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka}. \quad (8.32)$$

These differential forms clearly reduce to those of equilibrium Helmholtz and Gibbs free energy as $X_{ka} \rightarrow 0$, namely, as the system approaches equilibrium. For non-equilibrium problems these free energies are not as convenient as the thermodynamic potential $\hat{\Omega}$. This function will be called the non-equilibrium free energy. It must be noted that $\hat{\Omega}$ coincides with \mathcal{G} in the limit of $X_{ka} \rightarrow 0$, as is evident from their differential forms (8.27) and (8.32); one is a Legendre transform of the other.

8.4.1 Symmetry Relations

We discussed some symmetry relations between phenomenological thermodynamic coefficients when global differential forms were considered for thermodynamic functions in Chapter 5. It is possible to examine symmetry relations in the context of the local theory that parallel those in the global theory. We pay attention to the last Maxwell relation in Eq. (8.28), for example. If non-conserved variables $\hat{\Phi}_{ka}$ are expanded in a series of X_{ka}

$$\hat{\Phi}_{ka} = \sum_{lb} K_{ab}^{(kl)} X_{lb} + \sum_{lb} \sum_{qc} K_{abc}^{(klq)} X_{lb} X_{qc} + \dots, \quad (8.33)$$

where $K_{ab}^{(kl)}$, $K_{abc}^{(klq)}$, ..., are expansion coefficients which may be functions of temperature and densities, then the aforementioned generalized Maxwell relation supplies a symmetry relation as follows:

$$K_{ab}^{(kl)} + \sum_{qc} K_{abc}^{(klq)} X_{qc} + \dots = K_{ba}^{(lk)} + \sum_{qc} K_{bac}^{(lqk)} X_{qc} + \dots \quad (8.34)$$

Especially, if a linear approximation is made for $\hat{\Phi}_{ka}$ in the limit of $X_{ka} \rightarrow 0$ then there follows the symmetry relation

$$K_{ab}^{(kl)} = K_{ba}^{(lk)}, \quad (8.35)$$

which is the local theory counterpart of the global symmetry relation (5.6). By independence of the variables X_{qc} it is possible to deduce

$$K_{abc}^{(klq)} = K_{bac}^{(lqk)}, \quad \text{etc..} \quad (8.36)$$

These symmetry relations remind us of the Onsager reciprocal relations [11], but they are not Onsager reciprocal relations because Eq. (8.33), which is a constitutive relation between the non-conserved variables $\{\hat{\Phi}_{ka}\}$ and generalized potentials $\{X_{ka}\}$, is not a thermodynamic force-flux relation and, for example, $K_{ab}^{(kl)}$ are not phenomenological coefficients related to the dynamics of transport processes—for instance, diffusion coefficients, viscosity, thermal conductivity coefficients, and so forth. Nevertheless, symmetry relations (8.35) are useful because they enable us to deduce the relation of one non-conserved variable to $\{X_{ka}\}$ from the relations of other non-conserved variables to $\{X_{ka}\}$.

The symmetry relations such as Eqs. (8.35) and (8.36) arise from the geometry of the space \mathfrak{P} , whereas the Onsager reciprocal relations are dynamical in their origin. Indeed, as we will see later, the Onsager reciprocal relations emerge from the dissipation terms Λ_{ka} in the case of linear irreversible processes, and the dissipation terms stem from dynamics at the level of molecular motions in the system. On the other hand, the symmetry relations such as in Eq. (8.35) simply reflect that the calortropy $\hat{\Psi}$ is a paraboloid with regards to $\hat{\Phi}_{ka}$ in the limit of linear approximations for the relations between $\hat{\Phi}_{ka}$ and X_{ka} . The symmetry relations such as Eqs. (8.35) and (8.36) are another example for the value and role of irreversible thermodynamics that provide interrelationships of irreversible thermodynamic processes and an economy of thought, when macroscopic processes are phenomenologically related and studied.

8.4.2 Non-Equilibrium Free Energy

As an example of applying the extended Gibbs relation for $\hat{\Omega}$, we calculate $\hat{\Omega}$ and its tangents such as $\hat{\Psi}$ and $\hat{\Phi}_{ka}$.

Evaluation of $\hat{\Omega}$

To make the discussion as simple as possible we will consider a single component system for which there holds the differential form

$$d\hat{\Omega} = -\hat{\Psi}dT + vdp + \sum_{k=1}^m \hat{\Phi}_k dX_k, \quad (8.37)$$

where the species subscript a is omitted from the non-conserved variables $\hat{\Phi}_k$ and their conjugate variables X_k . In this case, if the mole number is denoted by n then

$$\hat{\Omega} = n\hat{\mu}, \quad (8.38)$$

where $\hat{\mu}$ is the non-equilibrium chemical potential of the substance.

Let us consider a process from the initial state $i \equiv (T_0, v_0, X_k^0 : k = 1, \dots, m)$ to the final state $f \equiv (T, v, X_k : k = 1, \dots, m)$ in the space $\mathfrak{P}^\Omega \equiv (T, v, X_k : k = 1, \dots, m)$. Therefore the integration in the subspace of $\{X_k\}$ is formally cast into the form of a line integral in the m -dimensional space

$$\hat{\Omega}_X \equiv \int_0^{\{X_k\}} d\mathbf{X} \cdot \hat{\Phi}.$$

Here the integral denotes a line integral in subspace $\{X_k\}$ of \mathfrak{P}^Ω . It is then possible to decompose the integration in the m -dimensional space into integrals along the edges of the hypercube starting from $\{X_k\} = \{0\}$ to $\{X_k\}$. There are $m!$ equivalent ways of reaching the point $\{X_k\}$ from the point $\{0\}$ because $\hat{\Omega}$ is a state function in the space \mathfrak{P}^Ω . Therefore the path of integration can be arbitrarily distorted so as to be suitable for integration of the differential form. For example, the path $i \rightarrow f$ in the space \mathfrak{P}^Ω can be decomposed into the following set of paths

$$i = (T_0, p_0, X_k^0 : 1 \leq k \leq m) \xrightarrow{1} 1 = (T, p_0, X_k^0 : 1 \leq k \leq m), \quad (8.39)$$

$$1 = (T, p_0, X_k^0 : 1 \leq k \leq m) \xrightarrow{2} 2 = (T, p, X_k^0 : 1 \leq k \leq m), \quad (8.40)$$

$$2 = (T, p, X_1^0, X_k^0 : 2 \leq k \leq m) \xrightarrow{3} 3 = (T, p, X_1, X_k^0 : 2 \leq k \leq m), \quad (8.41)$$

⋮

$$m+1 = (T, p, X_1, \dots, X_{m-1}, X_m^0) \xrightarrow{m+2} f = (T, p, X_k : 1 \leq k \leq m). \quad (8.42)$$

Assume p_0 to be sufficiently low and $X_k^0 = 0$ so that the fluid is ideal and at equilibrium at the initial state so that the thermodynamic reference state

is an ideal gas state. The path of integration is assumed to be free from phase transition points.

The overall change in $\widehat{\Omega}$ from the initial state i to the final state f therefore can be formally written in the form

$$\widehat{\Omega}(f) = \widehat{\Omega}(i) + \sum_{j=1}^{m+2} \int_j d\widehat{\Omega}, \quad (8.43)$$

where the index j denotes the path of integration defined in Eqs. (8.39)–(8.42). We calculate the integrals case by case.

For $j = 1$

$$\begin{aligned} \int_1 d\widehat{\Omega} &= \int_{T_0}^T dT \left(\frac{\partial \widehat{\Omega}}{\partial T} \right)_\xi = - \int_{T_0}^T dT \widehat{\Psi} \\ &= -T\widehat{\Psi}(T) + T_0\widehat{\Psi}(T)_0 + \int_{T_0}^T dT \widehat{C}_{p\xi}, \end{aligned} \quad (8.44)$$

where

$$\widehat{C}_{p\xi} = T \left(\frac{\partial \widehat{\Psi}}{\partial T} \right)_{p,\xi} \quad (8.45)$$

This is a non-equilibrium analog of specific heat at constant pressure and ξ . It must be remembered that the other variables for the integral in Eq. (8.44) are kept at p_0 and X_k^0 ($k = 1, \dots, m$).

For path $j = 2$

$$\begin{aligned} \int_2 d\widehat{\Omega} &= \int_{p_0}^p dp \left(\frac{\partial \widehat{\Omega}}{\partial p} \right)_{T,\xi} = \int_{p_0}^p dp v \\ &= nk_B T \ln \left(\frac{p}{p_0} \right) + \int_{p_0}^p dp \left(v - \frac{nk_B T}{p} \right). \end{aligned} \quad (8.46)$$

It must be noted that in the last integral $X_k = X_k^0$ ($k = 1, \dots, m$). Since $X_k^0 = 0$ for all k the two integrals in Eqs. (8.44) and (8.46) involve equilibrium attributes of the system.

For integration along paths $j \geq 3$

$$\int_j d\widehat{\Omega} = \int_{X_j^0}^{X_j} dX_j \left(\frac{\partial \widehat{\Omega}}{\partial X_j} \right)_{T,p,\xi} = - \int_{X_j^0}^{X_j} dX_j \widehat{\Phi}_j, \quad (8.47)$$

for which it must be remembered that along the path of integration

$$\widehat{\Phi}_j = F(X_1, \dots, X_j, X_{j+1}^0, \dots, X_m^0) = F(X_1, \dots, X_j, 0, \dots, 0), \quad (8.48)$$

the last equality being on account of the choice of $X_k^0 = 0$ for the initial state. By combining the results obtained so far we find the change in $\widehat{\Omega}$ between the initial and the final state:

$$\begin{aligned}\Delta\widehat{\Omega} &= \widehat{\Omega}(f) - \widehat{\Omega}(i) \\ &= T_0\Psi(i) - T\Psi(1) + \int_{T_0}^T dT \widehat{C}_{p\xi} + nk_B T \ln\left(\frac{p}{p_0}\right) \\ &\quad + \int_{p_0}^p dp \left(v - \frac{nk_B T}{p}\right) - \sum_{j=3}^{m+2} \int_0^{X_j} dX_j \widehat{\Phi}_j.\end{aligned}\quad (8.49)$$

Here it is useful to define the limit of $\Delta\widehat{\Omega}$ as $p_0 \rightarrow 0$:

$$\Delta\widehat{\Omega}^*(T) = \lim_{p_0 \rightarrow 0} \left[T_0\Psi(i) - T\Psi(1) - nk_B T \ln p_0 + \int_{T_0}^T dT \widehat{C}_{p\xi} \right], \quad (8.50)$$

which can be verified if $\Psi(1)$ is calculated in more detail in the subspace $\mathfrak{P}_1 \equiv (p, X_k : 1 \leq k \leq m)$ up to the point $p = p_0$ and $X_k = X_k^0$ at T ; see Eq. (8.39). In view of the choice for p_0 and X_k^0 , $\Delta\widehat{\Omega}^*$ is seen to be the equilibrium ideal gas limit of $\widehat{\Omega}$, and we finally obtain the expression

$$\begin{aligned}\Delta\widehat{\Omega} &= \Delta\widehat{\Omega}^*(T) + nk_B T \ln p + \int_0^p dp \left(v - \frac{nk_B T}{p}\right) \\ &\quad - \sum_{j=3}^{m+2} \int_0^{X_{j-2}} dX_{j-2} \widehat{\Phi}_{j-2}.\end{aligned}\quad (8.51)$$

Keeping with the tradition in equilibrium thermodynamics we may define the non-equilibrium fugacity $f(T, p, \{X_k\})$ by the formula

$$\begin{aligned}f(T, p, \{X_k\}) &= \exp\left[\frac{1}{nk_B T} \int_0^p dp \left(v - \frac{nRT}{p}\right)\right] \\ &\quad \times \exp\left[-\frac{1}{nk_B T} \sum_{j=3}^{m+2} \int_0^{X_{j-2}} dX_{j-2} \widehat{\Phi}_{j-2}\right].\end{aligned}\quad (8.52)$$

Then $\Delta\widehat{\Omega}$ can be put in the form

$$\Delta\widehat{\Omega} = \Delta\widehat{\Omega}^*(T) + nk_B T \ln[pf(T, p, \{X_k\})]. \quad (8.53)$$

The non-equilibrium fugacity f defined here reduces to the equilibrium fugacity as $X_k \rightarrow 0$ for all k . Finally, since $\widehat{\Omega} = n\widehat{\mu}$, Eq. (8.53) provides the formula for the chemical potential of the non-equilibrium fluid considered, and all other local thermodynamic quantities can be derived from $\widehat{\mu}$.

It is instructive to examine the integral over X_k in the non-equilibrium fugacity expression by using the expansion (8.33) for $\widehat{\Phi}_k$, which in the present case of a single component takes the form

$$\widehat{\Phi}_k = \sum_l K^{(kl)} X_l + \sum_l \sum_q K^{(klq)} X_l X_q + \dots . \quad (8.54)$$

Explicitly written out for evaluation, the integral consists of m integrals along the paths $3, \dots, m+2$:

$$\begin{aligned} \widehat{\Omega}_X &= \int_0^{\{X_k\}} d\mathbf{X} \cdot \widehat{\Phi} = \sum_{j=3}^{m+2} \int_0^{X_{j-2}} dX_{j-2} \widehat{\Phi}_{j-2} \\ &= \int_0^{X_1} dX_1 \widehat{\Phi}_1(X_1, 0, \dots) + \int_0^{X_2} dX_2 \widehat{\Phi}_2(X_1, X_2, 0, \dots) \\ &\quad + \dots + \int_0^{X_m} dX_m \widehat{\Phi}_m(X_1, X_2, \dots, X_m). \end{aligned} \quad (8.55)$$

It helps for gaining insight into the nature of the integral over $\{X_k\}$ to remark that the integrals are along the sides of m -dimensional hypercube, starting from a corner $\{X_k\} = \{0\}$ to the corner $\{X_k\}$ which is located diagonally to $\{0\}$ in the hyperspace. The value of the integral $\widehat{\Omega}_X$ is independent of the path taken, and there are $m!$ independent paths. Each integral on the right hand side can be evaluated on substitution of the expansion for $\widehat{\Phi}_k$ (8.54). On use of the symmetry relations we thus find

$$\widehat{\Omega}_X = \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m K^{(kl)} X_k X_l + \frac{1}{3} \sum_{k=1}^m \sum_{l=1}^m \sum_{q=1}^m K^{(klq)} X_k X_l X_q + \dots . \quad (8.56)$$

This result is evidently invariant under interchanging the order of integration, namely, distorting the path of integration along the sides of a hypercube in \mathfrak{P}^Ω in accordance with $d\widehat{\Omega}$ being an exact differential in the space \mathfrak{P}^Ω . In the linear approximation for the integral in Eq. (8.56) $\widehat{\Omega}$ becomes a quadratic function of $\{X_k\}$ and the matrix $(K^{(kl)})$ is found to be negative by the dictate of the second law of thermodynamics. Therefore $\widehat{\Omega}$ is minimum at $X_k = 0$ and a variation of the state of the system from the state $(T, p, 0, \dots, 0) \in \mathfrak{P}^\Omega$ to a state $(T, p, X_1, \dots, X_m) \in \mathfrak{P}^\Omega$ results in $\delta\widehat{\Omega} = \widehat{\Omega} - \widehat{\Omega}_{\text{eq}} \geq 0$. Note that $\widehat{\Omega}_{\text{eq}} = \mathcal{G}_{\text{eq}}$.

This consideration indicates that the irreversible thermodynamic theory employed for the discussion here makes it easy to understand the thermodynamic stability theory in the Gibbsian equilibrium thermodynamics [2, 3], in which one has to argue that the Clausius entropy or the free energies, which are defined for reversible processes only, reaches a maximum in the case of entropy as stated by Clausius for the second law of thermodynamics, or a minimum in the case of the free energies \mathcal{G}_e and \mathcal{A}_e , as

the system approaches equilibrium. However, the aforementioned quantities are the attributes of reversible processes or equilibrium, which do not depend on non-equilibrium variables and hence have no meanings away from equilibrium. Since $\widehat{\Psi}$ and $\widehat{\Omega}$ are defined for irreversible processes or non-equilibrium systems they do not have such a limitation inherent in the equilibrium attributes.

Evaluation of Calortropy Density $\widehat{\Psi}$

For its basic importance to the theory of irreversible processes developed here we now consider the calortropy of the fluid of interest in more detail. We will calculate its change in the space $\mathfrak{P}^G = \left(T, p, \widehat{\Phi}_{ka} : k \geq 1; r \geq a \geq 1 \right)$, which is the primitive variable set for \mathcal{G} . It must be recognized that the calortropy density is a characteristic function of the variables in the space \mathfrak{P} , but the choice of the primitive variable set \mathfrak{P}^G is most natural and compatible with the constitutive equations for non-conserved variables $\{\widehat{\Phi}_{ka}\}$. For the sake of simplicity we will consider a single-component fluid as for $\widehat{\Omega}$. Therefore we look for $\widehat{\Psi}$ such that

$$\widehat{\Psi} = \widehat{\Psi}(T, p, \{\widehat{\Phi}_k\}).$$

Then

$$d\widehat{\Psi} = \left(\frac{\partial \widehat{\Psi}}{\partial T} \right)_{p, \widehat{\Phi}} dT + \left(\frac{\partial \widehat{\Psi}}{\partial p} \right)_{T, \widehat{\Phi}} dp + \sum_{k=1}^m \left(\frac{\partial \widehat{\Psi}}{\partial \widehat{\Phi}_k} \right)_{T, p, \widehat{\Phi}'} d\widehat{\Phi}_k, \quad (8.57)$$

where the prime on the subscript $\widehat{\Phi}$ means that the variable $\widehat{\Phi}_k$ is excluded from the set $\{\widehat{\Phi}_j\}$. By using the definition of heat capacity and the generalized Maxwell relations arising from the differential form for \mathcal{G} in Eq. (8.32) we obtain Eq. (8.57) in the form

$$d\widehat{\Psi} = T^{-1} \widehat{C}_{p\xi} - \left(\frac{\partial v}{\partial T} \right)_{p, \widehat{\Phi}} dp + \sum_{k=1}^m \left(\frac{\partial X_k}{\partial T} \right)_{p, \widehat{\Phi}} d\widehat{\Phi}_k. \quad (8.58)$$

This differential form can be evaluated along the paths similar to those in Eqs. (8.39)–(8.42) in which $\{X_k\}$ should be replaced by $\{\widehat{\Phi}_k\}$. That is, the non-equilibrium part of the integration is from $\{0\}$ to $\{\widehat{\Phi}_k\}$ in the space \mathfrak{P}^G . We thus find

$$\begin{aligned} \widehat{\Psi}(f) &= \widehat{\Psi}(i) + \int_{T_0}^T dT T^{-1} \widehat{C}_{p\xi} - k_B \ln \left(\frac{p}{p_0} \right) \\ &\quad - \int_{p_0}^p dp \left[\left(\frac{\partial v}{\partial T} \right)_{p, \widehat{\Phi}} - \frac{k_B}{p} \right] + \sum_{k=1}^m \int_0^{\widehat{\Phi}_k} d\widehat{\Phi}_k \left(\frac{\partial X_k}{\partial T} \right)_{p, \widehat{\Phi}}. \end{aligned} \quad (8.59)$$

Here the integration along $\widehat{\Phi}_k$ is performed in the same manner as for $\widehat{\Omega}$ in Eq. (8.56). Define the limit of $\widehat{\Psi}(i)$, as $p_0 \rightarrow 0$, by $\widehat{\Psi}^*(T)$:

$$\widehat{\Psi}^*(T) = \lim_{p_0 \rightarrow 0} \left[\widehat{\Psi}(i) + k_B \ln p_0 + \int_{T_0}^T dT T^{-1} \widehat{C}_{p\xi}(T) \right]. \quad (8.60)$$

This is the equilibrium calortropy for the ideal gas, namely, the ideal gas entropy: $\widehat{\Psi}^*(T) = S_e^*(T)$. Then $\widehat{\Psi}(f)$ may be written as

$$\widehat{\Psi}(f) = S_e(T, p) + \sum_{k=1}^m \int_0^{\widehat{\Phi}_k} d\widehat{\Phi}_k \left(\frac{\partial X_k}{\partial T} \right)_{p, \widehat{\Phi}'}, \quad (8.61)$$

where

$$S_e(T, p) = S_e^*(T) - k_B \ln p - \int_0^p dp \left[\left(\frac{\partial v}{\partial T} \right)_{p, \widehat{\Phi}} - \frac{k_B}{p} \right]. \quad (8.62)$$

Since $S_e(T, p)$ is basically the equilibrium contribution owing to the fact that $\widehat{\Phi}_k^0 = 0$ along the paths of integration involved, the last integral in Eq. (8.61) represents the non-equilibrium contribution to the calortropy density. For example,

$$\widehat{\Phi}_k = \sum_l K^{(kl)} X_l$$

with the matrix $(K^{(kl)})$ being negative, not only the integral in Eq. (8.61) is quadratic with respect to $\{\widehat{\Phi}_k\}$, but also the quadratic form is negative.

Therefore the calortropy reaches a maximum as $\{\widehat{\Phi}_k\} \rightarrow \{0\}$, and the maximum is given by the equilibrium entropy. This formula for calortropy indicates that it is possible to construct a calortropy surface in the Gibbs space once the equation of state and the constitutive relations for X_k such as Eq. (8.54) are provided as functions of $\widehat{\Phi}_k$, p and T . Non-equilibrium statistical mechanics [4, 12] can provide some ideas about the constitutive relations, since the former facilitates calculation [13, 14] of the non-equilibrium partition functions for non-equilibrium systems undergoing irreversible processes, and relations of X_k and $\widehat{\Phi}_k$ can be calculated by using the non-equilibrium partition function.

8.5 Examples

It is useful to consider some illustrative examples for the calortropy in particular. Other thermodynamic functions can be derived from the results for the calortropy if suitable Legendre transformations are applied. To make the formulas as mathematically unencumbered as possible we consider a

single-component fluid which is near equilibrium so that a linear approximation for the constitutive relations for the generalized potentials X_k is appropriate. Under these assumptions the problem amounts to explicitly evaluating the calortropy given in Eq. (8.61).

8.5.1 Ideal Gas

We consider the case of an ideal gas. As was made evident in the general discussion in the previous section, it is convenient to calculate the calortropy as a correction to the equilibrium entropy. To make calculation as simple as possible without losing the point of illustration, we make some assumptions. It is assumed that the specific heat is independent of p for an ideal gas. The ideal gas has this property in any case. We will further assume that it does not depend on T . It is then easy to obtain the entropy

$$\mathcal{S}_e(T, p) = \mathcal{S}_e^0 + \hat{C}_p^0 \ln T - k_B \ln p. \quad (8.63)$$

Here \mathcal{S}_e^0 is the entropy at the reference state suitably chosen and \hat{C}_p^0 is the specific heat of the ideal fluid. The equation of state is $p = nk_B T$. In the linear approximation taken for this calculation the non-equilibrium contribution is given by

$$\sum_{k=1}^m \int_0^{\hat{\Phi}_k} d\hat{\Phi}_k \left(\frac{\partial X_k}{\partial T} \right)_{p, \hat{\Phi}'} = \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m \left(\frac{\partial M_{kl}}{\partial T} \right)_p \hat{\Phi}_k \hat{\Phi}_l, \quad (8.64)$$

where M_{kl} is an element of the inverse of matrix $(K^{(qs)})$:

$$M_{kl} = \left(K^{(qs)} \right)_{kl}^{-1}. \quad (8.65)$$

On combining these results together we obtain the calortropy in the form

$$\hat{\Psi}(T, p, \hat{\Phi}) = \mathcal{S}_e^0 + k_B \ln \left(\frac{T \hat{C}_p^0 / k_B}{p} \right) + \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m \left(\frac{\partial M_{kl}}{\partial T} \right)_p \hat{\Phi}_k \hat{\Phi}_l.$$

Using the equation of state and setting the constant term

$$\mathcal{S}_e^0 - k_B \ln(k_B)$$

equal to zero, we obtain $\hat{\Psi}$ in the space \mathfrak{P} in the form

$$\hat{\Psi}(T, v, \hat{\Phi}) = k_B \ln \left[\left(\mathcal{E} / \hat{C}_v^0 \right)^{3/2} \frac{v}{k_B} \right] + \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m \left(\frac{\partial M_{kl}}{\partial T} \right)_p \hat{\Phi}_k \hat{\Phi}_l, \quad (8.66)$$

where $\hat{C}_v^0 = \hat{C}_p^0 - k_B$. This is a calortropy surface in the Gibbs space \mathfrak{P}_G in the case of an ideal gas in a non-equilibrium state characterized by variables

$\{\hat{\Phi}_k\}$. It must be emphasized that the linear approximation has been used for X_k for this calculation. It contains the constitutive information of the ideal gas in the stated approximation. For this result to be consistent with the extended Gibbs relation for the calortropy in the space \mathfrak{P} the matrix $(K^{(kl)})$ must be such that

$$(\mathbf{K}^{-1})_{kl} = T \left(\frac{\partial M_{kl}}{\partial T} \right)_p = T \left(\frac{\partial M_{kl}}{\partial T} \right)_v - T \left(\frac{\partial M_{kl}}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v, \quad (8.67)$$

where the second equality follows on changing the variable set from $(T, p, \hat{\Phi})$ to $(T, v, \hat{\Phi})$. Note that M_{kl} are independent of $\{\hat{\Phi}_k\}$. The fugacity and, consequently, the non-equilibrium chemical potential can be easily calculated by using Eqs. (8.52) and (8.53). This exercise is left to the reader.

8.5.2 van der Waals Gas

If the van der Waals equation of state is assumed together with the assumption of constant specific heat then the equilibrium part of the calortropy is easily computed. It is in the form

$$\mathcal{S}_e = k_B \ln \left[\left(\frac{\mathcal{E} + a/v}{\hat{C}_v^0} \right)^{3/2} \frac{(v - b)}{k_B} \right], \quad (8.68)$$

where

$$\mathcal{E} = \frac{3}{2} k_B T - \frac{a}{v}$$

and a and b are the van der Waals constants:

$$\left(p + \frac{a}{v^2} \right) (v - b) = k_B T.$$

Since the non-equilibrium part remains the same as for an ideal gas considered earlier, the calortropy has the expression

$$\begin{aligned} \hat{\Psi}(\mathcal{E}, v, \hat{\Phi}) &= k_B \ln \left[\left(\frac{\mathcal{E} + a/v}{\hat{C}_v^0} \right)^{3/2} \frac{(v - b)}{k_B} \right] \\ &+ \frac{1}{2} \sum_{k=1}^m \sum_{l=1}^m \left(\frac{\partial M_{kl}}{\partial T} \right)_p \hat{\Phi}_k \hat{\Phi}_l. \end{aligned} \quad (8.69)$$

This function contains all the information about a van der Waals fluid subjected to non-equilibrium perturbations taken into account by the expansion (8.64) for $\{\hat{\Phi}_k\}$. For example, on differentiation w i $\mathfrak{E} \mathfrak{h} \mathfrak{u} \mathfrak{q}$ n d $\hat{\Phi}_k$

there follow the caloric equation of state, the van der Waals equation of state, and the constitutive relation for X_k given in terms of a linear combination of $\{\hat{\Phi}_l\}$, respectively. The non-equilibrium chemical potential can be calculated in a manner similar to that for an ideal gas.

8.5.3 Canonical Equation of State

In the calculations made for the examples in the two previous sections we have assumed an equilibrium form for the equation of state. They, however, are approximations for the equation of state of a substance in a non-equilibrium state, because, for example, the van der Waals parameters a and b can be dependent on non-equilibrium variables. A recent work [15, 16] on the canonical form of equation of state the virial equation of state can be cast into the form of van der Waals equation of state in which the van der Waals-like parameters are found to be dependent on density and temperature. The equation of state so obtained is called the generic van der Waals equation of state, and the parameters therein the generic van der Waals parameters. Such equation of state can be used even for calculating transport coefficients such as self-diffusion and diffusion coefficients of liquids [17, 18] and, in terms of the latter, the shear viscosity, bulk viscosity, and thermal conductivity of liquids [19, 20, 21, 22, 23]. According to the non-equilibrium ensemble theory [12] it is possible to calculate the non-equilibrium pair distribution function by means of the non-equilibrium Ornstein–Zernike equation [24]. This means that the equation of state for a non-equilibrium fluid can be also expressed in the generic van der Waals equation of state in which the generic van der Waals parameters depend on the density and temperature as well as the non-conserved variables $\{\hat{\Phi}_{ka}\}$.

In a manner similar to the case of equilibrium fluids [15], the generic van der Waals equation of state can be shown to have the form

$$[p + A(\rho, T, \hat{\Phi}) \rho^2] [1 - B(\rho, T, \hat{\Phi}) \rho] = \rho k_B T, \quad (8.70)$$

where $A(\rho, T, \hat{\Phi})$ and $B(\rho, T, \hat{\Phi})$ are the non-equilibrium generic van der Waals parameters. They depend on density $\rho = 1/v$, T , and $\hat{\Phi}_{ka}$. The equation of state in Eq. (8.70) will be referred to as the canonical equation of state. Therefore the canonical equation of state the information on interactions between molecules and effects of non-equilibrium is vested in the non-equilibrium generic van der Waals parameters. As an example of application of the canonical equation of state, we consider the compressibility of the fluid subjected to non-equilibrium perturbations. It is easily found

in the form

$$\begin{aligned}
 (\rho\kappa_T)^{-1} &= \left(\frac{\partial p}{\partial \rho} \right)_{T,\hat{\Phi}} \\
 &= \frac{k_B T}{(1 - B\rho)^2} + \frac{\rho^2 k_B T}{(1 - B\rho)^2} \left(\frac{\partial B}{\partial \rho} \right)_{T,\hat{\Phi}} \\
 &\quad - 2A\rho - \rho^2 \left(\frac{\partial A}{\partial \rho} \right)_{T,\hat{\Phi}}. \tag{8.71}
 \end{aligned}$$

The dynamic free volume v_f may be defined by

$$v_f = v(1 - B\rho) = \rho^{-1}(1 - B\rho). \tag{8.72}$$

The dynamic isothermal compressibility then can be expressed by the formula

$$(\rho\kappa_T)^{-1} = \frac{k_B T}{\rho^2 v_f^2} \left[1 + \rho^2 \left(\frac{\partial B}{\partial \rho} \right)_{T,\hat{\Phi}} \right] - 2A\rho - \rho^2 \left(\frac{\partial A}{\partial \rho} \right)_{T,\hat{\Phi}}. \tag{8.73}$$

If the phenomenological model [16] that was used to account for the critical behavior of simple fluids is employed to construct a model the generic van der Waals parameters for a fluid in non-equilibrium, we may take them in the forms

$$\begin{aligned}
 A(\rho, T, \hat{\Phi}) &= a + \frac{1}{3}\theta(T - T_c) a_3(\hat{\Phi})(\rho - \rho_c)^3 \\
 &\quad + \left[a_5(T, \hat{\Phi})(\rho - \rho_c)^3 + A_{5k}(T, \hat{\Phi})\rho^3 \right] |\rho - \rho_k|^{1+\delta}, \tag{8.74}
 \end{aligned}$$

$$\begin{aligned}
 B(\rho, T, \hat{\Phi}) &= b + \frac{1}{3}\theta(T - T_c) b_3(\hat{\Phi})(\rho - \rho_c)^3 \\
 &\quad + \left[b_5(T, \hat{\Phi})(\rho - \rho_c)^3 + B_{5k}(T, \hat{\Phi})\rho^3 \right] |\rho - \rho_k|^{1+\delta},
 \end{aligned}$$

where a and b are constants which turn out to be similar to the van der Waals constants; ρ_c and T_c are critical density and temperature, respectively; a_3 , a_5 , A_{5k} , b_3 , b_5 , and B_{5k} are empirical functions depending on either $\hat{\Phi}$ or both T and $\hat{\Phi}$; and $\theta(T - T_c) = 1$ for $T - T_c > 0$; $\theta(T - T_c) = 0$ for $T - T_c < 0$, that is, a Heaviside step function; and ρ_k ($k = 1, 2$) are density values, from the point of which A and B become discontinuous if $T - T_c < 0$ and vanish for $T - T_c > 0$. The T dependence of the aforementioned empirical functions is generally non-analytic and the exponent δ is a fractional number. As a matter of fact, the expansions for A and B may include a term depending linearly on $(\rho - \rho_c)$ so that they become more

general phenomenological models for A and B . With appropriate values for the empirical parameters in the expansions for A and B the density, temperature, and $\hat{\Phi}$ dependence of the compressibility may be studied in comparison with experiment. Other thermodynamic quantities may be similarly calculated by using the canonical equation of state postulated. The results of such calculations may be summarized as a surface for $\hat{\Psi}$ by following the procedure described earlier. The surface of $\hat{\Psi}$ so determined in the Gibbs space then may be regarded as the storage of information on the system of interest. Calculating tangents to this surface provides the necessary constitutive information on the system, and there lies the ultimate utility of thermodynamics and generalized thermodynamics. This line of study appears to promise a considerable potential for understanding non-equilibrium properties of liquids in the phenomenological theory approach.

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9

Thermodynamics of Linear Irreversible Processes

The theory of linear irreversible processes which we discuss here is a special case of the generalized thermodynamics of irreversible processes that is formulated up to this point in this work. Since the important position which the theory of linear irreversible processes [1, 2, 3, 4, 5] occupies historically and practically in irreversible thermodynamics warrants a more careful consideration, we devote this chapter to the subject. The main aim of this chapter is to examine how and under what condition the traditional linear theory of irreversible processes arises from the more general theory formulated in this work. However, the discussion will be limited only to the connection between the conventional theory of linear irreversible processes and the present generalized thermodynamics, because there are many monographs on the former in which the theory is delineated and its applications are extensively studied, and consequently there is no point to repeat them in this work.

In the discussion presented here we will limit the set of non-conserved variables to the stress tensor, the heat fluxes, and the diffusion fluxes, since only they are traditionally taken into account in the linear theory of irreversible processes. The theory, however, is applicable to both gases and liquids, provided appropriate material functions, such as viscosity, thermal conductivity, and diffusion coefficients are used in the constitutive equations.

The steady state linear irreversible thermodynamics has been well documented in the standard monographs such as those by De Groot and Mazur [4], Haase [5], and others. Therefore the reader is referred to them for the details of the linear theory of steady irreversible processes. In this work,

as applications of the mathematical formalism developed in this chapter, we would like to discuss some topics which are not generally discussed in the works on linear theory of irreversible processes mentioned. More specifically, we would like to discuss ultrasonic wave dispersion and absorption phenomena and viscoelasticity in the linear regime, in addition to the irreversible thermodynamic treatment of galvanic cells with liquid junctions. These topics are of current interest in physics and chemistry as well as in engineering. They are not strictly in the purview of the conventional linear irreversible thermodynamics theory since the evolution equations used for the shear stress, the excess normal stress, and the heat flux are not the conventional thermodynamic force–flux relations which are assumed for non-conserved variables in the linear theory of irreversible processes. Nevertheless, because the constitutive equations are linear with regard to the thermodynamic forces and the non-conserved variables, we have put them in this category by slightly broadening the scope of linear irreversible thermodynamics.

9.1 Clausius Entropy and Linear Irreversible Processes

Before proceeding further to the aim of this chapter we briefly examine the gist of the theory of linear irreversible processes as formulated by Onsager [1], Meixner [2], Prigogine [3], and so on [4, 5]. First, by interpreting the differentials of macroscopic observables to mean their substantial time derivatives, the equilibrium Gibbs relation for the Clausius entropy is cast into a local form which may be written as

$$d_t \mathcal{S}_e = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a^e d_t c_a \right), \quad (9.1)$$

where d_t is the substantial time derivative introduced earlier and \mathcal{S}_e , \mathcal{E} , and c_a are regarded as local densities of the Clausius entropy and the internal energy and the mass fraction of species a , respectively; $\hat{\mu}_a^e$ is the equilibrium chemical potential of species a . The identification of d_t with the substantial time derivative is an important step in the theory because it makes it possible for the theory to be built on the local forms of the conservation laws of mass, momentum, and energy. The theory of linear irreversible processes assumes the validity of the local equilibrium Gibbs formula (9.1), which then is combined with the conservation laws presented in the previous chapter. This assumption is called the local equilibrium hypothesis. If it is recalled that the equilibrium Gibbs relation for the Clausius entropy is for a uniform system where extensive as well as intensive variables are independent of position and time, assuming not only that the entropy exists

away from equilibrium but also that the variables are dependent on space and time presumes, in a logical leap, the validity of the equilibrium Gibbs relation beyond its range of validity. Therefore it is important for us to see in what sense the linear theory fits in with the theory of irreversible processes presented in earlier chapters.

On combining the local equilibrium hypothesis with a set of linear thermodynamic force–flux relations as the constitutive relations for fluxes appearing in the conservation laws, there follows in essence the theory of linear irreversible processes. The Onsager reciprocal relations are the essential ingredients of the linear thermodynamic force–flux relations—linear constitutive equations. Upon using the linear constitutive equations in the conservation equations for mass, momentum, and internal energy, closed field equations are obtained for the mass densities, velocity, and internal energy. The field equations in fact are the classical hydrodynamics equations, namely, the Navier–Stokes, the Fourier, and the Fick equation in the conventional hydrodynamics [6]. Therefore the classical hydrodynamics may be regarded as a continuum field theory at the level of linear irreversible thermodynamics and local equilibrium Gibbs relation (9.1).

It must be remembered that since the Clausius entropy can be defined only for reversible processes it is not clear under what conditions it is permissible to assume the local equilibrium hypothesis (9.1) when the process in question is not reversible. In fact, the theory of linear irreversible processes, when examined in depth, is contradictory to the definition of the Clausius entropy holding for reversible processes. This question was first raised by Meixner [7] who was also one of the formulators of the theory of linear irreversible processes. His attempt to resolve this vexing question was not successful, in retrospect, for the reason that the non-equilibrium version of entropy was not identified on the basis of the second law of thermodynamics. As has been shown in the previous chapters, Meixner's qualm does not arise in the theory presented in this work.

9.2 Linearized Constitutive Equations for Fluxes

In this section we show under what condition the theory of linear irreversible processes arises from the generalized theory presented in the previous chapters. The generalized theory thereby is shown to be inclusive of the existing theory of linear irreversible processes.

9.2.1 *Fluids with a Bulk Viscosity*

To make the discussion for the stated purpose as simple as possible we first consider the case of a single-component fluid with a non-vanishing bulk

viscosity. Dense simple liquids have a bulk viscosity, which vanishes as the density vanishes. The case of a fluid with internal rotational degrees of freedom will be considered separately. We assume that the fluid is sufficiently near equilibrium so that the magnitudes of the fluxes are sufficiently small. Under the assumption on the number of non-conserved variables taken into consideration in the present discussion the extended Gibbs relation is given by

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + pd_t v + \mathbf{X}_s : d_t \hat{\boldsymbol{\Pi}} + X_b d_t \hat{\Delta} + \mathbf{X}_q \cdot d_t \hat{\mathbf{Q}} \right), \quad (9.2)$$

where the subscript for the species is omitted and \mathbf{X}_s , X_b , and \mathbf{X}_q are the generalized potentials. The evolution equations for the stress tensor, the excess normal stress, and the heat flux for the fluid [8, 9, 10, 11, 12] in this case are the linear equations of the forms

$$\rho d_t \hat{\boldsymbol{\Pi}} = -2p[\nabla \mathbf{u}]^{(2)} - \frac{p}{\eta_0} \boldsymbol{\Pi}, \quad (9.3)$$

$$\rho d_t \hat{\Delta} = -\frac{2}{3}p \nabla \cdot \mathbf{u} - \frac{2p}{3\eta_b} \Delta, \quad (9.4)$$

$$\rho d_t \hat{\mathbf{Q}} = -\hat{C}_p T p \nabla \ln T - \frac{\hat{C}_p T p}{\lambda_0} \mathbf{Q}, \quad (9.5)$$

where \hat{C}_p is the specific heat per mass at constant pressure, η_0 is the viscosity, η_b is the bulk viscosity, and λ_0 is the thermal conductivity of the fluid. For dilute monatomic gases the bulk viscosity is absent and Eq. (9.4) must be ignored. In this section we consider the case of $\eta_b \neq 0$. The equations (9.3) and (9.5) were originally obtained by Maxwell [13] as transfer equations [14, 15] which he used to calculate the viscosity and the thermal conductivity of monatomic gases in his kinetic theory. The molecular expressions for the viscosity and thermal conductivity are available in the monographs of the kinetic theory of gases such as Chapman and Cowling's quoted previously. These equations are valid near equilibrium and are examples for linearized versions of the evolution equations listed in Table 6.1. The linearization of the full evolution equations for the fluxes entails making approximations for the generalized potentials¹ X_k as follows [8, 12]:

$$\mathbf{X}_s = -\frac{\boldsymbol{\Pi}}{2p}, \quad X_b = -\frac{3\Delta}{2p}, \quad \mathbf{X}_q = -\frac{\mathbf{Q}}{\hat{C}_p T p}. \quad (9.6)$$

¹ If the non-equilibrium ensemble method is used the generalized potentials can be theoretically calculated as functions of non-conserved variables and T from the non-equilibrium partition function for the system. This line of study in non-equilibrium statistical mechanics is in an early stage at present. For a method of calculating non-equilibrium partition functions in the presence of heat flow, see Al-Ghoul, M. and Eu, B.C. (2001) J. Chem. Phys., 115, 8481. Also see Farhat, H. and Eu, B.C. (1998) J. Chem. Phys., 109, 10169 for the case of sheared fluids.

These approximations for generalized potentials X_k are equivalent to truncating the expansions for X_k given in Eq. (8.54) at the linear order. Since there is no bulk viscosity in the case of dilute monatomic gases, $\Delta = \frac{1}{3}\text{Tr}\mathbf{P} - p = 0$. However, if there is an internal degree of freedom which is coupled to the translational motion, if there is a chemical reaction, or if the density is sufficiently high there is generally a non-vanishing bulk viscosity and the evolution equation for Δ should be included.

In the case of gases, unless the system is forced by an oscillating velocity or temperature field, $\mathbf{\Pi}$, Δ , and \mathbf{Q} relax to their steady state values on the time scale of the order of 10^{-10} s or shorter. Therefore on a time scale longer than that just mentioned the time derivatives in the constitutive equations (9.3)–(9.5) vanish and the evolution of the non-conserved variables reaches a steady state. At the steady state of $\mathbf{\Pi}$, Δ , and \mathbf{Q} in the reference frame moving at \mathbf{u} the constitutive equations—the evolution equations—then reduce to the Newtonian law of viscosity and the Fourier law of heat conduction:

$$\mathbf{\Pi} = -2\eta_0[\nabla\mathbf{u}]^{(2)}, \quad (9.7)$$

$$\Delta = -\eta_b \nabla \cdot \mathbf{u}, \quad (9.8)$$

$$\mathbf{Q} = -\lambda_0 \nabla \ln T, \quad (9.9)$$

and the extended Gibbs relation for the system reduces to the equilibrium Gibbs relation

$$d_t S_e = T^{-1}(d_t \mathcal{E} + pd_tv),$$

provided that $\widehat{\Psi} = S_e$. This equality is satisfied if $\mathbf{X}_s = X_b = \mathbf{X}_q = 0$. However, the vanishing substantial time derivatives of $\widehat{\mathbf{\Pi}}$, $\widehat{\Delta}$, and $\widehat{\mathbf{Q}}$ do not necessarily mean that the aforementioned generalized potentials vanish. Therefore it would make more sense if it is interpreted so that by local equilibrium we mean the differential form for the steady state calortropy $\widehat{\Psi}_s$

$$d_t \widehat{\Psi}_s = T^{-1}(d_t \mathcal{E} + pd_tv), \quad (9.10)$$

where the subscript s on the calortropy density stands for the steady state with regard to the non-conserved variables. This differential form expresses that the system is not in an equilibrium state because the conserved variables still evolve on a time scale much longer than those of the non-conserved variables, which decay much faster than the former, and the non-conserved variables are spatially non-uniform, as is evident from their constitutive relations (9.7)–(9.9). Because of the space–time dependent conserved variables and the space dependent non-conserved variables obeying the linear constitutive relations given earlier, the differential form (9.10), despite its mathematical similarity to the equilibrium Gibbs relation, is not exactly the same as the latter as far as its physical content is

concerned. This analysis indicates that the entropy used in the linear irreversible thermodynamics is really the steady state calortropy or its density from the viewpoint of the present generalized theory. Under this proviso the theory of linear irreversible processes is easily recovered from the general theory presented in this work if the fluxes are steady in the reference frame moving at the fluid velocity \mathbf{u} and the constitutive equations are linearized with respect to fluxes and thermodynamic forces. Since the substantial time derivatives appear naturally in the local formulation of the present generalized thermodynamic theory of irreversible processes, the discussion leading to Eq. (9.10) supports the interpretation of d_t used for the time derivatives in the linear theory of irreversible processes, which we have mentioned in the previous section.

With the approximation (9.6) and the evolution equations (9.3)–(9.5) the calortropy production Ξ_c takes the form

$$\Xi_c = T^{-1} \left(\frac{1}{2\eta_0} \mathbf{\Pi} : \mathbf{\Pi} + \frac{1}{\eta_b} \Delta^2 + \frac{1}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right) \geq 0, \quad (9.11)$$

which is simply the Rayleigh dissipation function [16]. The positivity of Ξ_c demands that the transport coefficients be positive. Therefore the phenomenological transport coefficients η_0 , η_b , and λ_0 appearing in the constitutive equations must be positive semi-definite, and this is the requirement for the material functions by the second law of thermodynamics. Note that Ξ_c also has the same form as the entropy production in the theory of linear irreversible processes. Therefore under the approximations made to recover the linear theory in this section the calortropy production Ξ_c should be interpreted as being coincident with the entropy production in the theory of linear irreversible processes, just as $d_t \hat{\Psi}_s$ may be interpreted as $d_t \mathcal{S}_e$, the local equilibrium hypothesis for \mathcal{S}_e . The consideration made here suggests that the local equilibrium hypothesis is simply a way of obtaining a special case of the calortropy density.

