Kinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized Hydrodynamics: Volume 1. Nonrelativistic Theories

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*Byung Chan EuKinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized HydrodynamicsVolume 1. Nonrelativistic Theories*The tenet under which this work is carried out is figuratively summarized by the hexahedron displayed above: three vertices of subjects in the middle are constrained and in conformation to the two fundamental principles of physics, mechanical laws and laws of thermodynamics, at the two apices at the top and the bottom Preface In this monograph, theories of nonequilibrium statistical mechanics of simple molecules are presented in density ranging from dilute gases to moderately dense gases to liquids. Both single and multiple components are considered for nonrelativistic and relativistic kinetic theories. The nonrelativistic kinetic theories are in classical formalism. In the case of relativistic kinetic theories, classical gases are treated with a relativistic Boltzmann equation, whereas radiation (photons) and matter are treated by means of quantum mechanical kinetic equationâ€"covariant Boltzmannâ€"Nordheimâ€"Uehlingâ€"Uhlenbeck kinetic equations for a mixture of photons and material gases. The nonrelativistic theories are presented in Volume 1 and the relativistic theories in Volume 2. The kinetic equations are postulates and hence their predictions are to be verified *a posteriori* against experiments. The laws of thermodynamics serve as the required benchmark for *a posteriori* verification for the

present kinetic theories. The postulational kinetic theories presented are formulated for nonequilibrium ensembles of fluids which obey irreversible time-reversal-invariance-breaking kinetic equations modeled after the Boltzmann kinetic equation. Being time-reversal symmetry breaking and hence irreversible, the kinetic equations employed are capable of providing molecular theoretic foundations for irreversible transport processes. The thermodynamic theory of irreversible processes obtained therewith is in full conformation with the laws of thermodynamics as we know of from the phenomenological theories of thermodynamics by S. Carnot, R. Clausius, and W. Thomson (Kelvin) and of J.W. Gibbs. Therefore the consequences of the present kinetic theory for the thermodynamics of irreversible processes and the accompanying hydrodynamics (more precisely, generalized hydrodynamics), may be said to be thermodynamically consistent. The germ of the present line of work was conceived by the author's realization that the celebrated Boltzmann equation is not derivable, but should be regarded as a postulate for a time-reversal symmetry breaking evolution equation for singlet distribution functions of dilute monatomic gas molecules in the phase space and that it should be also regarded as a phase-space evolution equation of a particular form for an ensemble of uncorrelated molecules. This strand of thought that initially was put forth in the papers [Ann. Phys. (NY) 118 , 187, 230 (1979); 120 , 423 (1979)] by the present author, however, has taken considerably roundabout ways to come to the present form that the Boltzmann equation should be regarded as a kinetic equation for a simplest possible dynamical ensemble of the many-particle systems consisting of a very dilute monatomic gas. It, in fact, is not derivable from the mechanical laws of motion alone since it requires *extra-mechanical* principles, for example, the probability theory. In this work we, therefore, abandon the pretension that the irreversible kinetic equations are somehow derived from the mechanical principles. This roundabout journey has taken many years, which took a more concrete form with the works underlying the monograph by this author entitled *Kinetic Theory and Irreversible Thermodynamics* published by John Wiley & Sons in 1992 and continued in its sequel, the monograph entitled *Nonequilibrium Statistical Mechanics* (Kluwer 1998) where the idea of the role of ensemble was broached along the line presented in one of my papers [J. Chem. Phys. 107 , 222, (1997)]. In the intervening years there have been made a number of developments and minor corrections in the course of thoughts and applications of the theories developed from the thoughts in the aforementioned monographs. Although there still remains a great deal of further work to be done, it is felt that it is an opportune time to gather materials studied and present a synthesis of them as best as possible in a coherent form. The present monograph is a product of such a sentiment on the part of this author. It is hoped that this work would be useful to readers interested in the subject matter. In the course of this work the author has experienced numerous physical travails, which I could not have overcome without the dedicated cares of numerous physicians and cardiac surgeons at the Royal Victoria Hospital, McGill University, who rescued me from the brink of the abyss of life, and last but not least, of the cares and devoted love of my wife Hui Young. That was about three years ago to this day. Without them this work would not have been possible. I would like to thank them all and, especially, for the encouragement of my wife for this work. I would also like to thank my former students and associates who shared the joys as well as labors with me during the journey along the course of this work. The thoughts of their camaraderie will be cherished. I would also gratefully acknowledge the valuable help from my son David for drawing figures despite his busy schedule. Byung Chan EuMontreal, CanadaMarch 2016Contents

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Kinetic theory of matter, or more specifically, gases and liquids, has a long history tracing back to the works of Maxwell [1] and Boltzmann [2] in mid 1860s and 1870s. It has evolved since then through the works of Gibbs [3], who established the ensemble theory of statistical mechanics and applied it to equilibrium ensembles, and numerous contributors, most prominently, Enskog [4] and Chapman [5], after him in the twentieth century and in the post-World War II, especially, those led by Bogoliubov [6], Born and Green [7], Kirkwood [8], and Yvon [9] and schools of theoreticians in statistical mechanics following their theoretical developments after 1946. In this work the author hopes to contribute to the ongoing efforts by numerous other research workers on the subject of nonequilibrium statistical mechanics and its relation to the thermodynamics of irreversible processes and hydrodynamics attendant thereto.In kinetic theory of matter, we hope to describe its macroscopic behavior from the molecular viewpoint in accordance with the particulate concept of matter composed of an astronomical number of particles (electrons, atoms, molecules, etc.). Although the evolution and behaviors of macroscopic material systems are governed not only by the principles of mechanics, classical or quantal, but also by the laws of thermodynamics according to the currently accepted tenets of science, it would not seem unfair to state that the aspects of thermodynamic laws had not been a foremost concern in most of kinetic theory literature. This aspect of kinetic theory has preoccupied the present author's study of kinetic theory beginning from the mid 1970s. This line of study [10] by the author has, unfortunately, evolved over the years unlike the works by some brilliant minds which we see sometimes in science appear to have been achieved in perfection in a single stroke,

