

Chapter 2

Mathematical Preliminaries and Notations

Abstract In the first part of this chapter we present the symbolic and the Cartesian tensor notations and show how these are applied in this book. Tensor calculus is presumed known to the reader; so, only specifics and peculiarities pertinent to the work are discussed. In the second part the elements of exterior calculus are explained, but only to the extent as they are used in the thermodynamic approach treated later on, in particular in Chap. 5.

2.1 Tensors

It is assumed that the reader is familiar with the elements of tensor algebra, analysis and calculus. There are many books which present this subject, among them e. g. BOWEN & WANG [15, 16] or CHADWICK [22] or KLINGBEIL [73].

Subsequently, not only symbolic but also index notation will be used, because often proofs and auxiliary results are easier to derive that way. Notation is a crucial issue and has to be treated with care. In particular, this is true for mixture theory. In the symbolic notation we choose Greek letters, $(\alpha, \beta, \gamma, \dots)$, to identify the constituents of the mixture and place them in the right lower corner of a quantity. In index notation, the Greek letters for the constituents are moved to the right upper corner. Indices identifying the Cartesian components of tensors are written in small Latin minuscules, (i, j, k, l, \dots) , in the lower right corner of a quantity. As usual, the EINSTEIN summation convention is used for the component indices but not for the Greek constituent indices. Consequently, summations over the constituents are always written out explicitly.

In ensuing calculations, we think of vectors and tensors over \mathbb{R}^3 as quantities that consist of components and an associated basis. Thus, we write

$$\mathbf{v} = v_i \mathbf{e}_i, \quad \mathbf{A} = A_{ij} \mathbf{e}_i \otimes \mathbf{e}_j, \quad \mathbf{B} = B_{ijk} \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k, \quad (2.1)$$

where an orthonormal basis \mathbf{e}_i ($i = 1, 2, 3$) is used that spans \mathcal{W} which is a three-dimensional vector space over \mathbb{R} . $\mathbf{e}_i \otimes \mathbf{e}_j$, $\mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k$, etc. represent *dyadic products* of these basis vectors. It follows that \mathbf{v} is an element of \mathcal{W} and the second rank tensor \mathbf{A} can be understood as a linear mapping of a vector from \mathcal{W} to \mathcal{W} . This statement can be written as

$$\mathbf{A}\mathbf{v} = A_{ij} (\mathbf{e}_i \otimes \mathbf{e}_j) v_k \mathbf{e}_k = A_{ij} v_k \delta_{jk} \mathbf{e}_i = A_{ij} v_j \mathbf{e}_i =: y_i \mathbf{e}_i . \quad (2.2)$$

Analogously, higher order tensors can be understood as multi-linear forms, for details see e. g. BOWEN & WANG [15]. In (2.2) the usual KRONECKER delta,

$$\delta_{ij} = \begin{cases} 1 & \text{for } i = j , \\ 0 & \text{for } i \neq j , \end{cases} \quad (2.3)$$

and the definition of the dyadic product

$$(\mathbf{a} \otimes \mathbf{b}) \mathbf{c} := \mathbf{a} (\mathbf{b} \cdot \mathbf{c}) , \quad (2.4)$$

have been used, where \mathbf{a} , \mathbf{b} and \mathbf{c} are any vectors in the vector space \mathcal{W} . The operation $\mathbf{a} \cdot \mathbf{b}$ of \mathbf{a} and \mathbf{b} is called the *scalar product* and reveals a scalar. Henceforth, the *dot product* $\mathbf{A} \cdot \mathbf{B}$ of two tensors \mathbf{A} and \mathbf{B} of the same, but arbitrary rank results in a scalar. For second, \mathbf{A} , \mathbf{B} , and third, \mathbf{C} , \mathbf{D} , rank tensors we define this product as

$$\mathbf{A} \cdot \mathbf{B} := A_{ij} B_{ij} , \quad \mathbf{C} \cdot \mathbf{D} := C_{ijk} D_{ijk} . \quad (2.5)$$

