Thermodynamics of Irreversible Processes

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Preface

In view of the large amount of recent work on the thermodynamics of non-equilibrium processes, there is a real need for a book giving a clear exposition of the thermodynamic formalism applicable to nonlinear thermodynamic processes at a mathematical level, accessible to physicists and to theoretically inclined biologists and chemists. This book attempts to fill this need by making a definite statement in regard to the present-day status of linear and nonlinear thermodynamics.

For the past two decades, two schools of non-equilibrium thermodynamics have dominated the literature: the school of 'rational' thermodynamics of Coleman and co-workers and the school of 'generalised' thermodynamics that is associated with the names of Glansdorff and Prigogine. Although both these schools praise themselves for their all-embracing coverage of the field, I have never seen 'generalised' thermodynamics applied to elastic materials with memory, nor have I seen 'rational' thermodynamics used in the analysis of chemical instabilities. The apparent incompatibility of the theories may bewilder the reader who wants to understand what non-equilibrium thermodynamics is all about.

Moreover, the vastly different usage of concepts and notations has not helped matters. A case in point is the ambiguity in the meanings of 'dissipation' and 'irreversibility'. These terms are often regarded as synonymous, and the precise meanings of each left in doubt. Confusion also arises over the meaning of the term 'nonlinear' in thermodynamics. While everyone knows what a nonlinear differential equation looks like, its usage in thermodynamics is far from being self-evident.

In this book I attempt to resolve such types of ambiguity and misconception. After the introductory chapter on equilibrium thermodynamics, which serves to form a common background and as a reference for all future developments, the book is divided into two parts. The first part (chapters 1–4) is a critical analysis of the classical theory of non-equilibrium thermodynamics and its more recent offshoots. The second part (chapters 5–9) deals with my own interpretation of what a theory of non-equilibrium thermodynamics should include. In the same way that equilibrium thermodynamics offers criteria for its validity so, too, non-equilibrium thermodynamics must provide for similar

criteria. My point of view is that these criteria must ultimately come from nonlinear mechanics and kinetic stability theory. This is to say that equilibrium thermodynamics itself does not provide a broad enough basis that will incorporate all types of kinetic process.

This book is formalistic rather than applicative in character. My feeling is that the presentation of a self-consistent and clear-cut thermodynamic formulation will automatically lead to its application. I hope that the interdisciplinary character of the book will allow the reader to draw upon the many interesting analogies that exist among the seemingly diverse branches of macroscopic physics, chemistry and theoretical biology.

I would like to express my deep gratitude to Gabriel Stein of the Hebrew University, Jerusalem, whose encouragement and advice had a great deal to do with making this book a reality. A very special role has been played by my wife Fanny, to whom I am greatly indebted.

Lucrino, Italy   BERNARD H. LAVENDA

Introduction

Formulations of non-equilibrium thermodynamics

In the first part of this book (chapters 1–4), there is given a brief exposition of classical equilibrium and linear thermodynamics and a critical review of two recent formulations of non-equilibrium thermodynamics.

Chapter 1 briefly presents the classic formulations of equilibrium thermodynamics. There is a twofold objective: (1) to accentuate the inherent differences between the axiomatic formulation of Carathéodory and the phenomenological approach of Gibbs, and (2) to evaluate the relative merits of the two equilibrium formulations for the construction of a non-equilibrium theory. The conclusion is reached that although Carathéodory's theory is mathematically more rigorous, it lacks the elements which would make it readily adaptable as a basis for the development of a theory of non-equilibrium thermodynamics.

Chapter 2 gives a chronological account of the developments in linear thermodynamics. Onsager's derivation of a class of reciprocal relations in which the flux is the time derivative of an extensive thermodynamic variable, forms the corner-stone of linear thermodynamics. The advantage of placing Onsager's derivation in its historical original form is that it affords a better grasp of the reciprocal relations and their specificity. An objection is raised concerning the Onsager–Casimir demonstration, in that their interpretation of the principle of microscopic reversibility at equilibrium is apparently incongruous with the non-conservative nature of the phenomenological regression laws.