9.2.2 The Navier–Stokes and Fourier Equations

When the linear thermodynamic force–flux relations, namely, the constitutive relations (9.7)–(9.9), are substituted into the momentum and internal energy balance equations, there follow the classical hydrodynamic equations which are constrained by the local form of the second law of thermodynamics (9.11):

$$\rho d_t \mathbf{u} = - \nabla p + 2\nabla \cdot (\eta_0 [\nabla \mathbf{u}]^{(2)}) + \nabla \cdot (\eta_b \nabla \mathbf{u}) + \rho \mathbf{F}, \quad (9.12)$$

$$\rho (d_t \mathcal{E} + pd_t v) = \nabla \cdot (\lambda_0 \nabla \ln T) + \eta_0 [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \eta_b (\nabla \cdot \mathbf{u})^2, \quad (9.13)$$

where it must be noted that

$$d_t \hat{h} = d_t \mathcal{E} + pd_t v \quad (9.14)$$

with \hat{h} denoting the enthalpy density. The substantial time derivative of the enthalpy density may be written as

$$d_t \hat{h} = \left(\frac{\partial \hat{h}}{\partial T} \right)_p d_t T = \hat{C}_p d_t T. \quad (9.15)$$

With this transformation and the assumption that the transport coefficients η_0 , η_b , and $\lambda'_0 = \lambda_0/T$ are independent of position we obtain the Navier–Stokes and Fourier equations [6] from (9.12) and (9.13)

$$\rho d_t \mathbf{u} = -\nabla p + 2\eta_0 \nabla \cdot [\nabla \mathbf{u}]^{(2)} + \eta_b \nabla^2 \mathbf{u} + \rho \mathbf{F}, \quad (9.16)$$

$$\rho \hat{C}_p d_t T = \lambda'_0 \nabla^2 T + \eta_0 [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \eta_b (\nabla \cdot \mathbf{u})^2. \quad (9.17)$$

It should be noted that this is for $\Delta \neq 0$, that is, for a non-vanishing bulk viscosity. This result shows that the classical hydrodynamics of Navier, Stokes, and Fourier is at the level of linear irreversible thermodynamics that assumes linear thermodynamic force–flux relations for the non-conserved variables and the local equilibrium hypothesis from the standpoint of irreversible thermodynamics.

9.2.3 Hyperbolic Partial Differential Equations

If the evolution of non-conserved variables are such that their substantial time derivatives are of the same order of magnitude as those of the conserved variables, the steady state approximation is not appropriate for the constitutive equations (9.3)–(9.5), but even in such a situation the hydrodynamic equations are still relatively simple partial differential equations

$$\rho d_t \mathbf{u} = -\nabla p - \nabla \cdot \boldsymbol{\Pi} - \nabla \Delta + \rho \mathbf{F}, \quad (9.18)$$

$$\rho (d_t \mathcal{E} + pd_t v) = -\nabla \cdot \mathbf{Q} - (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) : \nabla \mathbf{u}, \quad (9.19)$$

$$\rho d_t \hat{\boldsymbol{\Pi}} = -2p[\nabla \mathbf{u}]^{(2)} - \frac{p}{\eta_0} \boldsymbol{\Pi}, \quad (9.20)$$

$$\rho d_t \hat{\Delta} = -\frac{2}{3}p \nabla \cdot \mathbf{u} - \frac{2p}{3\eta_b} \Delta, \quad (9.21)$$

$$\rho d_t \hat{\mathbf{Q}} = -\hat{C}_p T p \nabla \ln T - \frac{\hat{C}_p T p}{\lambda_0} \mathbf{Q}, \quad (9.22)$$

which give rise to a set of hyperbolic type of partial differential equations of \mathbf{u} and T if it is assumed that the coefficients on the right hand side of the

constitutive equations are independent of position and time. It should be pointed out that the attendant thermodynamic description of the process represented by this set of evolution equations requires the extended Gibbs relation (9.2).

We note that this hyperbolicity [17] of the partial differential equations for the macroscopic variables has been one of the motivations of generalizing the classical hydrodynamic equations and the local equilibrium hypothesis for the Clausius entropy in some versions of extended irreversible thermodynamics [18, 19, 17, 20]. It is useful to have hyperbolic evolution equations, but even if the evolution equations are not hyperbolic they are not as embarrassing in non-relativistic theory as in relativistic theory and still remain useful. For example, the Navier–Stokes–Fourier equations are not hyperbolic, but they are capable of excellently describing diverse flow phenomena occurring near equilibrium. Furthermore, it is often sufficient to consider steady state processes for the non-conserved variables because the relaxation times for the non-conserved variables $\boldsymbol{\Pi}$, Δ , and \mathbf{Q} are much shorter than the hydrodynamic relaxation time, and in such cases the hyperbolicity question becomes moot. Therefore the hyperbolicity, although preferable to have, cannot be such an overriding issue in generalizing equilibrium thermodynamics; the thermodynamically consistent description of non-linear irreversible processes far removed from equilibrium provides a more important motivation for generalizing equilibrium thermodynamics. We will apply the linearized generalized hydrodynamic equations (9.18)–(9.22) to some linear flow problems later. They are, however, not too useful for non-linear flow problems in general, since the constitutive equations generally turn out to be non-linear for the latter class of phenomena.

9.2.4 Multi-Component Fluids

For multi-component fluids the evolution equations should include the mass fraction balance equations and the mass diffusion flux evolution equations in addition to the stress tensor and heat flux evolution equations cast in component forms. Such a set of evolution equations would make the description of processes comparable to that made in the previous subsection, namely, one comparable to the thirteen moment description for a single component system. If there are r components in the fluid the extended Gibbs relation in this case is given by

$$\begin{aligned} d_t \widehat{\Psi} = T^{-1} & \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a \right) \\ & + \sum_{a=1}^r \left(\mathbf{X}_{sa} : d_t \widehat{\boldsymbol{\Pi}}_a + X_{ba} d_t \widehat{\Delta}_a + \mathbf{X}_{qa} \cdot d_t \widehat{\mathbf{Q}}_a + \mathbf{X}_{da} \cdot d_t \widehat{\mathbf{J}}_a \right). \end{aligned} \quad (9.23)$$

The subscript a stands for the species in the system. The accompanying calortropy production is given by

$$\begin{aligned} \Xi_c = T^{-1} \sum_{a=1}^r & \left[\frac{1}{2\eta_{0a}} \boldsymbol{\Pi}_a : \boldsymbol{\Pi}_a + \frac{1}{\eta_{ba}} \Delta_a^2 + \sum_{b=1}^r \mathbf{Q}'_a \left(\frac{1}{\lambda_{ab}} \mathbf{Q}_a + \frac{1}{\kappa_{ab}^{(QJ)}} \mathbf{J}_b \right) \right. \\ & \left. + \sum_{b=1}^r \mathbf{J}_a \left(\frac{1}{D_{ab}} \mathbf{J}_b + \frac{1}{\kappa_{ab}^{(JQ)}} \mathbf{Q}'_b \right) \right] - T^{-1} \sum_{l=1}^m \mathcal{A}_l R_l, \end{aligned} \quad (9.24)$$

where parameters η_{ab} , $\eta_{ab}^{(b)}$, λ_{ab} and D_{ab} are, respectively, the shear viscosity, bulk viscosity, thermal conductivity, and diffusion coefficients of the mixture, and $\kappa_{ab}^{(QJ)}$ and $\kappa_{ab}^{(JQ)}$ are thermal diffusion coefficients. It should be recalled that $\mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a$ and the last term in Eq. (9.24) accounts for the contribution from the chemical reactions. The \mathcal{A}_l and R_l denote the affinity and the rate of chemical reaction l , respectively. In the case of a mixture the following approximations for the generalized potentials X_{ka} are used:

$$X_{sa} = -\frac{\boldsymbol{\Pi}_a}{2p_a}, \quad X_{ba} = -\frac{3\Delta_a}{2p_a}, \quad X_{qa} = -\frac{\mathbf{Q}'_a}{\hat{C}_{pa} T p_a}, \quad X_{da} = -\frac{\mathbf{J}_a}{\rho_a}. \quad (9.25)$$

These approximations are the multi-component versions of the approximations given in Eq. (9.6) and imply that the calortropy surface is quadratic with regards to $\boldsymbol{\Pi}_a$, Δ_a , \mathbf{Q}'_a , and \mathbf{J}_a . These approximations for X_{sa} and so on appear to be good enough for description of many irreversible processes. The attendant linearized generalized hydrodynamic equations are

$$\rho d_t \mathbf{v} = \nabla \cdot \mathbf{u}, \quad (9.26)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l, \quad (9.27)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot (p\boldsymbol{\delta} + \Delta\boldsymbol{\delta} + \boldsymbol{\Pi}) + \rho \mathbf{F}, \quad (9.28)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - (p\boldsymbol{\delta} + \Delta\boldsymbol{\delta} + \boldsymbol{\Pi}) : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (9.29)$$

$$\rho d_t \hat{\Pi}_a = -2p_a [\nabla \mathbf{u}]^{(2)} - \sum_{b=1}^r \frac{p_a}{\eta_{ab}} \Pi_b, \quad (9.30)$$

$$\rho d_t \hat{\Delta}_a = -\frac{2}{3} p_a \nabla \cdot \mathbf{u} - \sum_{b=1}^r \frac{2p_a}{3\eta_{ab}^{(b)}} \Delta_b, \quad (9.31)$$

$$\rho d_t \hat{\mathbf{Q}}'_a = -\hat{C}_{pa} T p_a \nabla \ln T - \hat{C}_{pa} T p_a \sum_{b=1}^r \left(\frac{\mathbf{Q}'_b}{\lambda_{ab}} + \frac{\mathbf{J}_b}{\kappa_{ab}^{(QJ)}} \right), \quad (9.32)$$

$$\rho d_t \hat{\mathbf{J}}_a = \rho_a \chi_a - \rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \rho_a \sum_{b=1}^r \left(\frac{\mathbf{J}_b}{D_{ab}} + \frac{\mathbf{Q}'_b}{\kappa_{ab}^{(JQ)}} \right), \quad (9.33)$$

where $1 \leq a \leq r$ and χ_a is the thermodynamic force for diffusion of species a defined by the formula

$$\chi_a = -(\nabla \hat{\mu}_a)_T + \mathbf{F}_a - \mathbf{F} + v \nabla p. \quad (9.34)$$

If the force is conservative then there exists the potential such that $\mathbf{F}_a = -\nabla \phi_a$, and the chemical potential in the external field may be defined by the formula

$$\hat{\mu}_{\phi a} = \hat{\mu}_a + \phi_a. \quad (9.35)$$

An example for $\hat{\mu}_{\phi a}$ is the electrochemical potential for ionic species subjected to an external electric field.

In the event that the non-conserved variables relax much faster than the conserved variables the former are at the steady state where the linear thermodynamic force–flux relations hold:

$$\Pi_a = -2 \sum_{b=1}^r \eta_{ab} [\nabla \mathbf{u}]^{(2)}, \quad (9.36)$$

$$\Delta_a = - \sum_{b=1}^r \eta_{ab}^{(b)} \nabla \cdot \mathbf{u}, \quad (9.37)$$

$$\sum_{b=1}^r \left(\frac{\mathbf{Q}'_b}{\lambda_{ab}} + \frac{\mathbf{J}_b}{\kappa_{ab}^{(QJ)}} \right) = -\nabla \ln T, \quad (9.38)$$

$$\sum_{b=1}^r \left(\frac{\mathbf{J}_b}{D_{ab}} + \frac{\mathbf{Q}'_b}{\kappa_{ab}^{(JQ)}} \right) = \chi'_a, \quad (9.39)$$

where

$$\chi'_a = \chi_a + (d_t \mathbf{u} - \mathbf{F}_a). \quad (9.40)$$

The constitutive relations (9.36)–(9.39) are the linear thermodynamic force–flux relations used in the linear theory of irreversible processes in a mixture.

The first two equations are Newton's laws for the shear viscosity and the bulk viscosity and the last two equations describe the thermo-diffusion phenomena in the fluid. The phenomenological coefficients η_{ij} , $\eta_{ij}^{(b)}$, λ_{ij} , D_{ij} , $\kappa_{ij}^{(QJ)}$, and $\kappa_{ij}^{(JQ)}$ satisfy the Onsager reciprocal relations. The thermodynamic description corresponding to these constitutive equations is provided by the steady state calortropy differential form

$$d_t \hat{\Psi}_s = T^{-1} \left(d_t \mathcal{E} + pd_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a \right). \quad (9.41)$$

As in the case of a single-component fluid, this differential form is not the same as the equilibrium Gibbs relation for \mathcal{S}_e despite its mathematical similarity to the latter, since the conserved variables vary in time and space and the non-conserved variables are not equal to zero but obey the steady state constitutive equations. It must be noted that in the linear theory of irreversible processes in the literature already cited $d_t \mathcal{S}_e$ is used instead of $d_t \hat{\Psi}_s$. On substituting the constitutive relations (9.36)–(9.39) into Eqs. (9.27)–(9.29) we obtain the classical hydrodynamic equations for the mixture. The constitutive equations for the shear stress, the excess normal stress, and the heat flux do not contain the contributions from the external forces because they are of higher order and thus neglected in the linearized equations presented. They should be restored if the processes are non-linear.

When charge transport processes are examined, it is convenient to consider the drift velocity of a charged species instead of the diffusion flux. The drift velocity evolution equation can be easily obtained from Eqs. (9.28) and (9.33):

$$d_t \mathbf{u}_a = \chi_a + \mathbf{F}_a - \sum_{b=1}^r \left(\frac{\mathbf{J}_b}{D_{ab}} + \frac{\mathbf{Q}'_b}{\kappa'_{ab}^{(JQ)}} \right), \quad (9.42)$$

where we have neglected the term $c_a^{-1} \mathbf{J}_a \nabla \cdot \mathbf{J}_a$. This is in the form of Langevin equation for charged particles subjected to an external force and concentration gradients in the presence of heat fluxes in the system. However, the last term is not stochastic but deterministic. The \mathbf{J}_b -dependent third terms on the right in Eq. (9.42) originate from the frictional effects on the charged particles moving relative to the fluid particle. Note that \mathbf{F}_a is the external force on the unit mass of species a . When this equation, coupled to the charge balance equation (9.27) and the Maxwell equations of electrodynamics, is solved, charge transport in a medium can be described.

9.3 Ultrasonic Waves in Monatomic Gases

The passage of sound wave through a medium periodically compresses or decompresses the medium. If the medium is viscous and diathermal such

a periodic process has an attendant energy dissipation which in turn results in an attenuation and dispersion of the sound wave. These phenomena [21, 22, 23, 24] are called sound wave dispersion and absorption, which can be exploited to measure material properties, notably, the bulk viscosity of the medium. If the medium is made up of molecules with an internal structure or is chemically reacting, measurement of sound or ultrasonic wave dispersion and absorption can be exploited to study the internal energy relaxation processes or the rates of chemical reactions in the medium. These phenomena have been studied rather extensively [21, 22, 23, 24] in the past by means of the classical hydrodynamics which comes within the framework of steady state linear irreversible thermodynamics. Here we show an application of the generalized hydrodynamics in the linear approximation, for which the evolution equations (9.3)–(9.5) or (9.30)–(9.33) for the non-conserved variables are used instead of their steady state forms, namely, Newton's law of viscosity, Fourier's law of heat conduction, and so forth. Application of the differential equations such as (9.3)–(9.5) represents a generalization of the classical hydrodynamic theory when the relaxation times of the non-conserved variables are relatively long and becomes comparable to the relaxation times of hydrodynamic conserved variables. Such situations would occur when the transport coefficients of the medium become sufficiently large.

Here for the sake of simplicity we will assume that the medium is of a single component monatomic fluid but with a bulk viscosity and not too far removed from equilibrium. This would make the use of linear constitutive equations valid. We also assume that there is no external field present. In the constitutive equations the transport coefficients and \hat{C}_p are assumed to be constants independent of position, time, and temperature as well as density of the medium. For the purpose of the problem in hand the density in the substantial time derivatives are approximated by the equilibrium density ρ_0 and the inertial term is neglected because the fluid velocity at equilibrium medium is equal to zero. The required evolution equations for the problem then consist of the linearized conservation laws of mass, momentum, and internal energy

$$\rho_0 \partial_t v = \nabla \cdot \mathbf{u}, \quad (9.43)$$

$$\rho_0 \partial_t \mathbf{u} = -\nabla p' - \nabla \cdot (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}), \quad (9.44)$$

$$\rho_0 \hat{C}_p \partial_t T = -\nabla \cdot \mathbf{Q}, \quad (9.45)$$

which are coupled to the linearized constitutive equations for the shear stress, excess normal stress, and heat flux—essentially Maxwell's stress

equation and the Cattaneo–Vernotte equation—of the fluid

$$\rho_0 \partial_t \widehat{\boldsymbol{\Pi}} = - 2p_0 [\nabla \mathbf{u}]^{(2)} - \frac{p_0}{\eta_0} \boldsymbol{\Pi}, \quad (9.46)$$

$$\rho_0 \partial_t \widehat{\Delta} = - \frac{2}{3} p_0 \nabla \cdot \mathbf{u} - \frac{2p_0}{3\eta_b} \Delta, \quad (9.47)$$

$$\rho_0 \partial_t \widehat{\mathbf{Q}} = - \widehat{C}_p p_0 \nabla T - \frac{\widehat{C}_p p_0}{\lambda'_0} \mathbf{Q}. \quad (9.48)$$

In these equations p_0 is the equilibrium pressure for which $\nabla p_0 = 0$, and $\lambda'_0 = \lambda_0/T$, which is assumed to be a constant. Therefore if we set

$$p = p_0 + p', \quad (9.49)$$

then $\nabla p = \nabla p'$.

We remark that in the classical theory of sound wave absorption based on the Navier–Stokes–Fourier theory of hydrodynamics the constitutive equations (9.46)–(9.48) are replaced with their steady state forms

$$\boldsymbol{\Pi} = - 2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad \Delta = - \eta_b \nabla \cdot \mathbf{u}, \quad \mathbf{Q} = - \lambda'_0 \nabla T.$$

The evolution equations (9.43)–(9.48) can be solved by Fourier transformation in space and time. The Fourier transforms of various variables, denoted by $q(\mathbf{r}, t)$, are defined by

$$\tilde{q}(\mathbf{k}, \omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp(i\omega t - i\mathbf{k} \cdot \mathbf{r}) q(\mathbf{r}, t). \quad (9.50)$$

In the case of non-conserved variables q stands for their densities in this formula. The inverse transform is

$$q(\mathbf{r}, t) = (2\pi)^{-4} \int d\mathbf{k} \int_{-\infty}^{\infty} d\omega \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r}) \tilde{q}(\mathbf{k}, \omega). \quad (9.51)$$

On inserting this into the evolution equations (9.43)–(9.48), we obtain the algebraic set of equations

$$\rho_0 \omega \tilde{v} = - \mathbf{k} \cdot \tilde{\mathbf{u}}, \quad (9.52)$$

$$\omega \tilde{\mathbf{u}} \cdot \mathbf{k} = k^2 v_0 \tilde{p}' + k^2 \tilde{\Delta} + \mathbf{k} \cdot \tilde{\mathbf{Q}}, \quad (9.53)$$

$$\widehat{C}_v \omega \tilde{T} + \frac{T_0 \alpha_p}{\kappa_T} \omega \tilde{v} = \mathbf{k} \cdot \tilde{\mathbf{Q}}, \quad (9.54)$$

$$(i\omega + \tau_s^{-1}) \mathbf{k}\mathbf{k} \cdot \tilde{\boldsymbol{\Pi}} = -i\frac{4}{3}p_0k^2\omega\tilde{v}, \quad (9.55)$$

$$(i\omega + \tau_b^{-1}) \tilde{\Delta} = -i\frac{2}{3}p_0\omega\tilde{v}, \quad (9.56)$$

$$(i\omega + \tau_q^{-1}) \mathbf{k} \cdot \tilde{\mathbf{Q}} = ip_0v_0\hat{C}_pk^2\tilde{T}, \quad (9.57)$$

where $v_0 = 1/\rho_0$,

$$\tilde{p}' = \frac{\alpha_p}{\kappa_T} \tilde{T} - \frac{1}{v_0\kappa_T} \tilde{v}, \quad (9.58)$$

the parameters τ_s , τ_b , τ_q are the relaxation times for the shear stress, the excess normal stress, and the heat flux defined by

$$\tau_s^{-1} = \frac{p_0}{\eta_0}, \quad \tau_b^{-1} = \frac{2p_0}{3\eta_b}, \quad \tau_q^{-1} = \frac{\hat{C}_p p_0}{\lambda'_0}, \quad (9.59)$$

and α_p and κ_T are the isobaric expansion coefficient and the isothermal compressibility, respectively:

$$\alpha_p = v_0^{-1} \left(\frac{\partial v}{\partial T} \right)_p, \quad \kappa_T = -v_0^{-1} \left(\frac{\partial v}{\partial p} \right)_T. \quad (9.60)$$

Upon eliminating $\tilde{\mathbf{u}}$, $\tilde{\boldsymbol{\Pi}}$, $\tilde{\Delta}$, and $\tilde{\mathbf{Q}}$ the coupled algebraic equations (9.52)–(9.57) can be reduced to the pair of algebraic equations for \tilde{v} and \tilde{T} :

$$\left[\omega^3 - \frac{k^2}{\kappa_T} - i \frac{k^2 \omega \eta_b}{1 + i\omega\tau_b} - i \frac{4k^2 \omega \eta_0}{3(1 + i\omega\tau_s)} \right] \tilde{v} + \frac{v_0 \alpha_p k^2}{\kappa_T} \tilde{T} = 0, \quad (9.61)$$

$$\frac{T_0 \alpha_p \omega}{\kappa_T} \tilde{v} + \left(\hat{C}_v \omega - i \frac{v_0 k^2 \lambda'_0}{1 + i\omega\tau_q} \right) \tilde{T} = 0. \quad (9.62)$$

The solvability condition of this algebraic set is the vanishing determinant of the linear equations (9.61) and (9.62) which is quartic with respect to k , and gives the dispersion relation as well as the absorption coefficient: written out in a polynomial of k , it is given by the equation

$$A_4 k^4 + A_2 k^2 + A_0 = 0. \quad (9.63)$$

The coefficients in this dispersion relation are given by the formulas

$$A_4 = \frac{i v_0 \lambda'_0}{\kappa_T (1 + i\omega\tau_q)} - \frac{v_0 \lambda'_0 \omega}{(1 + i\omega\tau_q)} \left[\frac{\eta_b}{1 + i\omega\tau_b} + \frac{4\eta_0}{3(1 + i\omega\tau_s)} \right], \quad (9.64)$$

$$A_2 = -v_0 \left[T_0 \left(\frac{\alpha_p}{\kappa_T} \right)^2 + \frac{\hat{C}_v}{v_0 \kappa_T} + i \frac{\omega \lambda'_0}{1 + i\omega\tau_q} \right] \omega - i \hat{C}_v \left[\frac{\eta_b}{1 + i\omega\tau_b} + \frac{4\eta_0}{3(1 + i\omega\tau_s)} \right] \omega^2, \quad (9.65)$$

$$A_0 = \hat{C}_v \omega^3. \quad (9.66)$$

Solution of Eq. (9.63) yields

$$k = \pm \left[\frac{-A_2 \pm \sqrt{A_2^2 - 4A_4 A_0}}{2A_4} \right]^{1/2}. \quad (9.67)$$

There are four modes of wave possible in the approximation used. The real part of the solution gives the dispersion of sound waves, and the imaginary part gives the absorption coefficient.

If ω is such that $\omega\tau_s, \omega\tau_b, \omega\tau_q \ll 1$, the classical description is recovered since the coefficients A_4 and A_2 become

$$A_4 = i \frac{v_0 \lambda'_0}{\kappa_T}, \quad (9.68)$$

$$A_2 = -v_0 \left[T_0 \left(\frac{\alpha_p}{\kappa_T} \right)^2 + \frac{\widehat{C}_v}{v_0 \kappa_T} \right] \omega - i \left(\widehat{C}_v \eta_b + \frac{4}{3} \widehat{C}_v \eta_0 + v_0 \lambda'_0 \right) \omega^2, \quad (9.69)$$

which coincide with the classical hydrodynamic results. The absorption coefficient of sound waves, defined by the imaginary part of the wave number determined through the dispersion relation, depends on the bulk viscosity coefficient and therefore can be used for measuring the bulk viscosity. This method [25, 26, 27, 28] has been a principal method of measuring the bulk viscosity. The generalized hydrodynamic result embodied by Eqs. (9.63)–(9.66) removes the assumption of short relaxation times $\omega\tau_s, \omega\tau_b, \omega\tau_q \ll 1$ made in the classical hydrodynamic theory.

9.4 Ultrasonic Waves in Rigid Diatomic Gases

The theory of ultrasonic wave absorption and dispersion developed in the previous subsection can be made slightly explicit with regards to the internal degrees of freedom of the molecule. In this subsection we consider the case of nitrogen and hydrogen treated as a rigid diatomic molecule. Therefore it is assumed that the vibrational degree of freedom is frozen. Furthermore, we assume that the temperature is such that the relaxation of rotational degrees of freedom is much faster than the hydrodynamic relaxation times. It then is possible to ignore the rotational energy relaxation equation in the set of evolution equations for the problem. By using the Boltzmann–Curtiss kinetic equation [29] for rigid diatomic gases it is possible to derive the full set of evolution equations for conserved and non-conserved variables. However, from the phenomenological standpoint it is not necessary to use the full set. The following linearized set [30] was shown to yield some reasonable results: namely, the linearized conservation laws

of mass, momentum, and internal energy

$$\rho_0 \partial_t v = \nabla \cdot \mathbf{u}, \quad (9.70)$$

$$\rho_0 \partial_t \mathbf{u} = -\nabla p - \nabla \cdot (\Pi + \Delta \delta), \quad (9.71)$$

$$\rho_0 \hat{C}_v \partial_t T = -\frac{T_0 \alpha_p}{\kappa_T} \nabla \cdot \mathbf{u} - \nabla \cdot \mathbf{Q}, \quad (9.72)$$

which are coupled to the linearized evolution equations for the shear stress, excess normal stress, and heat flux of the diatomic fluid

$$\rho_0 \partial_t \hat{\Pi} = -\nabla \cdot \psi^{(s)} - 2p_0 [\nabla \mathbf{u}]^{(2)} - \frac{p_0 \rho_0}{\eta_0} \hat{\Pi}, \quad (9.73)$$

$$\rho_0 \partial_t \hat{\Delta} = -\nabla \cdot \psi^{(b)} - \frac{2p_0 \hat{C}_{v\text{rot}}}{3\hat{C}_v} \nabla \cdot \mathbf{u} - \frac{2p_0 \hat{C}_{v\text{rot}} \rho_0}{3\hat{C}_v \eta_b} \hat{\Delta}, \quad (9.74)$$

$$\rho_0 \partial_t \hat{\mathbf{Q}} = -\nabla \cdot \psi^{(q)} - p_0 \hat{C}_p \nabla T - \frac{p_0 \hat{C}_p \rho_0}{\lambda'_0} \hat{\mathbf{Q}}. \quad (9.75)$$

In these constitutive equations κ_T and α_p are the isothermal compressibility and the isobaric expansion coefficient of the fluid, respectively, defined by

$$\kappa_T = -v_0^{-1} \left(\frac{\partial v}{\partial p} \right)_T^0, \quad \alpha_p = v_0^{-1} \left(\frac{\partial v}{\partial T} \right)_p^0, \quad (9.76)$$

$\hat{C}_{v\text{rot}}$ denotes the rotational specific heat per mass at constant volume, and

$$\nabla \cdot \psi^{(s)} = -\frac{2p_0 \lambda'_0}{3\rho_0 \hat{C}_p} [\nabla \nabla T]^{(2)}, \quad (9.77)$$

$$\psi^{(q)} = -p_0 v_0 (2\eta_0 [\nabla \mathbf{u}]^{(2)} + \eta_b \delta \nabla \cdot \mathbf{u}), \quad (9.78)$$

$$\psi^{(b)} = \frac{2\rho_0 \hat{C}_{v\text{rot}}}{3\hat{C}_v} \hat{\mathbf{Q}}. \quad (9.79)$$

This kind of closures is generally used in the Grad moment method [31] for the kinetic equation, but their kinetic theory and irreversible thermodynamic foundations are obscure. These closure relations are taken in an *ad hoc* manner for the non-conserved set of variables for this particular problem in the work cited.

The linearized evolution equations (9.70)–(9.75) can be solved by Fourier transform as for the evolution equations (9.43)–(9.48) in the previous subsection, and the resulting coupled algebraic equations for the Fourier expansion coefficients give rise to the dispersion relation, which is the solvability

condition. Since the procedure is the same as for the previous subsection, we present the result only. The dispersion relation, which appears as the solvability condition for the algebraic system of equations for the Fourier expansion coefficients for velocity and temperature, is given by the sixth order polynomial of reduced wave number k^*

$$B_6 k^{*6} + B_4 k^{*4} + B_2 k^{*2} + B_0 = 0, \quad (9.80)$$

where the coefficients are given by the formulas

$$\begin{aligned} B_0 &= -\frac{5}{2}, \\ B_2 &= \frac{5}{2} + i\omega^* \left(\frac{5}{2} f_b \xi_b + \frac{10}{3} \xi_s + \frac{19}{4} \xi_q \right), \\ B_4 &= -i \frac{95}{28} \omega^* \xi_q - \frac{19}{3} \omega^{*2} \left(\frac{2}{7} \xi_s + \frac{2}{7} \xi_q + \frac{3}{4} f_b \xi_b \right. \\ &\quad \left. + \frac{3}{14} f_b \xi_q - \xi_s \xi_q - \frac{3}{4} f_b \xi_b \xi_q \right), \\ B_6 &= \frac{361}{30} \omega^{*4} \xi_q \left(\frac{8}{21} \xi_s + f_b \xi_b \right) \left(1 + \frac{3}{4} f_b \right) \end{aligned} \quad (9.81)$$

Various quantities in these formulas are defined as follows:

$$c_0 = \sqrt{\frac{\gamma k_B T_0}{m}}, \quad \omega^* = \frac{\omega \eta_0 v_0}{c_0^2}, \quad k^* = \frac{k c_0}{\omega}, \quad f_b = \frac{\eta_b}{\eta_0}, \quad (9.82)$$

$$\xi_s = \left(1 + i \frac{7}{5} \omega^* \right)^{-1}, \quad \xi_q = \left(1 + i \frac{19}{10} \omega^* \right)^{-1}, \quad \xi_b = \left(1 + i \frac{21}{4} \omega^* \right)^{-1}, \quad (9.83)$$

with γ denoting the polytropic ratio $\gamma = 7/5$ for the diatomic gas. We note that c_0 is the speed of sound and f_b is the Eucken ratio of the viscosity coefficients. This ratio can be determined by fitting the sound wave absorption coefficient in the low frequency regime—the classical regime. This fitting in effect amounts to measuring the bulk viscosity, provided that the shear viscosity is known.

Although the dispersion relation can be exactly solved, the solutions are not in readily interpretable forms. Therefore it is useful to consider the low

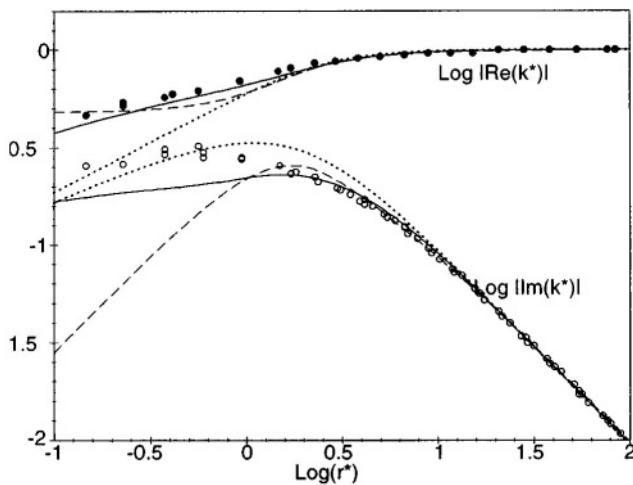


FIGURE 9.1. Sound wave absorption coefficient $\log|\text{Im } k^*|$ and dispersion $\log|\text{Re } k^*|$ vs. $\log r^*$ for nitrogen gas ($r^* = 1/\gamma\omega^*$). The ordinate is for either $\log|\text{Re } k^*|$ or $\log|\text{Im } k^*|$ in the common scale as indicated, and $r^* = 1/\gamma\omega^*$. The prediction by the present theory (solid curve) is compared with the experimental data by Greenspan (symbols), the Navier-Stokes theory (dotted curve), and the result (broken curve) of the Moraal-McCourt moment method. The value of f_b is 0.8. [Reproduced with permission from (2001) Physics of Fluids, 13, 744. © 2001 American Institute of Physics.]

frequency limits of the solutions. Since as $\omega^* \rightarrow 0$

$$B_6 \rightarrow 0,$$

$$B_4 \rightarrow -i \frac{95}{28} \omega^* - \left(\frac{205}{56} + \frac{19}{14} f_b \right) \omega^{*2},$$

$$B_6 \rightarrow \frac{5}{2} + i \left(\frac{97}{12} + \frac{5}{2} f_b \right) \omega^* + \left(\frac{1643}{120} + \frac{105}{8} f_b^2 \right) \omega^{*2},$$

we readily find the limiting solutions in the form

$$k^* = \pm \left[1 - i \frac{1}{2} \left(\frac{197}{105} + f_b \right) \omega^* - \left(\frac{8563}{4200} + \frac{16}{35} f_b + 3 f_b^2 \right) \omega^{*2} \right], \quad (9.84)$$

which are the sound modes, and the thermal modes are given by

$$k^* = \pm (1 - i) \sqrt{\frac{7}{19\omega^*}}. \quad (9.85)$$

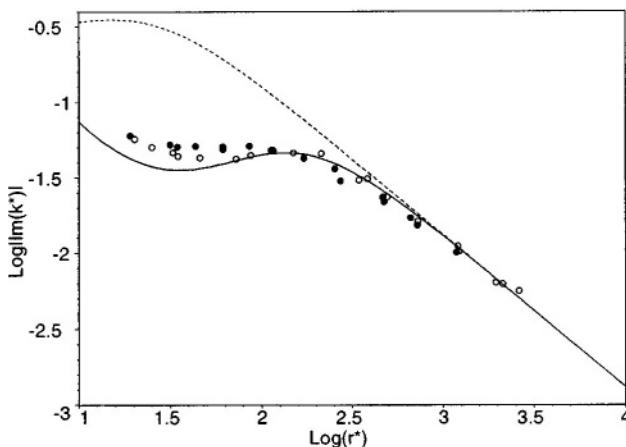


FIGURE 9.2. Sound wave absorption coefficient $\log |\text{Im } k^*|$ vs. $\log r^*$ for normal H_2 and para H_2 at $T_0 = 293\text{ K}$. The open circles are for normal H_2 and the filled circles are for para H_2 . The solid curve denotes the prediction by the present theory, and the broken curve the prediction by the Navier–Stokes theory. $f_b = 35$ and $\eta_0 = 88.2 \mu\text{P}$. [Reproduced with permission from (2001) Physics of Fluids, **13**, 744]. © 2001 American Institute of Physics.]

The absorption and dispersion of ultrasonic waves are characterized by the imaginary part and the real part of k^* , respectively. They can be numerically calculated by solving the dispersion relation (9.80). The result is plotted in Fig. 9.1 where comparison is made with the experimental data obtained for nitrogen by Greenspan [25] and also with the kinetic theory result obtained by Moraal and McCourt [32] who used a moment method for the Waldmann–Snider kinetic equation [33, 34]. The $|\text{Im}(k^*)|$ denotes the reduced absorption coefficient, and $|\text{Re}(k^*)|$ represents the reduced dispersion of sound wave. The agreement with experiment is excellent in the low frequency regime, but in the high frequency regime there is a considerable deviation from experiment. To improve the results in the high frequency regime it appears to be necessary to take into account the rotational energy relaxation process more precisely than the present theory. The theory can be also applied to the case of hydrogen, deuterium, and deuterium hydride. The results for the absorption and dispersion of ultrasonic waves in H_2 , HD, and D_2 are given in Fig. 9.2 and Fig. 9.3. These results show that the generalized hydrodynamic theory performs better than the classical hydrodynamics using the Navier–Stokes–Fourier theory with which the former agrees in the low frequency regime. The ultrasonic absorption measurement can be used for measuring the bulk viscosity of the gas. It is done by choosing the Eucken ratio f_b in the present phenomenological method. In fact, ultrasonic absorption measurement is just about the only practicable method of measuring bulk viscosity at present. Therefore it is

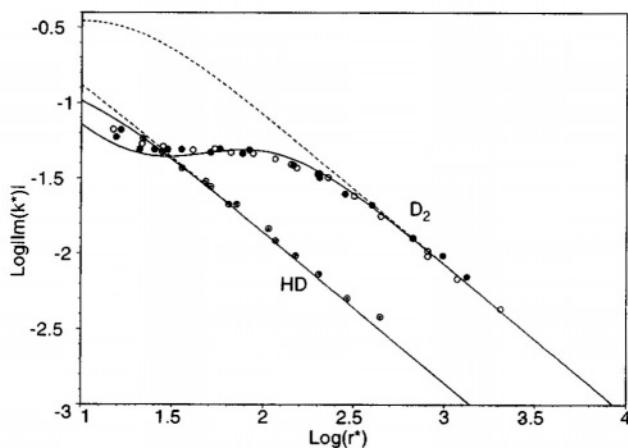


FIGURE 9.3. Sound wave absorption coefficient $\log |\text{Im } k^*|$ vs. $\log r^*$ for normal D_2 , ortho D_2 , and HD at $T_0 = 293\text{ K}$. The open circles are for normal D_2 , the filled circles are for ortho D_2 , and the dotted circles are for HD. The solid curves denote the predictions by the present theory, and the broken curves the predictions by the Navier–Stokes theory. $f_b = 22$ for D_2 and $\eta_0 = 123 \mu\text{P}$ for D_2 and $f_b = 2$ for D_2 and $\eta_0 = 108 \mu\text{P}$ for D_2 . [Reproduced with permission from (2001) Physics of Fluids, **13**, 744. © 2001 American Institute of Physics.]

important to study further the generalized hydrodynamic theory in order to improve the underlying theory of measuring ultrasonic absorption and dispersion in gases and liquids. Here the discussion presented gives a glimpse into the subject field.

9.5 Viscoelasticity of Fluids

On deforming some viscous substances such as polymer solutions or polymer melts, one observes that they tend to return to their original form after a time. This is a manifestation of the viscoelasticity of the substances. All viscous substances, in fact, have viscoelasticity in varying degrees, some with a noticeable extent. The viscoelasticity of materials can be characterized by a complex viscosity coefficient whose real and imaginary parts give the measure of rigidity (or elasticity) and of energy dissipation, respectively. We would like to examine viscoelasticity within the framework of irreversible thermodynamics [35] by using the linear evolution equations presented in this chapter. In general the proper description of viscoelasticity requires non-linear constitutive equations for stresses, but since our main aim here is an illustration of how the present generalized hydrodynamic theory can be applied to such problems, we make a linear approximation for the simplicity of mathematics involved.

In addition to the assumptions made earlier, it will be assumed that the temperature is maintained uniform over the system, which is made up of a single component fluid. It is also assumed that the fluid is incompressible. Therefore there is no need to consider the excess normal stress.

Under these assumptions there is only a pair of evolution equations to consider, namely, the momentum balance equation and the shear stress evolution equation:

$$\rho \partial_t \mathbf{u} = -\nabla \cdot \boldsymbol{\Pi}, \quad (9.86)$$

$$\rho \partial_t \hat{\boldsymbol{\Pi}} = -2p[\nabla \mathbf{u}]^{(2)} - \frac{\rho p}{\eta_0} \hat{\boldsymbol{\Pi}}. \quad (9.87)$$

Since the equations are linearized, the inertia terms are also neglected in these equations. By the assumptions made, ρ and p are independent of position and time, and it is assumed that η_0 is also a constant. Cast in these forms, the partial differential equations are hyperbolic.

In the momentum balance equation the pressure and the excess normal stress terms are absent because of the incompressibility assumption made. This fluid is Maxwellian, that is, it obeys the Maxwell equation for the shear stress. Eqs. (9.86) and (9.87) can be solved by Fourier transform. To make the analysis made here more specific we will consider a nonsteady, oscillating Couette flow configuration. That is, the fluid is confined between two parallel infinite plates, which are separated by distance D and oscillate back and forth at amplitude γ and frequency ω_0 . The plates are assumed to be parallel to the x axis and perpendicular to the y axis of the laboratory coordinate system. Therefore the velocity gradient is in the direction of the y axis. The fluid does not move in the z direction; it is a neutral direction. On analytic continuation of the variables we may regard the velocity and stress tensor as complex variables [35]. Therefore, in the aforementioned flow configuration the traceless symmetric part of the velocity gradient takes the form

$$[\nabla \mathbf{u}]^{(2)} = \gamma \exp(i\omega_0 t) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (9.88)$$

Here

$$\gamma = \frac{1}{2} \frac{\partial u_x}{\partial y} = \text{constant} \quad (9.89)$$

with u_x denoting the x component of fluid velocity \mathbf{u} . In the flow configuration under discussion here the momentum balance equation has the x component only, and the stress evolution equation the xy component only.

The velocity and stress tensor components can be decomposed in Fourier series:

$$u_x(x, t) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dk \exp(ikx - i\omega t) \hat{u}(k, \omega), \quad (9.90)$$

$$\hat{\Pi}_{xy}(x, t) = \frac{1}{4\pi^2} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dk \exp(ikx - i\omega t) \hat{\Pi}(k, \omega). \quad (9.91)$$

On inserting these expansions into the evolution equations there follow the algebraic equations for the Fourier components

$$-i\omega\rho\hat{u}(k, \omega) = -ik\rho\hat{\Pi}(k, \omega), \quad (9.92)$$

$$-i\omega\rho\hat{\Pi}(k, \omega) = -2p\gamma\delta(\omega - \omega_0)\delta(k) - \frac{\rho p}{\eta_0}\hat{\Pi}(k, \omega). \quad (9.93)$$

Solving these equations we obtain

$$\rho\hat{\Pi}(k, \omega) = -\frac{2\eta_0\gamma}{1 - i\tau\omega}\delta(\omega - \omega_0)\delta(k), \quad (9.94)$$

where τ is the stress relaxation time defined by

$$\tau = \frac{\eta_0}{p}. \quad (9.95)$$

Substitution of Eq. (9.94) into Eq. (9.92) yields

$$\rho\hat{u}(k, \omega) = -\frac{2\eta_0\gamma k}{\omega(1 - i\tau\omega)}\delta(\omega - \omega_0)\delta(k), \quad (9.96)$$

which suggests that

$$u_x(x, t) = 0 \quad (9.97)$$

and

$$\begin{aligned} \Pi_{xy}(x, t) &= \rho\hat{\Pi}_{xy}(x, t) \\ &= -\frac{1}{2\pi^2} \frac{\eta_0\gamma}{1 - i\tau\omega_0} \exp(-i\omega_0 t). \end{aligned} \quad (9.98)$$

The dynamic viscosity is defined by

$$\Pi_{xy}(x, t) = -2\eta(\omega_0)\gamma \exp(-i\omega_0 t). \quad (9.99)$$

Comparison of Eq. (9.98) with Eq. (9.99) identifies the dynamic viscosity [35, 36]

$$\begin{aligned} \eta(\omega_0) &= \eta'(\omega_0) + i\eta''(\omega_0) \\ &= \frac{\eta_0}{4\pi^2 [1 + (\tau\omega_0)^2]} + i\frac{\eta_0\tau\omega_0}{4\pi^2 [1 + (\tau\omega_0)^2]}. \end{aligned} \quad (9.100)$$

The real part $\eta'(\omega_0)$ of the dynamic viscosity gives the loss modulus, whereas the imaginary part gives the storage modulus of the viscoelastic substance. In the linear approximation used in the present discussion the moduli are independent of the shear amplitude γ . However, it is not the case in general. For more appropriate treatment of the subject non-linear evolution equations [35], namely, non-linear generalized hydrodynamic equations, are necessary.

9.6 Galvanic Cells

Galvanic cells are closed finite systems of electrolytes and non-electrolytes where irreversible processes and, in particular, chemical reactions and diffusion of matter, give rise to passage of an electrical current through the system. A galvanic cell consists of subsystems of a finite size which interact across their boundaries, and chemical reactions occur in some of subsystems while matter diffuses within them and across their boundaries. In textbooks [37] on physical chemistry galvanic cells are usually described by means of the equilibrium thermodynamics formalism by the force of tradition in which the electromotive force is measured in the no charge current condition by imposing an opposing potential difference on the cell. Such a formalism provides the Nernst equation for the electromotive force of the galvanic cell. Since galvanic cells are inherently irreversible, and irreversible processes therein imply unavoidable energy dissipation in various modes, it would be useful to formulate a thermodynamic theory of irreversible processes in galvanic cells, since such a theory could enable us to design galvanic cells which have a minimum energy dissipation possible. Besides this practical reason there is also the fundamental question of how to describe irreversible processes in galvanic cells, which are finite in size, and the precise mode of energy dissipation in them. In this section we consider the irreversible thermodynamics of galvanic cells as an example of applications to a finite system of the irreversible thermodynamics formalism developed earlier in this work.

There are two different categories of galvanic cells: cells without liquid junctions and cells with liquid junctions. Since the latter category requires formally a more general description which can be specialized to the former category, we will consider only the latter in this work.

In order to make the formalism as simple as possible without making it trivial, we will introduce some simplifications. First, we will assume that the temperature is uniform over the entire system, although this assumption can be readily removed, and a more general theory can be formulated at the expense of simplicity in formalism. It will also be assumed that there are no convection of the fluid and no stress present in the system. Then the only possible non-scalar irreversible process is the diffusion of matter

accompanying charge currents. The chemical reactions are the other irreversible processes, which are scalar, however.

A galvanic cell is assumed to consist of $(r + 1)$ components in which the $(r + 1)$ th component is assigned to the electrons. The remaining r components are electrically neutral. This mode of description is possible since ionic species can be regarded as consisting of the neutral species minus an appropriate number of electrons, namely, for example, $M^+ = M - e^-$, where M^+ is a univalent ion of M and e^- is the electron. The system is subjected to an electrostatic field \mathbf{E} which has the potential ϕ defined by the relation

$$\mathbf{E} = -\nabla\phi. \quad (9.101)$$

This potential enters the expression for the electrochemical potential of species a , which is written in the form

$$\hat{\mu}_{ea} = \hat{\mu}_a + z_a \mathcal{F}\phi, \quad (9.102)$$

where $\hat{\mu}_a$ is the material part of the electrochemical potential, z_a is the charge number per mass of species a , and \mathcal{F} stands for electric charge in Faraday units. This manner of writing the chemical potential is not operational since $\hat{\mu}_a$ and ϕ are not independently measured. However, it is possible to measure the electrostatic potential difference across a phase boundary under special conditions, and galvanic cells are devices that allow such measurement. Since such measurement requires more than one phase in the system, galvanic cells are necessarily multiphase systems. The phases will be distinguished by a superscript on the chemical potentials and other macroscopic variables involved. The material part $\hat{\mu}_a$ of the electrochemical potential $\hat{\mu}_{ea}$ can be determined such that if two phases α and β are at the same temperature and pressure and have the same composition, then

$$\hat{\mu}_a^{(\alpha)} = \hat{\mu}_a^{(\beta)}, \quad (9.103)$$

provided that there are no irreversible processes present in them. Insofar as the splitting of $\hat{\mu}_{ea}$ as in Eq. (9.102) is arbitrary, it is possible to subject the splitting to this condition.