but it has reached a point where a summing up of the extended study should be made, especially, of the gist of it. That is the aim of this work.Since the kinetic theory must be developed from the mechanical viewpoint of molecules or particles on the foundation of laws of thermodynamics, so believes this author, the beginning of the discourse on the subject matter in this work is opened with a phenomenological theory of irreversible processes in matter without restriction to the degree of displacement from equilibrium in Chap. [2]. Since the phenomenological theory of such unrestricted irreversible processes is itself not fully verifiable experimentally at present with only some spotty examples of experiment in rarefied gases, carrier mobilities in semiconductors, and some rheological phenomena, we have formulated it axiomatically mainly on the basis of our experience with the thermodynamic theory of linear irreversible processes and a plausible extension of it to nonlinear processes which can be far removed from equilibrium. This axiomatic theory of irreversible processes is formulated in a manner consistent with the principles of thermodynamics and as such it serves as a benchmark to the kinetic theory of irreversible phenomena in matter from the molecular theory point of view in this work. The kinetic theory of irreversible transport processes developed in this work, therefore, is thermodynamically consistent to the extent that the axiomatic theory of phenomenological irreversible processes in macroscopic matter is in conformation to the statistical mechanical representation of laws of thermodynamics.The phenomenological theory mentioned earlier makes use of Carnot's theorem [[11]] and the notion of *compensated and uncompensated heats* which Clausius [[12]] inferred from Carnot's theorem for the second law of thermodynamics and with which he formulated the Clausius inequality for the second law of thermodynamics and the notion of entropy for reversible processes. The Clausius inequality, together with the compensated and uncompensated heats, gives rise to the notion of *calortropy* for nonequilibrium (irreversible) processes in lieu of *entropy*, which was originally defined by Clausius *for reversible processes only*. The internal energy differential and the calortropy differential then can be deduced to give rise to *a pair of vanishing circular integrals in the manifold of thermodynamic variables* that include conserved and nonconserved variables representative of irreversible processes occurring in the system. Since the axiomatically constructed evolution equations for conserved and nonconserved variables are subordinate to the aforementioned pair of exact differential forms as representations of the first and second law of thermodynamics by virtue of the fact that they belong to the thermodynamic manifold described by the differential forms mentioned, the phenomenological theory so constructed is guaranteed to satisfy the thermodynamic laws. In this sense, the macroscopic theory of irreversible processes is consistent with the laws of thermodynamics, and consequently, we have *a continuum theory beacon* to chart the molecular theory of irreversible processes by means of kinetic equations for systems of matter consisting of an enormous number of molecules or particles. Our journey in the rest of this work on kinetic theory of matter is charted by the guiding light of the continuum theory beacon and hence may be said to be thermodynamically consistent since it is in conformation to the laws of thermodynamics.The first requirement for a molecular theory of irreversible macroscopic processes—namely, kinetic theory—is that the kinetic equation must be irreversible, which means that it must break time reversal invariance, so that it describes irreversible processes. There is available such a kinetic equation in the form of Boltzmann kinetic equation invented by Boltzmann [[2]] in the case of sufficiently dilute monatomic gases. One of his aims with his celebrated kinetic equation was to show the uniqueness of the Maxwell velocity distribution function that Maxwell [[1]] obtained from his kinetic equation less than a decade earlier. With the help of the *H* theorem for the kinetic equation he invented, which turned out to precede the Lyapounov stability theorem [[13]] that appeared much later, he was able to show the uniqueness of Maxwell's equilibrium velocity distribution function. Moreover, the *H* theorem enabled him to make connection with Clausius's entropy for reversible (equilibrium) processes [[14]], which Clausius discovered some 10 years earlier. These well-established features of the Boltzmann kinetic equation suggest that it would be possible to formulate a macroscopic theory of irreversible processes, at least, for dilute gases that would be thermodynamically consistent in the sense mentioned earlier. Therefore, in Chap. [3], we formulate a kinetic theory of irreversible processes in a dilute monatomic gas without restriction as to the degree of removal from

equilibrium, which is thermodynamically consistent. We say a macroscopic theory of irreversible processes, regardless of whether it is phenomenological or molecular, is thermodynamically consistent if the theory conforms to the requirement of the laws of thermodynamics, primarily, the first and second law of thermodynamics.To achieve the stated goal, it was necessary to recognize that the macroscopic variables for the system are, *mathematically*, projections of the distribution functions living in the phase space of molecules comprising the system onto a manifold spanned by macroscopic variables, whose numbers are extremely smaller than the number of particles (molecules) on the order of Avogadro's number comprising the system. Secondly, the nonequilibrium distribution function describing the macroscopic processes in an aforementioned macroscopic manifold of macroscopic variables itself is a "projection" of the phase space distribution function and hence is not exactly the same as the latter. In fact, the former, namely, the projected distribution function, is *a functional of the macroscopic variables spanning the manifold mentioned*—the thermodynamic manifold defined later more precisely—and therefore cannot, in practice, be the exact solution of the kinetic equation. This subtle distinction lies underneath the entire theoretical formulation of kinetic theory of irreversible processes presented throughout this work.The first step to take in the theoretical formulation of evolution equations for macroscopic variables is in identifying the leading element of the variable set. Since this set is a homologous hierarchy, once the seed element is chosen on the basis of physical phenomena desired to describe, the procedure of collecting the set is fairly easy to find and automatic. Since the phenomena of interest is irreversible flow processes in matter and the fundamental physical laws of nonrelativistic physics demand that the mass must be conserved in a nonrelativistic process, the mass conservation law is sought after from the molecular theory standpoint. Therefore we first look for a statistical mechanical representation of mass of the fluid.Thus the seed element—henceforth the set will be called moment set—is naturally chosen with the mean mass of particles making up the system. The statistical mechanical mean value—the average—can be readily defined by the local mechanical mass density which is averaged over the phase space weighted by the distribution function obeying the kinetic equation postulated for the system, for example, the Boltzmann kinetic equation in the case of a dilute monatomic gas. Differentiating with time the statistical mechanical expression for mass, or more precisely, the mass density, the mass balance equation is obtained, which turns out to be the conservation law of mass in the axiomatic phenomenological theory of irreversible phenomena formulated in Chap. 2. This conservation law expression is assured if the mean flux of mass appearing in the divergence term of the equation is identified with the local mean momentum of the flow process in the fluid of interest.The mean momentum is the moment succeeding the moment of mass—the seed moment of the homologous hierarchy. Thus the second element of the moment set—the hierarchy—is identified and its statistical mechanical formula is definitively defined. Then the evolution equation for the mean momentum density can be derived in exactly the same manner as for the first evolution equation, namely, the mass conservation law, and at the same time the statistical mechanical formula for the moment succeeding the momentum density in the moment set may be defined unambiguously. And it turns out to be the pressure tensor. Repeating this process of deriving all other elements of the moment set and identifying their statistical mechanical formulas, the entire set of evolution equations is derived for macroscopic mean values representing the variables describing flow process of interest.Sometimes it may be necessary to have additional homologous sets of moments which are distinctive from the homologous moment set led by mass. Then we may repeat the derivation process with an appropriately identified seed moment for each new homologous set and obtain desired evolution equations. In this manner, all the necessary evolution equations can be derived to describe irreversible flow processes in the system of interest and the formal theory of irreversible processes may be completed. However, it must be remembered that the systems of evolution equations are abstract and are not as yet assured of the thermodynamic consistency.Averaging a mechanical quantity over the phase space with the distribution function f as a statistical mechanical weight is a projection of f onto the manifold of mean macroscopic variables, which may be identified with the thermodynamic manifold to be defined later more precisely. The projection is accompanied by a contraction of information.Since