Chapter 3 presents a résumé of one school of thought which uses a formal statement of the second law, the so-called Clausius–Duhem inequality, as a restriction on the types of thermodynamic process that can occur in elastic materials. Why this restriction? Since the second law does not, in general, constitute a criterion of stability, this restriction would necessarily exclude various forms of nonlinear thermodynamic processes which are stable kinetically. In the last section of this chapter there is an example of where the restriction on the form of the constitutive relations leads to a contradiction; the results invalidate the Clausius–Duhem inequality.

Chapter 4 is a review of the work of still another school of thought, which

uses the sign criteria of the second variation of the entropy and its time-rate-of-change as criteria of stability in the small. The inability to make a direct connection with the second law, on account of the fact that the first variation of the entropy does not vanish in a non-equilibrium stationary state, makes it necessary to turn to a weaker justification of the proposed stability criteria based on an analogy with a Liapounov function. Notwithstanding the fact that Liapounov's second method is addressed to stability in the large, the analogy is found to be spurious. One of the two criteria of Liapounov's second method is satisfied automatically by supposing the system to be in a state of local equilibrium. The criteria of local equilibrium have nothing whatsoever to do with the asymptotic stability properties of kinetic processes. Furthermore, it is shown that the sign criterion of the time-rate-of-change of the second variation of the entropy does not coincide with the necessary and sufficient conditions of stability that are obtained from Liapounov's first method.

Quasi-thermodynamic approach to nonlinear thermodynamics

In the second part of the book (chapters 5–9), there is undertaken a detailed exposition of an approach to nonlinear thermodynamics which is based on a confluence of thermodynamic and kinetic concepts regarding evolution and stability. For the major part, the analyses are limited to thermodynamic systems that are found in the immediate neighbourhood of a non-equilibrium stationary state. Only in the last sections of chapters 7 and 9 is the approach extended to include the phenomena of nonlinear periodic processes in space and time that may occur at a finite distance from an unstable non-equilibrium stationary state.

The fundamental idea is that the principles of thermodynamics are compatible with, and can be sharpened by, the precise criteria of kinetic stability analysis. In carrying out the implications of the fundamental idea, it was found necessary to correlate thermodynamic variables, needed to specify the thermodynamic state, with mechanical variables that satisfy the same types of differential equation. This approach is to be regarded as 'quasi-thermodynamic' in character and this is what distinguishes it from the thermodynamic approaches that have been discussed in the first part of the book.

In chapter 5, the development of nonlinear thermodynamics is begun, having already appreciated the fact that linear thermodynamic processes evolve to a state of least dissipation of energy or equivalently to a state of minimum entropy production. This implies that the evolution of linear thermodynamic processes can be accounted for by a single thermodynamic potential. The relevant thermodynamic principle states that the entropy production is equal to the energy dissipated.

In nonlinear thermodynamics we are dealing with processes that occur in open systems in which the external forces prevent the system from relaxing to equilibrium. We can no longer expect that the linear thermodynamic principle will be valid or that the evolution of such processes can be accounted for in terms of the properties of a single thermodynamic potential. It is found

necessary to derive an extension of the thermodynamic principle which will govern the evolution of nonlinear thermodynamic processes.

It is now found that the dissipation function is no longer synonymous to the entropy production but rather that their difference is a measure of the absorbed power. This is to say, the absorbed power appears as the time-rate-of-change of the entropy less that which is dissipated. The thermodynamic principle of the balance of power forms the basis for the discussion of non-equilibrium variational principles in chapter 6 and the quasi-thermodynamic stability analysis of chapter 7.

In chapter 6, there is a fairly complete treatment of the variational principles of linear and nonlinear thermodynamics. How non-equilibrium thermodynamic variational principles are constructed is shown by applying constraints on the principle of least dissipation of energy. In linear thermodynamics, the principle of minimum entropy production is obtained as a corollary of the aforementioned principle and does not constitute a minimum principle in itself.

Throughout, this chapter deals with a 'conditioned' rather than a free minimum of the dissipation function. In other words, we are not merely interested in determining the values of the velocities for which the dissipation function becomes a minimum but we are asked, at the same time, to consider only those values of the velocities for which the nonlinear thermodynamic principle of the balance of power is simultaneously fulfilled.