On elimination of the material parts $\hat{\mu}_a^{(\alpha)}$ and $\hat{\mu}_a^{(\beta)}$ of the chemical potentials by using Eq. (9.102), it follows

$$\hat{\mu}_{ea}^{(\alpha)} - \hat{\mu}_{ea}^{(\beta)} = z_a \mathcal{F}(\phi^{(\alpha)} - \phi^{(\beta)}) = z_a \mathcal{F}\Delta\phi. \quad (9.104)$$

This provides $\Delta\phi$ on measurement of the observables $\hat{\mu}_{ea}^{(\alpha)}$ and $\hat{\mu}_{ea}^{(\beta)}$ by some means.

The electromotive force ε is defined as follows:

$$\lim_{I \rightarrow 0} I = \lim_{I \rightarrow 0} \frac{\Delta\phi - \varepsilon}{R_e} = 0, \quad (9.105)$$

where I is the electric current and \mathcal{R}_e is the resistance. That is, in the limit of vanishing electric current the electromotive force is determined by the potential difference in two phases:

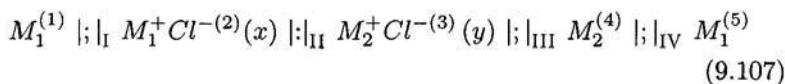
$$\varepsilon = \Delta\phi. \quad (9.106)$$

Because of this definition of electromotive force, if the electrodes of a galvanic cell are of different substances, the last phase adjacent to the second electrode, for example, of the cell must be identical with the first phase—the first electrode.

9.6.1 Galvanic Cells with Liquid Junctions

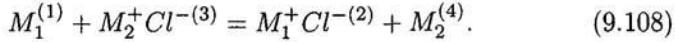
In galvanic cells phases are arranged in such a way that electric current is transmitted between phases as a result of chemical reactions in the terminal phases which are called the electrodes. The electric current passes from one electrode through the other phases to the other electrode. There is no accumulation of charges in the phases except for the terminal phases, namely, the electrodes. In the American convention for the cell configuration the oxidizing electrode phase is written on the left hand side, and the reducing electrode on the right hand side with the oxidized and reduced phases—for example, liquid solutions or mixtures—positioned in contact with the oxidizing and reducing electrodes, respectively. If the oxidized and reduced phases are liquid solutions there is an interphase (liquid junction) through which ions diffuse from one phase into the other. In this case another phase consisting of solutions of other electrolytes is usually inserted between the oxidized and reduced solution phases. Such a phase will be called the liquid junction phase. The liquid junction phase may consist of a solution containing an ion in common with the oxidized and reduced phases, which will be numbered 2 and 3, respectively, or solutions of ions different from those in phases 2 and 3. There are no chemical reactions in the liquid junction phase. The fluids are assumed to be incompressible for the simplicity of fluid dynamic description of the irreversible processes in the event it is desired. It is also assumed that phases 2 and 3 are uniform in concentration. Strictly speaking, this is not true, but the assumption is made in order to make the theory as simple as possible.

To be specific for the galvanic cell examined in this section, we will consider the example



where M_1 and M_2 are monovalent metals, x and y denote the concentrations of the compounds in suitable units, the superscripts mean the phases, the semicolon or the colon enclosed in the vertical bars with a subscript stand

for the interfaces and the liquid junction phase, respectively, which are numbered by Roman numerals. The overall cell reaction for this galvanic cell is



This cell reaction may be decomposed into two reactions

$$\begin{aligned} M_1(1) &= M_1^+(1) + e^-(1) \\ M_2^+(4) + e^-(4) &= M_2(4). \end{aligned} \quad (9.109)$$

The ionic species in phase 1 or 2 are in equilibrium with the solution phase 2 or 3, which is electrically neutral on account of the chlorine ions present and the boundaries I and III being impermeable to the electrons.

9.6.2 Local Hydrodynamic Equations

The relevant local hydrodynamic equations under the assumptions made earlier are the concentration balance equations for the species and the evolution equations for diffusion fluxes, which may be approximated by their linear steady state forms. If the mass fractions are denoted by c_a then

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l, \quad (9.110)$$

$$\mathbf{J}_a = \sum_{b=1}^r \rho_b k_{ab} \mathbf{E} - \rho \sum_{b=1}^r D_{ab} \nabla c_b, \quad (9.111)$$

where R_l is the reaction rate of reaction l , ν_{al} are stoichiometric coefficients times mass in the usual sign convention adopted in this work, k_{ab} are the mobilities, and D_{ab} are the diffusion coefficients. Since the concentrations are assumed to be uniform in various phases the concentration gradient terms do not contribute to the diffusion fluxes, which then may be written in the form

$$\mathbf{J}_a = \rho_a k_a \mathbf{E}, \quad (9.112)$$

where the mean mobility k_a is defined by

$$\rho_a k_a = \sum_{b=1}^r \rho_b k_{ab}. \quad (9.113)$$

If one desires to solve local hydrodynamic flow problems within the electrolyte solutions in the cell then it is necessary to add to these equations the momentum balance equation and one of the Maxwell equations

$$\nabla \cdot \mathbf{E} = \frac{4\pi\rho_c}{\epsilon}, \quad (9.114)$$

where ρ_c is the charge density and ϵ is the dielectric constant of the medium.

If the charge currents vary in time in the cell then the time-independent constitutive equation (9.111) for the diffusion fluxes must be replaced by a time-dependent evolution equation within the generalized hydrodynamic formalism developed earlier. We, however, will not deal with such a situation in this work. Once the present near-equilibrium theory is formulated, the generalization of the theory to such a situation is rather straightforward to achieve.

9.6.3 Calortropy Production in the Galvanic Cell

We are interested in the rate of change in global calortropy of the galvanic cell, as an electric current flows in the system under the conditions specified earlier in the present section. Since the system is a finite multiphase system, the desired quantity is an integral of the local rate of calortropy change, which is described by the calortropy balance equation:

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \rho \frac{d\hat{\Psi}}{dt} = \int_V d\mathbf{r} [-\nabla \cdot \mathbf{J}_c + \Xi(\mathbf{r}, t)] \quad (9.115)$$

in the standard notation for this work. Here the integral is over the volume of the entire multiphase system. The integral on the right hand side is decomposable into contributions from the various phases distinguished by the superscript s :

$$\frac{d\Psi}{dt} = \sum_{s=1}^{\nu} \int_{V^{(s)}} d\mathbf{r} \left[-\nabla \cdot \mathbf{J}_c^{(s)} + \Xi^{(s)}(\mathbf{r}, t) \right]. \quad (9.116)$$

Under the assumptions made for the galvanic cell the local calortropy flux \mathbf{J}_c and the local calortropy production Ξ in phase s are given by the formulas

$$\mathbf{J}_c^{(s)} = -T^{-1} \sum_{a=1}^{r+1} \widehat{\mu}_{ea}^{(s)} \mathbf{J}_a^{(s)}, \quad (9.117)$$

$$\Xi^{(s)} = -T^{-1} \sum_{a=1}^{r+1} \mathbf{J}_a^{(s)} \cdot \left(\nabla \widehat{\mu}_a^{(s)} - \mathbf{F}_a^{(s)} \right) - T^{-1} \sum_{l=1}^m \mathcal{A}_l^{(s)} R_l^{(s)}, \quad (9.118)$$

where the external force may be written as $\mathbf{F}_a = -z_a \mathcal{F} \nabla \phi$ since it is electrical, and \mathcal{A}_l is the chemical affinity of reaction l :

$$\mathcal{A}_l = \sum_{a=1}^{r+1} \nu_{al} \widehat{\mu}_{ea}. \quad (9.119)$$

The thermodynamic force in the first term on the right hand side of Eq. (9.118) therefore may be replaced by $\nabla \widehat{\mu}_{ea}^{(s)}$ given in terms of the electrochemical potential.

Compensated Heat

Inserting the expression for $\mathbf{J}_c^{(s)}$ in Eq. (9.117) into the divergence term in Eq. (9.116) and performing integration yields the compensated heat change

$$\frac{dQ_c}{dt} = \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \int_{B^{(s)}} d\mathbf{B}^{(s)} \cdot \mathbf{J}_a^{(s)} \hat{\mu}_{ea}^{(s)}, \quad (9.120)$$

where $\mathbf{B}^{(s)}$ is the surface vector of phase s in the sign convention adopted for surfaces in this work. For a single isolated system dQ_c/dt is counted as the compensated heat exchanged between the system and the surroundings per unit time, but for isolated galvanic cells consisting of many phases considered in this work the interphase exchange of matter must be counted in the energy dissipation within the system, which can result in a reduction of performance of the cell. If the mass of species a in phase s is denoted by $M_a^{(s)}$ the rate of mass change in phase s is given by the surface integral

$$\frac{d_e M_a^{(s)}}{dt} = - \int_{B^{(s)}} d\mathbf{B}^{(s)} \cdot \mathbf{J}_a^{(s)}. \quad (9.121)$$

If the electrochemical potential is uniform over the surface then the compensated heat change can be written as

$$\frac{dQ_c}{dt} = - \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \hat{\mu}_{ea}^{(s)} \frac{d_e M_a^{(s)}}{dt}, \quad (9.122)$$

which may be interpreted as a global Gibbs free energy change for phase s . If we assume that the phases are aligned along the x axis of the coordinate system and have translational symmetry along the y and z directions and that there is no flux in the y and z directions then Eq. (9.120) can be written in a more explicit form

$$\frac{dQ_c}{dt} = A \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \left[\hat{\mu}_{ea}^{(s)}(x_{s+1}) \mathbf{J}_a^{(s)}(x_{s+1}) - \hat{\mu}_{ea}^{(s)}(x_s) \mathbf{J}_a^{(s)}(x_s) \right], \quad (9.123)$$

where A is the cross section of the phase, x_{s+1} and x_s denote the coordinates of the right and left boundary of phase s and $\mathbf{J}_a^{(s)}(x_i)$ is the x component of the diffusion flux vector of species a at position x_i . Since Eqs. (9.122) and (9.123) are equivalent, Eq. (9.123) is an alternative way of expressing the rate of free energy change arising from material exchange between the phases.

For electrolytes mass diffusion fluxes may be related to the transport numbers. To achieve the desired relation we first express the electrical current I_a of ionic species a relative to the solvent velocity u_1

$$I_a = z_a c_a (u_a - u_1), \quad (9.124)$$

where the velocities u_a and u_1 stand for the x components of the ionic and solvent velocities. These velocities should be replaced by the appropriate vectors if the flow is multi-dimensional. The total current I is then given by

$$I = \sum_{a=1}^{r+1} z_a c_a (u_a - u_1). \quad (9.125)$$

The transport number t_a of ionic species a is then defined by the fraction of the electrical current carried by the ionic species a :

$$t_a = \frac{I_a}{I}. \quad (9.126)$$

The diffusion flux in this work is defined by the mass flux relative to the barycentric (mean) velocity \mathbf{u}

$$\mathbf{J}_a = \rho_a (\mathbf{u}_a - \mathbf{u}), \quad (9.127)$$

but a theory of diffusion may be equally well formulated by means of diffusion fluxes defined relative to the solvent velocity, although the definition (9.127) holds formalistic advantage when species are put on the equal footing in the description of flow. However, since measurement of transport numbers is conventionally made in the frame of reference relative to the solvent, which is assumed to be stationary, it is useful to modify the definition of diffusion fluxes accordingly. Thus we define

$$\mathbf{J}_a = \rho_a (\mathbf{u}_a - \mathbf{u}_1). \quad (9.128)$$

Then the electrical current I_a is related to \mathbf{J}_a , denoting the x component of mass flux, through the expression

$$I_a = z_a \mathbf{J}_a / \rho. \quad (9.129)$$

Therefore the diffusion flux \mathbf{J}_a of ionic species may be expressed in terms of the transport number t_a :

$$\mathbf{J}_a = \frac{t_a}{z_a} I \rho. \quad (9.130)$$

Substitution of this representation for \mathbf{J}_a into Eq. (9.123) yields the compensated heat change in the form

$$\frac{dQ_c}{dt} = \rho I A \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \left[\hat{\mu}_{ea}^{(s)}(x_{s+1}) \frac{t_a}{z_a}(x_{s+1}) - \hat{\mu}_{ea}^{(s)}(x_s) \frac{t_a}{z_a}(x_s) \right]. \quad (9.131)$$

This describes the total Gibbs free energy change arising from the passage of electric current I through the phase boundaries in the cell. This free energy change contributes to the calorimetry production in the galvanic cell

made up of subsystems (phases). This contribution is a measure of energy dissipation in the system that accompanies the passage of current I . It is usually ignored in the equilibrium thermodynamic theory of galvanic cells, but we clearly see that it makes a contribution to the global calortropy production.

Uncompensated Heat

The rate of uncompensated heat change, namely, the global calortropy production arising from the irreversible processes within the phases, is the volume integral of $\Xi_c^{(s)}$ summed over all phases. On use of Eq. (9.118) it is given by the expression

$$\Xi_c = - \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \int_{V^{(s)}} d\mathbf{r} \mathbf{J}_a^{(s)} \cdot \nabla \hat{\mu}_{ea}^{(s)} - \sum_{l=1}^m A_l^{(s)} R_l^{(s)} V^{(s)}. \quad (9.132)$$

The first term, representing the energy dissipation arising from irreversible diffusion process within the phases, may be written in terms of the transport numbers. Since the chemical potentials are assumed to be uniform within the phases except for the liquid junction phase it can be written as

$$\begin{aligned} \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \int_{V^{(s)}} d\mathbf{r} \mathbf{J}_a^{(s)} \cdot \nabla \hat{\mu}_{ea}^{(s)} &= \rho I \sum_{a=1}^{r+1} \int_{V^{(s)}} d\mathbf{r} \frac{t_a}{z_a} \cdot \nabla \hat{\mu}_{ea}^{(2)} \\ &= I \rho A \sum_{a=1}^{r+1} \int_{x_2}^{x_3} dx \frac{t_a}{z_a} \frac{\partial \hat{\mu}_{ea}^{(2)}}{\partial x} \\ &= I \rho A \sum_{a=1}^{r+1} \int_{x_2}^{x_3} dx \frac{t_a}{z_a} \frac{\partial \hat{\mu}_a^{(2)}}{\partial x} \end{aligned} \quad (9.133)$$

where we have used for the last equality the electro-neutrality condition

$$\sum_{a=1}^{r+1} c_a z_a = 0. \quad (9.134)$$

If the liquid junction phase consists of M_1^+ , M_2^+ , and Cl^- , the sum over a in Eq. (9.133) runs over the aforementioned three species. Thus the dissipative

contribution to the calortropy production is given by

$$\begin{aligned} (\Xi_c)_{\text{diss}} &= -I\rho A \sum_{a=1}^{r+1} \int_{x_2}^{x_3} dx \frac{t_a}{z_a} \frac{\partial \hat{\mu}_a^{(2)}}{\partial x} \\ &= -I\rho A \sum_{a=1}^{r+1} \int_{\hat{\mu}_a^{(2)}(x_2)}^{\hat{\mu}_a^{(2)}(x_3)} d\hat{\mu}_a^{(2)} \frac{t_a}{z_a}, \end{aligned} \quad (9.135)$$

where the integral in the second line is a line integral along the path of length L along the x direction.

To calculate explicitly the reactive contribution to the calortropy production within the phases of the cell, observe that there are only two phases where chemical reactions occur, namely, phases 1 and 4. The reactions in the aforementioned phases are given in Eqs. (9.108) and (9.109) and the corresponding affinities are

$$\mathcal{A}_L = \hat{\mu}_{eM_1^+}(1) + \hat{\mu}_{ee^-}(1) - \hat{\mu}_{eM_1}(1), \quad (9.136)$$

$$\mathcal{A}_R = \hat{\mu}_{eM_2}(4) - \hat{\mu}_{eM_2^+}(4) - \hat{\mu}_{ee^-}(4), \quad (9.137)$$

where the subscripts L and R denote the reaction in the left and the right electrode, respectively. Since upon the passage of current I a mole of charges (electrons) is created or consumed per unit time, it is clear that the left- and right-electrode reaction rate R_L and R_R are given by

$$R_L = I\rho L^{-1}, \quad R_R = I\rho L^{-1}. \quad (9.138)$$

Upon use of these results, we find the reactive contribution to the calortropy production

$$\begin{aligned} (\Xi_c)_{\text{reactive}} &= -I\rho AT^{-1} \left\{ \hat{\mu}_{eM_1^+}(1) + \hat{\mu}_{ee^-}(1) - \hat{\mu}_{eM_1}(1) \right. \\ &\quad \left. + \hat{\mu}_{eM_2}(4) - \hat{\mu}_{eM_2^+}(4) - \hat{\mu}_{ee^-}(5) \right\}, \end{aligned} \quad (9.139)$$

for which we have used the condition

$$\hat{\mu}_{ee^-}(4) = \hat{\mu}_{ee^-}(5) \quad (9.140)$$

for the last phase consisting of the same metal as for phase 1. Since $\hat{\mu}_{eM_1}(1) = \hat{\mu}_{M_1}(1)$, $\hat{\mu}_{eM_2}(4) = \hat{\mu}_{M_2}(4)$, and

$$\hat{\mu}_{ee^-}(5) - \hat{\mu}_{ee^-}(1) = \hat{\mu}_{e^-}(5) - \hat{\mu}_{e^-}(1) - \mathcal{F}(\phi^{(5)} - \phi^{(1)})$$

$$= -\mathcal{F}(\phi^{(5)} - \phi^{(1)}), \quad (9.141)$$

with the definition

$$\varepsilon = \phi^{(5)} - \phi^{(1)}, \quad (9.142)$$

the reactive contribution to the calortropy production finally is given by the formula

$$(\Xi_c)_{\text{reactive}} = -I\rho A (\mathcal{A}_{gc} + \mathcal{F}\varepsilon), \quad (9.143)$$

where \mathcal{A}_{gc} is the affinity of the galvanic cell defined by

$$\mathcal{A}_{gc} = \widehat{\mu}_{eM_1^+}(1) + \widehat{\mu}_{M_2}(4) - \widehat{\mu}_{M_1}(1) - \widehat{\mu}_{eM_2^+}(4). \quad (9.144)$$

Collecting the results for the dissipative and reactive contributions to the calortropy production together with the result for dQ_c/dt , we obtain the overall rate of calortropy change in the cell:

$$\begin{aligned} \frac{d\Psi}{dt} &= I\rho AT^{-1} \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \left[\widehat{\mu}_{ea}^{(s)}(x_{s+1}) \frac{t_a}{z_a}(x_{s+1}) - \widehat{\mu}_{ea}^{(s)}(x_s) \frac{t_a}{z_a}(x_s) \right] \\ &\quad - I\rho AT^{-1} \sum_{a=M_1^+, M_2^+, Cl^-} \int_{x_2}^{x_3} dx \frac{t_a}{z_a} \frac{\partial \widehat{\mu}_a^{(2)}}{\partial x} \\ &\quad - I\rho AT^{-1} (\mathcal{A}_{gc} + \mathcal{F}\varepsilon) \\ &\geq 0. \end{aligned} \quad (9.145)$$

We define the dissipative contribution to the calortropy production as the liquid junction potential

$$\mathcal{F}\varepsilon_L = - \sum_{a=M_1^+, M_2^+, Cl^-} \int_{x_2}^{x_3} dx \frac{t_a}{z_a} \frac{\partial \widehat{\mu}_a^{(2)}}{\partial x}. \quad (9.146)$$

Since I is arbitrary, for $d\Psi/dt$ to be maximum, there must hold the condition

$$\begin{aligned} -\mathcal{F}(\varepsilon - \varepsilon_L) &= - \sum_{s=1}^{\nu} \sum_{a=1}^{r+1} \left[\widehat{\mu}_{ea}^{(s)}(x_{s+1}) \frac{t_a}{z_a}(x_{s+1}) - \widehat{\mu}_{ea}^{(s)}(x_s) \frac{t_a}{z_a}(x_s) \right] \\ &\quad + \left[\widehat{\mu}_{eM_1^+}(1) + \widehat{\mu}_{M_2}(4) - \widehat{\mu}_{M_1}(1) - \widehat{\mu}_{eM_2^+}(4) \right]. \end{aligned} \quad (9.147)$$

If equilibrium is established between $M_1^+(1)$ and $M_1^+(2)$ across the boundary I and similarly for $M_2^+(3)$ and $M_2^+(4)$ across the boundary III then the chemical potentials $\widehat{\mu}_{eM_1^+}(1)$ and $\widehat{\mu}_{eM_2^+}(4)$ may be replaced, respectively, by the chemical potentials $\widehat{\mu}_{eM_1^+}(2)$ and $\widehat{\mu}_{eM_2^+}(3)$ in Eq. (9.147). If the first term on the right hand side, the contribution to the energy dissipation

from the interfacial transfer of ionic species, is neglected or is equal to zero because of material equilibrium established, then the electromotive force is given by the usual formula for galvanic cells with liquid junctions

$$-\mathcal{F}(\varepsilon - \varepsilon_L) = \left[\hat{\mu}_{eM_1^+}(2) + \hat{\mu}_{M_2}(4) - \hat{\mu}_{M_1}(1) - \hat{\mu}_{eM_2^+}(3) \right], \quad (9.148)$$

where we have made the aforementioned replacement of the chemical potentials for the ionic species. It is also appropriate to add the chemical potentials of the chlorine ions in phase 2 and 3 so that the electro-neutrality is preserved in each phase mentioned. In this event, the electrochemical potential can be replaced by its material part. The Nernst equation in the presence of a liquid junction potential arises on substitution of the expressions for the chemical potentials. It should be noted that the global calortropy formula (9.145) would have contained a contribution arising from diffusion of ionic species in phases 2 and 3, if the assumption of homogenous concentrations were removed. This assumption is strictly not true since the ionic species should have a steady concentration gradient in each phase as an electrochemical process is in progress. This contribution can be calculated in a manner similar to the calculation of the liquid junction potential.

The liquid junction potential can be calculated if Eqs. (9.110) and (9.111) are solved to calculate the concentration distribution functions and therewith the transport numbers given in terms of concentrations and mobilities, as was done by M. Planck [38]. The point we would like to make here is that irreversible thermodynamics of galvanic cells can be investigated by using the generalized hydrodynamics formalism. Further study of this subject is left to future work.

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10

Irreversible Thermodynamics of Steady States

Experiments are often performed in steady state conditions where non-conserved variables (*e.g.*, fluxes) remain stationary in time, relative to the conserved variables, in the moving coordinate system. Such examples can be seen in many transport processes [1] in fluids and solids including many rheological experiments [2]. They usually require steady state constitutive equations, which are generally non-linear with respect to the non-conserved variables and the thermodynamic forces, in contrast to the linear theory of irreversible processes, where linear thermodynamic force–flux relations are assumed as the constitutive equations of non-conserved variables. Just as the linear thermodynamic force–flux relations are steady state versions of linearized constitutive equations as has been already noted in the previous chapter, the aforementioned steady state constitutive equations for the non-conserved variables may be regarded as non-linear thermodynamic force–flux relations. Thermodynamic theory of irreversible processes employing such non-linear constitutive equations will be called non-linear irreversible thermodynamics. Since many irreversible phenomena are often non-linear and the linear theory of irreversible processes is incapable of describing such phenomena, they come under the purview of non-linear irreversible thermodynamics, and it is useful to consider non-linear phenomena and relate them to the present non-linear theory—generalized hydrodynamics.

In this chapter we consider steady state non-linear irreversible phenomena as generalizations of the linear irreversible phenomena considered in the previous chapter. Therefore, we will examine cases where the non-conserved variables are non-linear and do not change in time in the frame of reference moving at the fluid velocity \mathbf{u} . That is, we consider the cases of

$d_t \hat{\Phi}_{ka} = 0$. Henceforth in this chapter we use the term steady state to mean the steady state of non-conserved variables satisfying the aforementioned condition. The kinematic and dissipation terms in the evolution equations for $\hat{\Phi}_{ka}$, however, can be non-linear in contrast to those of linear evolution equations for Φ_{ka} already considered in the previous chapter.

If $d_t \hat{\Phi}_{ka} = 0$ for all k and a then the extended Gibbs relation for the steady state calortropy becomes

$$d_t \hat{\Psi}_{ss} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a \right), \quad (10.1)$$

where the subscript ss denotes the steady state of the non-conserved variables. Since the right hand side of Eq. (10.1) is simply the same in the mathematical form as the local equilibrium entropy change, the calortropy at the steady state appears to coincide with the local equilibrium entropy \mathcal{S}_e given by the same differential form as in Eq. (10.1). However, the meanings of the coefficients to the differentials are different since they now depend on the non-conserved variables $\hat{\Phi}_{ka}$. Therefore the thermodynamic space is still extended beyond that of the thermodynamic space of local equilibrium thermodynamics for which it is sufficient to consider the conserved variables $(\mathcal{E}, v, c_a : 1 \leq a \leq r)$ only. In this case, the local equilibrium hypothesis for the Clausius entropy

$$d_t \mathcal{S}_e = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a \right) \quad (10.2)$$

appears superficially to be an acceptable differential form for a thermodynamic description of the process in hand, provided that the steady state evolution equations are given by the equations¹

$$-\nabla \cdot \psi_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka} = 0 \quad (10.3)$$

for all k and a . See the examples for the kinematic and dissipation terms given in Table 6.1 in the case of dilute gases. The steady state evolution

¹In actual applications of the present theory the non-conserved variables require closure relations. For example, in the case of single component fluids it will be found useful to take the density, velocity, internal energy, stress tensor, and heat, flux as macroscopic variables and then assume the closure relations for higher order moments $\psi_{1a} = \psi_{3a} = 0$; see the previous chapter for this notation. It is appropriate to set the latter non-conserved variables equal to zero since once a set of variables with which to describe a process is chosen, all the variables not in the set must be neglected instead of expressing those outside the set in terms of the variables in the chosen set. Applications discussed in this chapter tacitly take this kind of closure relations when the non-conserved variables other than those chosen are simply neglected. For an application of the closure $\psi_{1a} = \psi_{3a} = 0$ to calculation of a non-equilibrium partition function, see Al-Ghoul, M. and Eu, B.C. (2001) J. Chem. Phys., **115**, 8481.

equations (10.3), in fact, give non-linear thermodynamic force–flux relations, namely, the constitutive equations for fluxes whose solutions yield non-linear transport coefficients.

It must, however, be pointed out that in the local equilibrium hypothesis taken for the entropy in the theory of linear irreversible thermodynamics, the constitutive variables such as p and $\hat{\mu}_a$ do not depend on the non-conserved variables. Therefore the similarity of two differential forms for $d_t \hat{\Psi}_{ss}$ and $d_t S_e$ is superficial, and conceptually misleading results can arise unless sufficient care is exercised in applying Eq. (10.2). For this reason we would like to refrain from using the local equilibrium hypothesis (10.2) in the development of the theory of steady state processes for fear it can cause confusion with regards to the subtle distinction between the equilibrium (Clausius) entropy and the calortropy applicable to irreversible processes. Perhaps the nature of Eq. (10.2) can be put in a better light if it is compared with (4.75), which was seen to hold for a cyclic process where the initial and final states A and B are embedded in the equilibrium part of the thermodynamic space. The embedded equilibrium states may be interpreted to be steady states which are characterized by Eqs. (10.2) and (10.3).

The solutions of Eq. (10.3) give Φ_{ka} , for example, the stress tensor, heat flux, and diffusion fluxes, and so on as functions of thermodynamic forces, temperature, density, and so forth. They may be written as functional relations

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = F_p(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (10.4)$$

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = F_q(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (10.5)$$

$$\mathbf{J}_a = F_a(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots) \quad (1 \leq a \leq r), \quad (10.6)$$

and in general

$$\Phi_{ka} = F_{ka}(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots). \quad (10.7)$$

The functions F_{ka} and F_a are generally non-linear tensor or vector functions of thermodynamic forces, $\nabla \mathbf{u}$, $\nabla \ln T$, and $(\nabla \hat{\mu}_a - \mathbf{F}_a)$, because the constitutive equations (10.3) are generally non-linear with respect to the non-conserved variables or the thermodynamic forces. On substitution, for example, of Eqs. (10.4)–(10.6) into Eqs. (8.1)–(8.4), we obtain hydrodynamics equations which generalize the classical hydrodynamic equations [3], such as the Navier–Stokes, Fourier, and Fick equations. It must be noted that in the present theory the steady state constitutive equations (10.3) are still subjected to the second law of thermodynamics since they must satisfy the inequality $\Xi_c \geq 0$ demanded by the second law.

The deduction made here from the general theory therefore shows that the theory of steady state non-linear irreversible phenomena can be put within the framework of the present extended theory in a form fully consistent with the second law of thermodynamics. If the theory of steady state irreversible phenomena for non-linear processes were formulated on the basis of the local equilibrium hypothesis, as usually is the case in the literature [4, 5, 6, 7], then the form for the entropy production would not be obvious and the second law of thermodynamics would not play a role in determining the non-linear forms for the constitutive equations for fluxes, as it does in the present theory. Some examples of steady state irreversible phenomena will be discussed later in this chapter.

Finally, we point out that the steady state description will be appropriate for non-conserved variables if they change on faster time scales than the conserved variables so that on the time scale of interest for the conserved variables the non-conserved variables have already decayed to their steady state values. There are many such situations realizable in laboratory experiments, and the steady state theory with non-linear constitutive equations can be sufficient for such situations. In fact, the steady state constitutive equations coincide with those in the adiabatic approximation, as will be seen presently.

10.1 Model Generalized Hydrodynamic Equations

To be specific in the discussion we use a model for the constitutive equations gleaned from the results of kinetic theory studies, especially, of gases. Although they are primarily for gases, they may be used for liquids if the transport coefficient therein are taken to be those for liquids. We have already presented this model in Table 6.1, but it is useful to list the generalized hydrodynamic equations for the sake of clarity of discussion. For a single component fluid free from external forces they are:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (10.8)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p - \nabla \cdot (\boldsymbol{\Pi} + \Delta\boldsymbol{\delta}), \quad (10.9)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - p \nabla \cdot \mathbf{u} - (\boldsymbol{\Pi} + \Delta\boldsymbol{\delta}) : \nabla \mathbf{u}, \quad (10.10)$$

$$\begin{aligned} \rho \frac{d\hat{\Pi}}{dt} = & -2p[\nabla \mathbf{u}]^{(2)} - 2\left[\Pi \cdot [\nabla \mathbf{u}]^{(2)}\right]^{(2)} - [\omega, \Pi] \\ & - \frac{2}{3}\Pi \nabla \cdot \mathbf{u} - \frac{p}{\eta_0}\Pi q(\kappa), \end{aligned} \quad (10.11)$$

$$\begin{aligned} \rho \frac{d\mathbf{Q}}{dt} = & -p\hat{C}_p T \nabla \ln T - \Pi \nabla \hat{h} + \nabla \cdot (p\delta + \Pi) \cdot \hat{\Pi} \\ & - \mathbf{Q} \cdot \left([\nabla \mathbf{u}]^{(2)} - \omega + \frac{1}{3}\delta \nabla \cdot \mathbf{u}\right) - \frac{p\hat{C}_p T}{\lambda_0} \mathbf{Q} q(\kappa), \end{aligned} \quad (10.12)$$

$$\rho \frac{d\Delta}{dt} = -p \frac{d}{dt} \ln(pv^{5/3}) - \frac{2}{3}\Pi : \nabla \mathbf{u} - \frac{2}{3}\Delta \nabla \cdot \mathbf{u} - \frac{2p}{3\eta_b} \Delta q(\kappa). \quad (10.13)$$

In these equations ω is the vorticity tensor defined by

$$\omega = \frac{1}{2} \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^t \right], \quad (10.14)$$

which forms an antisymmetric tensor with Π

$$[\omega, \Pi] = \omega \cdot \Pi - \Pi \cdot \omega \quad (10.15)$$

and $q(\kappa)$ is the non-linear factor defined before: $q(\kappa) = \sinh \kappa / \kappa$ with κ given by the Rayleigh dissipation function

$$\kappa = \frac{(mk_B T)^{1/4}}{\sqrt{2}p\sigma} \left(\Pi : \Pi + \frac{\eta_0}{\eta_b} \Delta^2 + \frac{\eta_0}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right)^{1/2} \quad (10.16)$$

Here m and σ are the mass and the diameter of the molecule, respectively, and η_0 , η_b , and λ_0 are the shear viscosity, bulk viscosity, and thermal conductivity of the fluid, respectively. We note that in writing the constitutive equations for Π , Δ , and \mathbf{Q} in Eqs. (10.11)–(10.13) we have used the convention taken for the Jaumann derivatives [10, 11, 12]. We will use these continuum equations as a model for generalized hydrodynamic equations describing various flow processes in single-component systems far removed from equilibrium. These equations are easily generalized to a mixture by appending the evolution equations for diffusion fluxes and replacing the stress and heat flux evolution equations with their component forms. They can be also applicable to liquids if some intermolecular force dependent terms are added to the kinematic terms \mathcal{Z}_{ka} . However, in many non-equilibrium phenomena in liquids Eqs. (10.8)–(10.13) may apply without such an addition of terms, provided that appropriate transport coefficients of the liquids are used for the viscosity, thermal conductivity, and bulk viscosity in the constitutive equations for the non-conserved variables.

The constitutive equations presented for Π , Δ , and \mathbf{Q} do not contain the divergence of higher order non-conserved variables $\psi^{(s)}$, $\psi^{(b)}$, and

$\psi^{(q)}$, which correspond to the flux of Π , Δ , and \mathbf{Q} , respectively. They are neglected on the basis of the closure of the non-conserved variables to the set $(\rho, v, \mathcal{E}, \Pi, \Delta, \mathbf{Q})$ in the description of irreversible processes. If the set is extended so as to include the neglected variables then the terms $-\nabla \cdot \psi^{(s)}$, $-\nabla \cdot \psi^{(b)}$, and $-\nabla \cdot \psi^{(q)}$ should appear on the right hand side of the constitutive equations for Π , Δ , and \mathbf{Q} , respectively, and the evolution equations for $\psi^{(s)}$ and so forth should be added to the set of evolution equations presented earlier. At the level of irreversible thermodynamics, the neglect of $\psi^{(s)}$, $\psi^{(b)}$, and $\psi^{(q)}$ also results in the absence of the $\psi^{(k)} \cdot \nabla X_k$ ($k = s, b, q$), where X_k are the generalized potentials conjugate to Π , Δ , and \mathbf{Q} , respectively, in the expression for the calortropy production Ξ_c , and the corresponding terms $\psi^{(k)} X_k$ ($k = s, b, q$) in the calortropy flux; see Eqs. (7.11) and (7.12). Consequently generalized hydrodynamic equations (10.11)–(10.13) represent an approximate description of irreversible processes in that sense.

In the case of dilute monatomic gases the excess normal stress vanishes: $\Delta = 0$. Therefore the evolution equation for Δ , Eq. (10.13), does not appear in the set of generalized hydrodynamic equations. If the flow problem of interest is non-steady and the relaxation times of non-conserved variables are comparable to the hydrodynamic relaxation time, then it will require the set of equations (10.11)–(10.13) for an appropriate description of the flow. We have examined such situations in the cases of ultrasonic wave absorption and dispersion and viscoelasticity in the previous chapter, albeit with linearized constitutive equations.

10.2 Reduced Evolution Equations

To show that steady state theory of irreversible processes arises from the generalized hydrodynamics in the adiabatic approximation it is convenient to use reduced evolution equations which enable us to see the time scales of change for conserved and non-conserved variables appearing in the generalized hydrodynamic equations.

10.2.1 Reduced Variables

There are time and length scales characteristic of the macroscopic variables, conserved and non-conserved variables, spanning the thermodynamic space. A fluid dynamic system generally has characteristic lengths and time scales of change for the velocity, temperature, and density. The material functions are usually the characteristic parameters involved in determining such scales. When properly scaled by the characteristic parameters, the hydrodynamic evolution equations generally become universal for the class of flow problems, and generalized hydrodynamic equations are no excep-

tion in that regard. To achieve this aim we reduce various hydrodynamic variables with respect to their reference values, which are denoted with the subscript r . The choice of the reference values depends on the phenomenon of interest. The following reduction scheme is used for the discussion in this chapter:

$$\begin{aligned}\xi &= \mathbf{r}L^{-1}, & \mathbf{u}^* &= \mathbf{u}u_r^{-1}, \\ \tau &= tt_r^{-1}, & p^* &= pp_r^{-1}, \\ \rho^* &= \rho\rho_r^{-1}, & T^* &= TT_r^{-1}, & \Pi^* &= \Pi L(\eta_r u_r)^{-1}, \\ \eta^* &= \eta_0\eta_r^{-1}, & \eta_b^* &= \eta_b\eta_{br}^{-1}, & \mathbf{Q}^* &= \mathbf{Q}LT_r(\lambda_r \Delta_T)^{-1}, \\ \lambda^* &= \lambda_0\lambda_r^{-1}, & \mathcal{E}^* &= \mathcal{E}\mathcal{E}_r^{-1}, & \Delta^* &= \Delta LT_r(\eta_{br} u_r)^{-1},\end{aligned}$$

Here L is the reference length, t_r is the reference time scale, $\Delta_T = T_2 - T_1$ with T_1 and T_2 denoting temperatures at two reference points in space, T_r may be taken as $T_r = \frac{1}{2}(T_1 + T_2)$, u_r is the reference speed, and so on. The following dimensionless fluid dynamic numbers (N_M , N_{Re} , N_{Kn} , N_{Pr} , N_E , N_{De} , N_A , N_δ) will occur frequently in the subsequent discussions:

Mach	$N_M = u_r / \sqrt{\gamma_0 \mathcal{R} T_r}$
Reynolds	$N_{Re} = \rho_r u_r L / \eta_r$
Knudsen	$N_{Kn} = l / L$
Prandtl	$N_{Pr} = \hat{C}_{pr} T_r \eta_r / \lambda_r$
Eckert	$N_E = u_r^2 / \hat{C}_{pr} \Delta_T$
Deborah	$N_{De} = (\eta_r / \Pi_r) / (L / u_r) = \tau_s / \tau_h$
Adiabaticity	$N_A = (h_r u_r / L^3) / Q_r = \tau_q / \tau_h$
Non-Uniformity	$N_\delta = \eta_r u_r / p_r L$

The non-uniformity number N_δ is an important fluid dynamic number for the generalized hydrodynamic discussed in this work, which is a composite fluid dynamic number, consisting of other fluid dynamic numbers, for example, as in

$$N_\delta = \gamma_0 N_M^2 N_{Re}^{-1}. \quad (10.17)$$

In the preceding definitions of fluid dynamic numbers \mathcal{R} is the gas constant per mass, \hat{C}_{pr} is the reference specific heat per mass at constant pressure, γ_0 is the polytropic ratio, and τ_s , τ_q , and τ_h are the characteristic time for stress, heat flux, and hydrodynamic relaxation, respectively. The adiabaticity number N_A characterizes the adiabatic approximation to be elaborated on later; it was previously called the Q number N_Q for want

of a suitable terminology for it [8, 9]. This number gives a measure of relaxation time of the heat flux relative to the relaxation times of the conserved variables, that is, the hydrodynamic relaxation time. Together with the Deborah number, which provides the same measure of time scale for the stress as the Weissenberg number in rheology, the adiabaticity number N_A gives a measure of deviation from the adiabatic approximation explained later. The non-uniformity number N_δ , formerly called the composite fluid dynamic number [8, 9], gives a measure of displacement from local equilibrium that gives rise to linear irreversible processes. For this reason it is a useful parameter for examining the relation of generalized hydrodynamics to the classical hydrodynamics. It is useful to note that the Reynolds number may be expressed in terms of the Mach and Knudsen numbers:

$$N_{Re} = \sqrt{\frac{\pi\gamma_0}{2}} \frac{N_M}{N_{Kn}}. \quad (10.18)$$

This kind of relation can be useful for transforming reduced equations from one context of flow to another. For example, on use of Relation (10.18) N_δ may be expressed in different forms as in the relations below

$$N_\delta = \frac{2}{\gamma_0} N_{Kn}^2 N_{Re} = \sqrt{\frac{2\pi}{\gamma_0}} N_M N_{Kn}. \quad (10.19)$$

Since N_δ appears in the dissipation terms in the evolution equations for the non-conserved variables and, as a matter of fact, in the Boltzmann collision term in the kinetic theory treatment of generalized hydrodynamics, the relations between N_δ and $N_M N_{Kn}$ or $N_{Kn}^2 N_{Re}$ in Eq. (10.19) is very useful for estimating the importance of various terms in the generalized hydrodynamic equations for various flow configurations. For example, some of the terms in the generalized hydrodynamic equations become increasingly meaningful as N_{Re} increases even if the value of N_{Kn} is small, although the conventional thought on this question is contrary to what the mathematical formula for the non-linear factor $q(\kappa)$ and other non-linear terms in the generalized hydrodynamic evolution equations suggest. We will return to this point later again.

10.2.2 Reduced Hydrodynamic Equations

When the generalized hydrodynamic equations are reduced by means of the reduction scheme presented in the previous subsection, dimensionless generalized hydrodynamic equations expressed in terms of reduced (asterisked) variables are obtained in which the aforementioned fluid dynamic numbers also appear as parameters. In order to make the notation as simple as possible we will omit the asterisk from the reduced variables but keep the fluid dynamic numbers. Therefore whenever such fluid dynamic

numbers appear in the generalized hydrodynamic equations it should be understood that they are reduced (dimensionless) equations.

To be more explicit with regards to the kinematic and dissipation terms in the evolution equations for the non-conserved variables we will use the models presented for them in Table 6.1. Another reason to use such specific forms for them is that such models will be applied to some gas dynamic problems later in this chapter. Therefore the present subsection can serve as an introduction to such applications. The reduced generalized hydrodynamic equations presented here are for the case of a single component fluid free from an external field, that is, $\mathbf{F} = 0$. This assumption is made for the relative brevity of the equations, but it is easy and straightforward to remove the assumption and obtain more complete generalized hydrodynamic equations.

The reduced generalized hydrodynamic equations for a single-component fluid according to the aforementioned model are:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (10.20)$$

$$\gamma_0 N_M^2 \rho \frac{d\mathbf{u}}{dt} = -\nabla p - N_\delta \nabla \cdot (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}), \quad (10.21)$$

$$\frac{\gamma_0 N_M^2}{N_E} \rho \frac{d\mathcal{E}}{dt} = -\frac{N_\delta}{N_{Pr} N_E} \nabla \cdot \mathbf{Q} - p \nabla \cdot \mathbf{u} - N_\delta (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) : \nabla \mathbf{u}, \quad (10.22)$$

$$\begin{aligned} N_\delta \rho \frac{d\hat{\boldsymbol{\Pi}}}{dt} &= -2p [\nabla \mathbf{u}]^{(2)} - 2N_\delta [\boldsymbol{\Pi} \cdot [\nabla \mathbf{u}]^{(2)}]^{(2)} - N_\delta [\boldsymbol{\omega}, \boldsymbol{\Pi}] \\ &\quad - \frac{2}{3} N_\delta \boldsymbol{\Pi} \nabla \cdot \mathbf{u} - \frac{p}{\eta_0} \boldsymbol{\Pi} q(N_\delta \kappa^*), \end{aligned} \quad (10.23)$$

$$\begin{aligned} \frac{N_\delta}{N_{Pr}} \rho \frac{d\mathbf{Q}}{dt} &= -p \hat{C}_p T \nabla \ln T + \frac{N_\delta N_E}{\gamma_0 N_M^2} \nabla \cdot (p \boldsymbol{\delta} + N_\delta \boldsymbol{\Pi}) \cdot \hat{\boldsymbol{\Pi}} \\ &\quad - \frac{N_\delta}{N_{Pr}} \mathbf{Q} \cdot \left([\nabla \mathbf{u}]^{(2)} - \boldsymbol{\omega} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u} \right) \\ &\quad - N_\delta \boldsymbol{\Pi} \nabla \hat{h} - \frac{p \hat{C}_p T}{\lambda_0} \mathbf{Q} q(N_\delta \kappa^*), \end{aligned} \quad (10.24)$$

$$\begin{aligned} N_\delta \rho \frac{d\hat{\Delta}}{dt} &= -p \frac{d}{dt} \ln(p v^{5/3}) - \frac{2}{3} N_\delta \boldsymbol{\Pi} : \nabla \mathbf{u} - \frac{2}{3} N_\delta \Delta \nabla \cdot \mathbf{u} \\ &\quad - \frac{2p}{3\eta_b} \Delta q(N_\delta \kappa^*). \end{aligned} \quad (10.25)$$

In these equations κ^* is the non-dimensionalized κ defined earlier:

$$\kappa^* = \frac{\kappa}{N_\delta} = \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma_0} \frac{T^{1/4}}{p\sqrt{\eta_0}}} \left(\boldsymbol{\Pi} : \boldsymbol{\Pi} + \frac{\eta_0}{\eta_b} \Delta^2 + 2\epsilon \frac{\eta_0}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right)^{1/2} \quad (10.26)$$

with ϵ denoting

$$\epsilon = \frac{\Delta_T}{T_r N_{Pr} N_E}. \quad (10.27)$$

It should be noted that the variables and parameters in κ^* in Eq. (10.26) are all reduced quantities. Perhaps it is worth noting that the reduction scheme for the Rayleigh dissipation function κ^2 must be adapted to the flow problem in hand, as will be found later, because some of fluid dynamic numbers may not be relevant to the problem of interest.

10.2.3 Navier–Stokes–Fourier Theory

At various occasions in the previous chapters allusions have been made to the situation that not only the present generalized hydrodynamics is inclusive of the classical hydrodynamics of Navier, Stokes, and Fourier but also the attendant theory of irreversible processes is a generalization of the theory of linear irreversible processes. This point can be seen in a mathematically precise manner if we make use of the non-uniformity number N_δ appearing in the evolution equations (10.23)-(10.25).