the Boltzmann entropy S represents the information content for the system from the information theory point of view, a set of quantities represented by the mean values discussed earlier contains far less information than the distribution function f itself that obeys the kinetic equation exactly and lives in the phase space of the system containing an astronomically large number of molecules or particles. The measure of information contraction of the projected space (or manifold) of macroscopic variables are described by what we call calortropy [15] denoted by . This calortropy cannot be equal to the Boltzmann entropy, but can be shown to be subjected to the laws of thermodynamics. As a matter of fact, because its differential can be shown to be exact in the thermodynamic manifold, it may be regarded as a representation of the second law of thermodynamics. In contrast to this, since the Boltzmann entropy S would not yield an exact differential form in *the thermodynamic manifold*, it is not possible to base the question of thermodynamic consistency on S. Therefore, with the help of the calortropy it is possible to construct a thermodynamically consistent theory of irreversible processes evolving in the thermodynamic manifold subject to the control of the calortropy, and consequently we have a thermodynamic theory of irreversible processes fully consistent with the laws of thermodynamics in the case of dilute monatomic gases obeying the Boltzmann kinetic equation. For the present formulation of theory of irreversible thermodynamics the Boltzmann entropy S plays only an indirect role providing the H theorem and the notion of calortropy.The underlying philosophy held for the concepts and procedures taken for formulating kinetic theories of macroscopic irreversible processes in Chap. 3 remains the same for other types of dilute gases, moderately dense gases, and liquids we have studied in this work. In Volume 1, nonrelativistic phenomena are discussed, whereas in Volume 2 relativistic theories are formulated for monatomic gaseous systems and also for a system composed of photons and relativistic gases. The kinetic equation employed in the latter system is quantal, since the Boltzmann–Nordholm–Uehling–Uhlenbeck kinetic equation [15–17], which is a quantal kinetic equation, is made covariant for the kinetic theory of relativistic particles. This treatment therefore would be an example for a macroscopic theory which combines a quantum theory and special relativity theory.The Boltzmann kinetic equation disguises the fact that the ensemble theory of statistical mechanics of J.W. Gibbs may be said to underlie it, perhaps, in a special form of ensemble of statistically uncorrelated particles. Once we realize this viewpoint in the general context, we may look for kinetic equations for statistically correlated interacting particle systems, which are also irreversible and break time reversal invariance as the Boltzmann equation does. We would like to keep these important features for kinetic equations of interacting particle systems. To implement these two crucially important properties in the kinetic theory we have in mind, in Chap. 4 we first briefly review the gist of equilibrium Gibbs ensemble theory, although we inject some important dynamical elements in the collisional evolution of the ensemble which are absent in the traditional discussion of the equilibrium Gibbs ensemble theory. This would prepare us for the implementation of the notion of ensemble and the heuristic formulations of the ensemble kinetic equations made in the subsequent chapters.With the aforementioned preparation we devise an ensemble kinetic equation for a moderately dense monatomic gas by recasting the irreversible Boltzmann equation for an ensemble of dilute uncorrelated particles, which may be regarded as a supersystem of one-particle members. Then by replacing the binary collision operator in the aforementioned ensemble kinetic equation with a many-particle collision operator so as to describe interactions of the members of the supersystem representative of the ensemble, we are able to construct an irreversible kinetic equation for a moderately dense gas of statistically uncorrelated particles and discuss irreversible processes therein. This topic is discussed in Chap. 5 in the spirit completely parallel to that taken in Chap. 3 on the Boltzmann kinetic equation. With the so-constructed irreversible kinetic equation and postulated for a moderately dense statistically uncorrelated system, we are not only able to recover the kinetic theory results which one may obtain from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY hierarchy theory [6–9] in sufficiently low density limit. But we are also able to show the transport coefficients obtained are free from the divergence difficulty arising in connection with the many-particle collision operator. The generalized hydrodynamic evolution equations are also derived in a manner consistent with the laws of

thermodynamics and their mathematical structures are shown to be completely parallel to the theory presented in Chap. [3], thanks to the irreversibility of the kinetic equation constructed for the ensemble.Adhering to the similar notions and postulates for kinetic equations for appropriate ensembles representative of the systems of molecules used in Chaps. [3] and [5], we are now able to construct and postulate irreversible kinetic equations for ensembles representative of single-component monatomic liquids and liquids mixtures to formulate the thermodynamic theory of irreversible processes, attendant generalized hydrodynamics, and a theory of transport processes in liquids and liquid mixtures. Such theories are presented, respectively, in Chap. [6] for simple single-component liquids and in Chap. [7] for simple liquid mixtures.In Chaps. [6] and [7], we have generalized the moment set to include the notion of mean volume of influence for interacting molecules—which we simply call the molar volume—and use it as another one of seed moments from which a new moment homologue begins. This "molar volume" enables us to discuss *volume transport phenomena* in fluid mechanics which Brenner [18] put forward in recent years on the phenomenological theory grounds. We have shown that his idea of new volume and associated flux may be formulated on the basis of molecular theory [19, 20] if we make use of the concept of Voronoi volume [21], and that a hydrodynamic theory of volume transport can be more cogently formulated in a logical manner from the molecular theory standpoint. The inclusion of volume transport phenomena represents an extension of the generalized hydrodynamics presented in Chaps. [3] and [5] not only with respect to the formalism itself, but also the scope of conceptual horizon in hydrodynamics. The generalized hydrodynamics presented in Chaps. [6] and [7] therefore may be regarded as a generalization of the generalized hydrodynamic formalism presented in Chaps. [3] and [5]. Inclusion of volume transport phenomena in the form presented in these two chapters also extends the thermodynamic manifold and at the same time eliminate, I believe, the uncertain and speculative features of the phenomenological formulation of the idea [18] of Brenner's "volume", which appears to be quite elusive to grasp. The generalized hydrodynamics with volume transport phenomena included in this work definitely broadens the horizon and range of traditional hydrodynamics.The generalized hydrodynamics formulated in this work necessarily accompanies the thermodynamic theory of irreversible processes and nonequilibrium statistical mechanics thereof, which can be carried through in a manner quite parallel to the equilibrium statistical mechanics, thanks to the nonequilibrium canonical or grand canonical distribution function underlying the nonequilibrium ensemble methods. As a matter of fact, the nonequilibrium statistical mechanics formalism accompanying the generalized hydrodynamics facilitates quantification of various intensive parameters appearing in the nonequilibrium canonical or grand canonical distribution functions with the help of the *extended Gibbs relation* for calortropy density—namely, the Pfaffian differential form for calortropy density—and its integrability condition, namely, the nonequilibrium Gibbs–Duhem equation . Thus with nonequilibrium canonical or grand canonical forms of distribution functions made use of for the calortropy, the extended Gibbs relation, and its integrability condition for the Pfaffian differential form for the calortropy, we are fully equipped with mathematical tools to carry out study of irreversible thermodynamics of transport processes both from the molecular and continuum theory viewpoints supported by the attendant generalized hydrodynamic equations.The generalized hydrodynamics includes the classical hydrodynamics of Navier, Stokes, Fourier, and Fick as a limiting case as the system tends toward the vicinity of equilibrium, and the accompanying steady-state constitutive equations together with the transport coefficients can be recovered from the generalized hydrodynamic equations. To achieve this goal, it is necessary to investigate the limiting processes required to obtain the limiting forms mentioned. For this purpose, approximate expansion forms—namely, linear approximations—are used for the generalized potentials conjugate to the fluxes, and a cumulant expansion method is used for the dissipation terms in the flux (nonconserved variable) evolution equations. However, some other methods of approximation may be used or explored in the future. As to the linear transport coefficients, in the limit of small fluxes the Chapman–Enskog transport coefficients [5] are recovered from the generalized hydrodynamic equations in the case of dilute monatomic gases, and in the case of liquids molecular-theory expressions for the linear transport coefficients are