One can think of several other products, e. g. in \mathbb{R}^3 the *cross product* of the two vectors \mathbf{a} and \mathbf{b}

$$\mathbf{a} \times \mathbf{b} := e_{ijk} a_i b_j \mathbf{e}_k , \quad (2.6)$$

where e_{ijk} stands for the alternator,

$$e_{ijk} := \begin{cases} 1 & \text{if } i, j, k \text{ are an even permutation of } 1, 2, 3 , \\ -1 & \text{if } i, j, k \text{ are an odd permutation of } 1, 2, 3 , \\ 0 & \text{else .} \end{cases} \quad (2.7)$$

Later in this chapter the *trace operator*

$$\text{tr}(\mathbf{A}^T \mathbf{B}) = \text{tr}(\mathbf{A} \mathbf{B}^T) := \mathbf{A} \cdot \mathbf{B} \quad (2.8)$$

will also be applied, where \mathbf{A} and \mathbf{B} are second rank tensors. It can be seen from its definition that the trace operator transforms $\mathbf{A} \mathbf{B}^T$ into a scalar. The *transpose* \mathbf{A}^T of the tensor \mathbf{A} is defined as follows

$$\mathbf{a} \cdot (\mathbf{A}^T \mathbf{b}) = \mathbf{b} \cdot (\mathbf{A} \mathbf{a}) , \quad \forall \mathbf{a}, \mathbf{b} \in \mathcal{W} . \quad (2.9)$$

As done in the literature, for calculations in index notation the bases of vector- and tensor-valued quantities are occasionally omitted. Tacitly assuming that we are always dealing with an orthonormal basis, we will follow the same line. Therefore, in place of

- $v_i \mathbf{e}_i$ we shall write v_i ,
- $A_{ij} \mathbf{e}_i \otimes \mathbf{e}_j$ we shall write A_{ij} ,
- $(B_{ik} \mathbf{e}_i \otimes \mathbf{e}_k)(a_j \mathbf{e}_j)$ we shall write $B_{ij} a_j$,

and we shall call v_i and $B_{ij} a_j$ vectors and A_{ij} a second rank tensor even though this is, strictly, not correct.

To make calculations easier we define

$$\begin{aligned} \text{sym}(\mathbf{A}) &:= \frac{1}{2} (\mathbf{A} + \mathbf{A}^T) , & [\mathbf{A}, \mathbf{B}] &:= \mathbf{AB} - \mathbf{BA} , \\ \text{skw}(\mathbf{A}) &:= \frac{1}{2} (\mathbf{A} - \mathbf{A}^T) , & \langle \mathbf{A}, \mathbf{B} \rangle &:= \mathbf{AB} + \mathbf{BA} , \end{aligned} \quad (2.10)$$

where the operators $\text{sym}(\cdot)$ and $\text{skw}(\cdot)$ extract the symmetric and the skew-symmetric parts of \mathbf{A} , respectively. The latter two definitions specify the LIE and JACOBI-brackets, respectively¹.

If we follow the notation of SVENDSEN & HUTTER [115] the temporal (or partial time) derivative of a general quantity φ (it can be a scalar-, vector- or tensor-valued function) is denoted by $\partial\varphi$ and its spatial (or partial space) derivative is given by $\nabla\varphi = \partial\varphi/\partial\mathbf{x} = \varphi_{i\dots j,k} \mathbf{e}_i \otimes \dots \otimes \mathbf{e}_j \otimes \mathbf{e}_k$.