The reduced evolution equations for the non-conserved variables $\boldsymbol{\Pi}$, Δ , and \mathbf{Q} suggest that the non-conserved variables are functions of the non-uniformity parameters among other parameters, because the magnitude of N_δ is a measure of the proximity to equilibrium of the system. Therefore in the neighborhood of N_δ much less than unity it is possible to expand the non-conserved variables in power series of N_δ :

$$\boldsymbol{\Pi} = \boldsymbol{\Pi}^{(0)} + \boldsymbol{\Pi}^{(1)} N_\delta + \boldsymbol{\Pi}^{(2)} N_\delta^2 + \dots, \quad (10.28)$$

$$\Delta = \Delta^{(0)} + \Delta^{(1)} N_\delta + \Delta^{(2)} N_\delta^2 + \dots, \quad (10.29)$$

$$\mathbf{Q} = \mathbf{Q}^{(0)} + \mathbf{Q}^{(1)} N_\delta + \mathbf{Q}^{(2)} N_\delta^2 + \dots. \quad (10.30)$$

The non-linear factor $q(N_\delta \kappa^*)$ then can be also expanded in the power series of N_δ

$$q(N_\delta \kappa^*) = \frac{\sinh(N_\delta \kappa^*)}{N_\delta \kappa^*} = 1 + \frac{1}{6} \kappa^{*2} N_\delta^2 + \dots, \quad (10.31)$$

where

$$\kappa_0^* = \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma_0} \frac{T^{1/4}}{p\sqrt{\eta_0}}} \left(\boldsymbol{\Pi}^{(0)} : \boldsymbol{\Pi}^{(0)} + \frac{\eta_0}{\eta_b} \Delta^{(0)2} + 2\epsilon \frac{\eta_0}{\lambda_0} \mathbf{Q}^{(0)} \cdot \mathbf{Q}^{(0)} \right)^{1/2} \quad (10.32)$$

Substitution of these expansions into (10.23)–(10.25) yields a hierarchy of constitutive equations at various orders of N_δ :

At the zeroth order of $N_\delta^0 = 1$

$$\boldsymbol{\Pi}^{(0)} = -2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (10.33)$$

$$\Delta^{(0)} = -\frac{3}{2}\eta_b \frac{d}{dt} \ln(p v^{5/3}) = -\eta_b \nabla \cdot \mathbf{u} - \frac{3}{2T} \eta_b \frac{dT}{dt}, \quad (10.34)$$

$$\mathbf{Q}^{(0)} = -\lambda_0 \nabla \ln T. \quad (10.35)$$

If the temperature is kept fixed over time then the zeroth order excess normal stress is given by the constitutive relation

$$\Delta^{(0)} = -\eta_b \nabla \cdot \mathbf{u}. \quad (10.36)$$

At the first order of N_δ

$$\begin{aligned} \boldsymbol{\Pi}^{(1)} &= -\frac{\eta_0}{p} \left(\rho \frac{d}{dt} \hat{\boldsymbol{\Pi}}^{(0)} + 2\boldsymbol{\Pi}^{(0)} \cdot [\nabla \mathbf{u}]^{(2)} - [\boldsymbol{\omega}, \boldsymbol{\Pi}^{(0)}] \right) \\ &\quad - \frac{2\eta_0}{3p} \boldsymbol{\Pi}^{(0)} \nabla \cdot \mathbf{u}, \end{aligned} \quad (10.37)$$

$$\Delta^{(1)} = -\frac{3\eta_b}{2p} \left(\rho \frac{d}{dt} \hat{\Delta}^{(0)} + \frac{2}{3} \boldsymbol{\Pi}^{(0)} : \nabla \mathbf{u} + \frac{2}{3} \Delta^{(0)} \nabla \cdot \mathbf{u} \right), \quad (10.38)$$

$$\begin{aligned} \mathbf{Q}^{(1)} &= -\frac{\lambda_0}{T \hat{C}_p p} \left(N_{\text{Pr}}^{-1} \rho \frac{d}{dt} \hat{\mathbf{Q}}^{(0)} - \frac{N_E}{\gamma_0 N_M^2} \boldsymbol{\Pi}^{(0)} \cdot \nabla p \right) \\ &\quad - \frac{\lambda_0}{T \hat{C}_p p N_{\text{Pr}}} \mathbf{Q}^{(0)} \cdot \left([\nabla \mathbf{u}]^{(2)} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u} \right) \\ &\quad - \frac{\lambda_0}{T \hat{C}_p p} \boldsymbol{\Pi}^{(0)} \cdot \nabla \hat{h} + \frac{\lambda_0}{T \hat{C}_p p N_{\text{Pr}}} \mathbf{Q}^{(0)} \cdot \boldsymbol{\omega}. \end{aligned} \quad (10.39)$$

In these equations $\hat{\boldsymbol{\Pi}}^{(i)} = \boldsymbol{\Pi}^{(i)} / \rho$ ($i = 0, 1, \dots$), and similarly for \mathbf{Q} and Δ . Substitution of Eqs. (10.33), (10.35), and (10.36) produces the reduced classical hydrodynamic equations, namely, the hydrodynamic equations of Navier, Stokes, and Fourier, which will be occasionally referred to as the

Navier–Stokes–Fourier equations [3]:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (10.40)$$

$$\gamma_0 N_M^2 \rho \frac{d\mathbf{u}}{dt} = -\nabla p + 2N_\delta \nabla \cdot \eta_0 [\nabla \mathbf{u}]^{(2)} + N_\delta \nabla (\eta_b \nabla \cdot \mathbf{u}), \quad (10.41)$$

$$\begin{aligned} \frac{\gamma_0 N_M^2}{N_E} \rho \frac{d\mathcal{E}}{dt} &= \frac{N_\delta}{N_{Pr} N_E} \nabla \cdot \lambda_0 \nabla \ln T + 2N_\delta \eta_0 [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} \\ &\quad - p \nabla \cdot \mathbf{u} + N_\delta \eta_b (\nabla \cdot \mathbf{u})^2. \end{aligned} \quad (10.42)$$

The derivation of the classical hydrodynamic equations presented here shows that the classical hydrodynamics is not only included in the generalized hydrodynamics, but also thermodynamically consistent to the lowest order in N_δ .

If the constitutive equations are used to the first order in N_δ then the Burnett order hydrodynamic equations [13, 14] arise. The Burnett order hydrodynamic equations, however, are generally inconsistent with the laws of thermodynamics [9]. Therefore they are not of interest to us in a thermodynamically consistent theory. Furthermore, since they involve higher-order spatial derivatives, which require additional boundary conditions not experimentally available, they are difficult to apply to practical flow problems without ambiguity. Nevertheless, it should be noted that there are some applications of the Burnett order equations made in the literature with additional approximations made of the higher-order derivatives in the equations.

10.2.4 Adiabatic Approximation

In many experiments and natural phenomena non-conserved variables and, in particular, the variables Π , Δ , and \mathbf{Q} change much faster than the conserved variables, perhaps, except when the non-conserved variables are forced to vary at a rate comparable to the former by an external force or agency. A typical example for this latter class of processes would be viscoelastic phenomena in which case the stress and strain vary on the same time and spatial scales as the fluid velocity. In such a class of phenomena the non-conserved variables reach a steady state on the same time scale of variation as for the conserved variables. Except for the latter cases of processes the non-conserved variables generally reach a steady state well before the conserved variables attain their steady states. In such a time scale it is sufficient to take the constitutive equations for the non-conserved variables in their steady state form. This is of course an approximation, and such an approximation is called the adiabatic approximation, because as the non-conserved variables reach their steady state, the conserved variables

remain invariant. We would like to examine how this approximation arises from the more exact set of evolution equations, namely, the full generalized hydrodynamic equations. With the closure of the variable set limiting the latter to those mentioned earlier, the evolution equations (10.20)–(10.25) well serve the purpose of our discussion intended. It is worth noting that the adiabatic approximation is similar in the basic idea to the center manifold approximation [15, 16, 17] used in non-linear dynamics.

In order to formulate what is said in the previous paragraph we examine the rates of change in, for example, the stress tensor and the fluid velocity. Their ratio may be taken in the following form:

$$\frac{\left(\frac{d\hat{\Pi}}{dt}\right)}{\eta_r (d\mathbf{u}/dt) L^{-1}} \sim \frac{(\Pi_r/\eta_r)}{u_r L^{-1}} \sim \frac{\tau_h}{\tau_s} = N_{De}^{-1}. \quad (10.43)$$

This ratio suggests that the rate of change in stress tensor is proportional to N_{De}^{-1} times that of velocity. Since $\tau_h \gg \tau_s$ in general, the stress tensor evolves much faster than the hydrodynamic velocity does. This means the stress tensor will reach the steady state well before the hydrodynamic velocity attains its steady state.

A similar consideration can be made for the heat flux evolution relative to the hydrodynamic velocity evolution. It is readily found that

$$\frac{\left(\frac{d\hat{\mathbf{Q}}}{dt}\right)}{\lambda_r (d\mathbf{u}/dt) L^{-1}} \sim \frac{(Q_r/\lambda_r)}{u_r L^{-1}} \sim \frac{\tau_h}{\tau_q} = N_A^{-1}. \quad (10.44)$$

Thus the constitutive equations for Π , Δ , and \mathbf{Q} can be reduced to the forms

$$\begin{aligned} N_{De}^{-1} \rho \frac{d\hat{\Pi}}{dt} &= -2p[\nabla \mathbf{u}]^{(2)} - 2\left[\Pi \cdot [\nabla \mathbf{u}]^{(2)}\right]^{(2)} - [\boldsymbol{\omega}, \Pi] \\ &\quad - \frac{2}{3}\Pi \nabla \cdot \mathbf{u} - \frac{p}{\eta_0} \Pi q(\kappa), \end{aligned} \quad (10.45)$$

$$N_{De}^{-1} \rho \frac{d\hat{\Delta}}{dt} = -p \frac{d}{dt} \ln(pv^{5/3}) - \frac{2}{3}\Pi : \nabla \mathbf{u} - \frac{2}{3}\Delta \nabla \cdot \mathbf{u} - \frac{2p}{3\eta_b} \Delta q(\kappa), \quad (10.46)$$

$$\begin{aligned} N_A^{-1} \rho \frac{d\hat{\mathbf{Q}}}{dt} &= -p \hat{C}_p T \nabla \ln T - \Pi \cdot \nabla \hat{h} + \nabla \cdot (p\delta + \Pi) \cdot \hat{\Pi} \\ &\quad - \mathbf{Q} \cdot \left([\nabla \mathbf{u}]^{(2)} - \boldsymbol{\omega} + \frac{1}{3}\delta \nabla \cdot \mathbf{u}\right) \\ &\quad - \frac{p \hat{C}_p T}{\lambda_0} \mathbf{Q} q(\kappa). \end{aligned} \quad (10.47)$$

Coupled to these constitutive equations are the mass, momentum, and internal energy balance equations

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (10.48)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p - \nabla \cdot (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}), \quad (10.49)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - p \nabla \cdot \mathbf{u} - (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) : \nabla \mathbf{u}. \quad (10.50)$$

Eqs. (10.45)–(10.47) suggest that the derivatives of $\hat{\boldsymbol{\Pi}}$, $\hat{\Delta}$, and $\hat{\mathbf{Q}}$ on the left are proportional to N_{De} and N_A and hence vanish in the limit of $N_{De}, N_A \rightarrow 0$: that is,

$$\frac{d\hat{\boldsymbol{\Pi}}}{dt} = 0, \quad \frac{d\hat{\Delta}}{dt} = 0, \quad \frac{d\hat{\mathbf{Q}}}{dt} = 0 \quad (10.51)$$

in the time scale of hydrodynamic evolutions of the conserved variables. Therefore, in the hydrodynamic time scale there hold the steady state constitutive equations in the moving coordinate system

$$\frac{p}{\eta_0} \boldsymbol{\Pi} q(\kappa) = -2p[\nabla \mathbf{u}]^{(2)} - 2[\boldsymbol{\Pi} \cdot [\nabla \mathbf{u}]^{(2)}]^{(2)} - [\omega, \boldsymbol{\Pi}] - \frac{2}{3} \boldsymbol{\Pi} \nabla \cdot \mathbf{u}, \quad (10.52)$$

$$\frac{2p}{3\eta_b} \Delta q(\kappa) = -p \frac{d}{dt} \ln(p v^{5/3}) - \frac{2}{3} \boldsymbol{\Pi} : \nabla \mathbf{u} - \frac{2}{3} \Delta \nabla \cdot \mathbf{u}, \quad (10.53)$$

$$\begin{aligned} \frac{p \hat{C}_p T}{\lambda_0} \mathbf{Q} q(\kappa) &= -p \hat{C}_p T \nabla \ln T - \boldsymbol{\Pi} \nabla \hat{h} + \nabla \cdot (p \boldsymbol{\delta} + \boldsymbol{\Pi}) \cdot \hat{\boldsymbol{\Pi}} \\ &\quad - \mathbf{Q} \cdot \left([\nabla \mathbf{u}]^{(2)} - \omega + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u} \right). \end{aligned} \quad (10.54)$$

These are the constitutive equations for $\boldsymbol{\Pi}$, Δ , and \mathbf{Q} in the adiabatic approximation. Physically this approximation means that in the time scale of change for the conserved variables over which the latter remain unchanged—thus the term adiabatic—the non-conserved variables have finished their temporal evolutions, although they are still inhomogeneous in the configuration space. These constitutive equations are highly non-linear because of the non-linear factor $q(\kappa)$, which accounts for the energy dissipation in the system. This non-linear factor plays crucial roles in accounting for flow behaviors of fluids far removed from equilibrium as will be shown in applications of the generalized thermodynamics.

Because of the conditions in Eq. (10.51), the calortropy change now takes the form

$$d_t \hat{\Psi}_{ss} = T^{-1} (d_t \mathcal{E} + p d_t v), \quad (10.55)$$

which has the same form as the local equilibrium hypothesis for the Clausius entropy in the theory of linear irreversible processes. However, as noted earlier, the system is not in equilibrium, but displaced from it by a high degree because of the non-linear terms contributing to the flow processes in the system. This point can be readily seen if the non-uniformity number N_δ is restored to the equations, since N_δ gives a measure of displacement of the system from equilibrium. In this regard it should be remarked that the argument of the non-linear factor $q(\kappa)$, when reduced, is $N_\delta \kappa^*$ [see Eqs. (10.26) and (10.32)] and hence $q(N_\delta \kappa^*)$ becomes increasingly important as either N_{Kn} and N_M or N_{Kn} and N_{Re} increase. This suggests that the generalized hydrodynamic equations should be also relevant to turbulent flows at large Reynolds numbers as well as rarefied gas and hypersonic flows, as the product $N_{Kn} N_M$ or $N_{Kn}^2 N_{Re}$ increases. We have alluded to this point earlier.

We remark that at the level of thermodynamic description the classical hydrodynamics shares the same differential form (10.55) with the generalized hydrodynamics in the adiabatic approximation, but the constitutive equations for the non-conserved variables are quite different, and they make significant and often crucial differences in the capabilities in their continuum theory description of flow processes. We will see examples for the differences as the generalized hydrodynamics in the adiabatic approximation is applied to some practical problems.

10.3 Simple Flows

Many macroscopic thermophysical processes occurring in matter, gaseous or condensed, can be effectively treated by means of continuum mechanics methods [18]. Evidence for the veracity of this viewpoint is amply provided by the classical hydrodynamics applications to numerous flow phenomena near equilibrium and for the cases where the gradients of temperature, density, or velocity are not too steep over the length scale of interest. When these limitations are removed the classical theories based on the Navier–Stokes–Fourier equations lose their power. The generalized hydrodynamics has been developed specifically to extend [19] the range of applicability of the classical hydrodynamics into such regimes. The power of generalized hydrodynamics lies not only in its thermodynamic consistency which enables us to develop approximation methods in a manner controlled by the second law of thermodynamics, but also, as a result and also additionally, in providing theories of flow processes in good accuracy. We will find that such thermodynamic consistency of continuum mechanics treatments of macroscopic flow phenomena invariably provides improved theories that better correlate with empirical observations made on flow. In this section we discuss some typical examples of application to steady state flow phe-

nomena of the generalized hydrodynamics within the framework of the adiabatic approximation. When it is considered appropriate and useful for the comprehensive picture of the matter in hand, the subjects considered in the previous monographs by this author will be repeated. Nevertheless, emphasis will be put on new applications of the theory.

10.3.1 Plane Couette Flow

A laminar flow is called parallel if the flow velocity is parallel to the axis of the channel in which the fluid is confined. The plane Couette flow is an example for such flows. We will consider the case of flow being parallel to the x axis in an infinitely long channel with the walls separated by a distance D in the y direction. The channel is extended to infinity in the direction of the z coordinate, which is the neutral direction. Consequently the flow is translationally invariant in the x and z directions. It is further assumed that the flow is incompressible and the temperature is uniform. Therefore heat flow is absent.

Under these assumptions it is sufficient to consider only the velocity and the shear stress as the relevant variables. The flow velocity, moreover, has the u_x component only and the equation of continuity is given by

$$\partial_x \rho u_x = 0. \quad (10.56)$$

This means that ρu_x is independent of x , but a function of y only, since the flow is assumed to be extended to infinity in the z direction. The boundary conditions on u_x at $y = \pm D/2$ are

$$u_x(\pm \frac{1}{2}D) = \pm \frac{1}{2}u_d,$$

where $\pm \frac{1}{2}u_d$ are the velocities of the walls at $y = \pm D/2$, to which the fluid is assumed to stick.

The steady momentum balance equation for the flow subjected to a pressure gradient $p_x = \partial_x p$ in the x direction is

$$\partial_y \Pi_{xy} + p_x = 0. \quad (10.57)$$

It is assumed that there are no normal stress differences, that is, $N_1 = \Pi_{xx} - \Pi_{yy} = 0$ and $N_2 = \Pi_{yy} - \Pi_{zz} = 0$. Furthermore, for the flow considered we have

$$\Pi_{xz} = \Pi_{zx} = 0.$$

Since there are no normal stress differences, under the assumptions on the flow made earlier, Eq. (10.52) for $\mathbf{\Pi}$ reduces to the equation

$$\Pi q(\kappa) = -2\eta_0 \gamma, \quad (10.58)$$

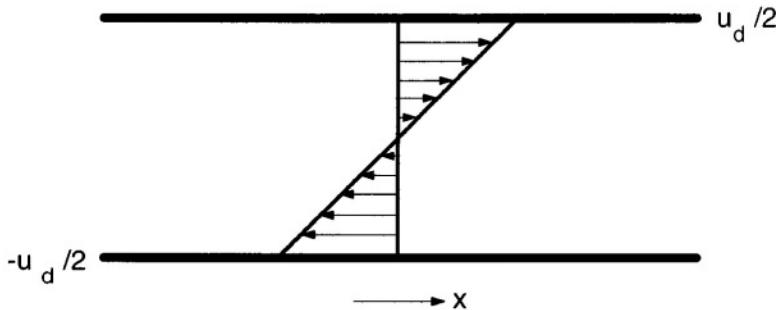


FIGURE 10.1 *Plane Couette flow configuration. The bold lines represent the plates which are separated by a distance D and move in opposite directions along the x axis at speed $u_d/2$*

where γ is the tensor of rank 2 defined by

$$\gamma = \begin{pmatrix} 0 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (10.59)$$

with γ standing for the shear rate

$$\gamma = \frac{1}{2} \frac{\partial u_x}{\partial y}. \quad (10.60)$$

On taking the doubly contracted scalar of Eq. (10.58) with itself and the square root of the result there follows the equation

$$(\Pi : \Pi)^{1/2} q(\kappa) = 2\eta_0 (\gamma : \gamma)^{1/2} = 2\sqrt{2}\eta_0\gamma. \quad (10.61)$$

Since $\kappa = \tau (\Pi : \Pi)^{1/2} / 2\eta_0$ under the assumptions made, the constitutive equation for the plane Couette flow follows from Eqs. (10.58) and (10.61) in the form

$$\Pi_{xy} = -2\eta\gamma, \quad (10.62)$$

where η is the non-Newtonian viscosity defined by the formula

$$\eta = \eta_0 \frac{\sinh^{-1}(\tau'\gamma)}{\tau'\gamma}. \quad (10.63)$$

In this viscosity formula τ' is a parameter with the dimension of time

$$\tau' = \sqrt{2}\tau = \frac{\sqrt{2}}{nk_B T d} \left[\eta_0 \sqrt{2m_r k_B T} \right]^{1/2}, \quad (10.64)$$

where n , m_r , and d denote the density, reduced mass, and diameter of the molecule, respectively. The factor $\sqrt{2}$ in front of τ arises because $\gamma : \gamma = 2\gamma^2$

for the flow configuration. The parameter τ' may be treated as a phenomenological parameter in the present discussion, although it descends from the kinetic theory of fluids [8, 9, 20, 21, 22]. The constitutive equation (10.62) is coupled to the momentum balance equation for the flow (10.57), which must be solved for u_x .

A. The case of $p_x = 0$

If $p_x = 0$ there follows from the momentum balance equation (10.57) the equation

$$\Pi_{xy} = \text{constant.}$$

On substitution of (10.62) into this equation and use of the boundary conditions on integration, there follows the velocity profile

$$u_x = \frac{u_d}{D}y, \quad (10.65)$$

where D is the width of the channel; see Fig. 10.1. Despite the non-Newtonian viscosity the velocity profile is linear in y , as is the case for the Newtonian viscosity.

Substitution of the formula (10.65) for velocity profile into (10.63) gives rise to the non-Newtonian viscosity formula and the shear stress in the forms

$$\eta = \eta_0 \frac{\sinh^{-1}(\tau' u_d / 2D)}{(\tau' u_d / 2D)} \quad (10.66)$$

and

$$\Pi_{xy} = -\frac{4\eta_0}{\tau'} \ln \left(\frac{\tau' u_d}{2D} + \sqrt{1 + \left(\frac{\tau' u_d}{2D} \right)^2} \right) \quad (10.67)$$

These results indicate the shear-thinning behavior of the fluid. In particular, (10.66) is known as the Eyring non-Newtonian viscosity formula [23], which was originally derived from the absolute reaction rate theory. The present formula, although treated as an empirical formula in this discussion, was derived from the kinetic equation and gives the molecular expression for the parameter τ' which in the absolute reaction rate theory appears as an empirical parameter. Formula (10.66) can be shown to account for the shear rate dependence of molecular dynamics simulation data on the viscosity of a Lennard-Jones fluid.

The result obtained here seems to be useful for examining the molecular dynamics algorithm [24, 25]. In the molecular dynamics simulation algorithm for flow the velocity gradient is taken as a constant even if the fluid is not Newtonian. The behavior (10.65) of u_x may be used to support such an algorithm taken in molecular dynamics simulations of flow. This assumption of a linear velocity profile, in fact, is taken for want of the advance knowledge of the flow profile before the simulations are performed, but

turns out to be fortuitously correct. If the flow configuration is changed to a tube flow configuration the velocity profile is no longer linear if the fluid is non-Newtonian. Consequently a linear profile would be an inappropriate assumption to take for such a flow configuration. For example, in the case of a Taylor–Couette flow the velocity profile [26] is no longer linear with respect to the radial distance if the fluid is non-Newtonian. This point can be readily seen from the calculation presented for a tube flow in the next subsection.

B. The case of $p_x \neq 0$

In the case where p_x is a non-vanishing constant the momentum balance equation (10.57) can be integrated to yield the velocity profile

$$u_x = \alpha u_d \left[\cosh\left(\frac{\delta}{2}\right) - \cosh\left(\frac{\delta y}{D}\right) \right], \quad (10.68)$$

where

$$\alpha = -\frac{4\eta_0}{\tau'^2 p_x u_d}, \quad \delta = -\frac{\tau' p_x D}{2\eta_0}. \quad (10.69)$$

The velocity profile in (10.68) reduces to the Newtonian form as the parameter δ becomes small in magnitude. The flow profile is plotted in Fig. 10.2 where $u_m = u_x/u_{\max}$. As δ increases, the boundary layer decreases and the flow behaves like a plug flow. It should be noted that the parameter δ is proportional to $N_M N_{Kn}$ or $N_M^2 N_{Re}$. Therefore as N_{Kn} or N_{Re} increases, the boundary layer thickness decreases and flow appears to be slipping at the boundary if the resolution of observation is low. This boundary layer thinning effect arises from the non-linear dissipation term in the evolution equation for the shear stress, namely, the non-linear factor $q(\kappa)$. Another quantity of physical interest here is the volumetric flow rate, namely, the volume of the fluid passing through unit area in unit time. It is given by the formula

$$\begin{aligned} Q_v &= \int_{-D/2}^{D/2} dz \int_{-D/2}^{D/2} dy \rho u_x(y) \\ &= \rho \alpha u D^2 \left[\cosh\left(\frac{\delta}{2}\right) - \frac{2}{\delta} \sinh\left(\frac{\delta}{2}\right) \right]. \end{aligned} \quad (10.70)$$

This may be cast in the form

$$Q_v = \frac{\rho D^4 \Delta p}{12\eta_0 L} F(\delta), \quad (10.71)$$

where $p_x = -\Delta p/L$ with L denoting the length of the channel, Δp the pressure difference, and

$$F(\delta) = \frac{12}{\delta^2} \left[\cosh\left(\frac{\delta}{2}\right) - \frac{2}{\delta} \sinh\left(\frac{\delta}{2}\right) \right]. \quad (10.72)$$

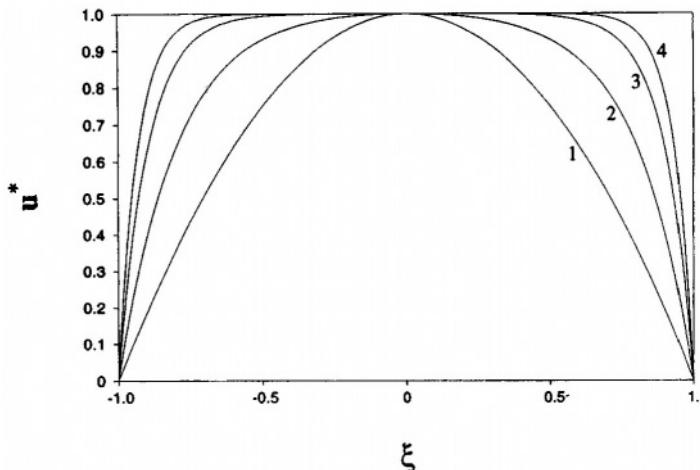


FIGURE 10.2 Velocity profiles of a channel flow in a non-Newtonian fluid. The flow profiles become increasingly rectangular as δ increases, and behave like a plug flow at very large values of δ [Reprinted with permission from (1990) Am J Phys, 58, 86 Copyright 1989 American Association of Physics Teachers]

This function, which reduces to unity as δ tends to zero, gives the non-Newtonian correction to the Hagen-Poiseuille volumetric flow rate which is given by the coefficient factor to $F(\delta)$ in (10.71).

It is interesting to calculate the calortropy production which gives a measure of energy dissipation in the flow. The reduced calortropy production for the flow is given by the formula

$$\hat{\Xi}_c = k_B^{-1} \Xi_c = g^{-1} \kappa \sinh \kappa, \quad (10.73)$$

where

$$g = \sqrt{\frac{m_r}{2k_B T}} (nd)^{-2}.$$

For both cases of $p = 0$ and $p \neq 0$ this formula, if written in terms of γ , has the same form

$$\hat{\Xi}_c = g^{-1} \tau' \gamma \sinh^{-1}(\tau' \gamma), \quad (10.74)$$

but, if the velocity profiles are explicitly used for the two different cases, different final results follow. In the case of $p = 0$ the calortropy production is given by the formula

$$\hat{\Xi}_c = g^{-1} \frac{\tau' u_d}{2D} \sinh^{-1} \left(\frac{\tau' u_d}{2D} \right), \quad (10.75)$$

which is a constant across the channel. On the other hand, in the case of $p \neq 0$ it follows from the velocity profile (10.68) that the calortropy

production is given by the formula

$$\hat{\Xi}_c = g^{-1} \frac{\delta}{D} y \sinh\left(\frac{\delta}{D} y\right). \quad (10.76)$$

Since it depends on y , the observable is the mean calortropy production, which may be defined by

$$\begin{aligned} \langle \hat{\Xi}_c \rangle &= \frac{1}{D} \int_{-D/2}^{D/2} dy \hat{\Xi}_c(y) \\ &= 2g^{-1} \left[\frac{\delta}{2} \cosh\left(\frac{\delta}{2}\right) - \sinh\left(\frac{\delta}{2}\right) \right]. \end{aligned} \quad (10.77)$$

Since

$$F(\delta) = \frac{6g}{\delta^3} \langle \hat{\Xi}_c \rangle,$$

the mean calortropy production for the flow is directly proportional to the volume flow rate

$$\langle \hat{\Xi}_c \rangle = g \frac{2\eta_0 L \delta^3}{\rho D^4 \Delta p} Q_v. \quad (10.78)$$

Therefore the measurement of volume flow rate yields the calortropy production for the flow.

10.3.2 Tube Flow

The non-Newtonian viscosity formula (10.63) used for the calculations in the previous subsection can be applied to a flow in cylindrical geometry. We consider it here since it not only illustrates an application of generalized hydrodynamics in a flow configuration different from the simple Cartesian flow configuration, for which plane Couette flow is an example, but also is more realistic from the viewpoint of experiment. Consequently the result obtained for the flow has a number of useful applications in connection with non-Newtonian fluids, including viscometry [2]. The point to remember is that although we are considering it in the context of gases the same results as obtained in this subsection can be produced for liquids obeying the same non-Newtonian viscosity formula, as is shown in Refs. [27]–[29]. Therefore the example considered here has general relevance to non-Newtonian fluids.

Let us assume that a fluid obeying the shear stress constitutive equation (10.52) flows in a cylinder of radius R and length L which is much larger than R . We assume that the flow is parallel to the axis of the cylinder, which is taken to be parallel to the z axis, and the temperature is uniform throughout the cylinder. Because of the cylindrical symmetry and the flow being laminar, flow variables do not depend on the angle θ of the coordinates and there is only the z component of the velocity to consider, if L is so long as to make the translational symmetry sufficiently valid. In this

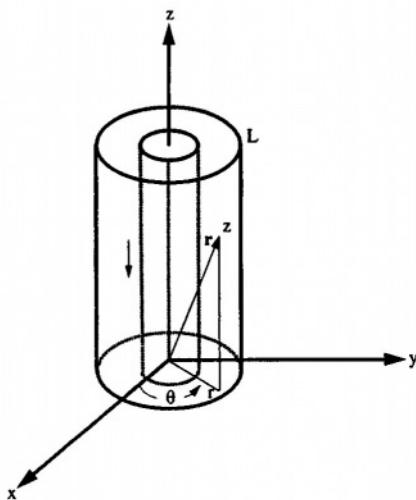


FIGURE 10.3 Cylindrical flow geometry. The inner cylinder represents an imaginary layer of the fluid.

case, we have $\mathbf{u} = (0, 0, u_z)$ for the velocity since the equation of continuity and the boundary condition demand that the radial velocity vanishes: $u_r = 0$. Note that $\rho \neq 0$. We also assume that there are no primary and secondary normal stress differences N_1 and N_2 . In the convention [30] used for defining the normal stress differences they are given by the formulas

$$N_1 = \Pi_{zz} - \Pi_{rr} = 0, \quad N_2 = \Pi_{rr} - \Pi_{\theta\theta} = 0.$$

Therefore there is only the shear component non-vanishing, which for the present flow configuration is given by

$$\Pi = \Pi_{rz} = \Pi_{rz}.$$

The momentum balance equation then has the form

$$\frac{1}{r} \frac{\partial}{\partial r} r \Pi = -p_z. \quad (10.79)$$

With regard to this equation we remark that the absence of the normal stress differences implies a pressure which is independent of r . The pressure gradient along the z direction is assumed independent of z owing to the translational invariance of flow in the z direction that arises from the assumption of an infinitely long tube. Under this set of assumptions, the relevant constitutive equation is given by

$$\Pi q(\kappa) = -2\eta_0 \gamma, \quad (10.80)$$

where

$$\gamma = \frac{1}{2} \frac{\partial u_z}{\partial r}, \quad (10.81)$$

and

$$q(\kappa) = \frac{\sinh \kappa}{\kappa}. \quad (10.82)$$

Since $(\Pi : \Pi)^{1/2} = \sqrt{2}\Pi$ and $(\gamma : \gamma)^{1/2} = \sqrt{2}\gamma$, as in the case of the plane Couette flow considered previously, it follows that

$$\kappa = \frac{\tau}{\sqrt{2}\eta_0} \Pi = \sinh^{-1}(\tau' \gamma). \quad (10.83)$$

On use of this result in Eq. (10.80) there follows the non-Newtonian viscosity formula

$$\eta = \eta_0 \frac{\sinh^{-1}(\tau' \gamma)}{\tau' \gamma} \quad (10.84)$$

even in the case of the tube flow under consideration.

It follows from Eq. (10.83) that the constitutive equation may be written as

$$\Pi = \frac{\sqrt{2}\eta_0}{\tau} \sinh^{-1}(\tau' \gamma).$$

Upon substituting this formula for Π in the momentum balance equation (10.79) there arises the non-linear second order differential equation for u_z

$$\frac{1}{r} \frac{\partial}{\partial r} r \sinh^{-1}(\tau' \gamma) = - \frac{\tau}{\sqrt{2}\eta_0} p_z. \quad (10.85)$$

We examine the solution of this differential equation by using two different boundary conditions: stick boundary conditions and Langmuir boundary conditions in the following two subsections.

10.3.3 Stick Boundary Conditions

The stick boundary conditions are usually taken in flow problems, especially if the density of the fluid is above the normal density value of gas. Here we first use the stick boundary conditions

$$u_z(R) = 0, \quad \left(\frac{\partial u_z}{\partial r} \right)_{r=0} = 0.$$

By using these boundary conditions on u_z we easily obtain from Eq. (10.85) the velocity profile in a simple analytic form [27, 28, 29]

$$u_z = \frac{2R}{\tau' \delta_c} \left[\cosh \delta_c - \cosh \left(\delta_c \frac{r}{R} \right) \right], \quad (10.86)$$

where

$$\delta_c = \frac{\tau' R \Delta p}{4\eta_0 L}. \quad (10.87)$$

Despite the geometry different from the plane Couette flow considered earlier the velocity profile for tube flow has a mathematical form similar to that for the channel flow shown in Eq. (10.68). Defining the Hagen–Poiseuille formula [31] in the cylindrical geometry by the formula

$$Q_{HP}^c = \frac{R^4 \Delta p}{8\eta_0 L N k_B T} \quad (N = \text{Avogadro's number}), \quad (10.88)$$

the volumetric flow rate can be calculated as follows:

$$\begin{aligned} Q_v^c &= 2\pi n \int_0^R dr r u_z(r) \\ &= Q_{HP}^c [1 + F_c(\delta_c)] p, \end{aligned} \quad (10.89)$$

where

$$F_c(\delta_c) = \frac{8}{\delta_c^2} \left[\frac{1}{2} \cosh \delta_c - \frac{\sinh \delta_c}{\delta_c} + \frac{\cosh \delta_c - 1}{\delta_c^2} \right] - 1. \quad (10.90)$$

As in the case of a plane Couette flow, the flow profile increasingly deviates from the parabolic behavior characteristic of a Newtonian fluid, becoming like a plug flow, since the boundary layer gets thinner as δ_c increases, as shown in Fig. 10.2. Again this parameter is proportional to $N_M N_{Kn}$ or $N_M^2 N_{Re}$. The principal cause for the boundary layer thinning effect is the non-linear energy dissipation described by the non-linear factor $q(\kappa)$.

The calortropy production for the flow is given by

$$\begin{aligned} \widehat{\Xi}_c &= g^{-1} \kappa \sinh \kappa \\ &= g^{-1} \frac{R^2 \Delta p^2}{4L^2 \eta_0 k_B T} \delta_c^{-1} \frac{r}{R} \sinh \left(\delta_c \frac{r}{R} \right), \end{aligned} \quad (10.91)$$

which on substitution of κ from (10.83) and integration over r gives the mean value

$$\begin{aligned} \langle \widehat{\Xi}_c \rangle &= \frac{1}{\pi R^2} \int_0^R dr 2\pi r \widehat{\Xi}_c(r) \\ &= g^{-1} \frac{R^2 \Delta p^2}{L^2 \eta_0 k_B T} \delta_c^{-2} \left[\frac{1}{2} \cosh \delta_c - \frac{\sinh \delta_c}{\delta_c} + \frac{\cosh \delta_c - 1}{\delta_c^2} \right] \\ &= g^{-1} \frac{N \Delta p}{R^2 L p} Q_v^c. \end{aligned} \quad (10.92)$$

This indicates that the calortropy production increases linearly with the volumetric flow rate Q_v^c . That is, the energy dissipation increases in direct proportion to the volumetric flow rate. As is for the plane Couette flow considered in the previous subsection, this is an example for a possibility of direct measurement of calortropy production by measuring the volumetric flow rate for a flow system.

The drag coefficient [32] gives a measure of friction by the flow past the body and is defined by the friction energy relative to the mean kinetic energy of the flow:

$$C_d = \frac{2\pi RL\Pi(R)}{2\pi RL\frac{1}{2}\rho \langle u_z \rangle^2}, \quad (10.93)$$

where

$$\langle u_z \rangle = \frac{1}{\pi R^2} \int_0^R dr 2\pi r u_z(r).$$

By using the result obtained earlier we find

$$C_d = \frac{\Gamma(\delta_c)}{N_{Re}}, \quad (10.94)$$

where

$$N_{Re} = \frac{\rho u_z(0)R}{\eta_0} = \frac{2R}{\tau' \delta_c (\cosh \delta_c - 1)}, \quad (10.95)$$

$$\Gamma(\delta_c) = \frac{4(\cosh \delta_c - 1)}{[1 + F_c(\delta_c)]^2}. \quad (10.96)$$

The drag coefficient reduces to the Newtonian flow value $16/N_{Re}$ in the limit of $\delta_c \rightarrow 0$.

We remark that the volumetric flow rate formula derived here can be used to resolve the Knudsen problem (paradox) observed by Knudsen [33] in 1909. The reader is referred to Ref. [28] and Ref. [34] cited therein. It can also be used to explain the laser-induced drift of gases in capillary [35].

10.3.4 Langmuir Boundary Conditions for Flows

Flow behavior and the characteristic length (*e.g.*, width) of the system has an important relation, especially in the case of gas flows. The Knudsen number is an important number appearing in such a relation. In the normal density gases contained in a volume of macroscopic size the Knudsen number is much less than unity, being of the order of 10^{-4} or less. As the fluid density is reduced to a sufficiently low value as to make the Knudsen number $O(10^{-1})$ or larger, the flow behavior changes markedly from the prediction by the classical hydrodynamic theory with stick boundary conditions. The generalized hydrodynamic theory can adequately provide

description of such flows, as has been demonstrated in a number of applications, including the examples given in the previous subsections.

In the classical hydrodynamics approach the anomalous behavior of flow is usually explained by employing slip boundary conditions in the tradition of Maxwell, who introduced for the first time the notion of slip [36] as a measure of repairing the predictions of the theory of transport processes based on his kinetic theory of gases [37], which were at variance with experiment [38]. The slip boundary conditions are in effect a way to patch up the inadequacy of the classical hydrodynamics which makes use of linear constitutive relations for stresses and heat fluxes and, in particular, Maxwell's prediction that the transport coefficients are independent of the density of the gas. We have shown that non-linear constitutive relations can replace the slip boundary conditions and achieve the same end in accounting for the observed flow behavior in rarefied gases. Nevertheless, it is true that as the fluid density diminishes, the interaction of molecules with the walls of the container of the fluid becomes important.

The slip boundary conditions make use of the interactions of the walls with the gas molecules, which appear in the form of accommodation coefficients in Maxwell's modified kinetic theory. On the other hand, since the fluid–wall interaction does not manifest itself in the stick boundary conditions, the effects of molecularity of the walls cannot be taken into account in the flow properties. In this sense the slip boundary conditions are more faithful to the molecularity of the whole flow system including the boundaries than the stick boundary conditions. For this reason alone, slip boundary conditions or their variations may be preferable.

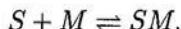
Such fluid–wall interactions modify the velocity and temperature of the gas in flow and consequently introduce a density dependence to the effective transport coefficients. In order to have a density dependence which was not present in the transport coefficients in the original version of his kinetic theory Maxwell [36] expanded flow variables in power series of the mean free path, and with the so obtained effective transport coefficients that depend on density he was able to account for the observed flow behavior in an *ad hoc* manner. However, it is true that such fluid–wall interactions alone are not sufficient to account for the basically non-linear nature of flows in high Knudsen number regime, and we believe that both non-linear constitutive equations and boundary conditions taking the fluid–wall interactions into account are necessary for satisfactory understanding of such flow phenomena.

In this subsection we develop a model for boundary conditions which enables us to take the surface–fluid molecule interactions into account in fluid dynamic calculations. With such modified boundary conditions we examine, within the framework of generalized hydrodynamics, the same flow problems as studied with the stick boundary conditions in earlier subsections. Therefore in the present approach the modification of boundary conditions is not a means of achieving the non-linear nature of flow processes

described by generalized hydrodynamics, but a way of taking into account the molecular nature of the walls interacting with the flow within the framework of generalized hydrodynamics.

The surface molecules or atoms comprising the walls of the container interact with the gas molecules in flow. It is known that the interaction energy between the gas molecules and the surface molecules of the wall is of the van der Waals attraction and long ranged because the mean interaction potential energy is proportional to the inverse cube of the distance between the particles [39]. For this reason the gas molecules get adsorbed even at low densities. It is, in fact, known in ultra-vacuum techniques [40] that such adsorption creates technical problems in achieving an ultra-high vacuum. Although adsorption is a problem for the aforementioned experimental techniques, it provides us with a way to treat the boundary conditions, because it is possible to examine the modification of flow variables such as velocity and temperature from the viewpoint of adsorption. For the purpose we exploit the basic idea of Langmuir [41] to formulate a method of calculating the boundary conditions [42, 43].

Let us assume that there are N sites per unit area of the surface making up the wall. These sites interact with the gas molecules. We now assume that a fraction θ of N sites is adsorbed by the gas molecules. It is further assumed that a quasi-stable complex is formed between the adsorbed molecule and the molecule of the wall on the sites. Therefore there are $N\theta$ of such quasi-stable complexes. The number of sites that are free is then $N(1 - \theta)$. The gas molecule will be denoted by M , and the molecule of the site by S . The adsorption-desorption of the gas molecule at the surface may be regarded as a chemical reaction



If the rate of adsorption and desorption process is assumed much faster than the flow speed, in the characteristic hydrodynamic time scale the chemical reaction may be regarded as being in equilibrium at temperature T_w of the wall, and the chemical equilibrium constant is given by

$$K = \frac{C_{SM}}{C_S C_M}, \quad (10.97)$$

where

$$C_{SM} = N\theta, \quad C_S = N(1 - \theta), \quad C_M = p/k_B T_w \quad (10.98)$$

with p denoting the gas pressure. The gas is assumed to be ideal. From Eqs. (10.97) and (10.98) follows the fraction θ given by the formula

$$\theta = \frac{bp}{1 + bp}, \quad (10.99)$$

where

$$b = \frac{K}{k_B T_w}. \quad (10.100)$$

The equilibrium constant can be calculated in terms of molecular partition functions.

Before calculating $K(T_w)$ and the temperature dependence of θ with it, we will calculate the apparent flow variables T_a and u_a in the interface near the wall by using the absorption–desorption model assumed earlier. Since θ in essence gives the fraction of species SM at thermal equilibrium with the wall, the apparent temperature T_a in the interface (boundary layer) near the wall may be regarded as the mean value of T_w and the gas temperature T_g within the stream in the following sense²:

$$T_a = \theta(T_w) T_w + [1 - \theta(T_w)] T_g, \quad (10.101)$$

where $T_w \neq T_g$. The gas temperature T_g may be taken as the gas temperature a fraction of a mean free path away from the wall for the following reason.

Let l be the mean free path and ϕ be the angle between the surface and the incident gas molecule. Then the normal component of the mean free path perpendicular to the surface is $l \sin \phi$. Because the incident angle ranges from 0 to π , the mean value of the normal component is

$$\langle l \sin \phi \rangle = \frac{1}{\pi} \int_0^\pi d\phi l \sin^2 \phi = \frac{l}{2}. \quad (10.102)$$

To be specific, we will consider the plane Couette flow configuration previously studied. If the distance between the walls is D and if D is comparable to l in the case of a sufficiently rarefied gas, it is reasonable to take T_g with the gas temperature at the midpoint between the walls, for example. Thus we may take

$$T_g = \frac{1}{2}(T_1 + T_2), \quad (10.103)$$

where T_1 and T_2 are the temperatures of the walls: $T_1 = T(\frac{1}{2}D)$ and $T_2 = T(-\frac{1}{2}D)$. In general, T_g will be taken as the temperature of the gas a fraction of a mean free path away from the wall.

²This formula can be justified by using the kinetic theory method, which yields the distribution function of the gas in the interface in the form

$$f(v, T_a) = \theta(T_w) f(v, T_w) + [1 - \theta(T_w)] f(v, T_g)$$

Since the temperature is defined by

$$\frac{3}{2} n k_B T = \left\langle \frac{1}{2} m v^2 f \right\rangle,$$

the temperature formula (10.101) follows.

A similar argument can be given for velocity, and we obtain

$$u_a = \theta(T_w) u_w + [1 - \theta(T_w)] u_g \quad (10.104)$$

with u_g denoting the fluid (gas) velocity in the stream one or less than a mean free path away from the wall; if the mean free path comparable with the channel width, it may be chosen with the midstream velocity, u_0 .

If we use in Formulas (10.101) and (10.104), for example, $T_1(l)$, $T_2(l)$, $u_1(l)$, and $u_2(l)$, which denote the temperatures and velocities a fraction of one mean free path away from the walls 1 and 2, respectively, the boundary conditions on temperature and velocity for the flow configuration in question read

$$T = \theta(T_1) T_1 + [1 - \theta(T_1)] T_1(l) \quad \text{at } y = \frac{1}{2}D, \quad (10.105)$$

$$T = \theta(T_2) T_2 + [1 - \theta(T_2)] T_2(l) \quad \text{at } y = -\frac{1}{2}D,$$

$$u = \frac{1}{2}\theta(T_1) u_d + [1 - \theta(T_1)] u_1(l) \quad \text{at } y = \frac{1}{2}D, \quad (10.106)$$

$$u = -\frac{1}{2}\theta(T_2) u_d + [1 - \theta(T_2)] u_2(l) \quad \text{at } y = -\frac{1}{2}D.$$

In these expressions T_1 and T_2 are the wall temperatures and $u_d = 2u_w$, if the walls move at velocities $u_w = \pm\frac{1}{2}u_d$ in plane Couette flow configuration.