obtained in terms of collision bracket integrals, which tend to the Chapman–Enskog theory results in the low density limit. They will appear in Chaps. 6 and 7 and also in Chap. 9.Deviation of distribution functions obeying the kinetic equation from the nonequilibrium canonical or grand canonical distribution function may be regarded as fluctuations. Therefore the difference between the *Boltzmann entropy S* and the *calortropy* may be attributed to fluctuations. Such fluctuations in distribution functions are characterized by the *relative Boltzmann entropy*. Mathematical and quantitative description of such fluctuations would require solution of the kinetic equation in the phase space. Evolution equations of the fluctuations can be generated from the kinetic equations. This part of investigation based on the kinetic equations considered here is rather sketchy primarily owing to the lack of time to study the subject in depth and, more importantly, because formulating the deterministic macroscopic theory from the kinetic theory standpoint is the primary task of the present work. But the relative Boltzmann entropy should be studied in the future for the general interest and completeness of the kinetic theory formulated here. Nevertheless, we would like to point out that with the help of the relative Boltzmann entropy it has been possible to establish a *thermodynamic uncertainty principle* by which various uncertainty inequalities have been established between conjugate variables spanning the thermodynamic manifold and its tangent manifold. Interestingly, they are parallel to the *quantum mechanical uncertainty relations*. This aspect was discussed in some detail, especially, in Chap. 3. It is quite interesting and insightful to see that the thermodynamic uncertainty relations exist in connection with the relative Boltzmann entropy and that they are associated with fluctuations of the Boltzmann entropy from the thermodynamic calortropy. Similar investigations can be made for dense gases, pure liquids, and liquid mixtures discussed in Chaps. 5, 6, and 7 by following the line of approach taken in Chap. 3. I believe that the surface is hardly scratched on this subject in the kinetic theory of irreversible processes and fluctuations.The nonequilibrium statistical mechanics and transport coefficients underlying the theories presented in Chaps. 5 through 7 would require practicable knowledge of many-particle collision dynamics of interacting molecules. The collision dynamical information in the present kinetic theory is vested in the collision integrals of the kinetic equations. More specifically, the information on molecular interactions of particles in the system is contained entirely in the form of collision operators in the collision bracket integrals defining transport coefficients. They have to be computed by some means if we wish to make the theory connect with experiments. For this important reason we digress to discuss a classical mechanical technique based on eigenfunctions and eigenvalues for classical Liouville operators and collision operators in Chap. 8. In this chapter is presented a detailed discussion on the eigenvalue problem [22] of classical Liouville operators with an aim to apply it to develop an algorithm to compute numerically—e.g., by using computer simulation techniques—the transport coefficients or collision bracket integrals for liquids and dense gases of interacting molecules. Such an algorithm is presented in Chap. 8 to facilitate computation of linear transport coefficients for liquids and dense gases. Through this study, we find that transport coefficients are expressible in formulas rather reminiscent of the autocorrelation functions in the linear response theory. They appear to be amenable to Monte Carlo simulation methods.In Chap. 9, the generalized hydrodynamic equations developed in Chaps. 3, 5, 6, and 7 are collected in the case of quasilinear and linear transport processes, and some of their applications are discussed in the case of dilute gas flows far removed from equilibrium—for example, hypersonic flows.Chapters 2 through 9 constitute Part I for nonequilibrium theories in Volume 1. Any kinetic theory study requires knowledge of methods of equilibrium statistical mechanics. For this reason we have added some results made in our study on them in the past, which we consider should be useful for implementing the kinetic theory results presented in Part I. They are presented in Chaps. 10 and 11 making up Part II of Volume 1 of this work. The materials presented are not at all complete nor are they published as yet, but it is hoped that they may be found useful for some readers.The relativistic kinetic theories are dealt with in Volume 2 for monatomic relativistic classical gas mixtures and a mixture of photons and material gases. Volume 2, consisting of three chapters, includes a relativistic kinetic theory of monatomic gases (Chap. 1) and a covariant formulation of kinetic theory of photons and material particles (Chap. 2), both of which are treated quantum mechanically, atleast, with respect to the

collision integrals. The linear transport coefficients arising from the generalized hydrodynamic theory of photons and gases are calculated explicitly for a radiative system of photons interacting with material particles in the last chapter (Chap. [3]) of the volume. The results of this chapter ascertain to some extents the validity of the relativistic kinetic theories presented in the previous two chapters of Volume 2.

References1.J.C. Maxwell, Philos. Trans. R. Soc. London **157**, 49 (1867) [CrossRef]2.L. Boltzmann, Wien. Ber. **66**, 275 (1872); Wien Anz. **9**, 23 (1872); Abh. **1**, 316 (1872); *Lectures on Gas Theory* (University of California, Berkeley, 1964) (trans: S.G. Brush)3.J.W. Gibbs, *Elementary Principles in Statistical Mechanics* (Yale University Press, New Haven, 1902)[MATH]4.D. Enskog, K. Svensk. Vet.-Akad. Handl. **63**(4) (1921); see also Ref. [5]5.S. Chapman, T.G. Cowling, *The Mathematical Theory of Nonuniform Gases*, 3rd edn. (Cambridge, U.P., London, 1970)6.N.N. Bogoliubov, J. Phys. (USSR) **10**(256), 265 (1946)7.M. Born, H.S. Green, Proc. R. Soc. London A **188**, 10 (1946); **190**, 455 (1947)8.J.G. Kirkwood, J. Chem. Phys. **14**, 180 (1946)[ADSCrossRef]9.J. Yvon, *La Theorie Statistique des Fluides et l'Equation d'Etat* (Herman et Cie, Paris, 1935)10.B.C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992) and references cited therein11.S. Carnot, *Refléxions sur la Puissance Motrice du Feu et sur les Machines (Bachelier, Paris, 1824); English translation* (Peter Smith, Gloucester, MA, 1977)12.R. Clausius, Philos. Mag. (Ser. 4) **2**, 1, 102 (1851); **24**, 81, 201 (1862)13.M.A. Lyapounov, Probléme generale de la stabilité de mouvement. Ann. Fac. Sci. Toulouse **9**, 203–474 (1907). Translated from *General problem of stability of motion* (Kharkov, 1893) (in Russian)14.R. Clausius, Ann. Physik. (Leipzig) **125**, 313 (1865)15.B.C. Eu, *Nonequilibrium Statistical Mechanics* (Kluwer, Dordrecht, 1998)[CrossRefMATH]16.N.N. Nordheim, Proc. R. Soc. London **119**, 689 (1932)[CrossRef]17.E.A. Uehling, G.E. Uhlenbeck, Phys. Rev. **43**, 552 (1932)[ADS CrossRef]18.H. Brenner, Phys. A **349**, 11 (2005); **349**, 60 (2005). Phys. Rev. E **70**, 061201 (2004)19. B.C. Eu, J. Chem. Phys. **129**, 094502 (2008)[ADSCrossRef]20.B.C. Eu, J. Chem. Phys. **129**, 134509 (2008)[ADSCrossRef]21.G.F. Voronoi, Zeit. Reine Angew. Math. **34**, 198 (1908)[MathSciNet]22.B.C. Eu, Bull. Korean Chem. Soc. **33**, 779 (2012)[CrossRef] Part INonrelativistic Theories © Springer International Publishing Switzerland 2016