An appreciation is gained of the relation between thermodynamic variational principles and those of classical mechanics. The thermodynamic variational principle is analogous to the classical Lagrangian function whose stationary value yields the phenomenological equations corresponding to the classical equations of motion. Rather than obtaining the principle of the conservation of energy through integration, we multiply the phenomenological equations by their conjugate velocities and sum them to obtain the thermodynamic principle of the balance of power.

In chapter 7, there is raised the question of whether thermodynamic stability criteria can supplement the necessary and sufficient conditions for asymptotic stability which are obtained from Liapounov's first method. The precise but particular results of Liapounov's first method are employed and general thermodynamic criteria of stability under certain circumstances are obtained.

The advantages of the quasi-thermodynamic analysis are: (1) it may provide general criteria for asymptotic stability that are not manifested by the integration of the variational equations, and (2) the stability analysis, under certain conditions, may be reduced to the application of definite criteria that have a thermodynamic significance. It is found that in all cases where the thermodynamic force is conservative, the necessary and sufficient conditions for asymptotic stability are that the dissipation function and the second variation of the entropy must be positive and negative definite, respectively. The vanishing of either quadratic form means that the stability is critical.

In chapter 7, Liapounov's first method is used to extract definite thermodynamic stability criteria from the complex power equation. Attention is then turned to the symmetries of the phenomenological coefficient matrices. These symmetries determine whether or not the exactness conditions are satisfied which guarantee the existence of scalar thermodynamic potentials. In turn, by

means of a mechanical analogy, the symmetries are related to conservative or non-conservative forces. The quasi-thermodynamic analysis provides a classification of the various forms of system motions in terms of their influence on system stability and prepares the way for the field analyses of the following chapter.

In chapter 8, methods to analyse nonlinear thermodynamic processes which are non-conservative are developed, recalling from the preceding chapter that the only case in which definite thermodynamic criteria of stability cannot be obtained is when a non-conservative thermodynamic force exists. In this chapter the situation is remedied.

The field analysis is particularly well adapted to two types of critical nonlinear thermodynamic phenomenon: (1) multistationary state transitions which are signalled by the vanishing of the second variation of a scalar potential called the velocity potential, and (2) rotational processes that are caused by non-conservative thermodynamic forces.

Methods are developed that use both velocity and force fields. When the system motion can be effectively reduced to a half-degree of freedom, the velocity potential method determines bifurcation points that are analogous to equilibrium critical points in second order phase transitions. Rotational processes require at least a single degree of freedom and the velocity field analysis can only describe the kinematics and not the dynamics of the motion.

The dynamics of rotational processes are obtained from a thermodynamic force field analysis which parallels the classical development of macroscopic field theories. The only difference is that real space is replaced by configuration space. Non-conservative forces are now shown to be derivable from thermodynamic vector potentials. Thermodynamic field principles and equations that govern the field are obtained from the constrained principle of least dissipation of energy. The new factor in the thermodynamic field principles is the presence of an energy flux density which implicates an external energy source in the maintenance of nonlinear thermodynamic rotational processes.

In chapter 9, there is formulated an internal state variable representation of thermodynamic processes belonging to the continua. After the derivation of a general thermodynamic principle of the continua, we limit ourselves to the analysis of isothermal processes under constant strain. These processes are governed by the following thermodynamic principle: the difference between the absorbed power and the energy flux across the surface of the system appears as the time-rate-of-change of the entropy less the energy which is dissipated. The thermodynamic principle allows non-equilibrium thermodynamic variational principles of the continua to be formulated and thus both the variational equations and the relevant thermodynamic stability criteria are obtained.