There now remains the temperature dependence of θ to calculate. To this end it is necessary to obtain the temperature dependence of the equilibrium constant K . It may be given in terms of the molecular partition functions

$$K = \frac{(q_{SM}/\Omega)}{(q_S/\Omega)(q_M/\Omega)}, \quad (10.107)$$

where q_i ($i = S, M, SM$) are the molecular partition functions and Ω is the volume in which the molecules are confined. Since the site molecules are fixed on the surface of the wall,

$$q_S = \Omega.$$

Since the gas is dilute and monatomic, q_M is simply the translational partition function of M :

$$q_M = (2\pi m k_B T_w / h^2)^{3/2} \Omega.$$

The precise form of the partition function q_{SM} depends on the model chosen for the complex. If it is assumed that the molecule is confined to a

rectangular volume $\Omega = A\bar{l}$, where A is the base area around the site and \bar{l} is the height in the direction perpendicular to the surface, and moves in Ω subjected to a constant attractive potential energy field, then

$$q_{SM} = A\bar{l} (2\pi m k_B T_w / h^2)^{3/2} \exp(D_e / k_B T_w),$$

where the exponential factor is inserted to account for the probability of the complex to break up on input of dissociation energy D_e .

The parameter b is then easily calculated to have the form

$$b = \frac{A\bar{l}}{k_B T_w} \exp(D_e / k_B T_w). \quad (10.108)$$

The length \bar{l} in this formula may be taken with $\bar{l} = D/2$. Instead of the model chosen for the motion of SM it is possible to assume that SM , confined to the base area A , execute a two-dimensional vibration of frequency v within the area and a one-dimensional translational motion perpendicularly to the surface subjected to a constant attractive potential energy field of depth D_e . For this model we obtain the formula for the parameter

$$b = \frac{\bar{l}}{2\pi m v^2} \exp(D_e / k_B T_w). \quad (10.109)$$

Either one of these formulas for b may be used in the formula for $\theta(T_1)$ and $\theta(T_2)$ in Eq. (10.99) and in the boundary conditions presented earlier. The model used for calculating b can, of course, be improved at the cost of simplicity of the formula for b . With the temperature dependence of $\theta(T)$ determined, the boundary conditions (10.105) and (10.25) can be used for the generalized hydrodynamics for the flow.

To test the boundary conditions we examine the following simple system. A rarefied gas is confined in a channel between two parallel plates which are aligned along the y direction and separated by distance D in the direction of the x axis in the coordinate system. The plates are positioned at $x = D/2$ and $x = -D/2$, respectively. The temperature of the upper plate is at T_2 and that of the lower plate is at T_1 , where $T_2 < T_1$. The gas is assumed to be stagnant. Therefore the velocity of the fluid is equal to zero. We assume that the thermal conductivity is given by

$$\lambda = \lambda_0 \frac{\sinh^{-1} \kappa}{\kappa}, \quad (10.110)$$

where

$$\kappa = \tau_q \left| \frac{d \ln T}{dx} \right| \quad (10.111)$$

with τ_q defined by

$$\tau_q = \left[\lambda_0 \sqrt{\frac{m_r}{2k_B T}} \right]^{1/2} (nk_B T d)^{-1}.$$

Here λ_0 is the thermal conductivity of the dilute gas, which may be taken for the Chapman–Enskog thermal conductivity [13]. The rest of the notation is the same as before. In the case of the Maxwell model for the interaction potential it is given by the formula

$$\lambda_0 = \frac{5C_v T}{2} \sqrt{\frac{2m}{a}} \frac{k_B T}{3\pi A_2(5)}, \quad (10.112)$$

where a is the Maxwell potential parameter and $A_2(5) \simeq 0.436$.

Since the direction of decreasing T , or increasing density, is taken with that of increasing x , the relevant generalized hydrodynamic equation

$$\frac{d}{dx} \lambda \frac{d \ln T}{dx} = 0 \quad (10.113)$$

can be put into the form

$$\frac{\lambda_0}{\tau_q} \sinh^{-1} \left[\tau_q \frac{d \ln T}{dx} \right] = C_1, \quad (10.114)$$

where C_1 is the integration constant. This is a non-linear differential equation for T because λ_0 and τ_q depend on T . Integrating it subject to the boundary conditions given in Eq. (10.105) we obtain the temperature profile as a function of x . Integrating Eq. (10.114) yields

$$\ln T = C + \int^x dx' \tau_q^{-1}(x') x' \sinh \left(\frac{\tau_q(x')}{\lambda_0} C_1 \right). \quad (10.115)$$

The solution of Eq. (10.115), in fact, can be numerically achieved by a shooting method to determine the integration constants C and C_1 , subject to the boundary conditions (10.105). Since the pressure can be shown to be constant throughout the channel, the density profile can be calculated from the so-obtained temperature profile with the equation of state

$$p = nk_B T.$$

Teagan and Springer [44] report on the density profile in the interval $0 < x/D < 1/2$. The density profile calculated³ theoretically is compared with the experimental data at various Knudsen numbers by Teagan and Springer in the Fig. 10.4. The parameter b taken for the comparison of the theoretical prediction with experiment was calculated from Eq. (10.108) with the parameter values $D_e = 7.2 \text{ KJ/mol}$ and $A = 5 \times 10^{-19} \text{ m}^2$. The n_0 is the density of the gas at $x = 0$, namely, at the midpoint of the channel.

³From the unpublished research notes of B.C. Eu, D.K. Bhattacharya, and R.E. Khayat, (1986) ‘Generalized Hydrodynamics and Flow Profiles: Heat Transfer between Parallel Plates’.

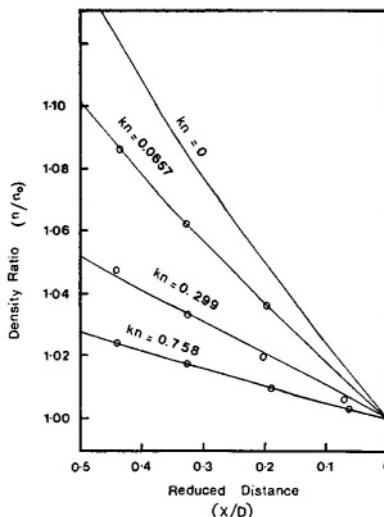


FIGURE 10.4 *Density profile of nitrogen gas above aluminum calculated under the Langmuir boundary conditions and compared with experiment by Teagan and Springer [44]. The symbols denote the experimental data, and the solid curves the theory at various Knudsen numbers (denoted by Kn)*

The agreement between the theory and experiment is excellent, supporting the method combining the generalized hydrodynamics and the Langmuir boundary conditions.

For another example of the effects of the modification of boundary conditions we consider the plane Couette flow in the case of $p_x \neq 0$, which was considered in subsection 10.2.1. We write out the flow equation (10.57) for the non-Newtonian fluid obeying the constitutive equation (10.63)

$$\frac{\partial}{\partial y} 2\eta_0 \frac{\sinh^{-1}(\tau' \gamma)}{\tau'} = p_x, \quad \gamma = \frac{1}{2} \frac{\partial u_x}{\partial y}. \quad (10.116)$$

Twice integrating this equation with regard to y , we find

$$u_x = -\alpha u_d (\cosh \delta \zeta \cosh C - \sinh \delta \zeta \sinh C) + C_1, \quad (10.117)$$

where C and C_1 are integration constants, α and δ have been defined earlier [see Eq. (10.69)], and $\zeta = y/D$. Let us take $u_g = u_0$, where u_0 is the velocity at $y = 0$. This choice is reasonable if the mean free path is comparable with the channel width. The boundary conditions in this case are

$$\begin{aligned} u_+ &= \frac{1}{2} \theta(T) u_d + [1 - \theta(T)] u_0 & \text{at } y = \frac{D}{2}, \\ u_- &= -\frac{1}{2} \theta(T) u_d + [1 - \theta(T)] u_0 & \text{at } y = -\frac{D}{2}, \end{aligned} \quad (10.118)$$

With these boundary conditions we obtain from Eq. (10.117) the equations

$$\begin{aligned} \frac{1}{2}\theta(T)u_d + [1 - \theta(T)]u_0 &= -\alpha u_d \cosh\left(\frac{\delta}{2} - C\right) + C_1, \\ -\frac{1}{2}\theta(T)u_d + [1 - \theta(T)]u_0 &= -\alpha u_d \cosh\left(\frac{\delta}{2} + C\right) + C_1. \end{aligned} \quad (10.119)$$

Upon solving these algebraic equations the constants C and C_1 are determined:

$$\begin{aligned} \cosh C &= \pm \sqrt{\frac{\theta^2}{4\alpha^2 \sinh^2 \frac{\delta}{2}} + 1}, \\ C_1 &= [1 - \theta(T)]u_0 \pm \alpha u_d \cosh \frac{\delta}{2} \sqrt{\frac{\theta^2}{4\alpha^2 \sinh^2 \frac{\delta}{2}} + 1}. \end{aligned} \quad (10.120)$$

The positive sign will be chosen. Finally, the solution u_x scaled by u_0 is given by the formula

$$\frac{u_x}{u_0} = 1 - \theta \frac{\cosh \delta \zeta - 1}{\cosh \frac{\delta}{2} - 1} + \frac{\theta^2 \sinh \delta \zeta}{(\cosh \frac{\delta}{2} - 1) \sqrt{\theta^2 + 4\alpha^2 \sinh^2 \frac{\delta}{2}}}. \quad (10.121)$$

This velocity profile reduces to the parabolic Poiseuille formula as $\delta \rightarrow 0$. The velocity u_0 at $\zeta = 0$ is found to be given by the formula

$$u_0 = \frac{u_d}{2\theta} \frac{(\cosh \frac{\delta}{2} - 1)}{\sinh \frac{\delta}{2}} \sqrt{\theta^2 + 4\alpha^2 \sinh^2 \frac{\delta}{2}}. \quad (10.122)$$

The parameter θ vanishes as p vanishes, that is, as the gas rarefies. In such a limit u_x becomes independent of ζ and thus the flow becomes rectangular and appears to be ballistic. We remark that instead of $u_g = u_0$ it is possible to take u_g as the velocity at a fraction of a mean free path from the wall. This choice will be made for u_g in Sec. 10.7 where microflows will be discussed.

10.4 Shock Waves in Monatomic Gases

Another example of applications of the present generalized hydrodynamic theory, which is of great practical importance, is the study of shock wave structures. Shock waves have been conventionally studied by means of Navier–Stokes–Fourier (NSF) theory [45, 46, 47], but unfortunately the NSF theory does not quantitatively predict the shock wave structure if the

Mach number exceeds the neighborhood of about 1.6. This failure of the classical continuum mechanics theory has been a major stumbling block in the gas dynamics research related to aeronautics and astronautics. In recent years the direct simulation Monte Carlo (DSMC) method [48, 49, 50] has been developed and replaced the classical hydrodynamic theory in the study of gas dynamics in the non-classical regimes. However, the DSMC method has its own limitations, its high computational cost and the limited range of applicability being two important examples of them. Therefore continuum mechanics approaches would be desired. Fortunately, it is found that the present generalized hydrodynamics theory provides excellent solutions [51] to the shock wave problems. The present and subsequent subsections are devoted to the topics.

To remedy the aforementioned situation with regard to the classical hydrodynamic theory the Burnett solutions of the Boltzmann equation have been explored [52, 53, 54] as a way to extend the NSF theory, but they have so far not yielded reliable and fully satisfactory solutions of the problem. The Grad moment method has also been used for the objective, but it has encountered a difficulty because the theory predicts that there is no shock solution beyond the critical Mach number which, contrary to experiments, appears at $N_M \approx 1.65$ according to Grad's own investigation [55], at $N_M = 1.851$ according to Holway [56], and at $N_M = 2.09$ according to Anile and Majorana [57]. These authors used a truncated set of Grad's moment equations where the moments beyond the first thirteen are expressed in terms of the lower-order moments to study the existence of shock solutions. The precise values for the upper limit of the Mach number appear to depend on how the moment series is truncated. One can, in fact, include a very large number of moments [58] beyond the first thirteen moments, but it is not possible to eliminate the maximum Mach number beyond which the shock solution does not exist. Ruggeri [59] examined the hyperbolic differential equation system obeyed by the moments given by the kinetic theory and obtained the theorem that there exists a maximum Mach number that is exactly the same as Grad's value of 1.65. Therefore it is clear that mere inclusion of a still larger number of moments is not going to yield the resolution of the problem, and shock waves still pose a theoretical challenge to the kinetic theory of gases. In this author's opinion this difficulty, however, is created in the kinetic theory approach because of an inappropriate interpretation of the meaning of what is commonly called the solution of the Boltzmann equation or equivalent kinetic equations for gas dynamic problems. Hydrodynamic equations derived from the Boltzmann equation must be in the branch of solutions consistent with laws of thermodynamics, but simply making the number of moments sufficiently large does not render the distribution function constructed with them a thermodynamically consistent solution of the kinetic equation. We will, however,

not discuss this point in this work, because the question⁴, being that of kinetic theory, is out of the scope of this monograph, which is limited to phenomenological theories.

In this subsection we take up the subject of shock waves and study it from the viewpoint of the generalized hydrodynamics formulated in the previous chapter. The generalized hydrodynamic theory of shock waves in monatomic gases was previously discussed in the monograph [9] on non-equilibrium statistical mechanics by this author, but we will discuss it here again as an integral part of a more comprehensive theory which includes shock wave structures in diatomic gases which are more interesting and useful in practice.

Conforming to the guiding spirit of the present monograph, the generalized hydrodynamic equations presented are basically empirical. We therefore do not concern ourselves with their molecular theory origin. However, they are certainly consistent with the laws of thermodynamics. The generalized hydrodynamic equations employed for the study of shock waves are not without some extensive tests [60, 61, 62, 63, 64, 65, 66, 67], because the applications of the steady constitutive equations used in this work have produced some results which are in quantitative agreement with experimental rheological data. Such agreement is rather assuring and provides a strong motivation to study shock wave structures with the generalized hydrodynamics.

10.4.1 Generalized Hydrodynamic Equations

We assume that flow is in the direction of the x coordinate. Since we are interested in one-dimensional steady shock waves, the balance equations are time-independent and one-dimensional. It must be noted, before we start writing down the evolution equations for the problem, that a one-dimensional model for shock phenomena is an approximation which is made reasonable under the assumption that flow variables vary at a much slower rate in the transversal directions than in the longitudinal direction. It therefore will be a reasonable description for the motion of the tip of shock wave. In these circumstances the balance equations for the conserved variables

⁴See Refs. [8] and [9] for the discussion of the thermodynamic branch of solutions for the Boltzmann equation and its significance to irreversible phenomena subjected to the laws of thermodynamics.

can be written in the form

$$\frac{d}{dx} \rho u = 0, \quad (10.123)$$

$$\frac{d}{dx} (\rho u^2 + p + \Pi_{xx}) = 0, \quad (10.124)$$

$$\frac{d}{dx} \left[\rho u \left(\mathcal{E} + \frac{1}{2} u^2 \right) + u(p + \Pi_{xx}) + Q_x \right] = 0, \quad (10.125)$$

where the notation is obvious by now.

Since the bulk viscosity vanishes for dilute monatomic gases it is possible to set $\Delta = 0$. Therefore the balance equations presented are supplemented by the evolution equations for Π_{xx} and Q_x only. Since we are interested in steady shock waves the steady state evolution equations for Π_{xx} and Q_x in the adiabatic approximation are sufficient for our purpose. Thus we take the one-dimensional versions of Eqs. (10.52) and (10.54) in the adiabatic approximation, which are given by the equations

$$\frac{p}{\eta_0} \Pi_{xx} q(\kappa) = -\frac{4}{3} \Pi_{xx} \partial_x u - \frac{4}{3} p \partial_x u, \quad (10.126)$$

$$\frac{\hat{h}_p}{\lambda_0} Q_x q(\kappa) = -Q_x \partial_x u - \Pi_{xx} u \partial_x u - \hat{h}(p + \Pi_{xx}) \partial_x \ln T. \quad (10.127)$$

In these equations \hat{h} is the enthalpy per mass, $\hat{h} = \hat{C}_p T$, and the non-linear factor $q(\kappa)$ is defined, as before, by $q(\kappa) = \sinh \kappa / \kappa$ where κ is defined by (10.26) with $\Delta = 0$. Other symbols are the same as before. Eqs. (10.126) and (10.127) are partial differential equations for velocity component u and temperature T .

Integration of the balance equations (10.123)–(10.125) yields the algebraic equations giving rise to the relations

$$\rho u = M, \quad (10.128)$$

$$(10.129)$$

$$\rho u^2 + p + \Pi_{xx} = P,$$

$$\rho u \left(\mathcal{E} + \frac{1}{2} u^2 \right) + u(p + \Pi_{xx}) + Q_x = Q, \quad (10.130)$$

where M , P , and Q are integration constants with the dimension of momentum per volume, momentum flux per volume, and energy flux per volume, respectively. These equations are also supplemented by the equation of state and the caloric equation of state for monatomic gas

$$p = \rho \mathcal{R} T, \quad \mathcal{E} = \frac{3}{2} \mathcal{R} T. \quad (10.131)$$

10.4.2 Reduced Hydrodynamic Equations

Let us define dimensionless variables

$$\begin{aligned} r &= P\rho M^{-2}, & \theta &= M^2 RTP^{-2}, & \phi &= pP^{-1}, \\ \nu &= MuP^{-1}, & \sigma &= \Pi_{xx}P^{-1}, & \varphi &= Q_xQ^{-1}, \\ \xi &= xl^{-1}, & & & & \alpha = MQP^{-2}. \end{aligned} \quad (10.132)$$

The upstream and downstream variables will be distinguished by subscripts 1 and 2. The length scale is provided by the mean free path l defined with the upstream momentum per volume, $M = \rho_1 u_1$:

$$l = \frac{\eta_{01}}{M}, \quad (10.133)$$

where η_{01} is the upstream Newtonian viscosity at the upstream temperature T_1 . The transport coefficients are reduced with respect to the upstream transport coefficients:

$$\eta^* = \frac{\eta_0}{\eta_{01}}, \quad \lambda^* = \frac{\lambda_0}{\lambda_{01}}. \quad (10.134)$$

With this reduced variables we cast (10.128)–(10.131) in the forms

$$\begin{aligned} \phi &= r\theta, \\ r\nu &= 1, \\ r\nu^2 + \phi + \sigma &= 1, \\ r\nu^3 + 5\phi\nu + 2\sigma\nu + 2\alpha\varphi &= \alpha. \end{aligned} \quad (10.135)$$

From these equations and reduced constitutive equations obtained from (10.126) and (10.127) follow the five evolution equations for the shock wave

of interest⁵

$$\theta = \phi\nu, \quad (10.136)$$

$$1 = \nu + \phi + \sigma, \quad (10.137)$$

$$\alpha = \nu^2 + 5\theta + 2\sigma\nu + 2\alpha\varphi, \quad (10.138)$$

$$\frac{1}{\eta^*} \phi\sigma q(\kappa) = -\frac{4}{3}\sigma\partial_\xi\nu - \frac{4}{3}\phi\partial_\xi\nu, \quad (10.139)$$

$$\frac{\alpha\beta}{\lambda^*} \theta\phi\varphi q(\kappa) = -\alpha\varphi\partial_\xi\nu - \nu\sigma\partial_\xi\nu - \frac{5}{2}\theta(\phi + \sigma)\partial_\xi\ln\theta. \quad (10.140)$$

Here the new dimensionless parameter β is defined by

$$\beta = \frac{N_{\text{Pr}}}{\theta_1} \quad (10.141)$$

with θ_1 denoting the reduced upstream temperature and the Prandtl number is defined with the upstream quantities: $N_{\text{Pr}} = \hat{C}_p T_1 \eta_{01} / \lambda_{01}$. The argument κ in the non-linear factor $q(\kappa)$ is given by the formula

$$\kappa = \frac{4}{(50\gamma_0 c^2 N_M^2)^{1/4}} \left(\frac{\theta}{\theta_1} \right)^{1/4} \frac{1}{\phi\sqrt{\eta^*}} \left(\sigma^2 + \frac{8}{15f\theta} \alpha^2 \varphi^2 \right)^{1/2}, \quad (10.142)$$

where γ_0 is the polytropic ratio and

$$c = \frac{l}{l_h}, \quad f = \frac{2\lambda_{01}}{3\hat{C}_p T_1 \eta_{01}} = \frac{2}{3N_{\text{Pr}}}$$

with l_h denoting the hard sphere mean free path defined by $l_h = 1/\sqrt{2\pi d^2 n}$. Therefore, for hard spheres, $c = 1$, $f = 1$, and $\eta^* = \sqrt{\theta/\theta_1}$. For a Maxwell gas / — 1, $\eta^* = \theta/\theta_1$, and

$$c = \frac{16}{15\sqrt{2\pi} A_2(5)} \sqrt{\frac{\theta_1}{E_d}},$$

where $A_2(5) = 0.432 \dots$ and $E_d = V_m M^2 / 4md^4 P^2$ with V_m denoting the potential parameter of the Maxwell model of interaction [13]. The E_d is a dimensionless Maxwell potential energy at the hypothetical contact point of two hard spheres of radius $d/2$. The dimensionless potential energy E_d

⁵The typographical errors of Ref. [9] in Eq. (8.190) and Eq. (8.191) as well as in the discussion on the reduction scheme given above Eq. (8.192) have been corrected in the following equations.

is set equal to unity by choosing parameter P so that $E_d = 1$, given the choice already made for M . With such a choice of reduction parameters, which are arbitrary, we obtain

$$\kappa = \left(\frac{3\pi}{5} \right)^{1/4} \sqrt{\frac{3A_2(5)}{N_M}} \cdot \frac{1}{\phi\theta^{1/4}} \left(\sigma^2 + \frac{8}{15\theta} \alpha^2 \varphi^2 \right)^{1/2}. \quad (10.143)$$

The parameter α is related to the upstream Mach number through the formula

$$N_M = \sqrt{\frac{1 + \frac{1}{5}\mu}{1 - \frac{1}{3}\mu}}, \quad (10.144)$$

where

$$\mu = \sqrt{25 - 16\alpha}. \quad (10.145)$$

Therefore, expressed in terms of the upstream Mach number defined by the usual formula

$$N_M = \frac{\nu_1}{\sqrt{\gamma_0\theta_1}},$$

the parameter μ is given by

$$\mu = \frac{3(N_M^2 - 1)}{N_M^2 + \frac{3}{5}}.$$

It ranges⁶ from 0 to 3 which occurs at $N_M = \infty$.

10.4.3 Boundary Conditions

To determine the boundary conditions on v , ϕ , and θ , we observe that $\sigma \rightarrow 0$ and $\varphi \rightarrow 0$ as $\xi \rightarrow \pm\infty$ and Eqs. (10.139) and (10.140) are identically satisfied in the limits if v and θ become independent of ξ at the boundaries. Therefore as $\xi \rightarrow \pm\infty$ in the downstream or upstream the following limits are attained by various variables:

$$\sigma, \phi \rightarrow 0, \quad (10.146)$$

$$\theta = \phi\nu, \quad (10.147)$$

$$\nu + \phi = 1, \quad (10.148)$$

$$\nu^2 + 5\theta = \alpha. \quad (10.149)$$

⁶This range of μ also follows from the values of v and θ in (10.150) and (10.151) given below. If $\alpha = 25/16$ clearly $\mu = 0$ and there is no shock wave. For an infinitely strong shock, ϕ must be equal to zero at one end. Therefore $\mu = 3$ for which $\alpha = 1$. It is not possible to have $v = 0$ instead of $\phi = 0$ at one end, since then $\mu = 5$ which implies a negative pressure.

The solutions of (10.147)–(10.149) are

$$\nu = \frac{1}{8} (5 \pm \mu), \quad (10.150)$$

$$\phi = \frac{1}{8} (3 \mp \mu), \quad (10.151)$$

$$\theta = \frac{1}{64} (15 \mp 2\mu - \mu^2). \quad (10.152)$$

The upper sign is for the upstream and the lower sign is for the downstream. These solutions provide the boundary conditions at the upstream and downstream. They also imply the boundary values for the reduced density

$$r = \frac{8}{5 \pm \mu}. \quad (10.153)$$

10.4.4 Differential Equations for Reduced Velocity and Temperature

With the help of Eqs. (10.136)–(10.138) the differential equations (10.139) and (10.140) may be cast into the following forms

$$\frac{d\nu}{d\xi} = \frac{3\theta(\nu^2 - \nu + \theta)}{4\eta^*\nu^2(1-\nu)} q(\kappa), \quad (10.154)$$

$$\begin{aligned} \frac{d\theta}{d\xi} = & -\frac{\theta}{5\nu^2(1-\nu)^2} \left[\frac{\beta\theta\nu(1-\nu)(\alpha + \nu^2 - 2\nu - 3\theta)}{\lambda^*} \right. \\ & \left. + \frac{3(\nu^2 - \nu + \theta)(\alpha - \nu^2 - 5\theta)}{4\eta^*} \right] q(\kappa). \end{aligned} \quad (10.155)$$

Here the argument κ in the non-linear factor $q(\kappa)$ can be expressed in terms of ν and θ by using Eqs. (10.136)–(10.138). These equations are solved subject to the boundary conditions in Eqs. (10.150)–(10.152). The second term on the right hand side of Eq. (10.155) stems from the thermo-viscous effect involving the second and third terms as well as the term $\hat{h}\Pi_{xx}\partial_x \ln T$ in Eq. (10.127). These, together with the second term in Eq. (10.126), are the terms which do not appear in the NSF theory.

To indicate the difference between the evolution equations in the classical (NSF) theory and the present theory and also to facilitate the solution procedure for Eqs. (10.154) and (10.155), the evolution equations are presented

for shock waves in the NSF theory [47]

$$\frac{dv}{d\xi} = \frac{3(\nu^2 - \nu + \theta)}{4\eta^*\nu}, \quad (10.156)$$

$$\frac{d\theta}{d\xi} = -\frac{\theta\beta(\alpha + \nu^2 - 2\nu - 3\theta)}{5\lambda^*}. \quad (10.157)$$

This pair of equations follow from Eqs. (10.136)–(10.140) on replacing Eqs. (10.139) and (10.140) with the Newtonian law of viscosity Eq. (10.33) and the Fourier law of heat conduction Eq. (10.35). We note that for a hard sphere gas the reduced transport coefficients η^* and λ^* depend on θ only:

$$\eta^* = \theta^{1/2}, \quad \lambda^* = \theta^{3/2}. \quad (10.158)$$

10.4.5 Shock Solutions and Shock Structure

The evolution equations (10.154) and (10.155) are quite different from the evolution equations for σ and φ appearing in the moment equation approach of Grad and the system of differential equations studied by Ruggeri [59] for his theorem. The evolution equations in the latter approach were found to fail to produce shock solutions for $N_M \geq 1.65$, as mentioned earlier. The differential equations for σ and φ in the Grad theory, primarily because of the particular closure relations for the higher order moments, inevitably involve their spatial derivatives which give rise to undesirable behavior of the solutions. As will be evident later when the existence of shock solutions is examined, the evolution equations (10.154) and (10.155) do not have such a defect.

Here we will examine the evolution equations in the case of the transport coefficients satisfying Eq. (10.158). For the NSF theory the equation for direction fields is given by

$$\frac{d\nu}{d\theta} = \frac{\omega(\nu^2 - \nu + \theta)}{\nu(3\theta + 2\nu - \nu^2 - \alpha)}, \quad (10.159)$$

where

$$\omega = \frac{15\lambda^*}{4\beta\eta^*\theta}. \quad (10.160)$$

It is independent of θ for the transport coefficients obeying Eq. (10.158). The singularities of the direction field [68] of the evolution equations in the NSF theory are given by

$$\nu^2 - \nu + \theta = 0,$$

$$\nu^2 - 2\nu - 3\theta + \alpha = 0, \quad (10.161)$$

$$\nu = 0.$$

There are three singular points:

$$P_0 : \quad \nu = \frac{1}{8}(5 + \mu), \quad \theta = \frac{1}{64}(15 - 2\mu - \mu^2),$$

$$P_1 : \quad \nu = \frac{1}{8}(5 - \mu), \quad \theta = \frac{1}{64}(15 + 2\mu - \mu^2),$$

$$P_2 : \quad \nu = 0, \quad \theta = 0.$$

Points P_0 and P_1 coincide with the boundary values given in Eqs. (10.150) and (10.152). By making linear stability analysis of the evolution equations, one can show that P_0 is a saddle, P_1 is an unstable node⁷, and P_2 is a spiral. The shock solution is a curve connecting P_0 and P_1 as $\xi \rightarrow \infty$ from $\xi = -\infty$. The shock solution⁸ lies in the domain bounded by the two parabolas in Eq. (10.161) that intersect at P_0 and P_1 . It is possible to show that there exists such a solution for every value of α . Therefore the NSF theory admits shock solutions for all values of the Mach number. We will find that P_0 , P_1 , and P_2 are also the singular points of the evolution equations (10.154) and (10.155) for the present theory.

We now examine the evolution equations (10.154) and (10.155) by using the equation for direction fields:

$$\frac{d\nu}{d\theta} = \frac{-\omega(1-\nu)(\nu^2 - \nu + \theta)}{\left[\nu(1-\nu)(\nu^2 - 2\nu - 3\theta + \alpha) + \frac{3}{4\beta}(\nu^2 - \nu + \theta)(\alpha - \nu^2 - 5\theta)\right]}. \quad (10.162)$$

The singularities of the direction field are given by the equations

$$1 - \nu = 0, \quad (10.163)$$

$$\nu^2 - \nu + \theta = 0, \quad (10.164)$$

$$\nu(1-\nu)(\nu^2 - 2\nu - 3\theta + \alpha) + \frac{3}{4\beta}(\nu^2 - \nu + \theta)(\alpha - \nu^2 - 5\theta) = 0. \quad (10.165)$$

The first two equations are for the loci of zero slopes whereas the last equation is for the loci of infinite slopes. Eq. (10.165) factorizes to the form

$$\frac{15}{4\beta} \left(\theta - B + \sqrt{B^2 + A} \right) \left(\theta - B - \sqrt{B^2 + A} \right) = 0, \quad (10.166)$$

⁷In Ref. [9] the singularity P_1 is said to be a stable node. This is incorrect. P_1 is an unstable node.

⁸A shock wave is described by a set of variables, say, $\{\phi_i\}$, which satisfy the upstream and downstream boundary conditions $\{\phi_{i1}\}$ and $\{\phi_{i2}\}$, respectively. It is said that there exists a shock solution if for $\{\phi_i\} = \{\phi_{i1}\}$ at $x = -\infty$

$$\lim_{x \rightarrow \infty} \{\phi_i\} = \{\phi_{i2}\}.$$

where

$$A = \frac{4\beta}{15}\nu(\nu - 1) \left[\left(1 - \frac{3}{4\beta}\right)\alpha + \left(1 + \frac{3}{4\beta}\right)\nu^2 - 2\nu \right], \quad (10.167)$$

$$B = \frac{2\beta}{5} \left[\left(1 - \frac{1}{\beta}\right)\nu^2 - \left(1 - \frac{5}{4\beta}\right)\nu - \frac{3}{4\beta}\alpha \right]. \quad (10.168)$$

There is an interval of ν where the discriminant $B^2 + A$ becomes negative and thus Eq. (10.166) represents an ellipse or rather a loop whereas it represents a pair of parabolas in the intervals where the discriminant is positive. The intersections of the five curves arising from Eqs. (10.163)–(10.165) are the following five points:

$$P_0 : \nu = \frac{1}{8}(5 + \mu), \quad \theta = \frac{1}{64}(15 - 2\mu - \mu^2),$$

$$P_1 : \nu = \frac{1}{8}(5 - \mu), \quad \theta = \frac{1}{64}(15 + 2\mu - \mu^2),$$

$$P_2 : \nu = 0, \quad \theta = 0,$$

$$P_3 : \nu = 1, \quad \theta = 0,$$

$$P_4 : \nu = 1, \quad \theta = \frac{1}{5}(\alpha - 1).$$

Notice that P_0 , P_1 , and P_2 are exactly the same not only in their values but also in their stability characters (i.e., P_0 is a saddle; P_1 an unstable node; P_2 a spiral) as for the NSF theory. An example of the loci of zero and infinite slopes for both the NSF and the present theory are plotted in the case of $N_M = 1.5$ in Fig. 10.5. The broken curve is the locus in the NSF theory whereas the solid curves are the loci in the present generalized hydrodynamic theory. Both theories share the same parabola (in bold) which intersects the broken line parabola and the ellipse at the same points P_0 and P_1 . This means that both theories share the same boundary conditions at upstream and downstream. In the case of the direction field equation for the present theory there appear additional singularities P_3 and P_4 . It must be noted that the line $\nu = 0$ is neither the locus of zero slopes nor the locus of infinite slopes. Linear analysis shows that P_0 is a saddle and P_1 is an unstable node. We emphasize that these characteristics of P_0 and P_1 are crucial for the existence of shock solutions for the system of differential equations. On the other hand, P_3 is neutral in one direction and unstable in the other, whereas P_4 is an unstable focus. As the Mach number increases, the intersections P_0 , P_3 , and P_4 coalesce at $\nu = 1$, which corresponds to the boundary value for velocity at infinite Mach number. This situation already is almost achieved at $N_M = 10$. The shock solution must connect P_0 and P_1 . The fact that the intersections P_0 and P_1 are shared by both theories and there is an intersection of domains where the slopes are negative strongly indicates that *a shock solution must exist for the evolution*

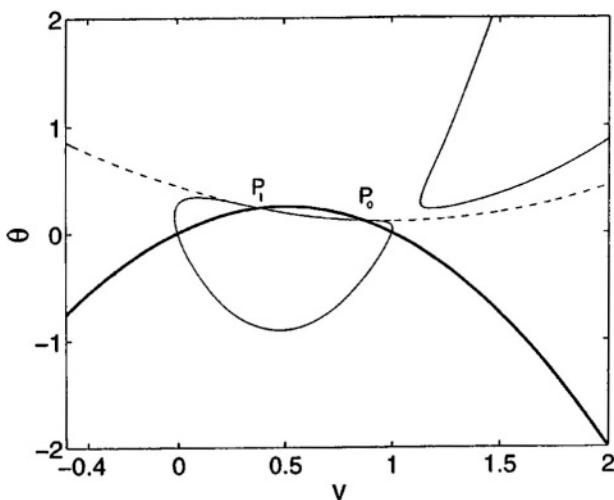


FIGURE 10.5 *Loci of zero and infinite slopes in the direction field for the NSF and generalized hydrodynamic theories. The broken curve is for the NSF theory whereas the light curves are for the generalized hydrodynamic theory. The bold curve is shared by both theories. Both theories also share the same points of intersection P_0 and P_1 . There is a parabola in the upper left-hand corner which does not show up in the scale used for the figure.* (Reproduced with permission from Al-Ghoul, M (1997) Ph D thesis, McGill University)

equations (10.154) and (10.155). Such solutions are demonstrated for the cases of $N_M \leq 10$ in Ref. [51], but they can be shown to exist for all Mach numbers.

In shock wave experiments reported in the literature the shock structures are characterized by the shock width δ defined by the formula

$$\delta = (n_2 - n_1) \left(\frac{dn}{dz} \right)_{\max}^{-1}, \quad (10.169)$$

where n denotes the number density and $(dn/dz)_{\max}$ is the maximum value of the number density derivative which occurs at the shock transition point. This definition of shock width does not most effectively characterize the structure of a shock wave, but is widely used to present experimental data. An example is given for inverse shock widths in Fig. 10.6 where the theoretical shock widths calculated by the evolution equations (10.154) and (10.155) for argon are compared with experimental data [70, 71, 72] over a range of Mach number. A line is drawn through the theoretical results to guide the eyes. A variable hard-sphere model mentioned earlier was used for the calculation with $s = 0.75$. Clearly, the generalized hydrodynamic theory is capable of accounting for the experimental data for the entire range of Mach number studied.

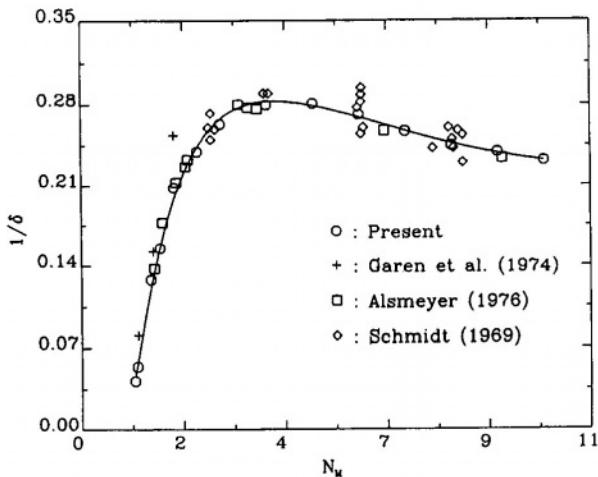


FIGURE 10.6. Inverse shock width vs Mach number in the case of argon (a variable hard sphere model with $s = 0.75$). The experimental data are from Refs. [70, 71, 72]. (Reproduced with permission from Al-Ghoul, M. (1997) Ph.D. thesis, McGill University.)

One can also calculate the calortropy production associated with a shock wave. This gives an idea of how and where energy dissipation occurs in the shock wave. Since the calortropy production for the present problem is given by

$$\Xi_c = k_B g^{-1} \kappa(\Pi, Q) \sinh \kappa(\Pi, Q), \quad (10.170)$$

where $g = \sqrt{m/k_B T}/2n^2 d^2$, we use the reduced calortropy production which may be written

$$\hat{\Xi}_c = \sqrt{\frac{\theta}{\theta_1}} \left(\frac{r_1}{r} \right)^2 \kappa(\sigma, \varphi) \sinh \kappa(\sigma, \varphi). \quad (10.171)$$

If this reduced calortropy production is plotted as a function of z , it is peaked around the shock transition point, and the results of calculation show that the reduced stress and heat flux are also peaked in the same region. Since the calortropy production is a measure of energy dissipation from a useful to a less useful form in an irreversible process, the behavior of reduced calortropy production indicates how the shock wave dissipates its energy and deteriorates. An equally interesting quantity to consider is the global calortropy production which is the sum total of the measure of energy dissipation. It is defined as a reduced integral calortropy production

$$\langle \hat{\Xi}_c \rangle = \int_{-\infty}^{\infty} d\xi \sqrt{\frac{\theta}{\theta_1}} \left(\frac{r_1}{r} \right)^2 \kappa(\sigma, \varphi) \sinh \kappa(\sigma, \varphi). \quad (10.172)$$

In the case of the Maxwell model considered, $\langle \hat{\Xi}_c \rangle$ increases with the Mach number in the following manner:

$$\langle \hat{\Xi}_c \rangle = \langle \hat{\Xi}_c \rangle_0 (N_M - a)^\epsilon, \quad (10.173)$$

where $\langle \hat{\Xi}_c \rangle_0$, a , and ϵ are constants. In the case of the variable hard sphere model used for argon earlier, $a = 0.87$ and $\epsilon = 2.98$ whereas $a = 0.85$ and $\epsilon = 3.14$ for the Maxwell model.

It may now be concluded that the generalized hydrodynamic equations presented represent a continuum hydrodynamic theory of shock waves and structures beyond the range of validity of the NSF theory, at least, for monatomic gases examined. An extension of the NSF theory is long sought after in the field of shock wave phenomena, and the present generalized hydrodynamic theory provides it, at least, for monatomic gases. It thus resolves one of the outstanding problems in gas dynamics for monatomic gases and displays its power to treat non-linear fluid dynamic problems in the regime far removed from equilibrium. In the next subsection we will see that a similar theory generalized for diatomic gases is equally successful for shock waves in such gases.

10.5 Shock Waves in Diatomic Gases

To study flow phenomena in molecular fluids the generalized hydrodynamic equations used for monatomic gases must be suitably extended to the former kind of gases. In a previous chapter we have already introduced to the reader a linearized version of such equations with which we have discussed ultrasonic wave absorption and dispersion in diatomic gases such as nitrogen, hydrogen, deuterium, and deuterium hydride. To carve out thermodynamically consistent generalized hydrodynamic equations for molecular fluids it was found useful to employ the Boltzmann–Curtiss equation [73] for rigid molecules, which yields a full set of evolution equations [74] for relevant macroscopic variables. Experience tells us that the evolution equations derived from kinetic theory do not yield satisfactory results for macroscopic flow problems unless they are suitably fashioned in such a way that they become thermodynamically consistent. For this purpose the notion of thermodynamic consistency that we have developed earlier in this work plays an indispensable role.

In conformity with the general spirit of this monograph we fashion a set of thermodynamically consistent generalized hydrodynamic equations from the kinetically derived evolution equations and then treat them as phenomenological equations, which are applied to practical flow problems and, in the present section, to shock waves in diatomic gases in particular [75, 76]. As we will see, the generalized hydrodynamic equations so constructed yield

not only shock solutions for all Mach numbers but also excellent numerical results in comparison with experiment. In this manner we not only establish a set of continuum mechanics equations for shock wave structures in diatomic gases, but also provide a practicable and, in fact, computationally simpler alternative to the numerical simulation methods for the problem. In this section the same notation as for the case of monatomic gases discussed before will be used unless stated otherwise.

10.5.1 Generalized Hydrodynamic Equations

In the case of molecular fluids the hydrodynamic field variables necessary for an appropriate description of flow in the fluids may consist of density ρ , velocity \mathbf{u} , internal energy \mathcal{E} , heat flux \mathbf{Q} , and stress tensor \mathbf{P} in addition to the energy for the internal degrees of freedom and rotational angular momentum. The internal degrees of freedom evolve on a faster time scale than the other hydrodynamic variables mentioned, unless their relaxation is inhibited for the reason of low temperature or other causes. We will limit the discussion to the case where their relaxation is faster than the hydrodynamic variables and consequently the evolution equations for the internal degrees of freedom may be suppressed.

Therefore in addition to the usual conservation laws of mass, momentum, and the internal energy, there are the constitutive equations for the heat flux and the stress tensor to fully describe shock phenomena in the diatomic gas of interest. For the sake of generality we first present them in general form:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u} \quad (v = 1/\rho), \quad (10.174)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot (\mathbf{\Pi} + \Delta \boldsymbol{\delta} + p \boldsymbol{\delta}), \quad (10.175)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - (\mathbf{\Pi} + \Delta \boldsymbol{\delta} + p \boldsymbol{\delta}) : \nabla \mathbf{u}. \quad (10.176)$$

In the case of diatomic gases the excess normal stress part certainly does not vanish and must be explicitly taken into account because the bulk viscosity of the fluid plays an important role in energy dissipation processes occurring in the flow. The pressure is described by a suitable equation of state, which in the case of dilute gases is still the ideal gas equation of state. The non-conserved variables $\mathbf{\Pi}$, Δ , and \mathbf{Q} are described by their evolution

equations which we propose to have the forms [74, 75]

$$\rho \frac{d\hat{\Pi}}{dt} = -2(p + \Delta)[\nabla \mathbf{u}]^{(2)} - 2[\Pi \cdot \nabla \mathbf{u}]^{(2)} - \frac{p}{\eta_0} \Pi q(\kappa), \quad (10.177)$$

$$\begin{aligned} \rho \frac{d\hat{\mathbf{Q}}}{dt} &= - (p + \Delta) \hat{C}_p T \nabla \ln T + \nabla \cdot (p\delta + \Delta\delta + \Pi) \cdot \hat{\Pi} \\ &\quad - \Pi \cdot \nabla \hat{h} - \mathbf{Q} \cdot \nabla \mathbf{u} - \frac{p\hat{C}_p T}{\lambda_0} \mathbf{Q} q(\kappa), \end{aligned} \quad (10.178)$$

$$\begin{aligned} \rho \frac{d\hat{\Delta}}{dt} &= - \frac{2}{3} p \frac{\hat{C}_{v\text{tot}}}{\hat{C}_v} (\Delta\delta + \Pi) : \nabla \mathbf{u} - \frac{2}{3} \frac{\hat{C}_{v\text{rot}}}{\hat{C}_v} p \nabla \cdot \mathbf{u} \\ &\quad - \frac{2}{3} \frac{\hat{C}_{v\text{rot}}}{\hat{C}_v} p \Delta q(\kappa). \end{aligned} \quad (10.179)$$

The set of field equations for the variables $(\rho, \mathbf{u}, \mathcal{E}, \Pi, \mathbf{Q}, \Delta)$ presented above constitutes the generalized hydrodynamic equations for flows in rigid diatomic gases, subject the assumptions mentioned earlier. The symbols \hat{C}_v and $\hat{C}_{v\text{rot}}$ stand, respectively, for the specific heat and rotational specific heat per mass of the molecule at constant volume and \hat{h} is the enthalpy per mass of the diatomic gas. Except for the evolution equation for Δ and the form of κ in the non-linear factor $q(\kappa)$ as well as the transport coefficients the structures of the remainder of the equations are the same as for the evolution equations for monatomic gases. The shear viscosity, bulk viscosity, and thermal conductivity [13] of the molecular gas are, respectively, denoted by η_0 , η_b , and λ_0 . The non-linear factor $q(\kappa)$ is defined by the same mathematical form as before

$$q(\kappa) = \frac{\sinh \kappa}{\kappa}, \quad (10.180)$$

but κ now has the form

$$\kappa = \frac{(mk_B T)^{1/4}}{\sqrt{2}pd} \left(\frac{1}{2\eta_0} \Pi : \Pi + \frac{\hat{C}_{v\text{rot}}}{\hat{C}_v} \frac{1}{\eta_b} \Delta^2 + \frac{1}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right)^{1/2} \quad (10.181)$$

The notation is the same as before. This is the factor much responsible for the non-linear behavior of the material functions for the gas and also for the non-linear modes of energy dissipation therein, because the calortropy production of the system is given by

$$\Xi_c = k_B g^{-1} \kappa \sinh \kappa \geq 0. \quad (10.182)$$

It is clearly positive for all values of the non-conserved variables in accordance with the second law of thermodynamics. In the sense that the first

and second laws of thermodynamics are satisfied by the generalized hydrodynamic equations presented, the latter are thermodynamically consistent, and so is the theory of shock waves developed here for diatomic fluids. As in the case of other flow problems studied in this work, we postulate the evolution equations for the shock wave problem and then justify their utility *a posteriori* in comparison with experiment.

In the event that in the domain of some physical parameters, such as temperature or the frequency of an external force, where the relaxation times of rotational energy and angular momentum are comparable to the hydrodynamic relaxation times, the rotational energy and angular momentum evolution equations should be added to the set of evolution equations presented earlier. These aspects remain to be studied in the future.