2. Thermodynamic Theory of Irreversible ProcessesByung Chan Eu1 (1)
Department of Chemistry, McGill University, Montreal, QC, Canada **Byung Chan Eu**Email: byung.eu@mcgill.caIn this work, we are interested in a molecular theory (i.e., statistical mechanics) of time- and space-dependent nonequilibrium (irreversible) processes in matter regarded as composed of many discrete particles. Statistical mechanics is a mathematical model theory of macroscopic observables of gross systems by means of which we hope to theoretically describe the collective state of matter consisting of an astronomical number of discrete constituent particles. By itself, such a mathematical model theory has no physical reality unless it is underpinned by an experimentally founded phenomenological theory of processes fully consistent with the laws of thermodynamics and until verified by experiments to a satisfactory accuracy. In this particular case of theory, it must be done so by an experimentally verifiable or verified phenomenological theory of thermodynamics of irreversible processes.For the sake of simplicity without losing the essential features of the theory we will begin the discussion with simple fluids. Once this task is accomplished, it then would be comparatively simple to generalize the theory to complex fluids consisting of non-simple molecules. We will assume in this work that the substance does not have an intrinsic angular momentum. We also assume that the system consists of an r-component non-reactive mixture. Therefore, the case of chemical reactions is excluded at the beginning, but it would be easy to modify the theory at the appropriate places to include the case of chemical reactions. After completing the formulation of the phenomenological theory under the assumptions taken, we will point out where the necessary modifications must be made to include chemical reactions. In this chapter we give a short survey of the essential features of the theory of thermodynamics of irreversible processes, subject to the assumptions mentioned, that we consider necessary in developing a theory of statistical mechanics of irreversible processes in

nonequilibrium systems.In the present work the term thermodynamics used alone without qualifiers will be reserved for equilibrium systems and processes in systems in thermal equilibrium, unless stated otherwise or modified by a suitable qualifier such as an adjective irreversible.

2.1 The Zeroth Law of Thermodynamics

2.1.1 The Zeroth Law of Thermodynamics for Temperature

If two bodies of different degrees of warmth are put into contact, the bodies eventually reach thermal equilibrium at an equal degree of warmth. This phenomenon is exploited to quantify the measure of hotness or coldness of systems. The zeroth law of thermodynamics [1–3] provides a general procedure of quantifying temperature as a measure of warmth of a system (or body). *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.* This literal statement can be expressed mathematically and more precisely: If there exists thermal equilibrium between A and C, there is a property called temperature such that if (2.1)and similarly for systems B and C (2.2)Then there follows the equality (2.3)In practice, these relations supply a means to devise thermometers and therewith quantify temperature precisely, as described in detail in the literature on measurements of temperature [4]. In our discussion, we will use the absolute temperature scale established in thermometry.Although the relations (2.1)–(2.3) are mathematically impeccable and are generally used in thermodynamics textbooks [3, 5], they are not too useful from the operational standpoint, especially for irreversible thermodynamics, because there is absent the concept of time duration in which thermal equilibrium is measured between the bodies. A more useful way of saying basically the same thing is to introduce a time interval in which the establishment of thermal equilibrium is monitored to a sufficient accuracy. Thus we write instead (2.4)where and so on. These expressions make it possible to deduce more practical means of measuring temperature and the meanings of temperature for systems where nonequilibrium processes may be in progress. For example, if the heat transfer per unit time from body A to body C is and the heat capacity is denoted by then we may write [6] (2.5)where is the heat transfer coefficient which is, together with the heat capacity, a characteristic of the materials involved. The and are non-vanishing quantities characteristic to the material considered. Therefore, for example, the first condition in (2.4) means that at thermal equilibrium of bodies A and C.Determination of the parameter requires thermal equilibrium between a body A and another body B (i.e., thermometer) if it is to be quantified as a well-defined value. However, the term 'thermal equilibrium' does not necessarily mean that body A itself is 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 , but the thermal equilibrium is between this body and another that is in contact with the former. The important point is that the value of remains constant over the time scale of measurement. This condition can be readily met if the irreversible processes in bodies A and B have reached a steady state at temperature within . 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 (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 points. 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 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 irrespective of possible irreversible processes within the bodies involved.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 may be 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 even if the body is in a nonequilibrium condition in another respect, and temperature becomes a field variable in such a case. If the irreversible process of interest is such that the conditions in (2.4) are not satisfied within the time interval achievable experimentally, then it is no longer possible to describe the process by means of a thermodynamic formalism on that time scale. In other words, thermodynamics has no meaning for such a process on the time scale in question.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 below. For this purpose, the notions of field variables are properly introduced and defined together with the notion of thermodynamic manifold, which is spanned by macroscopic observables that can be measured in principle in the laboratory on performing experiments on a set of irreversible processes. They include the conserved variables, which obey the conservation laws, and the nonconserved variables, which do not obey conservation laws, but instead are described by the constitutive equations (field equations) characteristic to the material considered.Definition 1 Thermodynamic manifold is spanned by the macroscopic variables The elements of this manifold are internal energy density , volume v, concentrations (mass density fraction) for conserved variables and additionally nonconserved variables (fluxes) density , if the fluid is monatomic. If the fluid has rotational degrees of freedom, the angular momentum and the related should be included. The species subscript a runs up to r for an r-component mixture, and the index for fluxes to s. The upper bound of index s can be as large as necessary depending on the fluid and processes of interest.For a global system the manifold is expressible asThe volume integral of may be expressible by the integral (2.6) The variables spanning manifold are extensive in the sense that when multiplied by density and integrated over the volume as in (2.6), they are extensive, being proportional to the mass of the system in V. In the conventional continuum mechanics the element v of manifold is generally taken as specific volume 1 –inverse –of the fluid. The thermodynamic manifold alone is not sufficient to characterize the state of a system (i.e., matter) thermodynamically. A manifold conjugate to is required for a thermodynamic description of it. It will be called the tangent manifold , which is defined as follows:Definition 2The manifold conjugate to is spanned by observables , each element in being conjugate to the element of in the same order of sequence of the two sets.Here , p, , , as they stand, are merely mathematical symbols for quantities conjugate to the elements of at the moment, but they will turn out to be, respectively, temperature, pressure, chemical potentials in a generalized sense, and generalized potentials . They are intensive macroscopic variables. The variable , p, and are counterparts of their concepts known in equilibrium phenomena, but the quantity , which we call the *generalized potential* for species a of process s in the nonequilibrium fluid, has no classical equivalent; they are new to the theory developed in this work. As a matter of fact, the operational meaning of parameter T has been already determined by means of the zeroth law of thermodynamics, but its quantitative determination in practice will be further clarified later. The phenomenological operational procedures for the remaining parameters p, , and can be formalized by applying the idea underlying the zeroth law of thermodynamics for temperature discussed earlier. We thus have extensions of the zeroth law of thermodynamics to parameters spanning the tangent manifold . Their irreversible thermodynamic meanings will be clarified as the theory of irreversible processes is further

developed.