Considered next are thermodynamic evolutionary criteria that are derived by means of the maximum principles of partial differential equations. It is appreciated that the internal configuration of continuous systems can be determined uniquely and solely from an analysis of the flows across their boundaries. A simple example is a system without any heat sources: the temperature at any point in the system cannot be greater than the temperature at the surface. Any heat flow resulting from a difference in temperature will be directed into the system. It is shown that a positive directional derivative of the

entropy flux at the surface of the system provides the condition for the absence of a positive maximum or a negative minimum in the spatial distribution of the variation of an internal state variable. These spatial distributions cause a decrease in the system entropy which must be compensated by an entropy influx from the surroundings.

Chapter 9 is concluded by an extension of the quasi-thermodynamic approach to the analysis of truly nonlinear processes. In much the same spirit that thermodynamic and kinetic concepts were interrelated in chapter 7, an averaged thermodynamic variational principle that employs the averaging techniques of nonlinear mechanics is now formulated. The method is directed to the analysis of the asymptotic evolution of nonlinear dissipative wavetrains and it is found, under certain conditions, that they give rise to a limit wave phenomenon. This brings us to the present-day frontiers of nonlinear thermodynamics.

Contents

1   Equilibrium Thermodynamics

.The purpose of this chapter is to compare the two different formulations of
equilibrium thermodynamics only in so far as they bear on the theories of linear
and nonlinear thermodynamics. The two formulations are generally associated
with the names of Carathéodory (1909, 1925) and Gibbs (1902). Carathéodory's
theory is axiomatic in character, whereas Gibbs's theory is phenomenological.
Although it has been suggested that Carathéodory's theory may eventually
provide a better mathematical basis for a theory of non-equilibrium thermodyn-
amics (Eckart, 1940), most of the recent theories of non-equilibrium thermodyn-
amics possess a predominantly Gibbsian character.

   Equilibrium thermodynamics is concerned with (1) the definition and proof
of existence of the entropy and absolute temperature, and (2) the methodology
by which equilibrium properties of thermodynamic systems can be character-
ised. Carathéodory's theory is concerned primarily with the axiomatisation of
(1), while Gibbsian thermodynamics is directed to (2). Although the two
formulations of equilibrium thermodynamics are consistent with one another,
they differ in their aims and points of view. There is no *a priori* reason why we
should select one over the other as a basis for non-equilibrium thermodynamics.

   The classical theory of equilibrium thermodynamics is therefore a blend of
two essentially different approaches. Carathéodory's theory is a mathematical
formulation of the empirical results of Clausius (1850) and Kelvin (Thomson,
1848). It sought to replace thermodynamic arguments based on Carnot cycles by
a differential geometry dealing with Pfaffian differential forms. In other words,
Carathéodory's theory allows us to obtain all the mathematical consequences of
the second law of thermodynamics without recourse to any particular physical
model (Chandrasekhar,   1939).   One   of   the   major   achievements   of
Carathéodory's theory is the definition and proof of existence of the entropy
solely in terms of mechanical variables, such as pressure and volume.
Carathéodory's axiomatic approach was developed and expounded upon by
Born (1921). Although the theory has been frequently discussed in the literature
(Born, 1949; Buchdahl, 1949, 1954, 1955; Chandrasekhar, 1939; Eisenschitz,
1955; Landé, 1926; Margenau and Murphy, 1943) there have been no substantial
advances made since 1921, with the important exception of Landsberg's (1956)
geometrisation of Carathéodory's axiomatic approach.

   Carathéodory's theory is not concerned with the characterisation of the

equilibrium properties of thermodynamic systems. In Gibbsian thermodynamics, on the other hand, attention is focused on the system. The primitive concepts of entropy and absolute temperature are assumed not to be needing definition or existence of proof. It uses these concepts to obtain a more detailed description of equilibrium thermodynamic systems in terms of their chemical and phase structures. One of the major advantages of Gibbsian thermodynamics, over Carathéodory's theory, is that it provides criteria for its validity. One assumes, in Carathéodory's theory, that all transformations are non-singular, whereas in Gibbs's theory the singularities of certain transformations are shown to coincide with the limits of system stability (e.g. critical points). However, one of the major disadvantages of Gibbsian thermodynamics is that an axiomatic approach, comparable to Carathéodory's theory, is still lacking (cf. Tisza, 1966).