10.5.2 One-Dimensional Shock Wave Equations

As for the shock waves in monatomic gases studied in the previous section, we consider a steady one-dimensional shock wave in the same flow configuration. We assume that flow is in the direction of the x coordinate in a fixed coordinate system. Thus the conservation laws for mass, momentum, and energy are time-independent and have the forms

$$\frac{d}{dx} \rho u = 0, \quad (10.183)$$

$$\frac{d}{dx} (\rho u^2 + p + \Delta + \Pi_{xx}) = 0, \quad (10.184)$$

$$\frac{d}{dx} \left[\rho u \left(\mathcal{E} + \frac{1}{2} u^2 \right) + u (p + \Delta + \Pi_{xx}) + Q_x \right] = 0. \quad (10.185)$$

These equations are the same as for dilute monatomic gases except for the excess normal stress Δ appearing in the momentum and internal energy balance equation. In the adiabatic approximation the non-conserved variables obey the one-dimensional steady state constitutive equations

$$\frac{p}{\eta_0} \Pi_{xx} q(\kappa) + \frac{4}{3} \Pi_{xx} \partial_x u + \frac{4}{3} p \partial_x u + \frac{4}{3} \Delta \partial_x u = 0, \quad (10.186)$$

$$\begin{aligned} & \frac{\hat{h}p}{\lambda_0} Q_x q(\kappa) + Q_x \partial_x u + (\Pi_{xx} + \Delta) u \partial_x u \\ & + \hat{h}(p + \Delta + \Pi_{xx}) \partial_x \ln T = 0, \end{aligned} \quad (10.187)$$

$$\frac{1}{3} p \Delta q(\kappa) + (\Delta + \Pi_{xx} + \frac{1}{3} p) \partial_x u = 0. \quad (10.188)$$

The first two equations are the same as for dilute monatomic gases except for those involving the excess normal stress Δ and the last equation for Δ

is a new feature. Eqs. (10.186)–(10.188) are partial differential equations for velocity component u and temperature T . Because of the adiabatic approximation, there do not appear partial derivatives of Π_{xx} , Δ , and Q_x in these equations. This is an important feature, as is for monatomic gases, which steers the theory away from troubles.

10.5.3 Reduced Hydrodynamic Equations

Integration of the balance equations (10.183)–(10.185) yields

$$\rho u = M, \quad (10.189)$$

$$\rho u^2 + p + \Delta + \Pi_{xx} = P, \quad (10.190)$$

$$2\rho u \left(\mathcal{E} + \frac{1}{2} u^2 \right) + 2u(p + \Delta + \Pi_{xx}) + 2Q_x = Q, \quad (10.191)$$

where M , P , and Q are integration constants with the dimension of momentum per volume, momentum flux per volume, and energy flux per volume, respectively. These equations are also supplemented by the equation of state and the caloric equation of state for the diatomic gas

$$p = \rho \mathcal{R} T, \quad \mathcal{E} = \frac{5}{2} \mathcal{R} T \quad (10.192)$$

in the same notation as before. Because the rigid diatomic gas is dilute there is no contribution to the equation of state from the internal degrees of freedom.

As is the case for monatomic gases, it is convenient to use dimensionless equations. In fact, the same reduction scheme as taken in Eq. (10.132) can be used in addition to the reduced excess normal stress defined by

$$\psi = \Delta P^{-1}. \quad (10.193)$$

The reduced distance $\xi = xl^{-1}$ is defined in the same manner as before with the length scale provided by the mean free path l , which is defined in terms of the upstream speed u_1 by the formula

$$l = \frac{\eta_{01}}{\rho_1 u_1}. \quad (10.194)$$

Henceforth the subscript 1 refers to the upstream whereas the downstream will be designated by subscript 2. In this notation, η_{01} therefore is the upstream Newtonian viscosity at the upstream temperature T_1 . The transport coefficients η_0 , η_b , and λ_0 are reduced with respect to the upstream transport coefficients η_{01} and λ_{01} , respectively:

$$\eta^* = \frac{\eta_0}{\eta_{01}}, \quad \eta_b^* = \frac{\eta_b}{\eta_{01}}, \quad \lambda^* = \frac{\lambda_0}{\lambda_{01}}. \quad (10.195)$$

With these reduced variables Eqs. (10.189)–(10.192) can be cast into the forms

$$\phi = r\theta,$$

$$r\nu = 1,$$

$$r\nu^2 + \phi + \sigma + \psi = 1,$$

$$r\nu^3 + 7\phi\nu + 2\sigma\nu + 2\psi\nu + 2\alpha\varphi = \alpha. \quad (10.196)$$

On reducing constitutive equations (10.186)–(10.188) and using Eq. (10.196) the following six equations can be obtained for six variables ϕ , θ , ν , σ , φ , and ψ :

$$\theta = \phi\nu, \quad (10.197)$$

$$1 = \nu + \phi + \sigma + \psi, \quad (10.198)$$

$$\alpha = \nu^2 + 7\theta + 2\sigma\nu + 2\psi\nu + 2\alpha\varphi, \quad (10.199)$$

$$\phi\sigma q(\kappa) = -\frac{4}{3}\eta^*(\sigma + \psi + \phi)\partial_\xi\nu, \quad (10.200)$$

$$\alpha\beta\theta\varphi\phi q(\kappa) = -\lambda^*(\alpha\varphi + \nu\sigma + \nu\psi)\partial_\xi\nu$$

$$-\frac{7}{2}\lambda^*\theta(\phi + \sigma + \psi)\partial_\xi\ln\theta, \quad (10.201)$$

$$\phi\psi q(\kappa) = -\eta_b^*\left(\sigma + \psi + \frac{1}{3}\phi\right)\partial_\xi\nu. \quad (10.202)$$

Here the dimensionless parameter β has the same form as β in Eq. (10.141) but with the Prandtl number N_{Pr} defined with the upstream quantities:

$$N_{\text{Pr}} = \left(\frac{\widehat{C}_p}{\widehat{C}_v}\right)f_{\text{E}}^{-1}. \quad (10.203)$$

In this formula f_{E} is the Eucken number [13] defined for the diatomic gas as

$$f_{\text{E}} = \frac{5}{2}\frac{\widehat{C}_{v\text{tr}}}{\widehat{C}_v} + \frac{\widehat{C}_{v\text{rot}}}{\widehat{C}_v}, \quad (10.204)$$

where $\widehat{C}_{v\text{tr}}$ is the translational part of \widehat{C}_v . The Eucken number is usually temperature and density dependent. However, we will assume that it is a

constant. Therefore $N_{\text{Pr}} = 14/19$ for a rigid diatomic gas. The appearance of the Eucken number is a new feature to the flow problems of diatomic gases which is not present in the theory for monatomic gases.

The Rayleigh dissipation function κ^2 can be shown to reduce to the form

$$\kappa = N_M \pi^{1/4} \sqrt{\frac{\gamma_0}{2}} \frac{\theta^{1/4}}{\phi \sqrt{\eta^*}} \left(\sigma^2 + \frac{4}{5} \frac{\eta^*}{\eta_b^*} \psi^2 + 2\varepsilon \frac{\eta^*}{\lambda^*} \varphi^2 \right)^{1/2}, \quad (10.205)$$

where the parameter ε is a constant made up of the Mach number

$$\varepsilon = \frac{49}{24} \sqrt{\frac{\pi \gamma_0}{2}} N_M \left[1 - 25 \left(\frac{N_M^2 - 1}{7N_M^2 + 5} \right)^2 \right]. \quad (10.206)$$

Here N_M is the upstream Mach number defined by

$$N_M = \frac{u_1}{\sqrt{\frac{7}{5} \mathcal{R} T_1}}. \quad (10.207)$$

Therefore the parameter a is related to N_M through the formula

$$N_M = \sqrt{\frac{1 + \frac{1}{7}\mu}{1 - \frac{1}{5}\mu}}, \quad (10.208)$$

where

$$\mu = \sqrt{49 - 24\alpha}. \quad (10.209)$$

The parameter μ should be compared with the corresponding parameter for monatomic gases; see Eq. (10.145). The difference in the numerical factors stems from the internal degrees of freedom of a diatomic gas. The value of μ ranges from 0 to 5 at which $N_M = \infty$. Therefore $\alpha = 1$ at $N_M = \infty$.

10.5.4 Boundary Conditions

To determine the boundary conditions on ν , ϕ , and θ we observe that $\sigma \rightarrow 0$, $\psi \rightarrow 0$, and $\varphi \rightarrow 0$ as $\xi \rightarrow \pm\infty$. Eqs. (10.200)-(10.202) are identically satisfied in the limits, if ν and θ become independent of ξ at the boundaries. Therefore, as $\xi \rightarrow \pm\infty$,

$$\sigma, \phi, \psi \rightarrow 0, \quad (10.210)$$

$$\theta = \phi\nu, \quad (10.211)$$

$$\nu + \phi = 1, \quad (10.212)$$

$$\nu^2 + 7\theta = \alpha. \quad (10.213)$$

The solutions of Eqs. (10.211)–(10.213) are

$$\nu = \frac{1}{12} (7 \pm \mu), \quad (10.214)$$

$$\phi = \frac{1}{12} (5 \mp \mu), \quad (10.215)$$

$$\theta = \frac{1}{144} (7 \pm \mu) (5 \mp \mu). \quad (10.216)$$

The upper sign is for the upstream and the lower sign is for the downstream. These solutions provide the boundary conditions at the upstream and the downstream. They also imply that on account of the equation of state the reduced densities at the boundaries are given by

$$r = \frac{12}{7 \pm \mu}. \quad (10.217)$$

10.5.5 Differential Equations for Reduced Velocity and Temperature

With the help of Eqs. (10.197)–(10.201), we can calculate the reduced excess normal stress ψ as a function of ν and θ :

$$\psi = \frac{3\eta_b^* \left(1 - \nu - \frac{2\theta}{3\nu}\right) \left(1 - \nu - \frac{\theta}{\nu}\right)}{\left[4\eta^*(1 - \nu) + 3\eta_b^* \left(1 - \nu - \frac{2\theta}{3\nu}\right)\right]}. \quad (10.218)$$

On elimination of variables other than ν and θ the differential equations (10.200) and (10.201) may be cast into the forms

$$\frac{d\nu}{d\xi} = \frac{3\theta}{4\eta^*\nu^2(1-\nu)}(\nu^2 - \nu + \theta + \nu\psi)q(\kappa), \quad (10.219)$$

$$\begin{aligned} \frac{d\theta}{d\xi} = & -\frac{\theta}{7\nu^2(1-\nu)^2} \left[\frac{3(\alpha - \nu^2 - 7\theta)(\nu^2 - \nu + \theta)}{4\eta^*} \right. \\ & + \frac{\beta\theta\nu(1-\nu)(\alpha + \nu^2 - 5\theta - 2\nu)}{\lambda^*} \\ & \left. + \frac{3(\alpha - \nu^2 - 7\theta)\nu\psi}{4\eta^*} \right] q(\kappa). \end{aligned} \quad (10.220)$$

These evolution equations for reduced velocity and temperature will be solved for shock profiles, subject to the boundary conditions in Eqs. (10.214)–(10.216). These equations generalize the evolution equations for v and θ in

the Navier–Stokes–Fourier theory as will be discussed presently, and also those in the generalized hydrodynamic theory of one-dimensional shock waves for monatomic gases, which we have discussed in the previous subsection.

10.5.6 Shock Solutions of the Evolution Equations

The second term on the right hand side of Eq. (10.220) stems from the thermo-viscous effect involving the second and third terms as well as the term $\hat{h}\Pi_{xx}\partial_x \ln T$ in Eq. (10.187). These, together with the second term in Eq. (10.186), are the terms that do not appear in the Navier–Stokes–Fourier theory [47] of shock waves. To indicate the difference between the evolution equations in the Navier–Stokes–Fourier theory and the present generalized hydrodynamic theory and also to facilitate the solution procedure for Eqs. (10.219) and (10.220), we present the evolution equations for one-dimensional shock waves in a diatomic gas in the Navier–Stokes–Fourier theory

$$\frac{d\nu}{d\xi} = \frac{(\nu^2 - \nu + \theta)}{\left(\frac{4}{3}\eta^* + \eta_b^*\right)\nu}, \quad (10.221)$$

$$\frac{d\theta}{d\xi} = -\frac{\theta\beta(\alpha + \nu^2 - 2\nu - 5\theta)}{7\lambda^*}. \quad (10.222)$$

These equations follow from Eqs. (10.197)–(10.202) if $q(\kappa)$ is set equal to unity and if σ , φ , and ψ are set equal to zero in the second term in Eq. (10.200), in the second and third terms in Eq. (10.201), and in the second term in Eq. (10.202) so that Eqs. (10.200)–(10.202) become, respectively, the Newtonian law of viscosity, the Fourier law of heat conduction, and the bulk viscosity law. Clearly Eqs. (10.221) and (10.222) are special cases of Eqs. (10.219) and (10.220). If the bulk viscosity is set equal to zero Eqs. (10.221) and (10.222) become the evolution equations considered in the Navier–Stokes–Fourier theory for shock waves in monatomic gases [47].

We note that for a rough hard sphere gas the reduced transport coefficients η^* and λ^* depend on θ only as follows [13]:

$$\eta^* = \left(\frac{\theta}{\theta_1}\right)^{1/2}, \quad \lambda^* = \left(\frac{\theta}{\theta_1}\right)^{3/2} \quad (10.223)$$

To facilitate comparison of the present evolution equations with the evolution equations in the literature, we note the relation between the reduced distance ξ in the present work and the reduced distance z in the literature:

$$\xi = \frac{x}{l_1}, \quad (10.224)$$

where l_1 is the upstream mean free path defined with the upstream velocity instead of the upstream sound speed. This relation is important to remember when the shock width is calculated and compared with the literature value.

In the following we examine the evolution equations (10.219) and (10.220) and the existence of shock solutions with the help of singularities of the direction field equation [68]. To this end we will examine the evolution equations in the case of the transport coefficients satisfying Eq. (10.223), which we take for simplicity of the formulas. The same conclusion as for the present model of transport coefficients can be drawn for different temperature dependence for the transport coefficients. In the Navier–Stokes–Fourier theory the direction field equation is given by

$$\frac{d\nu}{d\theta} = - \frac{\omega(\nu^2 - \nu + \theta)}{\nu(\alpha + \nu^2 - 2\nu - 5\theta)}, \quad (10.225)$$

where

$$\omega = \frac{(\frac{4}{3}\eta^* + \eta_b^*)\beta\theta}{7\lambda^*}. \quad (10.226)$$

It is independent of θ for the transport coefficients obeying Eq. (10.223). The singularities of the direction field are given by

$$(\nu^2 - \nu + \theta) = 0,$$

$$\nu(\nu^2 - 2\nu - 5\theta + \alpha) = 0, \quad (10.227)$$

which give rise to three singular points P_0 , P_1 , and P_2 :

$$\begin{aligned} P_0 : \quad & \nu = \frac{1}{12}(7 + \mu), & \theta = \frac{1}{144}(35 - 2\mu - \mu^2), \\ P_1 : \quad & \nu = \frac{1}{12}(7 - \mu), & \theta = \frac{1}{144}(35 + 2\mu - \mu^2), \\ P_2 : \quad & \nu = 0, & \theta = 0. \end{aligned} \quad (10.228)$$

It is interesting that P_0 and P_1 coincide with the boundary values given in Eqs. (10.214) and (10.216). They are also the singular points of the evolution equations (10.221) and (10.222) for the Navier–Stokes–Fourier theory where the derivatives $d\nu/d\xi$ and $d\theta/d\xi$ vanish. The eigenvalues of the linearized governing equations show that PQ is a saddle point, whereas P_1 is an unstable node and P_2 is a spiral. The shock solution is a curve connecting P_0 and P_1 as $\xi \rightarrow \infty$ from $\xi = -\infty$. There exists a unique such solution [47, 55] for every value of a since the aforementioned nature of P_0 and P_1 remains invariant for all Mach numbers. Therefore the Navier–Stokes–Fourier theory admits shock solutions for all values of Mach number in the case of diatomic gases. The problem of the Navier–Stokes–Fourier theory is that it yields too narrow shock widths that incorrectly behave

with regard to the Mach number. This situation is similar to that of shock solutions for monatomic gases.

We now examine the evolution equations (10.219) and (10.220) by using the direction field equation

$$\frac{d\theta}{d\nu} = - \frac{(\alpha - \nu^2 - 7\theta)}{7(1-\nu)} - \frac{\omega' \nu (\alpha + \nu^2 - 5\theta - 2\nu)}{7(\nu^2 - \nu + \theta + \nu\psi)}, \quad (10.229)$$

where

$$\omega' = \frac{4\eta^* \beta \theta}{3\lambda^*}. \quad (10.230)$$

By using Eq. (10.218) for ψ the right hand side of this equation may be written as

$$\begin{aligned} & \frac{(\alpha - \nu^2 - 7\theta)(\nu^2 - \nu + \theta)}{7(1-\nu)(\nu^2 - \nu + \theta)} \\ & + \frac{3\eta_b^* \omega'}{28\eta^*} \cdot \frac{\nu(\alpha + \nu^2 - 5\theta - 2\nu)[4\eta^*(1-\nu) + 3\eta_b^*(1-\nu - 2\theta/3\nu)]}{(1-\nu)(\nu^2 - \nu + \theta)}. \end{aligned}$$

It is interesting to see that the non-linear factor $q(\kappa)$ does not appear in this equation and thus the singularities of the direction field are not affected by the non-linear factor.

The singularities of the direction field are therefore given by the equations

$$(1-\nu)(\nu^2 - \nu + \theta) = 0, \quad (10.231)$$

$$(\alpha - \nu^2 - 7\theta)(\nu^2 - \nu + \theta) + \omega' \nu (1-\nu)(\alpha + \nu^2 - 5\theta - 2\nu) \quad (10.232)$$

$$\times \left[1 - \nu + \frac{3\eta_b^*}{4\eta^*} \left(1 - \nu - \frac{2\theta}{3\nu} \right) \right] = 0.$$

Eq. (10.232) can be written as a product of two factors as follows:

$$\left(A\theta + B + \sqrt{B^2 + AC} \right) \left(A\theta + B - \sqrt{B^2 + AC} \right) = 0, \quad (10.233)$$

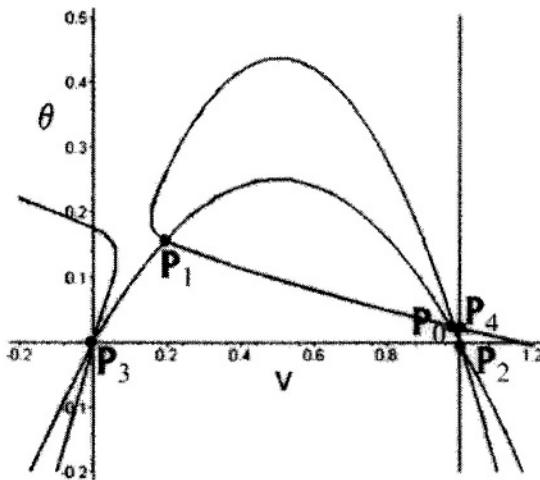


FIGURE 10.7. Loci of the direction field singularities. The singular points P_0 and P_1 are, respectively, a saddle and an unstable node for all Mach numbers. The shock solutions pass through these two singular points. This means such shock solutions exist for all Mach numbers. [Reproduced with permission from (2001) Phys. Rev. E **64**, 046303. Copyright 2001 American Physical Society.]

where

$$A = 7 - \frac{5\eta_b^*}{2\eta^*} \omega'(1 - \nu), \quad (10.234)$$

$$2B = 7\nu(1 - \nu) + \nu^2 - \alpha + \frac{\eta_b^*}{2\eta^*} \omega'(\alpha + \nu^2 - 2\nu) \\ + 5\omega' \left(1 + \frac{3\eta_b^*}{4\eta^*}\right) \nu(1 - \nu)^2, \quad (10.235)$$

$$C = \omega' \left(1 + \frac{3\eta_b^*}{4\eta^*}\right) \nu(1 - \nu)^2 (\alpha + \nu^2 - 2\nu) \\ + \nu(1 - \nu)(\alpha - \nu^2). \quad (10.236)$$

Therefore Eqs. (10.231) and (10.233) indicate that the loci of the infinite and zero slopes of the direction field are either parabolas or ellipses (or closed curves) in the (θ, ν) plane. See Fig. 10.7, where the singular points P_0, \dots, P_4 are indicated. Notice the similarity of this figure to the one for monatomic gases shown earlier in Fig. 10.4.

The solutions of Eqs. (10.231) and (10.232) are obtained as follows. If there holds

$$1 - \nu = 0, \quad (10.237)$$

then

$$(\alpha - 1 - 7\theta)\theta = 0, \quad (10.238)$$

which means

$$\theta = 0, \quad \theta = \frac{1}{7}(\alpha - 1). \quad (10.239)$$

If

$$\nu^2 - \nu + \theta = 0, \quad (10.240)$$

then

$$\nu(1 - \nu)(\alpha + \nu^2 - 5\theta - 2\nu) \left[1 - \nu + \frac{3\eta_b^*}{4\eta^*} \left(1 - \nu - \frac{2\theta}{3\nu} \right) \right] = 0. \quad (10.241)$$

This means

$$\nu = 0, \quad \theta = 0 \quad (10.242)$$

or

$$\alpha + \nu^2 - 5\theta - 2\nu = 0 \quad (10.243)$$

or

$$1 - \nu + \frac{3\eta_b^*}{4\eta^*} \left(1 - \nu - \frac{2\theta}{3\nu} \right) = 0. \quad (10.244)$$

Solving Eqs. (10.240) and (10.243) we find

$$\nu = \frac{7 \pm \sqrt{49 - 24\alpha}}{12}, \quad \theta = \nu - \nu^2. \quad (10.245)$$

The other pair is Eqs. (10.240) and (10.244) from which follows the equation

$$(1 - \nu) + \frac{\eta_b^*}{4\eta^*}(1 - \nu) = 0.$$

This equation is redundant since it yields the solution which was obtained earlier:

$$\nu = 1, \quad \theta = 0.$$

Eqs. (10.231) and (10.232) therefore yield the five singular points P_0, \dots, P_4 given below:

$$\begin{aligned} P_0 : \quad & \nu = \frac{1}{12}(7 + \mu), & \theta = \frac{1}{144}(35 - 2\mu - \mu^2), \\ P_1 : \quad & \nu = \frac{1}{12}(7 - \mu), & \theta = \frac{1}{144}(35 + 2\mu - \mu^2), \\ P_2 : \quad & \nu = 1, & \theta = 0, \\ P_3 : \quad & \nu = 0, & \theta = 0, \\ P_4 : \quad & \nu = 1, & \theta = \frac{1}{7}(\alpha - 1) = \frac{1}{168}(25 - \mu^2). \end{aligned} \quad (10.246)$$

It is useful to compare these singular points with those of the shock wave evolution equations in the case of a vanishing bulk viscosity:

$$\begin{aligned}
 P_0 : \quad & \nu = \frac{1}{8}(5 + \mu), & \theta = \frac{1}{64}(15 - 2\mu - \mu^2), \\
 P_1 : \quad & \nu = \frac{1}{8}(5 - \mu), & \theta = \frac{1}{64}(15 + 2\mu - \mu^2), \\
 P_2 : \quad & \nu = 1, & \theta = 0, \\
 P_3 : \quad & \nu = 0, & \theta = 0, \\
 P_4 : \quad & \nu = 1, & \theta = \frac{1}{5}(\alpha - 1) = \frac{1}{80}(9 - \mu^2).
 \end{aligned} \tag{10.247}$$

The number of singularities and their structures and natures are similar between the two cases, and the similarity indicates that the present case will also admit shock solutions. The linear stability analysis of Eq. (10.229) reveals that P_0 is a saddle and P_1 is an unstable node for all Mach numbers. A shock solution exists whenever one of the singular points is a saddle and the other is an unstable node for a given Mach number. In this case, any trajectory which enters the saddle will slide toward the node, being confined within the region bounded by the curves between P_1 and P_0 , and eventually pass through the node out of the region. The situation is very similar to a heteroclinic connection in the theory of non-linear differential equations [77]. In fact, since $\mu \rightarrow 5$ as $N_M \rightarrow \infty$ it follows that $P_0, P_4 \rightarrow P_2$, whereas P_1 tends to a point other than P_3 . It is significant that P_0 tends toward P_2 ($\nu = 1, \theta = 0$) as $N_M \rightarrow \infty$, because this means that the shock solution exists for all Mach numbers. Therefore the one-dimensional generalized hydrodynamic equations presented describe shock phenomena in one dimension for all Mach numbers, and there remains only the verification of the numerical accuracy of the shock solutions obtained from the differential equations (10.219) and (10.220). It must be remembered that the existence of shock solutions does not guarantee the accuracy of the solutions. The required verification is done in the following.

10.5.7 Comparison with Experiment

The differential equations (10.219) and (10.220) are ordinary and straightforward to solve by using a suitable integrator. They are integrated subject to the boundary conditions specified by Eqs. (10.214)–(10.216) at various Mach numbers. The solutions for the differential equations (10.219) and (10.220) are numerically obtained by using the temperature dependence of reduced transport coefficients in the following forms

$$\eta^* = \left(\frac{\theta}{\theta_1} \right)^{0.78}, \quad \lambda^* = \left(\frac{\theta}{\theta_1} \right)^{1.78}, \quad \eta_b^* = \frac{2}{3}\eta^*. \tag{10.248}$$

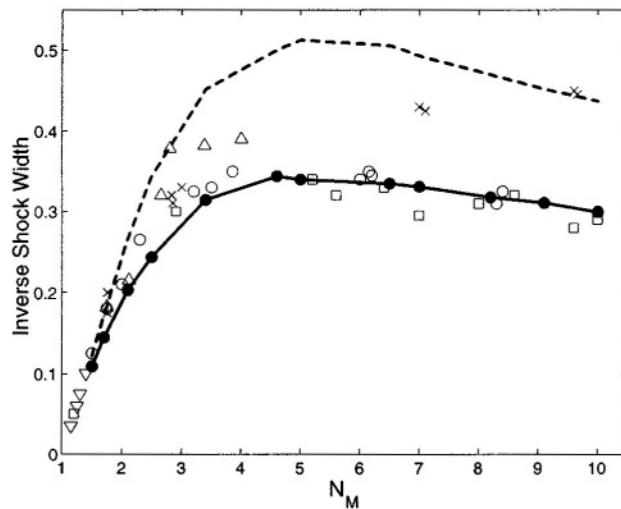


FIGURE 10.8. *Inverse shock width vs Mach number for nitrogen gas. The filled circles (●) are theoretical values, which are connected by the solid curve to guide the eyes. The other symbols are the experimental values by: Greene and Hornig (▽); by Linzer and Hornig (△); by Camac (□); by Robben and Talbot (×); and by Alsmeyer (○). The broken curve is obtained by the Navier–Stokes–Fourier theory.* [Reproduced with permission from (2001) Phys. Rev. E, **64**, 046303. Copyright 2001 American Physical Society.]

These are patterned after the Sutherland model [13] used for monatomic gases interacting through a non-hard sphere potential such as the Lennard–Jones potential. These representations of the temperature dependence of the transport coefficients, generally used in the literature in connection with shock structures, should be taken as empirical relations. The inverse shock width is defined by the usual formula given in Eq. (10.169).

The shock profiles for the reduced stress tensor, heat flux, and excess normal stress are found to be peaked around the transition point where energy dissipates, causing the velocity to diminish rapidly to the downstream value. As is for the case of monatomic gases, a measure of shock structure is given by the inverse shock width, which is plotted as a function of N_M in Fig. 10.8, where the filled circles (●) are the values predicted by the present theory and other symbols are experimental values reported in the literature: (▽) by Greene and Hornig [78]; (△) by Linzer and Hornig [79]; (□) by Camac [80]; (×) by Robben and Talbot [81]; and (○) by Alsmeyer [70]. Beyond $N_M \approx 1.5$ the Navier–Stokes–Fourier theory gives the inverse shock widths much too large compared with experimental values. The theoretical values are computed up to $N_M = 10$, which is the maximum Mach number experimentally studied. As shown in the previous section, the present theory is capable of giving shock solutions for all Mach numbers. The agreement

between the theory and experiment is found to be excellent for the entire range of Mach number examined experimentally. The comparison presented strongly supports the validity and thus the utility of the phenomenological model based on the generalized hydrodynamics for diatomic fluids.

Since the reduced calortropy production,

$$\hat{\Xi}_c = \Xi_c g / k_B = \kappa \sinh \kappa \geq 0, \quad (10.249)$$

is a function of the reduced stress tensors and heat flux, which are peaked at the transition point, it also has a maximum at the transition point. It is found to be positive throughout the range examined, suggesting that the second law of thermodynamics is satisfied in the range studied. Since the present theory ensures the positivity of Ξ_c it is thermodynamically consistent for all Mach numbers. This calortropy production is a measure of energy dissipation from the useful form (a higher velocity) to a less useful form (a lower velocity). Clearly, such energy dissipation occurs in a narrow region around the transition point. The width of the reduced calortropy production is wider than the case for the Navier–Stokes–Fourier theory.

10.6 Two-Dimensional Shock Waves

In the last two subsections the generalized hydrodynamics equations were specialized to a one-dimensional shock wave configuration and successfully applied to shock waves in monatomic and diatomic gases. The one-dimensional treatment was made because of the computational ease provided by the approximation. The success of the one-dimensional model of the generalized hydrodynamic equations is encouraging and assures that a more general treatment of shock and other flow phenomena may be equally accurate. Nevertheless, since a one-dimensional model for shock wave phenomena does not necessarily guarantee the reliability of the general theory from which the one-dimensional model was derived, it is important to test the general theory for higher-dimensional shock waves and flow problems. The high degree of non-linearity of the generalized hydrodynamics equations makes the task of testing them look computationally non-trivial and challenging.

Such a challenge has been successfully met by the recent work of Myong [82, 83, 84], who developed a computational algorithm that is practicable with moderate computational resources and yields accurate results for flow properties. Myong has numerically solved the two-dimensional version of the generalized hydrodynamic equations in the adiabatic approximation, (10.48)–(10.50) and (10.52)–(10.54) for shock waves in the cases of both monatomic and diatomic gases and also for flows incident on a blunt body. When compared with the results by the direct simulation Monte Carlo (DSMC) method or experiment the numerical results obtained are reliable

and robust. The computational details of the two-dimensional studies are referred to the work quoted. Since the generalized hydrodynamic approach requires a fraction of computational cost and additionally provides insights into flow problems of interest as is generally the case for continuum mechanics approaches, it promises to be of considerable potential use in fluid dynamics.

10.7 Flow in Microstructures and Nanostructures

Microstructures or nanostructures are commonly fabricated in scientific and technological fields at present, but flows of fluids in such structures are not very well understood and there is much exploration of continuum mechanical theories to handle them in the literature at present. It is generally known that the classical Navier–Stokes–Fourier equations are not capable of accounting for the flow properties of gases in microstructures [86, 87], if non-slip (or stick) boundary conditions are employed. Even with slip boundary conditions there are some fundamental questions of whether the classical hydrodynamics is appropriate, because the thermodynamic gradients are enormous in the spatial scales of microstructures and thus the systems should be far removed from equilibrium. We know from our studies carried out in the previous chapter and also in this chapter that the classical hydrodynamics must be suitably generalized for systems in such non-equilibrium conditions far removed from equilibrium. Since when the system size gets so small as to be at the microscale or even smaller as to be comparable to the mean free path of fluid molecules, the ratio of the surface area to the characteristic length becomes so large that the surface characteristic begins to play an important role in determining the system properties including the flow properties. Therefore it is essential to take the surface–fluid interaction into consideration in order to properly understand flow properties in addition to the equally essential non-linear thermodynamic force (thermodynamic gradient) dependence of the constitutive relations for the substance of interest.

In proceeding in this manner, we are in fact putting forward the viewpoint that not only the classical hydrodynamic equations—the Navier–Stokes–Fourier equations—must be modified, but also the boundary conditions must be altered from the stick boundary conditions to ‘slip’ boundary conditions if flows in micro or nanostructures are to be studied by a continuum mechanics method. The term slip is used here in deference to the tradition of Maxwell. A more appropriate term would be Langmuir boundary conditions, which have already been used in a previous section, since they explicitly take into account the interactions of surface and fluid molecules. The basic difference of the stick and Langmuir boundary conditions is that

the former conditions correspond to the case of fluid particles completely covering and thus sticking at the surface, whereas the latter conditions correspond to a partial coverage of the surface by the fluid molecules. In the approach taken in this section, the Langmuir boundary conditions are used primarily to take into account the effects of surface on the flow properties, but not to produce a ‘slip’ behavior of flow, which has been the traditional purpose of using slip boundary conditions, as was done by Maxwell [36] for the first time. It will, however, be found that Langmuir boundary conditions tend to contribute significantly to the slip flow behavior, but we emphasize that slip flow can be accounted for without slip boundary conditions, as has been shown in the earlier sections by using non-linear constitutive equations for non-conserved variables.

In this section we argue that the generalized hydrodynamic equations have the necessary features which can be employed for studying flows in microstructures and, perhaps, in nanostructures. Some indirect evidence for this line of argument is already available in the field of charge carrier transport in semiconductors, for which it has been shown that the generalized hydrodynamics can be used for accounting for current–voltage characteristics of semiconductors [85, 88]. In the case of semiconductor charge carriers a dilute electron gas flows in a small semiconductor device subjected to a high field gradient. Therefore the situation is not too different from that of gas flows in a microdevice.

10.7.1 Generalized Hydrodynamic Equations

To be specific we will consider a flow in a rectangular channel of finite length L and width D , aligned along the x axis of the laboratory coordinate system suitably chosen. We will also assume that flow is two-dimensional and steady for the simplicity of the equations involved without being trivial, the temperature is uniform, and the fluid is of a single component. We emphasize that these assumptions can be readily removed and a more complete theory developed on the basis of the generalized hydrodynamic equations presented in Sec. 10.1 in this chapter.

Under the assumptions the constitutive equations in the generalized hydrodynamic equations are for the shear stress and the excess normal stress in the adiabatic approximation. The generalized hydrodynamic equations consist of the mass balance equation and the x and y components of the momentum balance equation

$$\frac{\partial}{\partial x} \rho u_x + \frac{\partial}{\partial y} \rho u_y = 0, \quad (10.250)$$

$$\rho \left(u_x \frac{\partial}{\partial x} + u_y \frac{\partial}{\partial y} \right) u_x = - \frac{\partial p}{\partial x} - \left(\frac{\partial}{\partial x} \Pi_{xx} + \frac{\partial}{\partial y} \Pi_{yx} \right), \quad (10.251)$$

$$\rho \left(u_x \frac{\partial}{\partial x} + u_y \frac{\partial}{\partial y} \right) u_y = - \frac{\partial p}{\partial y} - \left(\frac{\partial}{\partial x} \Pi_{xy} + \frac{\partial}{\partial y} \Pi_{yy} \right), \quad (10.252)$$

which are coupled to the constitutive equations for the primary normal stress difference ($\Pi_{xx} - \Pi_{yy}$) and the shear stress Π_{xy} in the adiabatic approximation [9]

$$\begin{aligned} \frac{p}{\eta_0} q(\kappa) (\Pi_{xx} - \Pi_{yy}) &= -2p \left(\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} \right) + \left(\Pi_{xx} \frac{\partial u_x}{\partial x} - \Pi_{yy} \frac{\partial u_y}{\partial y} \right) \\ &\quad + \Pi_{xy} \left(\frac{\partial u_y}{\partial x} - \frac{\partial u_x}{\partial y} \right), \end{aligned} \quad (10.253)$$

$$\begin{aligned} \frac{p}{\eta_0} q(\kappa) \Pi_{xy} &= -p \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right) - \Pi_{xy} \left(\frac{\partial u_y}{\partial y} + \frac{\partial u_x}{\partial x} \right) \\ &\quad - \Pi_{xx} \frac{\partial u_y}{\partial x} - \Pi_{yy} \frac{\partial u_x}{\partial y}. \end{aligned} \quad (10.254)$$

The $q(\kappa)$ is the non-linear factor made up of the Rayleigh dissipation function, which is by now well recognizable. Nevertheless, we write it out again for the sake of clarity:

$$q(\kappa) = \frac{\sinh \kappa}{\kappa}, \quad \kappa = \frac{\tau}{2\eta_0} \left(\Pi_{xy}^2 + \frac{1}{2} N_1^2 \right)^{1/2} \quad (10.255)$$

with $\tau = (\eta_0 \sqrt{2m_r k_B T})^{1/2} (nk_B T \sigma)^{-1}$. The rest of the notation is standard in this work.

Since the shear stress tensor $\mathbf{\Pi}$ is the traceless and symmetric part of the stress (or pressure) tensor it follows that

$$\Pi_{xx} + \Pi_{yy} = 0. \quad (10.256)$$

With the definition of the primary normal stress difference

$$N_1 = \Pi_{xx} - \Pi_{yy} = 2\Pi_{xx} = -2\Pi_{yy},$$

the constitutive equations can be cast into the forms

$$\begin{aligned} \frac{p}{\eta_0} q(\kappa) N_1 &= -2p \left(\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} \right) \\ &\quad + \Pi_{xy} \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right) + \frac{1}{2} N_1 \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right), \end{aligned} \quad (10.257)$$

$$\begin{aligned} \frac{p}{\eta_0} q(\kappa) \Pi_{xy} &= -\Pi_{xy} \left(\frac{\partial u_y}{\partial y} + \frac{\partial u_x}{\partial x} \right) + \frac{1}{2} N_1 \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right) \\ &\quad - p \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right). \end{aligned} \quad (10.258)$$

Since the ideal gas equation of state holds if the gas is sufficiently dilute gases and since the temperature is uniform the steady state equation of continuity can be written as

$$\frac{\partial}{\partial x} p u_x + \frac{\partial}{\partial y} p u_y = 0. \quad (10.259)$$

In summary, the generalized hydrodynamic equations in the adiabatic approximation for the flow problem are

$$\begin{aligned} \frac{\partial p u_x}{\partial x} + \frac{\partial p u_y}{\partial y} &= 0, \\ \frac{p}{k_B T} \left(u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} \right) &= -\frac{\partial p}{\partial x} - \left(\frac{1}{2} \frac{\partial}{\partial x} N_1 + \frac{\partial}{\partial y} \Pi_{xy} \right), \\ \frac{p}{k_B T} \left(u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} \right) &= -\frac{\partial p}{\partial y} - \left(\frac{\partial}{\partial x} \Pi_{xy} - \frac{1}{2} \frac{\partial}{\partial y} N_1 \right), \\ \frac{p}{\eta_0} q(\kappa) N_1 &= -2p \left(\frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} \right) + \frac{1}{2} N_1 \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) \\ &\quad + \Pi_{xy} \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right), \\ \frac{p}{\eta_0} q(\kappa) \Pi_{xy} &= -p \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right) - \Pi_{xy} \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) \\ &\quad + \frac{1}{2} N_1 \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right). \end{aligned} \quad (10.260)$$

We remark that in the present forms there is nothing in these equations that reminds us of a flow in a microstructure. Some aspects of the system size will manifest themselves when the equations are properly scaled by the characteristic lengths of the system.

10.7.2 Reduced Hydrodynamic Equations

To see the importance of various terms for the microchannel flow under consideration and fashion a model simplified further for the problem, it is convenient to make the evolution equations non-dimensional by using a suitable reduction scheme. To implement such a scheme it is convenient to define some non-dimensional fluid dynamic numbers:

$$\varepsilon = \frac{D}{L}, \quad N_{\text{Re}} = \frac{\rho_e u_e D}{\eta_0}, \quad N_{\text{M}} = \frac{u_e}{\sqrt{\gamma k_B T}}, \quad (10.261)$$

where γ is the polytropic ratio. The N_{Re} and N_{M} are the Reynolds and Mach number, respectively, at the channel entrance and ε is the aspect ratio. Define the mean free path l by the relation

$$\eta_0 = \frac{1}{2} m \rho_e u_e l, \quad (10.262)$$

where η_0 is the Chapman–Enskog shear viscosity for hard spheres [89]. It is given by the formula

$$\eta_0 = \frac{5}{16} \frac{\sqrt{m k_B T}}{\sqrt{\pi} \sigma^2}, \quad (10.263)$$

where m is the mass of the molecule and σ is its diameter. This implies that the mean free path has the expression

$$l = \frac{5}{16\sqrt{2}} \frac{1}{\sigma^2 \rho_e}. \quad (10.264)$$

For this we have taken the reference speed to be the root mean square speed

$$u_e = \sqrt{\frac{8k_B T}{\pi m}}. \quad (10.265)$$

Although the formula for mean free path can vary depending on the formula for viscosity or other transport coefficients used, the present definition is good enough for our purpose here. With the mean free path so determined, the transversal Knudsen number is defined by

$$N_{\text{Kn}} = \frac{l}{D}. \quad (10.266)$$

This suggests that there exists the relation among three fluid dynamic numbers N_{M} , N_{Re} , and N_{Kn} :

$$N_{\text{M}} = \sqrt{\frac{2}{\gamma \pi}} N_{\text{Re}} N_{\text{Kn}} \quad (10.267)$$

and therefore the non-uniformity number N_δ appearing in the Rayleigh dissipation function is related to the Knudsen and Mach, or Reynolds,

numbers by the relations

$$N_\delta = \gamma N_M^2 N_{Re}^{-1} = \frac{2}{\pi} N_{Kn}^2 N_{Re} = \sqrt{\frac{2\gamma}{\pi}} N_M N_{Kn}. \quad (10.268)$$

These are relations of fluid dynamic numbers well known to us by now. Since the non-uniformity number appears in the Rayleigh dissipation function in the generalized hydrodynamic equations, we begin to see the roles of non-dimensional fluid dynamic numbers in the hydrodynamic treatment of microflows.

The variables appearing in the generalized hydrodynamic equations are then reduced to non-dimensional forms in the following manner:

$$\begin{aligned} \xi &= xL^{-1}, & \zeta &= yD^{-1}, \\ u &= u_x/u_e, & v &= u_y/\varepsilon u_e, \\ \phi &= p/p_e, & \psi &= \frac{N_\delta \Pi_{xy}}{(\eta_0 u_e / D)}, & \varphi &= \frac{N_\delta N_1}{(\eta_0 u_e / D)}. \end{aligned} \quad (10.269)$$

Notice that the longitudinal distance is scaled by the channel length L whereas the transversal distance is scaled by the channel width D ; u_e and p_e are, respectively, the speed of flow and the pressure at the channel entrance. It therefore follows that the Rayleigh dissipation function for the flow problem is reducible as follows:

$$\kappa = \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{\phi} \left(\psi^2 + \frac{1}{2} \varphi^2 \right)^{1/2}. \quad (10.270)$$

This suggests that although N_δ does not appear explicitly in this expression for κ , the non-linear factor $q(\kappa)$ exerts influence on the flow as the Reynolds or Mach number and the Knudsen number change locally since the flow condition locally changes rapidly. Of course, in the simple channel flow under consideration such a rapid change in flow condition does not occur, but in a more complex flow configuration such a rapid change cannot be ruled out. The generalized hydrodynamic equations considered here should also apply to such flow configurations.

If the reduction scheme described earlier is used, the generalized hydrodynamic equations for the flow problem are reduced as follows. The reduced equation of continuity and the reduced momentum balance equations are

given by

$$\varepsilon \frac{\partial \phi u}{\partial \xi} + \varepsilon \frac{\partial \phi v}{\partial \zeta} = 0, \quad (10.271)$$

$$\frac{\partial \psi}{\partial \zeta} + \varepsilon \frac{\partial}{\partial \xi} \left(\phi + \frac{1}{2} \varphi \right) + \varepsilon \gamma N_M^2 \phi \left(u \frac{\partial u}{\partial \xi} + v \frac{\partial u}{\partial \zeta} \right) = 0, \quad (10.272)$$

$$\varepsilon \frac{\partial}{\partial \zeta} \left(\phi - \frac{1}{2} \varphi \right) + \varepsilon^2 \frac{\partial \psi}{\partial \xi} + \varepsilon^3 \gamma N_M^2 \phi \left(u \frac{\partial v}{\partial \xi} + v \frac{\partial v}{\partial \zeta} \right) = 0, \quad (10.273)$$

whereas the reduced constitutive equations are given by

$$\begin{aligned} q(\kappa) \psi &= - \left(N_\delta - \frac{2}{\pi} N_{Kn} \frac{\varphi}{\phi} \right) \frac{\partial u}{\partial \zeta} - \frac{4}{\pi} N_{Kn} \varepsilon \frac{\psi}{\phi} \left(\frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \zeta} \right) \\ &\quad - \varepsilon^2 \left(N_\delta + \frac{2}{\pi} N_{Kn} \frac{\varphi}{\phi} \right) \frac{\partial v}{\partial \xi}, \end{aligned} \quad (10.274)$$

$$\begin{aligned} q(\kappa) \varphi &= \frac{4}{\pi} N_{Kn} \frac{\psi}{\phi} \frac{\partial u}{\partial \zeta} - 2\varepsilon N_\delta \left(\frac{\partial u}{\partial \xi} - \frac{\partial v}{\partial \zeta} \right) \\ &\quad + \frac{2}{\pi} N_{Kn} \varepsilon \frac{\varphi}{\phi} \left(\frac{\partial u}{\partial \xi} + \frac{\partial v}{\partial \zeta} \right) - \varepsilon^2 \frac{4}{\pi} N_{Kn} \frac{\psi}{\phi} \frac{\partial v}{\partial \xi}. \end{aligned} \quad (10.275)$$

The solutions of these equations are such that the influx of matter must be equal to the outflux:

$$\int_0^1 d\zeta \rho^* u(\xi, \zeta) |_{\xi=0} = \int_0^1 d\zeta \rho^* u(\xi, \zeta) |_{\xi=1}, \quad (10.276)$$

which, written in another way, is

$$\int_0^1 d\zeta \phi(\xi, \zeta) u(\xi, \zeta) |_{\xi=0} = \int_0^1 d\zeta \phi(\xi, \zeta) u(\xi, \zeta) |_{\xi=1}. \quad (10.277)$$

In Eq. (10.276) ρ^* is the reduced density denoted by $\rho^* = \rho/\rho_e$. By setting

$$f(\xi) = \int_0^1 d\zeta \phi(\xi, \zeta) u(\xi, \zeta), \quad (10.278)$$

we may express the condition (10.277) in the form

$$\frac{df}{d\xi} = 0. \quad (10.279)$$

This provides an equation necessary for determining the pressure distribution in the microchannel. Instead of Eq. (10.279) it is possible to use the

vanishing transversal velocities v —namely, the boundary conditions on v —at the walls, since the fluid cannot penetrate into the wall. On use of the boundary conditions on v at the walls, there arises the differential equation for pressure as the solvability condition. We will use such boundary conditions to calculate the pressure distribution because it is more convenient to use.