2.1.2 The Zeroth Law of Thermodynamics Extended

The parameters p, , and and their temporal behaviors can be quantified through the relations [6] similar to (2.5)

(2.7)

where , , with the subscripts 1 and 2 denoting the two systems in contact, and , , and are the susceptibilities of the quantities V, , and to the changes , , and , respectively. The time derivatives , , and are functions of the variables in manifolds and , which may be empirically determined. The , , and are the associated transfer coefficients . The differential equations in (2.7) are the zeroth law analogs for pressure, chemical potentials, and generalized potentials. For, as , , and , the derivatives on the left vanish : (2.8) and the systems in contact reach equilibrium with regards to the variables p, , and . They thereby can be quantified experimentally, just as the 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. It should be noted, however, that the time scale for may not be necessarily the same as for those of the conjugate variables to the conserved variables, namely, T, p, and . These time scales, however, are not known *a priori* in phenomenological theories, but should be found through experiments, or calculated theoretically if molecular theories are available for them. In any case, (2.5) and (2.7) empirically establish the evolution equations for elements of manifold . In the subsequent chapters, their evolution equations will be found derived by means of a kinetic theory. They may be also regarded as constitutive equations of the material considered. The natures of these quantities will be clarified as the theory is developed.

To carry out unambiguous discussions of thermodynamic processes it is necessary to establish sign conventions on heat transfer and work performed. We take the following sign conventions: Convention on heat transfer: *Heat transfer is counted negative if heat is given up by the system to the surroundings, and positive if heat is taken up by the system from the surroundings.* Convention on work: *Work is counted as positive if it is done on the system by the surroundings, and negative if it is done on the surroundings by the system.*

2.2 The First Law of Thermodynamics

The first law of thermodynamics was a culmination of the understanding of what is meant by heat and its relation to energy. Referring the historical account of the genesis of the idea of equivalence of heat and energy to the literature [3, 9 –11], we will simply state it below. The First Law of Thermodynamics may be stated in two equivalent forms:*1. The energy of an isolated system is constant. 2. It is impossible to construct a perpetual machine of the first kind––a machine that, working in a cycle, expends no heat to produce an equivalent work.* The first statement due to Clausius [12] is a little obtuse, but, 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.

The second equivalent statement, in essence due to Planck [13], can be given a mathematical representation as follows. For this purpose we need the concept of internal energy.

2.2.1 Internal Energy

To obtain a mathematical representation of the first law of thermodynamics in the case of an infinitesimal process let us denote the differential heat change by and the differential work by accompanying the process. The first law of thermodynamics then implies that there exists a quantity called the internal energy E whose differential , under the sign conventions adopted earlier for heat and work, must be given by the expression (2.9) whether the process is reversible or irreversible. Thus for a cyclic process[2] the first law of thermodynamics may then be expressible as a vanishing circular integral (2.10) where the cyclic integral is to be performed over the path of a cycle in the space of macroscopic variables characterizing the thermodynamic state of the system—namely, the thermodynamic manifold (). For by the requirement of the first law the energy of the initial state must be exactly the same as the energy of the final state in the cyclic process. If time is used as a parameter for E, then the circular integral in (2.10) may be written as an integral over a period of the cyclic motion in the thermodynamic manifold (2.11) It must be reiterated that the first law holds irrespective of whether the process is reversible or irreversible although in equilibrium thermodynamics it is tacitly restricted to a reversible process.

Mathematically, the vanishing circular integral (2.10)

means that dE is an exact differential in the aforementioned thermodynamic manifold (). Equation (2.10) is also equivalent to the statement that heat is a form of energy, since on substitution of (2.9) into (2.10) we obtain (2.12) demonstrating that heat is equal to work (energy) with signs appropriately attached to them. It must be remarked that the mathematical representation (2.10) of the first law is for the global system performing the cycle, namely, the working substance in the whole system which goes through the cyclic process in question. We also note that dQ and dW are not by itself an exact differential[3] in the path of the cyclic change unlike dE is, but the sum of them, dE, is an exact differential according to the first law of thermodynamics, thus giving rise to (2.10).

2.2.2 Work

The meaning of work W or its differential form dW will depend on the mechanical task of the cycle (process) in question. It may 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 the volume of the system under an external pressure, or work may be done by the system as it transfers a portion of mass to its surroundings under a material potential (chemical potential) 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 or, more precisely, the densities of extensive variables of . 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 nonconserved variables, *which is nonclassical*, it is possible to imagine that the system responds by adjusting the value of "flux" to the driving force . The driving forces are all in the set of variables belonging to introduced earlier, which are conjugate to those in . If the aforementioned driving forces are in operation, the work done by the system per unit time can be written in the form [6] (2.13) 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 , between the system and the surroundings; 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 denotes the transfer (or exchange) rate of the quantity between the system and the surroundings. Since extensive quantities such as and can also change within the system owing to its inherent internal processes, their total rates of change consist of two components, one arising from the transfer of the quantity mentioned earlier, and the other arising from its internal change [6]: (2.14) where stands for the internal rate of change in A, which contains basically constitutive information on the substance of interest and the rate of transfer of A between the system and the surroundings. The time derivatives and will be referred to as the transfer time derivative and the internal time derivative of A, respectively.

In the conventional theory of macroscopic processes and thermodynamics there is no physical mechanism taken into consideration for an internal volume change and hence the transfer time derivative of volume is simply equal to the total time derivative dV / dt in the case of V. Therefore there is no need to express the volume derivative as in (2.14) in the the conventional theory of thermodynamics and attendant hydrodynamics. This viewpoint would be certainly plausible if we knew nothing of the fluid structure in terms of molecules and the volume inherent to molecules constituting the matter beyond the volume of the hard core of the molecules. If this average inherent volume is called the molar volume of the fluid molecule, then it is reasonable to examine the internal volume change of the fluid. The overall volume derivative of the fluid may be also written as in (2.14). The internal volume

then must be regarded as belonging to the submanifold of nonconserved variables of manifold in the terminology introduced in this work.[4] Likewise, the heat transfer rate associated with the internal energy conservation law will be denoted by 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 (see the subsection on the second law of thermodynamics below), which will be denoted by dQ / dt. Since the two quantities are not necessarily the same, we set [14] (2.15)The difference must be elucidated by some means, and it will be done when the second law of thermodynamics is discussed. It should be remarked here that this internal transfer rate is essentially in the same level as of other internal changes mentioned earlier and, in fact, would be related to them in irreversible thermodynamics.With the work made more explicit about the nature of its composition as in (2.13) and with the heat transfer rate denoted as indicated, the first law of thermodynamics may be expressed in the form (2.16)Albeit restricted to within the bounds of the operational meanings of p, , and , the form (2.16) will be useful for developing a generalized form of thermodynamics for global processes in a finite bounded system; see Ref. [15]. By using (2.15) the differential form (2.16) for a global irreversible process may be written as (2.17)Before closing this subsection, we would like to examine the notion of 'work of the task' . *A work will be called the 'work of the task' if it is the mechanical work specifically 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 the task of work in question. 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 of the device performing the cycle. We illustrate this point with the example of pressure–volume work for the work of the task. Over a cycle it is given by (2.18)On substitution of the pressure–volume work term from (2.17) there follows the equation (2.19)where (2.20)and Q may be expressed as a difference between the input and the output of heat (2.21)Therefore if it is possible to identify Q in (2.21) with that in (2.12) we find (2.22)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 (2.20) for unavailable work clearly indicates that its precise meaning depends on what is. For example, if is that of transferring a mass involving the third term on the right hand side of (2.17), then the second integral on the right hand side of (2.20) for is replaced by the circular integralthe pressure–volume work, and hence the meaning of is accordingly altered from that of the unavailable work given in (2.20). 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*, but when irreversible processes are considered, the notion of unavailable work becomes relevant and worth recognizing its presence to examine its nature.2.2.3 Local Forms of Evolution EquationsThe variables spanning manifold can be endowed their evolution equations and more precise mathematical meanings in this and following subsections. These evolution equations, especially the balance equations for conserved variables, are well established in fluid (or continuum) mechanics, quite apart from the question of irreversible thermodynamics. 2.2.3.1 Local Forms of the Conservation LawsMany macroscopic processes in nature are described from the local theory viewpoint. Typical examples will be various flow processes in fluid mechanics where local field variables of fluids are assumed to obey partial differential equations—field equations. Since flow phenomena in fluids must obviously be subjected to thermodynamic laws as any macroscopic phenomena should be, it is

necessary to cast the internal energy conservation law, namely, the first law of thermodynamics, in local form. 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. This is easily done by following the method of continuum mechanics [16]. We will simply accept them as phenomenological expressions for the conservation laws and present them as a proposition without going through the details of their derivations.