The two formulations of equilibrium thermodynamics can be discussed in terms of the geometrical structure of their relevant spaces. A major tool in equilibrium thermodynamics is the geometrical method based on the 'thermodynamic' space. In Carathéodory's theory, the space is spanned by all the independent variables that are needed to describe the thermodynamic system. The only criterion for their presence in the thermodynamic space is that they must be physically measurable. Hence, in Carathéodory's formulation no specific choice of the space is made; in particular, no geometrical distinction is made between extensive and intensive thermodynamic variables. This was first pointed out by Ehrenfest (1911), who concluded that the geometrical distinction between extensive and intensive variables requires additional axioms than those contained in Carathéodory's theory. The geometrisation of Carathéodory's theory was accomplished by Landsberg (1956, 1961).

In contrast, Gibbsian thermodynamics requires a particular space — the Gibbs space — which is spanned by all the independent extensive variables. Although in the original presentation (Gibbs, 1902), the construction of the Gibbs space was *ad hoc*, it did lead to the representation of thermodynamic potentials as quadratic forms which form the primitive surfaces in the Gibbs space. The achievements of Gibbs's geometrisation of his thermodynamic theory is really quite remarkable when it is realised that the basic geometrical elements of metric and orthogonality are wanting.

The mathematical foundations were discovered, at a later date, by Blaschke (1923) who showed that the geometry of the Gibbs space is an affine differential geometry. Although a metric cannot be defined, it is possible to define a parallel projection which replaces the orthogonal projection in the ordinary Riemann theory of curvature. Furthermore, by representing the entropy as a quadratic form, it is possible to obtain something similar to a metric. That is, the Gibbs space is one in which 'volumes' but not 'lengths' are measurable. The volume is represented by the determinant of the matrix that is associated with the quadratic form. Therefore, in contrast to Euclidean geometry, parallelism replaces orthogonality, and volumes but not lengths are measurable in the Gibbs space. In addition, different spaces can be generated that are spanned by both extensive and intensive variables, through the Legendre transforms which replace extensive variables by their conjugate intensive variables in the fundamental expression for the thermodynamic potential.

The attributes of the axiomatic and phenomenological formulations of equilibrium thermodynamics are now considered in greater detail. Since the laws of thermodynamics are formulated with the greatest amount of logical simplicity in Carathéodory's theory, his formulation will be considered first. There will then follow a discussion of Gibbsian thermodynamics which takes many of the concepts, introduced by Carathéodory, and makes practical use out of them.

1.1 Carathéodory's theory

1.1.1 Definitions and conditions of equilibrium

Thermodynamic systems are classified according to whether they are 'isolated', 'closed' or 'open'. In an isolated system there is no communication with the outside world; that is, there is neither energy nor matter transfer between the system and its environment. In a closed system there is energy but no matter exchange with the outside world. Finally, in an open system there is both an exchange of energy and matter between the thermodynamic system and its environment.

Since equilibrium thermodynamics deals with isolated systems, how is it possible to establish the conditions of equilibrium? In other words, if the isolated system is not in equilibrium then there is the problem of defining a thermodynamic potential for the non-equilibrium state. Alternatively, if the system is in equilibrium it is no longer possible to determine the conditions of equilibrium. To resolve this paradoxical problem, Carathéodory introduced the ingenious device of 'composite systems' which was later carried over into Gibbsian thermodynamics (cf. section 1.2). That is, in order to obtain the conditions of equilibrium, in a theory that does not define non-equilibrium states, it is necessary to introduce partitions that divide the isolated system into a number of subsystems. The partition or 'wall' permits the passage of a certain form of energy which thereby forces a new relation upon the parameters of the subsystems that it separates (Landsberg, 1956).

Carathéodory's theory considers only two types of partition that are involved with the transfer of heat: (1) an adiabatic partition which is restrictive to the passage of thermal energy, and (2) a diathermal partition which allows the passage of thermal energy. Diathermal partitions are used to establish the conditions of thermal equilibrium. But as Landsberg (1956) points out, the definition of a diathermal partition precedes the introduction of the notions of heat and thermal equilibrium in the axiomatic formulation. This is only one of a number of criticisms that can be lodged against Carathéodory's formulation (cf. Landsberg, 1956).