The evolution equations (10.271)–(10.275) with κ given by Eq. (10.270) may be solved numerically, subject to suitable boundary conditions, to determine flow characteristics in the channel flow. The evolution equations, however, may be further simplified so that the problem can be reduced to a much simpler form.

10.8 Model Equations for MicroChannel Flow

Eqs. (10.271)–(10.275) indicate the order of the various terms contributing to the flow variables. They also appear to provide some useful insights for even the Prandtl boundary layer theory [32]. For the present flow problem they suggest that since we are interested in creeping flows of a low N_M in a channel with a small aspect ratio, if only the terms of up to $O(\varepsilon)$ and $O(N_M)$ are retained, then the following equations arise for the flow problem

$$\varepsilon\phi \frac{\partial u}{\partial \xi} + u\varepsilon \frac{\partial \phi}{\partial \xi} + \varepsilon\phi \frac{\partial v}{\partial \zeta} + \varepsilon v \frac{\partial \phi}{\partial \zeta} = 0, \quad (10.280)$$

$$\frac{\partial \psi}{\partial \zeta} + \varepsilon \frac{\partial}{\partial \xi} \left(\phi + \frac{1}{2}\varphi \right) = 0, \quad (10.281)$$

$$\varepsilon \frac{\partial}{\partial \zeta} \left(\phi - \frac{1}{2}\varphi \right) = 0, \quad (10.282)$$

$$q(\kappa)\psi = - \left(N_\delta - \frac{2}{\pi} N_{K_B} \frac{\varphi}{\phi} \right) \frac{\partial u}{\partial \zeta}, \quad (10.283)$$

$$q(\kappa)\varphi = 0. \quad (10.284)$$

These equations are rather reminiscent of the flow equations for a rarefied gas flowing in an infinite channel [8] except for the continuity equation and the last equation. Because of Eqs. (10.280) and (10.282) the pressure gradient in the channel is not a constant but varies with ξ , namely, along the channel axis. The set of equations (10.280)–(10.284) is reducible to a single non-linear ordinary differential equation for the reduced pressure as will be shown.

10.8.1 Profile for the Streamwise Velocity

First, the streamwise velocity u can be determined from Eqs. (10.281) and (10.283). For this purpose we observe that Eqs. (10.282) and (10.284) suggest that ϕ depends on ξ only:

$$\phi = \phi(\xi). \quad (10.285)$$

It therefore follows that

$$\varepsilon\phi \frac{\partial u}{\partial \xi} + u\varepsilon \frac{\partial \phi}{\partial \xi} + \varepsilon\phi \frac{\partial v}{\partial \zeta} = 0, \quad (10.286)$$

and the Rayleigh dissipation function is given by the formula

$$\kappa = \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi} (\psi^2)^{1/2} = \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi} |\psi|. \quad (10.287)$$

Consequently from Eq. (10.283) there follows the equation

$$\psi = 2\sqrt{\frac{\gamma}{\pi^{3/2}}} \phi \sinh^{-1} \left(-N_\delta \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi} \frac{\partial u}{\partial \zeta} \right). \quad (10.288)$$

Taking the derivative with respect ζ and using Eq. (10.281) we obtain from Eq. (10.288)

$$\frac{\partial}{\partial \zeta} \sinh^{-1} \left(-N_\delta \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi} \frac{\partial u}{\partial \zeta} \right) = \beta, \quad (10.289)$$

where the positive parameter β is denoted by

$$\beta = -\frac{1}{\mu} \frac{\partial \ln \phi}{\partial \xi}, \quad \mu = \frac{2}{\varepsilon} \sqrt{\frac{\gamma}{\pi^{3/2}}}. \quad (10.290)$$

On integrating with respect to ζ , Eq. (10.289) yields the equation

$$N_\delta \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi} \frac{\partial u}{\partial \zeta} = -\sinh(\beta\zeta + C), \quad (10.291)$$

where C is a constant. Define the abbreviation

$$\alpha = N_\delta \sqrt{\frac{\pi^{3/2}}{\gamma}} \frac{1}{2\phi}. \quad (10.292)$$

Integration of Eq. (10.292) gives the solution for u :

$$\alpha u = -\frac{1}{\beta} \cosh(\beta\zeta + C) + C_1, \quad (10.293)$$

where C_1 is an integration constant. The integration constants are determined by imposing the boundary conditions. We consider two cases of boundary conditions: stick (non-slip) boundary conditions and Langmuir boundary conditions developed in an earlier section. These two different sets of boundary conditions yield different flow profiles. We consider both of them, since the comparison of the flow profiles obtained by the two sets of boundary conditions will make it possible to appreciate the effects of the surface on flows in microsystems.

Stick Boundary Conditions

The stick boundary conditions on u are

$$u(\zeta = 0) = 0, \quad u(\zeta = 1) = 0. \quad (10.294)$$

Upon imposing these boundary conditions on u given in Eq. (10.293) there follow the two algebraic equations for the integration constants

$$\begin{aligned} \beta C_1 &= \cosh C, \\ \beta C_1 &= \cosh(\beta + C). \end{aligned} \quad (10.295)$$

The solutions of these algebraic equations are

$$C = -\frac{\beta}{2}, \quad \beta C_1 = \cosh \frac{\beta}{2}. \quad (10.296)$$

On using these results the solution for u is obtained:

$$u = \frac{1}{\alpha\beta} \left\{ \cosh \frac{\beta}{2} - \cosh \left[\beta \left(\zeta - \frac{1}{2} \right) \right] \right\}. \quad (10.297)$$

It should be noted that α and β still contain ϕ and its derivative $\partial\phi/\partial\xi$. They must be determined to obtain a complete solution for the flow problem of interest.

The midstream velocity u_m is then given by

$$u_m = \frac{1}{\alpha\beta} \left(\cosh \frac{\beta}{2} - 1 \right). \quad (10.298)$$

Therefore it is possible to express the velocity profile in a more insightful form

$$u = u_m \left\{ 1 - \frac{\cosh[\beta(\zeta - \frac{1}{2})] - 1}{\cosh(\beta/2) - 1} \right\}, \quad (10.299)$$

which reduces to the well known Poiseuille formula for u in the limit of small β . The parameter β must be determined by using the pressure distribution. This condition yields a differential equation for ϕ through β , which must be solved to determine the pressure profile. The differential equation for ϕ will be given later.

Langmuir Boundary Conditions

Instead of the stick boundary conditions for which it is presumed that fluid molecules stick on the surface of the walls and cover it fully, the Langmuir boundary conditions can be used for the velocity u in order to incorporate into the flow characteristics the wall–fluid interaction and a partial coverage of the surface by the fluid molecules. The Langmuir boundary conditions for u are

$$u_a = \theta(T) u_w + [1 - \theta(T)] u_l, \quad (10.300)$$

where $u_a = u(\zeta = 0)$ or $u_a = u(\zeta = 1)$, u_w is the wall velocity, u_l is the flow velocity a fraction of a mean free path away from the wall, and $\theta(T)$ is defined by

$$\theta(T, \phi) = \frac{bp}{1 + bp} = \frac{b^* \phi}{1 + b^* \phi} \quad (10.301)$$

with $b^* = b/p_e$ and

$$b = \frac{K}{k_B T}, \quad K = \text{equilibrium constant.} \quad (10.302)$$

The distance away from the wall, at which u_l is evaluated, is a free parameter to be chosen suitably and at that position u_l must be determined self-consistently from the velocity profile, which has been already calculated by solving the generalized hydrodynamic equations. The equilibrium constant in θ may be determined by means of statistical thermodynamics in the manner discussed in Subsec. 10.2.3 by taking into account a surface–gas interaction model. Here T is the wall temperature. The equilibrium constant K depends on the wall temperature and wall–gas interaction parameters. It can be specifically calculated, but for the present discussion it is not essential to know its temperature dependence.

The modified boundary conditions (10.300) alter the velocity profile from that described by Eq. (10.299). Using the boundary conditions (10.300) we find at the wall at $\zeta = 0$

$$\alpha\beta(1 - \theta)u_l = -\cosh C + \beta C_1 \quad (10.303)$$

and at the wall at $\zeta = 1$

$$\alpha\beta(1 - \theta)u_l = -\cosh(\beta + C) + \beta C_1. \quad (10.304)$$

Solving these algebraic equations for C and C_1 , we obtain

$$C = -\frac{\beta}{2}, \quad C_1 = \alpha\beta(1 - \theta)u_l + \cosh \frac{\beta}{2}. \quad (10.305)$$

Therefore the velocity u is given by

$$u = \frac{1}{\alpha\beta} \left\{ \cosh \frac{\beta}{2} - \cosh \left[\beta \left(\zeta - \frac{1}{2} \right) \right] + \alpha\beta(1 - \theta)u_l \right\}, \quad (10.306)$$

which has a term arising from the surface effects in addition to the terms making up the velocity profile in the case of stick boundary conditions.

Let ζ_l denote the distance a fraction of a mean free path away from the wall. Then u_l is self-consistently determined from the velocity profile (10.306):

$$u_l = \frac{1}{\theta\alpha\beta} \left\{ \cosh \frac{\beta}{2} - \cosh \left[\beta \left(\zeta_l - \frac{1}{2} \right) \right] \right\}. \quad (10.307)$$

Since ζ_l is a reduced distance scaled by the channel width D , if ζ_l is on the order of a mean free path then it is $O(N_{Kn})$. Therefore for definiteness of calculation let us choose

$$\zeta_l = \frac{N_{Kn}}{1 + \sigma N_{Kn}}, \quad (10.308)$$

where σ is an adjustable parameter larger than 2. This lower limit of σ is dictated by the fact that the midstream is the maximum distance away from the wall to be taken into account for the situation because of the symmetry of flow in question. This means that for the two walls of the channel

$$\zeta_l - \frac{1}{2} = \pm \frac{1 + (\sigma - 2) N_{Kn}}{2(1 + \sigma N_{Kn})} \quad (10.309)$$

with the + and — signs applying to the walls, respectively, at $\zeta = 1$ and $\zeta = 0$. On use of these values for ζ_l in Eq. (10.307) it follows that for the channel flow

$$u_l = \frac{1}{\theta\alpha\beta} \left\{ \cosh \frac{\beta}{2} - \cosh \left[\beta \frac{1 + (\sigma - 2) N_{Kn}}{2(1 + \sigma N_{Kn})} \right] \right\}. \quad (10.310)$$

In summary, the velocity profile in the Langmuir boundary conditions is given by the formula

$$u = \frac{1}{\alpha\beta} \left\{ \cosh \frac{\beta}{2} - \cosh \left[\beta \left(\zeta - \frac{1}{2} \right) \right] + (\theta^{-1} - 1) u_{kn} \right\}, \quad (10.311)$$

where

$$u_{kn} = \cosh \frac{\beta}{2} - \cosh \left[\beta \frac{1 + (\sigma - 2) N_{Kn}}{2(1 + \sigma N_{Kn})} \right]. \quad (10.312)$$

This velocity profile reduces to that of stick boundary conditions as the fluid molecules fully cover the surface of the walls, that is, as $\theta \rightarrow 1$, and the effects of the walls consequently do not manifest themselves in the limit. However, as θ becomes smaller than unity, the effects of the walls begin to show up. It should be also noted that as β becomes small, the flow profile tends to the Poiseuille velocity profile for the channel flow in the limit of $\theta \rightarrow 1$.

10.8.2 Differential Equation for ϕ

We now derive the pressure equation in using the velocity profile for the Langmuir boundary conditions, which is more general than the stick boundary condition result and can be evidently reduced to the latter in the limit of $\theta \rightarrow 1$. We will derive the pressure equation by using the equation of continuity (10.286).

On substitution of the velocity profile given in Eq. (10.311) into Eq. (10.286), which is rearranged to the form

$$\frac{\partial v}{\partial \zeta} = -\frac{\partial u}{\partial \xi} + \mu u \frac{\partial \beta}{\partial \xi},$$

and changing the independent variable ζ to z defined by

$$z = \zeta - \frac{1}{2}$$

so that the interval $0 \leq \zeta \leq 1$ changes to $-\frac{1}{2} \leq z \leq \frac{1}{2}$ and consequently the symmetry property of the equation becomes more transparent, we obtain the differential equation for the transversal velocity in the form

$$\frac{\partial v(z)}{\partial z} = v_t^0 - \frac{\mu}{\alpha} \cosh \beta z - \frac{\cosh \beta z}{(\alpha \beta)^2} \frac{\partial \alpha \beta}{\partial \xi} + \frac{z \sinh \beta z}{\alpha \beta} \frac{\partial \beta}{\partial \xi}. \quad (10.313)$$

In this equation v_t^0 is defined by

$$v_t^0 = \frac{\cosh(\beta/2) + (\theta^{-1} - 1) u_l}{(\alpha \beta)^2} \frac{\partial \alpha \beta}{\partial \xi} - \frac{\sinh(\beta/2) + 2(\theta^{-1} - 1)(\partial u_l / \partial \beta)}{2 \alpha \beta} \frac{\partial \beta}{\partial \xi} + \frac{\mu}{\alpha} \cosh \frac{\beta}{2}. \quad (10.314)$$

The right hand side of Eq. (10.313) is even with respect to z . This means that

$$v(-z) = -v(z).$$

Integrating Eq. (10.313) over z yields

$$v(z) = V_0 + v_t^0 z - \frac{\mu}{\alpha \beta} \sinh \beta z - \frac{\sinh \beta z}{\beta (\alpha \beta)^2} \frac{\partial \alpha \beta}{\partial \xi} + \frac{\beta z}{\alpha \beta^3} \left(\cosh \beta z - \frac{\sinh \beta z}{\beta z} \right) \frac{\partial \beta}{\partial \xi}, \quad (10.315)$$

where V_0 is the integration constant. Upon imposing the boundary conditions $v = 0$ at $z = \pm \frac{1}{2}$ we find $V_0 = 0$ and, as the solvability condition, the

differential equation for the pressure

$$\begin{aligned} v_t^0 - \frac{2\mu}{\alpha\beta} \sinh \frac{\beta}{2} - \frac{2 \sinh(\beta/2)}{\beta(\alpha\beta)^2} \frac{\partial\alpha\beta}{\partial\xi} \\ + \frac{\beta}{\alpha\beta^3} \left(\cosh \frac{\beta}{2} - \frac{2}{\beta} \sinh \frac{\beta}{2} \right) \frac{\partial\beta}{\partial\xi} = 0, \end{aligned} \quad (10.316)$$

where v_t^0 is given by Eq. (10.314). Since α and β depend on p this is a differential equation for p which describes the pressure distribution along the channel axis. With $V_0 = 0$ deduced from the boundary conditions and v_t^0 given by Eq. (10.314) Eq. (10.315) can be used for calculating the transversal velocity component $v(z)$ of the flow.

By noting that

$$\frac{\partial \ln \theta}{\partial \ln \phi} = 1 - \theta$$

and

$$\frac{1}{\alpha\beta} \frac{\partial\alpha\beta}{\partial\xi} = \mu\beta + \frac{1}{\beta} \frac{\partial\beta}{\partial\xi},$$

we obtain from Eq. (10.316) the differential equation for reduced pressure in the form

$$L_1(\beta) \frac{\partial\beta}{\partial\xi} + \mu\beta^2 L_2(\beta) = 0. \quad (10.317)$$

In this equation the coefficients L_1 and L_2 are defined by the formulas

$$\begin{aligned} L_1 &= \frac{4}{\beta} \sinh \frac{\beta}{2} - 2 \cosh \frac{\beta}{2} + \frac{\beta}{2} \sinh \frac{\beta}{2} \\ &\quad - (\theta^{-1} - 1) u_{kn} + \beta(\theta^{-1} - 1) \frac{\partial u_{kn}}{\partial\beta}, \end{aligned} \quad (10.318)$$

$$L_2 = \frac{4}{\beta} \sinh \frac{\beta}{2} - 2 \cosh \frac{\beta}{2} - (\theta^{-1} - 1) u_{kn}.$$

Eq. (10.317) is the desired differential equation β or ϕ . However, it is highly non-linear and does not appear to be possible to solve in a closed analytical form.

10.8.3 Approximate Pressure Distribution

It appears useful to examine an approximate form for the differential equation (10.317) in order to gain some insights into the pressure distribution predicted by the present theory. For the purpose we will be content with the lowest order approximation. By using the identities

$$\frac{\partial\beta}{\partial\xi} = \frac{1}{2\mu\phi^2} \left(\frac{\partial^2\phi^2}{\partial\xi^2} - 4\phi \frac{\partial^2\phi}{\partial\xi^2} \right)$$

and

$$\frac{\partial}{\partial \xi} \phi \left(\frac{\partial \phi}{\partial \xi} \right)^{-1} = 1 - \phi \left(\frac{\partial \phi}{\partial \xi} \right)^{-2} \frac{\partial^2 \phi}{\partial \xi^2},$$

it is possible to recast Eq. (10.317) into the form

$$\frac{\partial}{\partial \xi} \beta^{-1} = \mu - \frac{\mu}{2\theta} \beta \left[\sinh \frac{\beta}{2} + 2(1-\theta) \frac{\partial u_{kn}}{\partial \beta} \right] L_1^{-1}(\beta). \quad (10.319)$$

This appears to be the most convenient of the forms for the pressure equation to investigate.

Since β is $O(\varepsilon)$ the β -containing terms in Eq. (10.319) may be expanded in power series of β . We thereby obtain the equation

$$\frac{\partial \beta^{-1}}{\partial \xi} = \mu - \frac{6\mu}{(3-\theta)} \frac{\left(1 + \frac{1}{24}\beta^2 + \dots \right)}{\left[1 - \frac{3}{80} \left(\frac{5-\theta}{3-\theta} \right) \beta^2 + \dots \right]}. \quad (10.320)$$

To the lowest order in β for the right hand side, the pressure equation becomes

$$\frac{\partial \beta^{-1}}{\partial \xi} = -\mu \left(\frac{3+\theta}{3-\theta} \right). \quad (10.321)$$

This equation can be easily solved to yield the pressure distribution. On use of the boundary conditions on pressure at the entrance and exit of the channel, there follows the approximate pressure distribution

$$\phi(\xi) = \phi_0 \left\{ 1 - \left[1 - \left(\frac{\phi_1}{\phi_0} \right)^{\frac{3+\theta}{3-\theta}} \right] \xi \right\}^{\frac{3-\theta}{3+\theta}}, \quad (10.322)$$

where ϕ_0 and ϕ_1 are the reduced pressure at the entrance and the exit, respectively. The approximate β corresponding to this pressure distribution is

$$\beta = \frac{1}{\mu} \left(\frac{3-\theta}{3+\theta} \right) \left[1 - \left(\frac{\phi_1}{\phi_0} \right)^{\frac{3+\theta}{3-\theta}} \right] \left\{ 1 - \left[1 - \left(\frac{\phi_1}{\phi_0} \right)^{\frac{3+\theta}{3-\theta}} \right] \xi \right\}^{-1}. \quad (10.323)$$

The reduced flow rate at the exit is given by the value of $f(\xi)$ at the exit, $\xi = 1$. By using Eq. (10.278) we find to the lowest order approximation corresponding to ϕ given in Eq. (10.322) the formula for $f_1 = f(\xi = 1)$:

$$f_1 = \frac{1}{\alpha_1 \beta_1} \left(\cosh \frac{\beta_1}{2} - \frac{2}{\beta_1} \sinh \frac{\beta_1}{2} + c^* N_{Kn} u_{kn} \right), \quad (10.324)$$

for which we have put θ in the following form in terms of N_{Kn} :

$$\theta = \frac{1}{1 + c^* N_{Kn}}. \quad (10.325)$$

The constant parameter c^* is related to the parameter b in Eq. (10.302). It depends on the surface–fluid molecule interaction parameters and temperature of the surface—that is, the wall.

The behavior of ϕ is qualitatively correct in that it is concave downward, and the limiting behavior of f_1 is as follows:

$$\begin{aligned} f_1 &\rightarrow N_{Kn}^{-1} \quad \text{as } N_{Kn} \rightarrow 0, \\ f_1 &\rightarrow N_{Kn} \quad \text{as } N_{Kn} \rightarrow \infty. \end{aligned} \tag{10.326}$$

These limiting behaviors imply that since $f_1 > 0$ there exists a minimum at a positive value of N_{Kn} . In fact, with a reasonable choice of parameters it is possible to show that the minimum occurs around $N_{Kn} \simeq 1$ and thus the present model equations capture the important features of the microchannel flow with regard to the pressure distribution and the Knudsen number dependence of the flowrate; that is, *the Knudsen paradox is resolved* [28, 90, 91, 92] for microchannel flow considered. Clearly, the results presented here with the lowest order solution for the pressure equation can be improved by obtaining a higher order solution or by means of a numerical solution method for the pressure equation. The capability of the model equations having been demonstrated, such an investigation is left to the reader as an exercise.

The pressure distribution obtained can be used in the velocity formulas as well as other flow variables in order to calculate their ξ dependence along the channel. For example, we note that the stress tensor ψ can be readily calculated by means of Eqs. (10.288), (10.322), and (10.323). In the approximation taken here it is given by the formula

$$\psi = 2\sqrt{\frac{\gamma}{\pi^{3/2}}}\phi\beta\left(\zeta - \frac{1}{2}\right) = -\varepsilon\frac{\partial\phi}{\partial\xi}\left(\zeta - \frac{1}{2}\right), \tag{10.327}$$

which satisfies Eq. (10.281). The transversal component of the flow velocity can be similarly calculated from Eq. (10.315).

In this section we have examined a generalized hydrodynamics approach to microchannel flows and thereby have shown that the method should be capable of treating flows in conditions far removed from equilibrium because either N_{Kn} or N_{Re} or their product is large. The non-uniformity parameter N_δ , made up of N_{Kn} and N_{Re} or N_{Kn} and N_M , is the parameter characterizing such flow conditions, and it provides a way to systematically treat the important non-linear dissipation processes in the system. It should be emphasized that non-linear constitutive equations for non-conserved variables and Langmuir boundary conditions are important ingredients of the theory for the microchannel flow considered.

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Variational Principles

In the previous chapters the thermodynamic formalisms have been discussed by means of which the evolution of the local calortropy density or the global calortropy of a system can be calculated, provided that the balance equations are given for mass, momentum, and internal energy in addition to the evolution equations for non-conserved variables, namely, the constitutive equations for the material functions of the substance. Since such evolution equations constitute the field equations of generalized hydrodynamics, the details of the local calortropy density or global calortropy evolution will be described in terms of hydrodynamic field variables of the fluid in space-time, if the generalized hydrodynamic equations are solved for irreversible processes occurring in the system. The calortropy surface thus constructed contains and furnishes the information on its tangents in the thermodynamic space, such as pressure, heat capacity, and the generalized potentials conjugate to the non-conserved variables, p , $\hat{C}_{p\xi}$, $\hat{\mu}_a$ ($1 \leq a \leq r$), and X_{ka} ($1 \leq a \leq r$; $k \geq 1$), which can be generally given in terms of the variables spanning the thermodynamic space \mathfrak{P} .

The extended Gibbs relation indicates formal relations between the calortropy and the aforementioned tangents $(p, \hat{C}_{p\xi}, \hat{\mu}_a, X_{ka} : 1 \leq a \leq r; k \geq 1)$, the set of which will be called the tangent space. However, it is not possible to deduce directly the spatial and temporal evolution of the tangents from the extended Gibbs relation itself, since they are, in fact, contained in, and only accessible through, the solutions of the generalized hydrodynamic equations, which can be obtained if the tangent set is provided as constitutive relations. In other words, the generalized hydrodynamic equa-

tions satisfying the thermodynamic laws make us learn about the local or global calortropy and associated quantities in terms of the variables in the space \mathfrak{P} with the help of the constitutive relations for the tangent set phenomenologically supplied.

Our thoughts in irreversible thermodynamics up to this point have been framed in the thermodynamic space \mathfrak{P} , while treating the tangents to the calortropy surface, or its equilibrium limit the entropy surface, as algebraic constitutive relations phenomenologically postulated. Furthermore, the tangent set made up of the constitutive relations is conferred no particular status other than being just constitutive equations. This viewpoint is rather confining and in fact deprives us of mathematical tools available to mechanics. Here we abandon this viewpoint and extend the space so as to include the thermodynamic space \mathfrak{P} and the elements making up its tangent set as independent variables. This extended space will be denoted by $\mathfrak{T}_{\mathfrak{P}}$. The union of \mathfrak{P} and $\mathfrak{T}_{\mathfrak{P}}$ will be called the ‘thermodynamic phase space’ $\Gamma_T = \mathfrak{P} \cup \mathfrak{T}_{\mathfrak{P}}$. This thermodynamic phase space is underlying the variational principle formulated here.

The variational procedure of starting from the balance equations as well as constitutive equations for the non-conserved variables will be called the ‘downward scheme’ in irreversible thermodynamics. However, it would be convenient to have this procedure in reverse and make the calortropy, calortropy flux, and calortropy production, that is, irreversible thermodynamics, the source of information on the tangent set and generalized hydrodynamics by means of which flows in systems of interest can be studied. This reverse procedure will be called the ‘upward variational scheme’ in irreversible thermodynamics or, simply, the upward scheme.

It may be said that the upward scheme often implies a variational principle of some sort, which starts from a suitable variational functional that compactly summarizes the continuum theory description of flows in a manner consistent with the laws of thermodynamics. From this viewpoint one of the important motivations for studying the downward scheme in irreversible thermodynamics may be said to be in learning about a way to ultimately implement the upward scheme, because it compactly summarizes the macroscopic physics of matter and, more specifically, generalized hydrodynamics with the attendant constitutive relations.

There are variational principles [1, 2] in irreversible thermodynamics known in the literature that should be regarded as restricted variational principles because variations are performed in a restricted sense. A most prominent example would be the variational principle of Onsager [1] for linear processes, which Onsager termed the ‘principle of least dissipation of energy’. Therefore, it is fair to say that, unfortunately, there is as yet no full variational principle, such as we know in mechanics, that is satisfactorily established and furnishes a complete set of equations of motion for a macroscopic dynamic system removed from equilibrium at arbitrary

degree. It would therefore be worthwhile to explore the possibility of some sort of variational principle in theory of irreversible processes.

In a previous chapter the zeroth law of thermodynamics and its extended forms for intensive variables other than temperature have been expressed in mathematical terms. The zeroth law and its equivalents will be simply called the zeroth law in the subsequent discussion. In this chapter we show that if the role of the zeroth law is given an appropriate place in the theory by extending the thermodynamic space to the thermodynamic phase space Γ_T , a variational principle can be formulated¹ without the kind of restriction imposed in the Onsager variational principle. The first important task in the variational method in mind then is to find an appropriate variational functional. For this purpose we will rely on the analogy provided by the d'Alembert principle in mechanics [4].

In this work we have subjected the generalized hydrodynamic equations to the constraint of the second law of thermodynamics so that the resulting continuum theory is consistent with the laws of thermodynamics. This constraint is imposed in the form of a positive calortropy production, which, as the seat of energy dissipation in the system, is the place where the hydrodynamic and material information also reside that is relevant to the energy dissipation modes in the system. In the variational principle explored in this chapter a variational functional is deduced in the downward scheme. The variational functional then can be used in the upward scheme to derive the conservation laws and the constitutive equations, provided that the zeroth law is given the proper status in the variational method. This point is crucial in formulating a variational principle for irreversible thermodynamics without using the restrictions imposed in the variational principles known in the literature on irreversible thermodynamics, such as Onsager's and other authors'.

11.1 Thermodynamic d'Alembert Principle

d'Alembert recast the Newtonian equation of motion in a manner which looks rather trivial, but we know that it underlies a principle and a powerful viewpoint of mechanics. In the d'Alembert principle in mechanics [4] the Newtonian law of motion may be expressed by a variational form

$$\sum_i (\mathbf{F}_i - m_i \mathbf{A}_i) \cdot \delta \mathbf{R}_i = 0, \quad (11.1)$$

¹In a paper with Ichiyanagi [3] a restricted variational principle was investigated. The method used in the paper was limited in its capability because the role of the zeroth law was not clearly understood. In the present chapter we are able to remove the limitations of the restricted variational principle of Eu and Ichiyanagi.

where \mathbf{F}_i is the force impressed on particle i of mass m_i , \mathbf{A}_i is the acceleration (inertial force), and $\delta\mathbf{R}_i$ is the virtual displacement of the position of particle i . d'Alembert called $-m_i\mathbf{A}_i$ the inertial force, and it balances the impressed force \mathbf{F}_i on the body. At first glance this variational equation appears to be a trivial rewriting of the Newtonian equation of motion. However, the power of this trivial rewriting of the Newtonian equation of motion is well recognized in classical mechanics because it endows the classical mechanics with flexibility not accorded to the Newtonian formulation of mechanics. The Lagrange and Hamilton action principles all descend from the d'Alembert principle.

In this section we would like to show that there is an irreversible thermodynamics analog [3] of the d'Alembert principle, which will be called the thermodynamic d'Alembert principle. The well known restricted variational principle of Onsager [1] may be regarded as a variation of the thermodynamic d'Alembert principle, as will be seen in the course of the discussion. We illustrate this point for the case of near-equilibrium processes, for which the constitutive equations are linear.

Let us assume a macroscopic continuum fluid consisting of r components, which do not react. The assumption of no chemical reactions is made for the simplicity of the theory. It is not difficult to remove it. The fluid is assumed to be near equilibrium. For simplicity the external force is assumed to be absent. The system contained in the elementary volume will be called a fluid particle in keeping with the terminology often used in continuum mechanics and also in this work. In the present case of a near-equilibrium thermodynamic continuum system contained in an elementary volume at position \mathbf{r} and time t , the evolution of the fluid particle is assumed to be described by the balance equations of mass, momentum, and internal energy (8.1)–(8.4). The balance equations, therefore, may now be regarded as analogs of the Newtonian equation of motion in the theory of irreversible processes under consideration. Indeed, the momentum balance equation is a generalization of the Newtonian equation of motion in the case of a body subjected to an external stress on the surface.

The thermal, mechanical, and material states of the fluid particle at \mathbf{r} and t are characterized by the local temperature T , the local pressure p , and the local chemical potentials $\hat{\mu}_a$ per mass of species a . These parameters are independent of the mass of the fluid particle and are intensive variables, which are distinct from the variables obeying the aforementioned balance equations, namely, field variables. These intensive variables can be measured, as discussed in a previous chapter, by inserting measuring instruments, such as a thermometer, a manometer, and so on into the elementary volume of interest and letting the elementary volume come into equilibrium with the measuring device with regard to the parameter measured. The spatial and temporal distributions of the intensive variables can be empirically established by measuring them over the whole system and over a time span of interest. In thermodynamics the extensive and intensive variables are stud-

ied together and related to each other through thermodynamic relations furnished by the Gibbs relation.

If the system is in non-equilibrium the distributions of these parameters will evolve toward those of equilibrium. It is therefore possible to formulate a theory of thermal, mechanical, and chemical evolution of the system if it is subjected to virtual variations in temperature, pressure, and chemical potentials and then the system is monitored of its response to the virtual variations in the aforementioned variables.

To simplify the notation we will define the often used symbols:

$$\beta = \frac{1}{T}; \quad \bar{p} = \frac{p}{T}; \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}; \quad \bar{X}_{ka} = \frac{X_{ka}}{T}.$$

The generalized potentials X_{ka} will be used in a later section. The manner in which the system responds to virtual variations in these variables is formulated by using the following variational principle similar to the d'Alembert principle in mechanics. Because the intensive variables are varied, the variational principle used here is the opposite of the Onsager variational principle in which the heat flux is varied while the temperature distribution is fixed. Despite the different viewpoints taken in the two variational principles, the formal results obtained are mostly the same, as will be seen, although the present method yields more than the Onsager variational method because the fluxes are also allowed to vary.

In order to implement the thermodynamic d'Alembert principle in the equilibrium subspace of the thermodynamic phase space Γ_T it is necessary to introduce the evolution equations for the intensive variables which we have earlier referred to as the ‘zeroth law of thermodynamics’:

$$\rho d_t \theta = L^{(\theta)}, \quad (11.2)$$

$$\rho d_t \bar{\mu}_a = L_a^{(\bar{\mu})} \quad (1 \leq a \leq r), \quad (11.3)$$

where θ stands for the intensive variables β and \bar{p} and the terms $L^{(\theta)}$ ($\theta = \beta, \bar{p}$) and $L_a^{(\bar{\mu})}$ on the right are defined by

$$L^{(\beta)} = -\frac{\partial \mathbf{Q}}{\partial \mathcal{E}} \cdot \nabla \beta + \beta \frac{\partial \mathbf{P}}{\partial \mathcal{E}} : \nabla \mathbf{u} + \sum_{a=1}^r \frac{\partial \mathbf{J}_a}{\partial \mathcal{E}} \cdot \nabla \bar{\mu}_a \quad (11.4)$$

$$L^{(\bar{p})} = -\frac{\partial \mathbf{Q}}{\partial v} \cdot \nabla \beta + \beta \frac{\partial \mathbf{P}}{\partial v} : \nabla \mathbf{u} + \sum_{a=1}^r \frac{\partial \mathbf{J}_a}{\partial v} \cdot \nabla \bar{\mu}_a \quad (11.5)$$

$$L_a^{(\bar{\mu})} = \frac{\partial \mathbf{Q}}{\partial c_a} \cdot \nabla \beta - \beta \frac{\partial \mathbf{P}}{\partial c_a} : \nabla \mathbf{u} - \sum_{b=1}^r \frac{\partial \mathbf{J}_b}{\partial c_a} \cdot \nabla \bar{\mu}_b \quad (11.6)$$

These evolution equations empirically state that the intensive variables are driven by the gradients comprising $L^{(\beta)}$, $L^{(\bar{p})}$, and $L_a^{(\bar{\mu})}$. The partial

derivatives multiplied to the gradients are constitutive relations in the linear theory under consideration here.

The thermodynamic variational principle then states that a virtually displaced system evolves in such a way that the following variational form vanishes:

$$\begin{aligned} \mathbb{V}_l = & (\rho d_t \mathcal{E} + \nabla \cdot \mathbf{Q} + \mathbf{P} : \nabla \mathbf{u}) \delta \beta + (\rho d_t v - \nabla \cdot \mathbf{u}) \beta \delta p \\ & - \sum_{a=1}^r (\rho d_t c_a + \nabla \cdot \mathbf{J}_a) \delta \bar{\mu}_a + \sum_{a=1}^r \left(\rho d_t \bar{\mu}_a - L_a^{(\bar{\mu})} \right) \delta c_a \\ & - \left(\rho d_t \bar{p} - L^{(\bar{p})} \right) \delta v - \left(\rho d_t \beta - L^{(\beta)} \right) \delta \mathcal{E} \\ = & 0. \end{aligned} \quad (11.7)$$

Here β is multiplied with the second term to make it dimensionless, as are the other terms. As it stands, it is not evident that there is a monogenic function for the right hand side of this equation.

The fluid momentum balance equation is left out since there is no gradient of a thermodynamic intensive parameter that drives the fluid particles—infinitesimally small packets of the fluid in an elementary volume—to acquire a velocity and thus can be deemed thermodynamically associated with the fluid velocity in non-relativistic thermodynamics. Note that in the Eulerian description of a fluid the motion of the fluid is described in the coordinate system moving at the fluid velocity \mathbf{u} . For this reason the fluid velocity plays no explicit role except for the energy dissipation mechanism in the local thermodynamic description of matter. Therefore the velocity gradient $\nabla \mathbf{u}$ occupies a special status in the theory of irreversible processes, which is different from other gradients such as the temperature, pressure, and concentration gradients, in non-relativistic thermodynamics.

In any case, the variational form (11.7) is sufficient for examining the Onsager variational principle from the viewpoint of the thermodynamic d'Alembert variational principle. Just like the mechanical d'Alembert variational principle (11.1) the thermodynamic d'Alembert variational principle (11.7) appears to be a trivial rewriting of the local conservation laws of mass, energy, and concentrations-as well as the evolution equations for the intensive variables. However, it contains deeper insights. It should be emphasized that $\delta \beta$, $\delta \bar{p}$, $\delta \bar{\mu}_a$, $\delta \mathcal{E}$, δv , and δc_a are not differentials but virtual displacements of the variables, the displacements being reversible. Another important point which must be clearly recognized is that the tangents to the entropy surface β , \bar{p} , and $\bar{\mu}_a$ are endowed the status of variables independent of the variables spanning the equilibrium thermodynamic space. The union of the spaces thus constructed is akin to the phase space in mechanics. We have introduced earlier the concept of thermodynamic phase space. The substantial time derivatives are abbreviated by d_t .

Define the symbols

$$\Omega_l = -\mathbf{Q} \cdot \nabla \delta \beta + \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \delta \bar{\mu}_a + (\mathbf{P} - p\boldsymbol{\delta}) : \nabla \mathbf{u} \delta \beta, \quad (11.8)$$

$$\mathfrak{F}_s = \mathbf{Q} \delta \beta - \sum_{a=1}^r \mathbf{J}_a \delta \bar{\mu}_a. \quad (11.9)$$

We remark that the right hand side of these equations is not a Pfaffian differential form in the equilibrium thermodynamic space and, as they stand, Ω_l and \mathfrak{F}_s are merely the symbols for the right hand side in each equation; they do not mean differentials of functions in the equilibrium thermodynamic space.

Then the variational form (11.7) can be recast into the form

$$\begin{aligned} \mathbb{V}_l &= \rho \left(\delta \beta d_t \mathcal{E} + \delta \bar{p} d_t v - \sum_{a=1}^r \delta \bar{\mu}_a d_t c_a \right) + \nabla \cdot \mathfrak{F}_s - \Omega_l \\ &\quad - \left(\rho d_t \beta - L^{(\beta)} \right) \delta \mathcal{E} - \left(\rho d_t \bar{p} - L^{(\bar{p})} \right) \delta v + \sum_{a=1}^r \left(\rho d_t \bar{\mu}_a - L_a^{(\bar{\mu})} \right) \delta c_a \\ &= 0. \end{aligned} \quad (11.10)$$

We will consider an integral of this form in space-time:

$$\delta I_l \equiv \int d^4x \mathbb{V}_l(x) = 0, \quad (11.11)$$

where $d^4x = dt dx dy dz = dt dr$ in the Cartesian coordinate system. The time integral is from $t = t''$ to $t = t'$ whereas the space integrals are confined to the volume V in which the system is contained. By taking an integral form of the thermodynamic d'Alembert principle we are making a slight departure from the original form of the principle, and this departure is akin to what the Lagrange principle makes from the d'Alembert principle in mechanics. This departure gives a mathematical advantage over the variational form (11.10). To proceed further from this equation let us examine the terms in the integral (11.11). For example,

$$\begin{aligned} \int d^4x \rho \delta \beta d_t \mathcal{E} &= \int_V dr \int_{t''}^{t'} dt \rho \delta \beta d_t \mathcal{E} \\ &= \int_V dr \int_{t''}^{t'} dt \rho [\delta(\beta d_t \mathcal{E}) - \beta d_t \delta \mathcal{E}] \\ &= \int d^4x \rho [\delta(\beta d_t \mathcal{E}) + \delta \mathcal{E} d_t \beta], \end{aligned} \quad (11.12)$$

where the second term in the third line is the result of integration by parts over time. It should be noted that ρd_t must be regarded as a single operator in performing integration by parts as a shortcut for performing integration by parts separately in time and space. Application of the same procedure to other terms with regards to time and space integrals puts Eq. (11.10) in the form

$$\begin{aligned} \delta I_l = & \int d^4x \delta(\rho d_t \mathcal{S} + \nabla \cdot \mathfrak{J}_s - \mathfrak{D}_l) + \int d^4x (\delta \mathbf{Q} \cdot \nabla \beta + L^{(\beta)} \delta \mathcal{E}) \\ & + \int d^4x (L^{(\bar{P})} \delta v - \beta \delta \mathbf{P} : \nabla \mathbf{u}) - \sum_{a=1}^r \int d^4x (\delta c_a L_a^{(\bar{\mu})} + \delta \mathbf{J}_a \cdot \nabla \bar{\mu}_a) \\ = & 0, \end{aligned} \quad (11.13)$$

where $d_t \mathcal{S}$ is given by the local equilibrium Gibbs relation

$$d_t \mathcal{S} = \beta d_t \mathcal{E} + \bar{P} d_t v - \sum_{a=1}^r \bar{\mu}_a d_t c_a \quad (11.14)$$

and \mathfrak{J}_s and \mathfrak{D}_l are, respectively, the entropy flux and the linear irreversible thermodynamics form of the entropy production. They are, respectively, defined by

$$\mathfrak{J}_s = \beta \mathbf{Q} - \sum_{a=1}^r \bar{\mu}_a \mathbf{J}_a, \quad (11.15)$$

$$\mathfrak{D}_l = -\mathbf{Q} \cdot \nabla \beta + \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \bar{\mu}_a + \beta (\mathbf{P} - p \boldsymbol{\delta}) : \nabla \mathbf{u}. \quad (11.16)$$

It should be recognized that \mathfrak{D}_l and \mathfrak{J}_s are not integrals of the variational forms Ω_l and \mathfrak{F}_s in Eqs. (11.8) and (11.9), which are not monogenic. Because they are not monogenic the integrands in the second, third, and fourth integrals on the right hand side of Eq. (11.13) have arisen. Owing to the absence of the monogenicity of the aforementioned quantities restrictions of either fixed gradients of intensive variables or fixed fluxes must be imposed in the Onsager variational principle.

Since the thermodynamic space considered here is limited to the conserved variables \mathcal{E} , v , and c_a , the variables \mathbf{Q} , \mathbf{P} , and \mathbf{J}_a are dependent variables. Therefore the variations of the latter may be expressed in terms

of the variations of the conserved variables:

$$\begin{aligned}\delta \mathbf{Q} &= \frac{\partial \mathbf{Q}}{\partial \mathcal{E}} \delta \mathcal{E} + \frac{\partial \mathbf{Q}}{\partial v} \delta v + \sum_{a=1}^r \frac{\partial \mathbf{Q}}{\partial c_a} \delta c_a, \\ \delta \mathbf{P} &= \frac{\partial \mathbf{P}}{\partial \mathcal{E}} \delta \mathcal{E} + \frac{\partial \mathbf{P}}{\partial v} \delta v + \sum_{a=1}^r \frac{\partial \mathbf{P}}{\partial c_a} \delta c_a, \\ \delta \mathbf{J}_a &= \frac{\partial \mathbf{J}_a}{\partial \mathcal{E}} \delta \mathcal{E} + \frac{\partial \mathbf{J}_a}{\partial v} \delta v + \sum_{b=1}^r \frac{\partial \mathbf{J}_a}{\partial c_b} \delta c_b.\end{aligned}\quad (11.17)$$

On inserting these expansions into Eq. (11.13) and rearranging the terms, we find that the second, third, and fourth integrals taken all together vanish, and obtain

$$\begin{aligned}\delta I_l &= \int d^4x \delta(\rho d_t \mathcal{S} + \nabla \cdot \mathbf{J}_s - \mathcal{D}_l) \\ &= 0.\end{aligned}\quad (11.18)$$

In other words, there exists a variational functional \mathfrak{L} such that

$$\mathbb{V}_l = \delta \mathfrak{L} \quad (11.19)$$

or in the integral form the variational functional

$$I = \int d^4x \mathfrak{L}_l, \quad (11.20)$$

where

$$\mathfrak{L} = \rho d_t \mathcal{S} + \nabla \cdot \mathbf{J}_s - \mathcal{D}_l. \quad (11.21)$$

The thermodynamic system evolves in the equilibrium thermodynamic phase space such that I is an extremum, that is,

$$\delta I_l = \int d^4x \delta \mathfrak{L}_l = 0. \quad (11.22)$$

The necessary and sufficient conditions for this to hold are the evolution equations for the thermodynamic phase space variables for equilibrium, namely, $(\mathcal{E}, v, c_a, \beta, \bar{p}, \bar{\mu}_a : 1 \leq a \leq r) \in \Gamma_T$. We recognize these equations are the local equations that describe the evolution of the internal energy, specific volume, mass fractions and their conjugate variables, temperature, pressure, and chemical potentials, when the system is displaced from equilibrium at which $d_t \beta = d_t \bar{p} = d_t \bar{\mu}_a = 0$ ($1 \leq a \leq r$) Therefore Eqs. (11.2)

and (11.3) with $L^{(\theta)}$ ($\theta = \beta, \bar{p}$) and $L_a^{(\bar{\mu})}$ defined, respectively, by Eqs. (11.4)–(11.6) are the local dynamics forms of the zeroth law of thermodynamics for the intensive variables, and the system reaches thermodynamic equilibrium as the time and spatial derivatives of β , \bar{p} , and $\bar{\mu}_a$ vanish in the course of time. The variational functional \mathfrak{L} thus contains the information on the balance equations and the evolution equations for the constitutive parameters β , \bar{p} , and $\bar{\mu}_a$, namely, the zeroth law of thermodynamics in dynamical form.

The variational principle of Onsager starts with the variational functional \mathfrak{L}_l , but because there are absent the conditions (11.2)–(11.6) or equivalents thereof, his variational principle is of necessity restricted by the conditions of fixed temperature distribution and so on. By starting from the thermodynamic d'Alembert principle in integral form—a thermodynamic Lagrange principle—and extending the space to Γ_T we have been able to remove the restriction imposed in the restricted variational principle of Onsager. However, the variational principle is limited to linear irreversible processes in the formulation given in the present section.

The variational functional \mathfrak{L}_l can be expressed in another form if there exists a positive semi-definite function \mathfrak{R} of the variables of the equilibrium subspace $(\mathcal{E}, v, c_a, \beta, \bar{p}, \bar{\mu}_a : 1 \leq a \leq r)$ of Γ_T such that

$$\rho d_t \mathcal{S} + \nabla \cdot \mathfrak{J}_s = \mathfrak{R}. \quad (11.23)$$

The positivity of \mathfrak{R} is a local form of the second law of thermodynamics. Upon using this entropy balance equation the variation functional I_l can be expressed in the form

$$I_l = \int d^4x (\mathfrak{R} - \mathfrak{D}_l) \quad (11.24)$$

and the system evolves along the path extremizing this variation function, namely,

$$\delta I_l = \int d^4x \delta (\mathfrak{R} - \mathfrak{D}_l) = 0. \quad (11.25)$$

The significance of this form will be seen in the following section.