Proposition 1

For non-reacting fluids without a rotational angular momentum the local conservation laws hold for the conserved variables in the following forms:

mass: (2.23) *mass fractions*: (2.24) *momentum*: (2.25) *energy*: (2.26)

The symbol stands for the substantial time derivative

(2.27)

with . In this description, time derivative is calculated in the frame of reference moving with the fluid particle velocity.[5] Henceforth the symbol is reserved for the substantial time derivative.

In the conservation laws presented, is the specific volume of the fluid; is the (mass) density; is the fluid velocity; is the mass fraction (2.28) with denoting the (mass) density of species *a*; (2.29) with denoting the velocity of species *a*, is the diffusion flux of species *a*; is the heat flux; is the external (body) force per mass density of species *a* at position ; and (2.30) the total force density. The internal energy density is related to *E* by the integral (2.31) where the integral is over the volume *V* of the fluid. If the assumption of simple fluids—fluids with no internal molecular degrees of freedom such as rotational or vibrational degrees of freedom—is removed, the conserved variables should include the angular momentum and the conservation law, i.e., the angular momentum balance equation.

The pressure tensor can be decomposed into species-component pressure tensors : (2.32) and, similarly, the heat flux into species-component heat fluxes : (2.33) Equations (2.23)–(2.26) are the local forms for the mass, mass fractions, momentum, and internal energy conservation laws, respectively. These are the field equations for local macroscopic field variables *v* or , , , and . We notice that these field equations contain variables , , and in addition to the conserved variables, which are so called by the terminology since they obey the conservation laws or balance equations without a dissipation term in them.

2.2.3.2 Local Forms for the Evolution Equations of Nonconserved Variables

The additional variables , , and are examples of nonconserved variables which we have collectively denoted by ; they span the manifold defined in the previous subsection. In the theory of linear irreversible processes or in the conventional classical hydrodynamics they are specified by means of constitutive relations characterizing the processes in the substance of interest. The constitutive relations traditionally used in the steady-state linear theory [17, 18] of irreversible processes are not necessarily the most general forms to describe evolutions of the nonconserved variables. There is a considerable body of experimental and kinetic theory evidence that they require suitable generalizations for non-steady and nonlinear regimes. Examples for such necessity can be found in hydrodynamics, rheology [19] and other nonlinear phenomena in semiconductor physics [20], heat transport [21], plasmas [22], etc., covering the entire gamut of macroscopic physics and engineering science. The nonconserved variables where and , for which the upper bound of *s* is finite in practice, but can be left unspecified at this point in development, are suitably ordered as follows:

Here the superscript *t* stands for transpose of the tensor; the boldface denotes the unit second rank tensor; the *hydrostatic* pressure of species *a*; and the enthalpy per unit mass of species *a*. The set of nonconserved variables can include as many nonconserved variables as necessary for proper description of the system in hand. The variable is regarded as nonconserved variable since its evolution equation is accompanied by energy dissipation represented by a source term. In some cases, the nonconserved variables may change on different, usually faster time scales and shorter spatial scales than the conserved variables. Since we are looking for a general formalism for macroscopic phenomena in this work, the conserved and nonconserved variables will be provisionally put on formally equal footing with regard to time and spatial variables. On actual applications of the theory thus formulated, we

may take into consideration the relative magnitudes of time and spatial scales of the two classes of field variables and develop approximate theories therewith. This turns out to be usually the case in practice. With this proviso, we now make the following proposition for the evolution equations for nonconserved variables . Since the nonconserved variables are also field variables, they obey partial differential equations, which take forms of balance equation, but with a source term, which will turn out related to energy dissipation because they are not conserved in time; it is a distinguishing feature from the conserved variables. It will be found convenient to assume a general form for the evolution equation for as below: Proposition 2The nonconserved variables ; in manifold obey the evolution equation (2.34) *where* is the flux of , is called the kinematic term , which contains, at least, a term driving the process among other terms that nonlinearly depend on nonconserved variables and gradients of the conserved variables, and is called the dissipation term which is responsible for energy dissipation arising from the process . The dissipation term may also be a nonlinear function of variables of the thermodynamic manifold *and its tangent manifold* .The dissipation terms are generally algebraic functions of conserved and nonconserved variables, satisfying the constraint imposed by the local form of the second law of thermodynamics. They also depend on material parameters such as transport coefficients, density, pressure, etc. Since the kinematic and dissipation terms have different physical origins and characteristics, we have put them as separate terms in the evolution equation ([2.34](#)). It is possible to give statistical mechanical definitions for the kinematic and dissipation terms, as will be shown in later chapters on kinetic theory, and calculate them in terms of molecular properties of the fluid. However, their explicit forms in terms of conserved and nonconserved variables are not necessary for the formal theory of irreversible processes we develop axiomatically in this chapter. As will be seen, they will be subject to the constraint of *the second law of thermodynamics*. In this sense, the theory of irreversible processes developed here is fully consistent with the second law of thermodynamics at the formal theory level. Exploiting this thermodynamic consistency and, particularly, making use of the minimum principle provided by the second law of thermodynamics, we may develop a variational method of determining the kinematic and dissipation terms from the standpoint of thermodynamics of irreversible processes.It should be noted that the linearized versions of the evolution equations for the stress tensor and heat flux were known to Maxwell [[23](#)] as transfer equations on which he based his calculation of transport coefficients under the steady-state assumption, and Chapman [[24](#)] later used their steady state form in his kinetic theory of linear transport processes in dilute gases on the basis of the Boltzmann kinetic equation. This aspect will be discussed explicitly in chapters on kinetic theories. It is remarkable to note that the phenomenological theory of irreversible processes can make progress if the laws of thermodynamics are taken advantage of for the kinetic theory of irreversible processes. Here lies the crucial value of the thermodynamic theory of irreversible processes developed axiomatically in this chapter.2.3 The Second Law of ThermodynamicsUnlike the first law of thermodynamics, which does not dictate the direction in which a reversible or irreversible macroscopic process proceeds, the second law of thermodynamics endows spontaneous natural processes with a quality of progressing in a preferred direction in time. This law is a summary of inviolable experimental facts of the unidirectional evolution in which spontaneous macroscopic processes in nature progress. It is presented as an axiom in this work. For a more detailed discussion on it the reader may be referred to *The Second Law of Thermodynamics* edited by Kestin [[25](#)] in which history and discussions of the law are given in detail.2.3.1 Carnot TheoremHistorically, the unidirectional temporal evolution of natural phenomena is phrased in a theorem proposed by Carnot [[26](#)] as a conclusion of his study of cycles of heat engines. It can be stated as follows[6]: Carnot 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 and that of an irreversible cycle by ,