In Gibbsian thermodynamics, the classes of partitions are increased so that other criteria of equilibrium can be obtained in addition to those of thermal equilibrium. Both adiabatic and diathermal partitions are impermeable to the transfer of matter. The two other types of partition, that are considered in Gibbsian thermodynamics, are: (3) a semipermeable partition that restricts the passage of certain constituents, and (4) a permeable partition which is non-restrictive to the passage of matter. Both these partitions permit the exchange of

thermal energy between the subsystems. It can be appreciated that partitions (3) and (4) establish the conditions of chemical equilibrium only after the system has attained thermal equilibrium. This is entirely reasonable since energy, but not matter, can be exchanged, the converse of which is certainly not true.

In order to obtain the conditions of thermal equilibrium, an isolated system is divided into a number of subsystems by means of diathermal partitions. For simplicity, consider the case of a single diathermal partition which separates two subsystems. Each of the subsystems is assumed to be fully characterised in terms of their pressures, p and p', and their volumes, V and V'. In order for there to exist an equilibrium between the two subsystems, the four parameters must enter into a relation of the form

$$F(p, V, p', V') = 0 \qquad (1.1.1)$$

that depends only on the properties of the two subsystems. In Carathéodory's theory, (1.1.1) is the condition of thermal equilibrium. The condition of thermal equilibrium may be extended to any number of subsystems by the transitive property: if two subsystems are in equilibrium with another subsystem, then they will be in thermal equilibrium with each other when they are brought into thermal contact. This means that the condition of thermal equilibrium has the form

$$T(p, V) - T'(p', V') = 0 \qquad (1.1.2)$$

where T and T' are the empirical temperatures of the two subsystems. Thermal equilibrium then implies the equivalence of the empirical temperatures, namely $T = T'$.

Another set of definitions concerns the types of thermodynamic process that can be performed. A 'quasi-static' process is one that is carried out infinitely slowly so that the system can be considered as passing through a continuous series of equilibrium states. Here there exists an ambiguity in the definitions of a quasi-static process and a "reversible' process (Landsberg, 1956). The two types of process are generally regarded as being synonymous. Any other process is called 'non-statical' which has the connotation of being 'irreversible'.

1.1.2 The first law
The first law of thermodynamics is nothing more than the principle of conservation of energy that applies to systems where heat is produced or absorbed (Planck, 1954). In Carathéodory's theory, the internal energy is defined solely in mechanical terms in contrast to the concept of heat which is a derived one, having no independent significance apart from the first law (Chandrasekhar, 1939).

In an adiabatic process which brings the system from an initial state (1) to a final state (2), the work done on the system is equal to the increase in its internal energy, namely

$$E_2 - E_1 = \int_1^2 dW \qquad (dQ = 0) \qquad (1.1.3)$$

The internal energy E is a function of state; it depends only on the initial and final states. If the transition $1 \to 2$ were to occur along a non-adiabatic path ($dQ \neq 0$), the work W would depend upon the path. For a non-adiabatic path, the

quantity of heat supplied to the system is

$$\int_1^2 dQ = E_2 - E_1 - \int_1^2 dW \tag{1.1.4}$$

It is a remarkable fact that, whereas the work done on the system and the heat supplied to the system are not point functions, their sum, the internal energy, is a point function. This means that dW and dQ are not 'exact' or 'perfect' differentials of scalar functions. Only their sum

$$dE = dW + dQ \tag{1.1.5}$$

is a perfect differential. In physical terms, we can attribute a certain internal energy with a given thermodynamic state but we cannot speak about the quantity of heat that the system possesses in that state. Moreover, if two subsystems are separated from one another by an adiabatic partition, then by definition

$$E = E_1 + E_2 \tag{1.1.6}$$

Expressed in words, the internal energy of the system is equal to the sum of its components. This will, in general, not be true when two subsystems are brought into contact. There will then be an additional energy due to the contact. The contact energy is proportional to the surface area in common between the subsystems, so that if the volume to surface ratio is large, as might be expected in all thermodynamic systems, then the additional energy is negligible and we suppose the additive law (1.1.6) always to be valid.