11.2 Thermodynamic Lagrangian for Linear Processes

For the discussion of a variational principle and the thermodynamic Lagrangian for linear irreversible processes in this section it is convenient to simplify the notation. Let us denote the intensive variables β , $-\hat{\mu}_a$, and the velocity components u_x , u_y , and u_z by x_q ($q \geq 1$) and the Cartesian

component of ∇ by ∂_j . Thus the spatial derivatives of β , $-\hat{\mu}_a$, and u_x , u_y , and u_z will be denoted by $\partial_j x_q$. We summarize these definitions below:

$$\nabla_j \beta = \partial_j x_p, \quad \nabla_j \hat{\mu}_a = -\partial_j x_q, \quad \nabla_j u_i = \partial_j x_s, \quad (11.26)$$

where the subscripts i and j denote x , y , and z , whereas the subscripts p , q , and s are ordered upward beginning from 1 according to the ordering made for the set $(\beta, -\hat{\mu}_a, u_x, u_y, u_z)$. The variable conjugate to $\partial_j x_q$ will be denoted by F_q^j . The definitions of F_q^j are summarized in the following:

$$F_p^j = Q_j, \quad F_q^j = J_{aj}, \quad F_s^j = \beta(P_{ji} - p\delta_{ij}), \quad (11.27)$$

where the subscripts p , q , and s run over the range appropriate for the ordering of the intensive variables. It should be noted that, for example, Q_j is conjugate to $\nabla_j \beta$, J_{aj} to $-\nabla_j \hat{\mu}_a$, and $\beta(P_{ji} - p\delta_{ij})$ to $\nabla_j u_i$ in this scheme of ordering.

Consider the quadratic form

$$L_D = \frac{1}{2} \partial_j x_p \partial_j x_q R^{qp}, \quad (11.28a)$$

for which the Einstein convention is used for repeated indices and R^{qp} are constant phenomenological coefficients which are symmetric in accordance with the Onsager reciprocal relations:

$$R^{qp} = R^{pq}. \quad (11.29)$$

We may regard L_D as a thermodynamic Lagrangian and define the ‘momentum’ conjugate to x_q by the derivative

$$F_q^j = \frac{\partial L_D}{\partial(\partial_j x_q)}. \quad (11.30)$$

It then follows that

$$F_q^j = \partial_j x_p R^{qp}. \quad (11.31)$$

Substitution of this result into Eq. (11.28a) yields L_D in the bilinear form

$$L_D = \frac{1}{2} F_q^j \partial_j x_q \quad (11.32)$$

and

$$\mathfrak{D}_l = -2L_D = -F_q^j \partial_j x_q. \quad (11.33)$$

Denoting the inverse of matrix (R^{qp}) by (M_{pq}) so that

$$M_{sq} R^{qp} = \delta_{sp} \quad (11.34)$$

we define the quadratic form—the Rayleigh dissipation function [5]

$$\mathfrak{R}_l = M_{pq} F_q^j F_p^j. \quad (11.35)$$

It then follows that

$$L_D = \frac{1}{2} \mathfrak{R}_l. \quad (11.36)$$

The Rayleigh dissipation function is positive, provided that the matrix M is positive, which we assume to be the case. Then the entropy balance equation consistent with the second law of thermodynamics may be given by

$$\rho d_t S + \nabla \cdot \mathfrak{J}_s = \mathfrak{R}_l, \quad (11.37)$$

where $\mathfrak{R}_l \geq 0$. It should be emphasized that S is the local equilibrium entropy. Eq. (11.37) implies that the variational principle (11.22) derived earlier may be written as

$$\int d^4x \delta (\mathfrak{R}_l - \mathfrak{D}_l) = 0, \quad (11.38)$$

which is simply the variational principle used by Gyarmati [2]. If \mathfrak{R} in Eq. (11.25) is identified with \mathfrak{R}_l then the variational principle (11.38) coincides with the variational principle (11.25) derived from the thermodynamic d'Alembert principle. This shows that the integral form of the thermodynamic d'Alembert principle which we have discussed in the previous section is the precursor to the restricted variational principle of Onsager and that of Gyarmati, at least, for irreversible processes near equilibrium.

11.3 Generalized Treatment

It is now possible to generalize the thermodynamic d'Alembert principle in the spirit of generalized thermodynamics; in other words, the equilibrium thermodynamic space spanned by the conserved variables and their conjugate variables is extended to include the non-conserved variables and their conjugate variables in addition to the variables spanning the equilibrium thermodynamic space considered up to this point in this chapter. In this section we consider the full thermodynamic space for generalized thermodynamics and the associated thermodynamic phase space Γ_T .

11.3.1 Downward Scheme

The thermodynamic d'Alembert principle is now given a generalized treatment in the full thermodynamic space \mathfrak{P} , namely, the downward scheme is implemented in the thermodynamic space or, more precisely, in the thermodynamic phase space that is extended to include the non-conserved variables and the conjugate generalized potentials. We add as constraints the constitutive equations for non-conserved variables to the set of balance equations for mass, concentrations, and internal energy considered in the case of near-equilibrium processes in the previous section of this chapter

as well as the evolution equations for the intensive variables conjugate to the variables in \mathfrak{P} . The ‘zeroth law of thermodynamics’ is expressed by the evolution equations²

$$\rho d_t \phi = M^{(\phi)} \quad (\phi = \beta, \bar{p}), \quad (11.39)$$

$$\rho d_t \bar{\mu}_a = M_a^{(\bar{\mu})} \quad (1 \leq a \leq r), \quad (11.40)$$

$$\rho d_t \bar{X}_{ka} = M_{ka}^{(\bar{X})} \quad (1 \leq a \leq r; k \geq 1), \quad (11.41)$$

where the terms $M^{(\phi)}$ ($\phi = \beta, \bar{p}$), $M_a^{(\bar{\mu})}$, $M_{ka}^{(\bar{X})}$ on the right are defined by

$$M^{(\beta)} = - \sum_{a=1}^r \sum_{k \geq 1} \bar{X}_{ka} \frac{\delta (\mathcal{Z}_{ka} + \Lambda_{ka})}{\delta \mathcal{E}}, \quad (11.42)$$

$$M^{(\bar{p})} = \beta \frac{\delta p}{\delta v} \nabla \cdot \mathbf{u} - \sum_{a=1}^r \sum_{k \geq 1} \bar{X}_{ka} \frac{\delta (\mathcal{Z}_{ka} + \Lambda_{ka})}{\delta v}, \quad (11.43)$$

$$M_a^{(\bar{\mu})} = \sum_{b=1}^r \sum_{k \geq 1} \bar{X}_{kb} \frac{\delta (\mathcal{Z}_{kb} + \Lambda_{kb})}{\delta c_b}, \quad (11.44)$$

$$M_{ka}^{(\bar{X})} = \Theta_{ka} - \sum_{b=1}^r \sum_{l \geq 1} \left[\frac{\delta \psi_{lb}}{\delta \hat{\Phi}_{ka}} \cdot \nabla \bar{X}_{lb} + \bar{X}_{lb} \frac{\delta (\mathcal{Z}_{lb} + \Lambda_{lb})}{\delta \hat{\Phi}_{lb}} \right]. \quad (11.45)$$

with Θ_{ka} denoting the sum of products of partial derivatives of \mathbf{Q} , \mathbf{P} , and \mathbf{J}_a and the spatial gradients of β , \mathbf{u} , and $\bar{\mu}_a$

$$\Theta_{ka} = - \frac{\partial \mathbf{Q}}{\partial \hat{\Phi}_{ka}} \cdot \nabla \beta + \beta \frac{\partial \mathbf{P}}{\partial \hat{\Phi}_{ka}} : \nabla \mathbf{u} + \frac{\partial \mathbf{J}_a}{\partial \hat{\Phi}_{ka}} \cdot \nabla \bar{\mu}_a. \quad (11.46)$$

These equations generalize to non-linear processes the evolution equations for the intensive variables conjugate to the variables in the thermodynamic space \mathfrak{P} , which we have referred to as the zeroth law of thermodynamics. Thus as a generalization of the thermodynamic d'Alembert principle considered for linear irreversible processes we have the d'Alembert

²In a recent paper [6] Gambar, Martinas, and Markus apply Hamilton's principle to irreversible thermodynamics and obtain a set of evolution equations for intensive variables. Their equations, however, are not the same as the evolution equations presented below.

principle in generalized thermodynamics

$$\begin{aligned}
 \mathbb{V} = & (\rho d_t \mathcal{E} + \nabla \cdot \mathbf{Q} + \mathbf{P} : \nabla \mathbf{u}) \delta \beta + \left(\rho \frac{dv}{dt} - \nabla \cdot \mathbf{u} \right) \delta \tilde{p} \\
 & - \sum_{a=1}^r \left(\rho \frac{dc_a}{dt} + \nabla \cdot \mathbf{J}_a \right) \delta \bar{\mu}_a \\
 & + \sum_{a=1}^r \sum_{k \geq 1} \left(\rho \frac{d\hat{\Phi}_a}{dt} + \nabla \psi_{ka} - \mathcal{Z}_{ka} - \Lambda_{ka} \right) \delta \bar{X}_{ka} \\
 & - \left(\rho d_t \beta - M^{(\beta)} \right) \delta \mathcal{E} - \left(\rho d_t v - M^{(\tilde{p})} \right) \delta v \\
 & + \sum_{a=1}^r \left(\rho d_t c_a - M_a^{(\bar{\mu})} \right) \delta c_a - \sum_{a=1}^r \sum_{k \geq 1} \left(\rho d_t \bar{X}_{ka} - M_{ka}^{(\bar{X})} \right) \delta \hat{\Phi}_a \\
 = & 0. \tag{11.47}
 \end{aligned}$$

The integral form for this is

$$\delta I = \int d^4x \mathbb{V}(x) = 0. \tag{11.48}$$

Proceeding in the same manner as in Sec. 11.1 and with the definitions of various quantities

$$\mathfrak{J}_c = \beta \mathbf{Q} - \sum_{a=1}^r \bar{\mu}_a \mathbf{J}_a + \sum_{a=1}^r \sum_{k>1} \bar{X}_{ka} \psi_{ka}, \tag{11.49}$$

$$\begin{aligned}
 \Xi_l = & \mathbf{Q} \cdot \nabla \beta - \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \bar{\mu}_a - \beta (\mathbf{P} - p\delta) : \nabla \mathbf{u} \\
 & + \sum_{a=1}^r \sum_{k \geq 1} \psi_{ka} \cdot \nabla \bar{X}_{ka}, \tag{11.50}
 \end{aligned}$$

$$\Lambda = \sum_{a=1}^r \sum_{k \geq 1} \bar{X}_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}), \tag{11.51}$$

we obtain δI in the form

$$\begin{aligned}
 \delta I = & \int d^4x \delta \left(\rho d_t \hat{\Psi} + \nabla \cdot \mathfrak{J}_c - \Xi_l - \Lambda \right) \\
 = & 0. \tag{11.52}
 \end{aligned}$$

This result suggests that there exists a variational functional \mathfrak{L} such that

$$\mathbb{V} = \delta \mathfrak{L}, \quad (11.53)$$

where

$$\mathfrak{L} = \rho d_t \hat{\Psi} + \nabla \cdot \mathbf{J}_c - \Xi_l - \Lambda. \quad (11.54)$$

Thus the irreversible process evolves such that the variational functional

$$I = \int d^4x \mathfrak{L} \quad (11.55)$$

is an extremum. That is,

$$\delta I = \int d^4x \delta \mathfrak{L} = 0. \quad (11.56)$$

If there exists a positive semi-definite function $\Xi \geq 0$ in the thermodynamic phase space such that

$$\rho d_t \hat{\Psi} + \nabla \cdot \mathbf{J}_c = \Xi,$$

then the variational principle can be written as

$$\delta I = \int d^4x \delta (\Xi - \Xi_l - \Lambda) = 0. \quad (11.58)$$

This generalizes the variational principle derived for linear irreversible processes discussed in Sec. 11.1.

It is useful to make a remark about the evolution equations for the intensive variables presented earlier and, in particular, their right hand sides, Eqs. (11.42)–(11.45). We note that the functional derivatives of \mathbf{Q} , $\mathbf{\Pi}$, Δ , and \mathbf{J}_a with respect to the conserved variables vanish, namely,

$$\frac{\delta \mathbf{Q}}{\delta \mathcal{E}} = \frac{\delta \mathbf{\Pi}}{\delta v} = \frac{\delta \Delta}{\delta v} = \frac{\delta \mathbf{J}_a}{\delta c_a} = 0, \quad (11.59)$$

because \mathcal{E} , \mathbf{Q} , \mathbf{J}_a , c_a , and so on are independent variables in the space Γ_T . Therefore the term Θ_{ka} defined by Eq. (11.46) will contribute only for those of $\hat{\Phi}_{ka}$ corresponding to \mathbf{Q} , $\mathbf{\Pi}$, Δ , or \mathbf{J}_a . The evolution equations (11.39)–(11.41) for the intensive variables with $M^{(\phi)}$ ($\phi = \beta, \bar{p}$), $M_a^{(\bar{\mu})}$, and $M_{ka}^{(\bar{X})}$ defined, respectively, by Eqs. (11.42)–(11.45) determine the evolution of the intensive variables in space-time when the system is displaced from equilibrium, and the system reaches equilibrium as their time and spatial derivatives vanish. Inasmuch as the calortropy balance equation describes the mode of energy dissipation arising from irreversible processes in the system, this variational principle specifies the processes of least energy dissipation. It should be noted that the integrand in the variational functional was, in fact, the local calortropy balance equation which has been used in

the local theory of irreversible processes in the previous chapters in this work. This variational principle in the upward scheme, as will be discussed, gives rise to the balance equations and the constitutive equations as well as the local forms of the zeroth law of thermodynamics for the intensive variables.

11.3.2 Upward Scheme

We now verify whether this variational principle gives rise to the balance and constitutive equations as well as the zeroth law of thermodynamics, given the extended Gibbs relation and the definitions of Ξ_l and Γ ; see Eq. (11.50) and (11.51). This upward scheme can be implemented by extremizing the variational functional (11.55) with the help of the calortropy differential

$$\begin{aligned} d_t \hat{\Psi} &= T^{-1} \left[d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right] \\ &\equiv \sum_{q \geq 1} x_q d_t y_q. \end{aligned} \quad (11.60)$$

Here we observe, incidentally, that it is possible to regard $\rho d_t y_q$ as \dot{y}_q , namely, the velocity of y_q conjugate to x_q .

Since there has been no approximation or assumption made to arrive at the variational principle (11.56), it is clear that the procedure can be traced back exactly and we will get the desired equations mentioned earlier.

If the extended Gibbs relation is used in the variational integral (11.56), it may be written in a form a little more familiar to us:

$$\delta I = \int d^4x \delta \left(\sum_{q \geq 1} x_q \rho d_t y_q + \nabla \cdot \mathfrak{J}_c - \Xi_l - \Lambda \right) = 0. \quad (11.61)$$

It is interesting to note that with the interpretation of $\rho d_t y_q$ as \dot{y}_q given earlier the terms

$$\sum_{q \geq 1} x_q \dot{y}_q - \Xi_l - \Lambda$$

look reminiscent of those making up the Lagrangian in mechanics, provided that $\Xi_l + \Lambda$ is interpreted as a ‘potential energy’ in the thermodynamic space. The divergence term in Eq. (11.61) does not contribute to the integral if the variations at the boundaries are required to vanish. On varying the rest of the terms it is straightforward to verify that the upward procedure gives rise to the balance equations for the conserved variables

and the constitutive equations for the non-conserved variables as well as the zeroth law equations for x_q . In implementing this procedure Λ should be varied with regards to the variables in the space \mathfrak{P} . Removal of this restriction would require suitable modifications of the balance equations, but the physical reason for the assumption is that the intensive variables reach the equilibrium state on a faster time scale than the thermodynamic variables of the space \mathfrak{P} so that they may be regarded as fixed as far as Λ is concerned. Of course, this is the situation we are dealing with in irreversible thermodynamics, in which the evolution of the thermodynamic variables of the space \mathfrak{P} is the principal interest, given the local values of intensive variables. Under this condition the upward scheme provides the entire set of evolution equations for the variables in the thermodynamic phase space:

$$\rho d_t v - \nabla \cdot \mathbf{u} = 0, \quad (11.62)$$

$$\rho d_t c_a + \nabla \cdot \mathbf{J}_a = 0, \quad (11.63)$$

$$\rho d_t \mathcal{E} + \nabla \cdot \mathbf{Q} + \mathbf{P} : \nabla \mathbf{u} = 0, \quad (11.64)$$

$$\rho d_t \hat{\Phi}_a + \nabla \cdot \psi_{ka} - \mathcal{Z}_{ka} - \Lambda_{ka} = 0, \quad (11.65)$$

together with Eqs. (11.39)–(11.45) except for the momentum balance equation, which does not play an explicit role in non-relativistic irreversible thermodynamics. In the sense that the generalized hydrodynamic equations (11.62)–(11.65) and Eqs. (11.39)–(11.45) are contained in the variational functional \mathfrak{L} , which consists of the calortropy and associated quantities \mathfrak{J}_c , Ξ_l , and Λ , the calortropy, calortropy flux, and calortropy production may be regarded as the information storage for the system under consideration. In acquiring such information storage lies the ultimate motivation for studying thermodynamic theory of irreversible processes.

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12

Contact Form in Thermodynamics

In his textbook [1] on thermodynamics H. Callen discusses a possibility of studying thermodynamics in terms of tangents to the entropy surface in the equilibrium thermodynamic Gibbs space. These tangents give rise to the constitutive relations for the system of interest and, as such, contain all the constitutive information on the system. In 1973 R. Hermann [2] realized this idea in a mathematically concrete form by making these tangents the contact elements to a $(2n + 1)$ -dimensional contact manifold M with the thermodynamic space as an n -dimensional base space E_n . The idea of Hermann in studying classical thermodynamics from the viewpoint of contact space structure can be implemented if a vector field X_f is constructed from a real-valued function f defined on the contact manifold M with coordinates specified by the extensive and intensive thermodynamic variables appearing in the equilibrium Gibbs relation. In particular, when f vanishes on a Legendre submanifold S of M (an integral manifold closely associated with the Gibbs relation in thermodynamics) the orbits of X_f can be regarded as a thermodynamic process on S in the contact space corresponding to the thermodynamic variable space. The Lie derivative associated with the vector field is the generator of contact transformations and describes the evolution of the contact form in the manifold. In this section¹ we take some examples to show that they display some of thermo-

¹The material in this section is based on the unpublished manuscript entitled ‘On the Contact Form in Thermodynamics’ prepared jointly with M. Chen in May, 1995. The aforementioned theory was formulated on the basis of local generalized hydrodynamics in the case of irreversible processes, which in retrospect was inappropriate. In the present

dynamic information for the system, given the choice made for the function f . Since this function basically contains the constitutive information about the thermodynamic system, constructing it amounts, in effect, to finding the solution of the thermodynamics of the system in hand. Therefore, its construction is not trivial. We give three examples—an ideal gas, a van der Waals gas with a constant heat capacity, and a general case—for the function f . The first two examples clearly show that the orbit equations are indeed thermodynamic constitutive equations or the Gibbs relation. The third example recovers all the formal aspects of thermodynamics including the Gibbs–Duhem equation as the integrability condition [3] of the Gibbs relation in the Legendre submanifold. We thereby show that the function f indeed can represent realistic thermodynamic systems and serve as the thermodynamic information storage. The third example giving rise to the general formal structure of thermodynamics, albeit incapable of delivering the constitutive relations, is particularly relevant to irreversible systems since it seems to suggest a variational functional, and a similar functional indeed can be constructed for irreversible processes. Later we apply the same idea to a non-equilibrium van der Waals fluid subjected to shearing in plane Couette flow geometry. Again, it is possible to show that the orbit equations are constitutive equations for the non-equilibrium fluid. When they are integrated in the Legendre submanifold, there follow the nonequilibrium caloric equation of state and the non-equilibrium equation of state, both of which generalize the equilibrium counterparts for the van der Waals fluid to non-equilibrium. Both constitutive equations contain the shear stress among the variables. We discuss some physical aspects of the results obtained for the constitutive equations.

12.1 Vector Field

In thermodynamics the basic equation is the equilibrium Gibbs equation

$$dS_e = A_\alpha d\phi^\alpha, \quad (12.1)$$

where S_e is the (Clausius) entropy, ϕ^α are the extensive variables such as internal energy, volume, mole numbers, and so on, and A_α are the conjugate variables to the extensive variables ϕ^α ; they may be T^{-1} , p/T , and $-\mu_i/T$ where T , p , and μ_i are temperature, pressure, and chemical potentials of species i , respectively. Here the Einstein summation convention is used for the repeated indices (subscripts or superscripts). The conjugate variables A_α represent the constitutive information on the system and must be empirically supplied. Let $(q^0, q^\alpha, p_\alpha; \alpha = 1, 2, \dots, n)$ be the coordinate

version the theory is formulated for global irreversible processes, which do not require local generalized hydrodynamic equations and their solutions.

system of the contact manifold M whose contact structure is specified by the one-form :

$$\Theta = dq^0 - p_\alpha dq^\alpha. \quad (12.2)$$

According to Hermann [2] the Gibbs relation (12.1) is exactly the zero of the contact form Θ . Consider a regular map Φ from the base space E_n with coordinates $(q^\alpha; \alpha = 1, 2, \dots, n)$ to the graph space $\mathfrak{G} = E_n \times \mathfrak{N}$ defined by [4]

$$q^0 = g(\phi^\alpha), \quad q^\alpha = \phi^\alpha.$$

Extend Φ to a map of E_n into M by requiring $\Phi^*\Theta = 0$ where Φ^* is the pull back map induced by Φ . Then $dS_e = dq^0 = p_\alpha dq^\alpha$ and hence $p_\alpha = \partial q^0 / \partial q^\alpha = A_\alpha$.

We now consider a 1-parameter group of mappings from M into M that preserves the contact structure of M . This 1-parameter group of contact transformations is generated by a vector field X on the tangent space TM by the condition

$$\mathcal{L}_X \Theta = \lambda \Theta, \quad (12.3)$$

where \mathcal{L}_X is the Lie derivative associated with X and λ is a non-vanishing function of $(q^0, q^\alpha, p_\alpha)$ defined on M . Here $\mathcal{L}_X \Theta$, the Lie derivative of Θ with respect to X , is computed by the formula [4]

$$\mathcal{L}_X \Theta = X \lrcorner d\Theta + d(X \lrcorner \Theta) \quad (12.4)$$

with \lrcorner denoting the pulling down operation (linear functional). Such a vector field X satisfying (12.3) is called an isovector field. The Lie derivative is defined in terms of pull back exponential operator $\exp(tX)^*$ corresponding to the vector field X . This Lie derivative is the generator of contact transformations in M . The contact structure of M specified by Θ is preserved along the orbits (flows) of X generated by the contact transformation. Let X be given by

$$X = v^0 \partial_0 + v^\alpha \partial_\alpha + v_\beta \partial^\beta, \quad (12.5)$$

where $\partial_0 = \partial/\partial q^0$, $\partial_\alpha = \partial/\partial q^\alpha$, $\partial^\beta = \partial/\partial p_\beta$, and v^0, v^α , and v_β are functions of $(q^0, q^\alpha, p_\alpha)$ defined on M . These functions are to be determined in terms of a function f of $(q^0, q^\alpha, p_\alpha)$. To determine the isovector field X we make use of the condition (12.3). Since $d\Theta = -dp_\alpha \wedge dq^\alpha$, it is easy to calculate that

$$X \lrcorner d\Theta \equiv \langle X, d\Theta \rangle = v^\alpha dp_\alpha - v_\beta dq^\beta$$

and

$$d(X \lrcorner \Theta) = dv^0 - d(p_\beta v^\beta).$$

By using these results in (12.4) for $\mathcal{L}_X\Theta$ and combining the result with (12.3), we find the following set of equations

$$\begin{aligned}\lambda &= \partial_0 v^0 - p_\alpha \partial_0 v^\alpha, \\ -\lambda p_\alpha &= \partial_\alpha v^0 - p_\beta \partial_\alpha v^\beta - v_\alpha, \\ 0 &= \partial^\alpha v^0 - p_\beta \partial^\alpha v^\beta.\end{aligned}\tag{12.6}$$

This set of equations gives rise to the conclusion that there exists an arbitrary function f of q^0, q^α , and p_α on M which defines the vector field X :

$$\begin{aligned}v^0 &= f - p_\alpha \partial^\alpha f, \\ v_\alpha &= \partial_\alpha f + p_\alpha \partial_0 f, \\ v^\alpha &= -\partial^\alpha f.\end{aligned}\tag{12.7}$$

By (12.3) $\lambda = \partial_0 f$. Hence to every scalar-valued function f defined on M , there exists a corresponding vector field $X_f = v^0 \partial_\alpha + v^\alpha \partial_\alpha + v_\alpha \partial^\alpha$ such that the contact structure of M is preserved along the orbits of X . The orbit equations of motion corresponding to the vector field X are given by

$$\frac{dq^0}{dt} = f - p_\alpha \partial^\alpha f,\tag{12.8}$$

$$\frac{dp_\alpha}{dt} = \partial_\alpha f + p_\alpha \partial_0 f,\tag{12.9}$$

$$\frac{dq^\alpha}{dt} = -\partial^\alpha f.\tag{12.10}$$

Here $1 \leq \alpha \leq n$.

A Legendre submanifold \mathcal{S} of the contact manifold M with the contact structure given by the one-form $\Theta = dq^0 - p_\alpha dq^\alpha$ is the graph space $\mathfrak{G} = \{(q^0, q^\alpha, p_\alpha) \in M \mid q^0 = g(q^\alpha), p_\alpha = \partial^\alpha g\}$. For example, the entropy surface S_e (the integral submanifold of the Gibbs relation) is a Legendre submanifold of M with $\Theta = dS_e - A_\alpha d\phi^\alpha$. Since $X_f \lrcorner df = f \partial_0 f$, X_f is tangent to \mathcal{S} if f vanishes on S . In that case, the orbits of X_f can be integrated as a thermodynamic process on the Legendre surface.

12.2 Examples in Equilibrium Thermodynamics

12.2.1 Ideal Gas Thermodynamics

Let us consider a mole of an ideal monatomic gas in the Gibbs space (base space E_n) with coordinates ($q^1 = E, q^2 = V$). Let M be a contact manifold with coordinates $(q^0, q^1, q^2, p_1, p_2)$. The contact structure of M is specified by $\Theta = dq^0 - p_\alpha dq^\alpha$. Suppose Φ is a mapping from E_n to $E_n \times \mathfrak{R}$ defined by $q^\alpha = q^\alpha, \alpha = 1, 2, q^0 = S_e(q^\alpha)$ where S_e is the Clausius entropy of the system. Extend Φ from E_n into M by requiring $\Phi^*\Theta = 0$. Then $p_1 = (\partial S_e / \partial q^1) = T^{-1}$ and $p_2 = (\partial S_e / \partial q^2) = pT^{-1}$. We now choose f as follows:

$$f = q^0 + R \ln(p_1^{3/2} p_2), \quad (12.11)$$

where R is the gas constant. Substituting this f into the orbital equations (12.8)-(12.9) and solving them under the initial conditions

$$\begin{aligned} E(0) &= \frac{3R}{2p_1(0)}, \\ V(0) &= \frac{R}{p_2(0)}, \end{aligned} \quad (12.12)$$

$$S_e(0) = -R \ln[p_1^{3/2}(0)p_2(0)],$$

where $E(0) = q^1(0), V(0) = q^2(0)$, and $S_e(0) = q^0(0)$, we obtain

$$pV = RT, \quad (12.13)$$

$$E = \frac{3}{2}RT, \quad (12.14)$$

$$S_e = -R \ln \left(p_1^{3/2} p_2 \right). \quad (12.15)$$

On elimination of p_1 and p_2 the entropy S_e can be written as

$$S_e = R \ln \left[\left(\frac{E}{C_v} \right)^{3/2} \frac{V}{R} \right]. \quad (12.16)$$

Here $C_v = 3R/2$. This form of entropy contains all the thermodynamic information on the ideal gas since it generates T and p by differentiation, that is, (12.13) and (12.14), respectively. Note that these derivatives are tangents to the Legendre submanifold. Thus, we see that the Legendre submanifold annihilates the function f and the vector field X_f is tangent

to the Legendre submanifold. We note that the contact transformation in this case is isobaric since $p_1/p_2 = p_1(0)/p_2(0)$ as follows from the orbit equations for p_α . It is useful to remark that the same thermodynamic results as given above can be obtained if f is taken

$$f = q^0 - R \ln \left[\left(\frac{q^1}{C_v} \right)^{3/2} \frac{q^2}{R} \right] \quad (12.17)$$

instead of the form given in (12.11). In this case the contact transformation is isochoric. Therefore it may be said that the two forms of f in (12.11) and (12.17) represent two different surfaces in the contact manifold for the system which intersect on the Legendre submanifold to produce the same thermodynamics of the system.

12.2.2 van der Waals Fluid

Next we consider the case that gives rise to the thermodynamics of a van der Waals gas with a constant heat capacity. As in Subsec. 12.2.1, $q^0 = S_e(q^1, q^2) = S_e(E, V)$, $p_1 = T^{-1} = (\partial S_e / \partial q^1)$, and $p_2 = pT^{-1} = (\partial S_e / \partial q^2)$. We then choose

$$f = q^0 - R \ln \left[\left(\frac{q^1 + a/q^2}{C_v} \right)^{3/2} \frac{(q^2 - b)}{R} \right], \quad (12.18)$$

where a and b are constants and $C_v = 3R/2$. Using this function in the orbit equations and integrating them, we find

$$E = E(0), \quad V = V(0), \quad (12.19)$$

and with the initial conditions

$$p_1(0) = \frac{3R}{2} [E(0) + a/V(0)]^{-1},$$

$$p_2(0) = \frac{R}{V(0) - b} - \frac{3R}{2} \frac{aV(0)^{-2}}{E(0) + a/V(0)},$$

$$S_e(0) = R \ln \left[\left(\frac{E(0) + a/V(0)}{C_v} \right)^{3/2} \frac{(V(0) - b)}{R} \right],$$

the following results for p_1 , p_2 , and S_e can be obtained:

$$p_1 = (E + a/V)^{-1}, \quad (12.20)$$

$$p_2 = \frac{R}{V - b} - \frac{3R}{2} \frac{aV^{-2}}{E + a/V}, \quad (12.21)$$

$$S_e = R \ln \left[\left(\frac{E + a/V}{C_v} \right)^{3/2} \frac{(V - b)}{R} \right]. \quad (12.22)$$

From (12.20) and (12.21) arise the following constitutive equations for energy and pressure, respectively:

$$E = \frac{3RT}{2} - \frac{a}{V}, \quad (12.23)$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (12.24)$$

Thus, we again see that all the thermodynamic information is contained in the orbit equations given by the function f chosen. Therefore the contact form provides a way to put the thermodynamics of the gases considered in a geometric setting in the contact space corresponding to the equilibrium Gibbs relation. Note that since $X \lrcorner df = 0$ the vector field X is tangent to the Legendre submanifold.

12.2.3 A General Form for f

Instead of choosing specific forms for function f as is done in the previous examples, one can choose a more formal but generic form for the function. Here we would like to add an additional piece of information which we find quite illuminating with regard to thermodynamics associated with the contact form Θ in (12.2). This also has a more direct implication for irreversible thermodynamics we are going to discuss shortly.

We choose the function f in the form

$$f = q^0 - p_\alpha q^\alpha. \quad (12.25)$$

This form, when substituted into (12.8)–(12.10), yields the orbit equations

$$\frac{dq^0}{dt} = q^0, \quad (12.26)$$

$$\frac{dp_\alpha}{dt} = 0, \quad (12.27)$$

$$\frac{dq^\alpha}{dt} = q^\alpha, (1 \leq \alpha \leq n). \quad (12.28)$$

Integrating these equations we obtain

$$q^0 = q^0(0)e^t, \quad (12.29)$$

$$q^\alpha = q^\alpha(0)e^t, \quad (12.30)$$

$$p_\alpha = p_\alpha(0). \quad (12.31)$$

To eliminate t we construct the sum

$$p_\alpha q^\alpha = p_\alpha(0)q^\alpha(0)e^t.$$

Dividing this equation with (12.29) side by side we obtain

$$\frac{q^0}{q^0(0)} = \frac{p_\alpha q^\alpha}{p_\alpha(0)q^\alpha(0)}.$$

This implies that there exists a 1-parameter family of solutions to the orbit equations—a one-parameter family of surfaces in the Legendre submanifold:

$$q^0 = Cp_\alpha q^\alpha, \quad (12.32)$$

where C is a constant. The surface of $C = 1$ annihilates f . Again, let Φ be the mapping from E_n to $E_n \times \mathfrak{R}$ defined by $q^\alpha = q^\alpha$ and $q^0 = g(q^\alpha) = p_\alpha q^\alpha$. In fact,

$$\mathfrak{G} = \left\{ (q^0, q^\alpha, p_\alpha) \mid q^0 = g(q^\alpha), p_\alpha = \frac{\partial g}{\partial q^\alpha} \right\}$$

is the Legendre submanifold of M , which is also the integral submanifold of the Gibbs relation

$$\Theta = 0, \quad dq^0 = p_\alpha dq^\alpha.$$

Secondly, we have the Gibbs–Duhem relation

$$q^\alpha dp_\alpha = 0. \quad (12.33)$$

This relation in fact can be directly deduced from (12.27) if q^α is multiplied to it and summed over α . Finally, since

$$q^0 = g(q^\alpha) = p_\alpha q^\alpha = \left(\frac{\partial g}{\partial q^\alpha} \right) q^\alpha,$$

it is possible to conclude that $q^0 = g(q^\alpha)$ is a homogeneous function of q^α of degree 1, whereas p_α is a homogeneous function of q^α of degree 0. If the function f is given by the form in (12.25) the orbit equations do not provide the constitutive information required to describe fully the thermodynamic system of interest, but yield general equilibrium thermodynamic relations. That is, the function f in (12.25) with the orbit equations (12.26)–(12.28) is a thermodynamic theory of a system, if constitutive relations are supplied.

12.3 Sheared Non-Equilibrium Real Fluids

In the case of non-equilibrium systems the extensive variables ϕ^α additionally contain a set of non-equilibrium flux (non-conserved) variables,

whereas the intensive variables respectively include the generalized potentials conjugate to the former; see Ref. [3] for the description of such a theory of irreversible processes. Even for such non-equilibrium systems it is still possible to introduce the contact form $\Theta = dq^0 - p_\alpha dq^\alpha$ in which the second term includes the non-equilibrium contribution consisting of non-conserved variables. However, since the equilibrium (Clausius) entropy is defined only for reversible processes or for equilibrium, it must be suitably generalized. If it is replaced by the calorropy Ψ the content of the previous subsection can be generalized to irreversible processes since all the relevant equations remain unchanged. However, a specific example for function f generating the isovector field is not generally known at present in a form as explicit as for the case of the ideal and van der Waals gases if all the irreversible processes are included in the consideration. To find it, it is generally necessary to solve the generalized hydrodynamic equations [5, 6] for the irreversible processes of interest. Their solutions are not trivial to obtain. However, there is one case for which an analytic solution is known for generalized hydrodynamics. It is the case of plane Couette flow in a simple fluid. Here we will assume the fluid at equilibrium obeys the equation of state and the caloric equation of state as considered for the van der Waals fluid in the previous section. We consider a global system where the flux variables appear in global form since they are the results of integration over the configuration space. To the set of coordinates q^α and p_α of contact manifold M defined in Subsec. 12.2.2, we add the coordinates $q^3 = \Pi$ where Π is the density of stress tensor, namely, the stress tensor per volume, and its conjugate variable p_3 which is related to the generalized potential $X^{(1)}$ that in turn is a function of Π , and finally $q^0 = \Psi$. The generalized potential is a constitutive quantity which may be approximated by $X^{(1)} = -\Pi/2p$. This is the approximation for the generalized potential we will take in this discussion. The aforementioned non-equilibrium variables depend on time only, since they are averages over the configuration space of the corresponding local variables. Furthermore, we will assume that the viscosity η_0 of the fluid is constant and the stress relaxation time k^{-1} is also a constant. These assumptions make the equations involved in the theory mathematically manageable. We will denote the distance between two plates of the plane Couette cell D . The following symbols will be defined to simplify the notation:

$$\Pi_0 = -\eta_0 \frac{u_0}{D}, \quad (12.34)$$

$$A(t) = 1 - \exp(-2kt), \quad (12.35)$$

where u_0 is the speed of the moving plate of the plane Couette cell. Therefore, u_0/D is the shear rate and Π_0 is the static shear stress. The time-dependent function $A(t)$ describes the relaxation of the shear stress Π as will be seen.

It then follows that the contact manifold M is spanned by the coordinates $(q^0, q^1, q^2, q^3, p_1, p_2, p_3)$ and the contact structure of M is given by

$$\Theta = dq^0 - p_\alpha dq^\alpha. \quad (12.36)$$

We now choose f for the fluid under consideration as follows:

$$\begin{aligned} f = & -4kq^0 + 4kNk_B \ln \left[\left(\frac{M(t, q)}{C_v} \right)^{3/2} \frac{(q^2 - b)}{Nk_B} \right] \\ & -2k\Pi_0 A(t)p_3 + 2kp_3q^3, \end{aligned} \quad (12.37)$$

where the parameters a , b , and C_v have the same meanings as before,

$$M(t, q) = q^1 + a/q^2 - B(t)q^3(q^2)^2 \quad (12.38)$$

and

$$B(t) = \frac{\epsilon\Pi_0 A(t)}{8k\eta_0 \bar{v}}. \quad (12.39)$$

Here $\epsilon = (\partial \ln \eta_0 / \partial \ln T)_p$ which may be regarded as a constant and \bar{v} is the molar volume of the molecule in the system. This volume is also regarded as a constant. The logarithmic function in the function f has the argument with a dimension, but it can be easily made dimensionless by scaling the argument with a constant factor of the same dimension. Since such a scaling does not change the result obtained in this paper, we will not be concerned with it. The function f gives rise to the following orbit equations:

$$\frac{dp_1}{dt} = -4kp_1 + \frac{4kC_v}{M(t, q)}, \quad (12.40)$$

$$\frac{dp_2}{dt} = -4kp_2 + \frac{4kNk_B}{q^2 - b} - \frac{4kC_v \left[a + 2B(t)q^3 (q^2)^3 \right]}{M(t, q) (q^2)^2}, \quad (12.41)$$

$$\frac{dp_3}{dt} = -2kp_3 - \frac{4kC_v B(t) (q^2)^2}{M(t, q)}, \quad (12.42)$$

$$\frac{dq^0}{dt} = -4kq^0 + 4kNk_B \ln \left[\left(\frac{M(t, q)}{C_v} \right)^{3/2} \frac{(q^2 - b)}{Nk_B} \right], \quad (12.43)$$

$$\frac{dq^1}{dt} = 0, \quad (12.44)$$

$$\frac{dq^2}{dt} = 0, \quad (12.45)$$

$$\frac{dq^3}{dt} = 2k [\Pi_0 A(t) - q^3]. \quad (12.46)$$

These orbit equations are solved under the following initial conditions:

$$p_1(0) = \frac{C_v}{q^1(0) + a/q^2(0)}, \quad (12.47)$$

$$p_2(0) = \frac{Nk_B}{q^2(0) - b} - \frac{aC_v}{q^2(0)[q^1(0)q^2(0) + a]}, \quad (12.48)$$

$$q^0(0) = R \ln \left\{ \left[\frac{q^1(0) + a/q^2(0)}{C_v} \right]^{3/2} \frac{[q^2(0) - b]}{Nk_B} \right\}, \quad (12.49)$$

$$p_3(0) = q^3(0) = 0. \quad (12.50)$$

We then find the solutions to the orbit equations:

$$q^1(t) = q^1(0), \quad (12.51)$$

$$q^2(t) = q^2(0), \quad (12.52)$$

$$q^3(t) = \Pi_0 [(2kt + 1) A(t) - 2kt], \quad (12.53)$$

$$\begin{aligned} q^0(t) &= e^{-4kt} \phi_0 + 4kNk_B \int^t d\tau \exp [4k(\tau - t)] \\ &\times \ln \left[\left(\frac{M(t, q)}{C_v} \right)^{3/2} \frac{(q^2 - b)}{Nk_B} \right], \end{aligned} \quad (12.54)$$

$$\begin{aligned} p_1(t) &= \frac{C_v}{q^1 + a/q^2} + e^{-4kt} \phi_1 - 4kC_v \int^t d\tau \frac{\exp [4k(\tau - t)]}{q^1 + a/q^2} \\ &+ 4kC_v \int^t d\tau \frac{\exp [4k(\tau - t)]}{M(t, q)}, \end{aligned} \quad (12.55)$$

$$\begin{aligned} p_2(t) &= \frac{Nk_B}{q^2 - b} - \frac{aC_v}{(q^2)^2 (q^1 + a/q^2)} + e^{-4kt} \phi_2 \\ &+ 4kaC_v \int^t d\tau \frac{\exp [4k(\tau - t)]}{(q^2)^2 (q^1 + a/q^2)} \\ &- 4kC_v \int^t d\tau \exp [4k(\tau - t)] \frac{[a - 2B(\tau)q^3 (q^2)^3]}{M(t, q)(q^2)^2}, \end{aligned} \quad (12.56)$$

$$p_3(t) = e^{-2kt} \phi_3 - 4kC_v \int^t d\tau \exp [2k(\tau - t)] \frac{B(\tau) (q^2)^2}{M(t, q)}. \quad (12.57)$$

Here ϕ_0, \dots, ϕ_3 are the integration constants which can be determined with the help of the initial conditions presented earlier. Note that q^1 and q^2 in the integrals in these solutions are independent of t . The integrals in Eqs. (12.55)–(12.54) may be approximately evaluated to $O(\Pi^2)$. We obtain from Eqs. (12.55) the caloric equation of state to $O(\Pi^2)$:

$$E = \frac{3}{2} Nk_B T - \frac{a}{V} + \frac{\epsilon V^2 \Pi^2}{8k\eta_0 \bar{v}} + O(\Pi^4), \quad (12.58)$$

for which we have used $p_1 = T^{-1}$ and $C_v = \frac{3}{2} Nk_B$ as well as $q^1 = E$, $q^2 = V$, $q^3 = \Pi$. Notice that the last term is the contribution to the internal energy of the substance from shearing which tends to increase the internal energy. The van der Waals term, namely, the second term on the right in Eq. (12.58), is negative meaning attraction, whereas the shear contribution is positive and thus may be interpreted as a repulsive potential energy. Since according to Eq. (12.53) Π relaxes to Π_0 as $t \rightarrow \infty$, the internal energy asymptotically approaches the value given by

$$E = \frac{3}{2} Nk_B T - \frac{a}{V} + \frac{\epsilon V^2 \Pi_0^2}{8k\eta_0 \bar{v}} \quad (12.59)$$

in the limit of a steady shear. Evaluating the integral in Eq. (12.56) to $O(\Pi^2)$, using Eq. (12.58) in the result, and recalling $p_2 = p/T$, we obtain the equation of state for the sheared van der Waals fluid

$$\left[p + \frac{a}{V^2} + \left(1 + \frac{a}{3VNk_B T} \right) \frac{\epsilon V \Pi^2}{4k\eta_0 \bar{v}} \right] (V - b) = Nk_B T. \quad (12.60)$$

By integrating Eq. (12.57), we obtain

$$p_3 = - \frac{\epsilon V \Pi}{4k\eta_0 \bar{v} T} + O(\Pi^3). \quad (12.61)$$

The calortropy Ψ is obtained to $O(\Pi^2)$ from Eqs. (12.54) and (12.58) in the following form

$$\Psi = Nk_B \ln \left[\left(\frac{E + a/V}{C_v} \right)^{3/2} \frac{(V - b)}{R} \right] - \frac{\epsilon V^2 \Pi^2}{8k\eta_0 \bar{v} T} + O(\Pi^4). \quad (12.62)$$

This result means that $f = 0 + O(\Pi^4)$. The asymptotic formulas for the equation of state and the calortropy for the sheared van der Waals fluid can be deduced similarly to the asymptotic internal energy in Eq. (12.59). As shearing is turned off, the calortropy Ψ becomes the Clausius entropy S_e given in Eq. (12.22). Note that $\Psi < S_e$ in accordance with the second law of thermodynamics.

Since the equation of state is obtained for the sheared van der Waals fluid it is interesting to calculate the critical parameters for the fluid. By using

the equation of state, Eq. (12.60), we can estimate the effects of shearing on the critical parameters P_c , V_c , and T_c for the van der Waals fluid. To the order of Π^2 , we find

$$V_c = 3b - \frac{81b^4\epsilon}{4k\eta_0\bar{v}a}\Pi^2, \quad (12.63)$$

$$T_c = \frac{8a}{27Nk_Bb} - \frac{b^2\epsilon}{k\eta_0Nk_B\bar{v}}\Pi^2, \quad (12.64)$$

$$p_c = \frac{a}{27b^2} - \frac{49b\epsilon}{32k\eta_0\bar{v}}\Pi^2, \quad (12.65)$$

where $T_c^0 = 8a/27Nk_Bb$ is the critical temperature of the unsheared fluid. This result shows how the critical volume, temperature, and pressure are shifted by shearing and, furthermore, they change in time as the shear stress evolves to Π_0 . The effect in the asymptotic time limit is in qualitative agreement with experiment on shear-induced critical phenomena [7, 8]; in fact, the Π dependence is that of the mean field theory and hence not quite correct. This inaccuracy is traceable to the form of f assumed. In any case, the present contact manifold approach seems to present a new possibility to study such phenomena from a purely thermodynamic standpoint.

The example considered here shows how we may apply the idea of contact structure even to the case of nonequilibrium processes in a real fluid. Furthermore, this study suggests it is possible to frame macroscopic studies on nonequilibrium processes within the theory of irreversible processes described in Ref. [5]. The theory can be further refined for nonequilibrium processes if the nonequilibrium part of the function f in contact manifold M is made more elaborate. Such refinements, however, are left to future study.

In conclusion, in this chapter we have shown some examples which explicitly demonstrate the essential point of using the idea of contact space in thermodynamics and the functions generating isovector fields X_f can be chosen to contain all the constitutive information of the system in an explicit and concise manner. However, this theory does not tell us how to construct the functions f in contact space for physically realistic systems. That task is generally the subject of thermodynamics and irreversible thermodynamics themselves. As a matter of fact, once f is constructed for a substance undergoing an irreversible process the mission of thermodynamics is accomplished. The mathematics of contact manifolds is not helpful in constructing an appropriate function f . Nevertheless, this approach might be useful for deductive studies in irreversible thermodynamics and, in particular, for non-linear irreversible processes, especially if one approaches the latter problems from the macroscopic viewpoint since the concept of contact manifold seems to provide new mathematical tools to solve them.

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