then regardless of the materials used and the modes of operationThe is a function of only the temperatures of the heat reservoirs of the Carnot cycle, and the prime denotes another reversible cycle.Suppose two cycles (e.g., engines) of the same working material and mode of operation which operate between two heat reservoirs of different temperatures. One cycle is reversible and the other is irreversible. The reversible cycle does work whereas the irreversible cycle does work W, both having received the same amount of heat from the higher temperature heat reservoir. The Carnot theorem then implies that . Therefore, the following can be concluded [3] as a corollary to 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 all available to the irreversible cycle.* If that amount of unavailable work is denoted by as we have earlier, then the reversible work may be decomposable into the form (2.35)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 [12].2.3.2 Clausius and Kelvin Principles The theorem of Carnot led Clausius [27] and Kelvin (Thomson) [28] to formulate the second law of thermodynamics as follows. 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 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 can be shown [1] that these two principles are equivalent7 to each other and also to the Carnot theorem. We note that the second law of thermodynamics is phrased in terms of, and for, cycles only, and for no others. Since even the present form of the second law has not as yet been given a full mathematical expression taking the uncompensated heat into consideration, it must be the goal for theory of irreversible processes before an alternative or amended form of the second law is proposed or formulated, as has been occasionally seen in the literature. Any amended form could be liable to give rise to an unwarranted confusion in the as-yet uncompleted field of thermodynamic theory of irreversible processes.Either one of the aforementioned literally stated forms of the second law of thermodynamics must be represented in a precise mathematical form, so that it can be used as the starting point of a thermodynamic theory of processes. 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's representation of the Carnot theorem for a Carnot cycle in the following manner.Imagine the aforementioned pair of irreversible and reversible cycles operating between two heat reservoirs of temperatures and where . The two cycles take the same amount of heat from the higher temperature reservoir and perform work. The irreversible cycle does work W, discharging heat to the lower temperature reservoir, whereas the reversible cycle does a maximum work . The efficiency of the reversible cycle iswhereas the efficiency of the irreversible cycle isBy the Carnot theorem (2.36)Clausius [12] rearranges (2.36) to the form (2.37)and argues that this inequality can be cast in an integral form by imagining a series of infinitesimal Carnot cycles (see, for example, Sect. 4.4, Ref. [3].): (2.38)for which the sign convention for heat transfer introduced earlier is used.An infinitesimal Carnot cycle is the cycle that operates between two heat reservoirs of an infinitesimally small temperature difference. The terminology *infinitesimal* 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 entire 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. This is an amount of heat that is intrinsic to the system when the system undergoes the irreversible cyclic process in question. It is one of the central quantities that must be elucidated[8] in order to formulate a thermodynamic theory of irreversible processes.2.3.3 Clausius InequalityFollowing Clausius, we denote the uncompensated heat by and express the Clausius inequality ([2.36]) as (2.39)The uncompensated heat 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 [[12]] suggested to calculate by using ([2.39]) where the circular integral must be computed along an irreversible path, which includes at least one irreversible step. His suggested procedure is mathematically correct since it maintains intact the relation between the compensated and uncompensated heats. However, it ignores his original recognition that the compensated heat $dQ\,/\,T$ and the uncompensated heat are two physically distinctive quantities, which cannot tell us about each other. *Here, we keep Clausius's original understanding of the uncompensated and compensated heats as two independent entities of a natural process and try to elucidate them in terms of the system properties for the irreversible process involved.* As a first step to initiate this endeavor, let us recall that there are two independent physical entities of similar kinds appearing in the guise of work-related quantities in the corollary to the Carnot theorem. According to this corollary, the reversible work is larger by than the irreversible work *W* for the pair of reversible and irreversible cycles in question and, furthermore, is positive semidefinite, 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: (2.40)This means that there exists a positive semidefinite quantity such that (2.41)This vanishes for reversible processes by the Carnot theorem. By using the notion of infinitesimal cycles and the sign convention for heat transfer introduced earlier, we may cast this equation in the form (2.42)which gives rise to ([2.39]) when passage is made from the sum to the cyclic integral. Clearly, the uncompensated heat 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. The difference between available work and unavailable work is evidently intrinsic to the system and the irreversible cycle in hand, and the unavailable work should be treated as a separate entity from the compensated heat. It is reasonable to consider an energy dissipation to the task of work in question, as we have mentioned in an earlier subsection of this chapter.2.3.4 Clausius EntropySince a precise mathematical representation for the uncompensated heat was not known to Clausius except that there should exist such a quantity, he limited the consideration to reversible processes for which identically, and developed thereby the theory of equilibrium thermodynamics of reversible processes, namely, thermostatics, with which we are all familiar at present through numerous textbooks on equilibrium thermodynamics. If is thus set equal to zero for a reversible cyclic process,[9] then there holds the equality (2.43)which implies that must be an exact differential in (thermodynamic manifold) for reversible processes and there exists a state function . Clausius called it the entropy [[12]] of the system and defined by the differential relation (2.44)so that (2.45)In other words, in mathematical terminology is an exact differential in the thermodynamic (variable) space characteristic of the reversible cyclic process. The differential form combined with the differential form ([2.9]) for the first law of thermodynamics is called the equilibrium Gibbs relation (2.46)It is the fundamental equation of equilibrium thermodynamics. It is important to keep in mind that *the Clausius entropy is defined for reversible processes only, but not for a nonequilibrium process. Such an entropy will be called the Clausius entropy in this work in order to distinguish it from the Boltzmann entropy defined by the H theorem in his kinetic theory.*Before proceeding further to consider irreversible processes in a general context, we briefly mention the gist of the theory of linear irreversible processes as formulated by Onsager [[29]], Meixner [[30]], Prigogine [[31]], and so on. First, by interpreting the differentials of macroscopic

observables in ([2.46](#)) 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 (2.47)where , , and are local densities of the Clausius entropy, internal energy, and work, respectively. It is important to recognize that the derivatives in ([2.](#)

This book presents the fundamentals of irreversible thermodynamics for nonlinear transport processes in gases and liquids, as well as for generalized hydrodynamics extending the classical hydrodynamics of Navier, Stokes, Fourier, and Fick. Together with its companion volume on relativistic theories, it provides a comprehensive picture of the kinetic theory formulated from the viewpoint of nonequilibrium ensembles in both nonrelativistic and, in Vol. 2, relativistic contexts.

Theories of macroscopic irreversible processes must strictly conform to the thermodynamic laws at every step and in all approximations that enter their derivation from the mechanical principles. Upholding this as the inviolable tenet, the author develops theories of irreversible transport processes in fluids (gases or liquids) on the basis of irreversible kinetic equations satisfying the H theorem. They apply regardless of whether the processes are near to or far removed from equilibrium, or whether they are linear or nonlinear with respect to macroscopic fluxes or thermodynamic forces. Both irreversible Boltzmann and generalized Boltzmann equations are used for deriving theories of irreversible transport equations and generalized hydrodynamic equations, which rigorously conform to the tenet. All observables described by the so-formulated theories therefore also strictly obey the tenet.

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