1.1.3 The second law

The first law of thermodynamics does not provide for a unique determination of physical processes. For example, the conservation of energy cannot tell us in which direction the heat is flowing between hot and cold bodies. In other words, the first law does not determine the direction in which a process takes place. From the viewpoint of the first law, initial and final states are entirely equivalent (Planck, 1954).

The second law of thermodynamics can be considered a law of 'impossibility'. It tells us which processes are physically unrealisable. The empirical basis of the second law is found in the Clausius–Kelvin principle. One phrasing of the second law is: without 'compensation', it is impossible to transfer heat from a cold to a hot body (Chandrasekhar, 1939). The mathematical formulation of the second law is due to Carathéodory, who showed that the absolute temperature is an integrating denominator for dQ. The second law can then be expressed as the inability to reach states arbitrarily near to a given state by means of an adiabatic process. In order to appreciate Carathéodory's theorem it is necessary to consider the mathematical properties of Pfaffian differential equations (Chandrasekhar, 1939; Goursat, 1922; Margenau and Murphy, 1943; Schouten and van der Kulk, 1949).

Consider a Pfaffian differential expression in two variables

$$dQ = X(x, y)dx + Y(x, y)dy \tag{1.1.7}$$

If

$$\int_1^2 dQ \neq Q(x_2, y_2) - Q(x_1, y_1) \tag{1.1.8}$$

then dQ is not the true differential of a certain function. This means that dQ cannot be integrated; it depends on the path from $1 \rightarrow 2$. For if dQ were a perfect differential of some scalar function f, with $dQ = df$, we would have

$$df = \partial_x f \, dx + \partial_y f \, dy \tag{1.1.9}$$

Comparing (1.1.7) and (1.1.9) we find

$$X(x, y) = \partial_x f \qquad \text{and} \qquad Y(x, y) = \partial_y f \tag{1.1.10}$$

or

$$\partial_y X = \partial_x \partial_y f = \partial_x Y \tag{1.1.11}$$

which is the exactness or integrability condition for the scalar function f. Condition (1.1.11) is, in general, not satisfied.

The Pfaffian differential equation, corresponding to (1.1.7), is

$$dQ = X \, dx + Y \, dy = 0 \tag{1.1.12}$$

Equation (1.1.12) defines a direction in the tangent plane to the one parametric family of curves which are the solutions to (1.1.12) at any given point. This is to say that we can equally as well write (1.1.12) as

$$d_x y = -X / Y \tag{1.1.13}$$

which is tangent to the curve

$$f(x, y) = C = \text{const} \tag{1.1.14}$$

at a given point. From (1.1.14) it follows that $d_x f = 0$ which is expressed explicitly as

$$\partial_x f + \partial_y f \, d_x y = 0 \tag{1.1.15}$$

Inserting (1.1.13) into (1.1.15), we obtain

$$\partial_x f - \partial_y f \, X / Y = 0 \tag{1.1.16}$$

or

$$Y \partial_x f = X \partial_y f = XY/\Theta, \text{ say} \tag{1.1.17}$$

where Θ is a function of x and y. (If $dQ = df$ then $\Theta = 1$.) We can now write (1.1.17) as

$$X = \Theta \, \partial_x f \qquad \text{and} \qquad Y = \Theta \, \partial_y f \tag{1.1.18}$$

Then the substitution of (1.1.18) into (1.1.7) leads to

$$dQ = \Theta(\partial_x f \, dx + \partial_y f \, dy) = \Theta \, df \tag{1.1.19}$$

In other words, if we divide the Pfaffian expression (1.1.7) by the integrating denominator Θ we obtain an exact differential. This is not surprising since a Pfaffian expression in two variables will always admit an integrating denominator. Moreover, if a Pfaffian differential expression admits one integrating denominator, it will admit an infinity of them. We can replace f by any function $S = S[f(x, y)]$ for which

$$S[f(x, y)] = C = \text{const} \tag{1.1.20}$$