In the thermodynamic analysis we will be dealing with dependent constitutive quantities \mathbf{f} (\mathbf{f} stands e. g. for the CAUCHY stress tensor or the heat flux vector, ...) and independent (constitutive) variables

$$\vec{x} = (x_1, \dots, x_K) .$$

Examples for x_s ($s = 1, \dots, K$) are the temperature field, the velocity of a constituent or its gradient etc. The dependence of \mathbf{f} on \vec{x} is written as

$$\mathbf{f} = \hat{\mathbf{f}} \circ \vec{x} = \hat{\mathbf{f}}(\vec{x}) .$$

Due to the chain rule, the temporal and spatial derivatives of \mathbf{f} take the forms

$$\begin{aligned} \partial\mathbf{f} &= \sum_{I=1}^K \hat{\mathbf{f}}_{,x_I} (\partial x_I) , \\ \nabla\mathbf{f} &= \sum_{I=1}^K \hat{\mathbf{f}}_{,x_I} (\nabla x_I) , \end{aligned} \quad (2.11a)$$

¹ In the sequel, the brackets $[\cdot, \cdot]$ and $\langle \cdot, \cdot \rangle$ will exclusively be used for the LIE and JACOBI operations, (2.10)_{2,4}.

$$\begin{aligned} \nabla \cdot \mathbf{f} &:= (\mathbf{f})_{i(\dots)jk,k} \mathbf{e}_i \otimes \dots \otimes \mathbf{e}_j \\ &= \sum_{I=1}^K \frac{\partial (\hat{\mathbf{f}})_{i(\dots)jk}}{\partial x_I} \frac{\partial x_I}{\partial x_k} \mathbf{e}_i \otimes \dots \otimes \mathbf{e}_j . \end{aligned} \quad (2.11b)$$

The partial derivative $\mathbf{f}_{,x_I}$ which occurs in equations (2.11) can be defined according to FRÉCHET. For a detailed definition of this type of partial derivative the reader is referred e. g. to MARSDEN & HUGHES [83], EDELEN [35], or CASEY [20], where explicit definitions and calculations of some important derivatives can also be found.

2.2 Results from Exterior Calculus

The mathematically complete introduction to exterior calculus can be found in the book ‘Applied Exterior Calculus’, by D.G.B. EDELEN [35]. Its formal treatment goes beyond the mathematical knowledge that is commonly absorbed by geophysicists and engineers; so, the intention here is to present those results established in this special mathematical field which are useful in the ensuing developments and facilitate the algebraic manipulations in the calculations of the thermodynamic analysis in Chapters 5 to 7. In this book only those aspects are of significance which concern so-called *differential* or *Pfaffian forms* and inferences which can be drawn from them when these forms are *total* or *perfect*. Alternative presentations of exterior calculus to [35] are by CARTAN [18, 19] and HEIL [53]. Here we follow mainly the beautiful ‘down to earth’ presentation by BAUER [10] in Chapter 4 to his Ph.D. dissertation ‘Thermodynamische Betrachtung einer gesättigten Mischung’, which we present here in our own English version, with additions and alterations where felt necessary. A formal exposition of the Exterior Calculus, presenting the ground work of what follows in the summary below is given in Appendix A

2.2.1 What is integrability?

Let

$$dF = \sum_{i=1}^n X_i(x_j) dx_i \quad (2.12)$$

be a *differential form* dF , which is expressed as a linear combination of differentials dx_i with coefficient functions X_i ($i = 1, \dots, n$) which depend on some or all of the x_j ($j = 1, \dots, n$). Equation (2.12) is also called a *Pfaffian form*. Under what conditions is the denotation dF on the left-hand side of (2.12) justified in the sense that the expression (2.12) represents a

total differential? In other words, under what conditions does integration over the right-hand side of (2.12) deliver a value that is independent of the path of integration in ‘configuration space’ of the ‘independent’ variables x_i ($i = 1, \dots, n$)?² If this is true, this value will only depend upon the initial and final points of the integration. If this should not be the case and $\sum_i X_i dx_i$ does not represent a total differential, there still remains the question: can we alter this situation by multiplying the right-hand side of (2.12) with an adequate function? Under those situations this function is called an *integrating factor*.³ In order to geometrically interpret the roles played by the variables X_i and the differential forms dx_i , it is advantageous to write (2.12) in vectorial form

$$dF = \mathbf{X} \cdot d\mathbf{x} , \quad (2.13)$$

where $\mathbf{X} \in \mathbb{R}^n$ and $\mathbf{x} \in \mathbb{R}^n$ are ordered arrays $\mathbf{X} = (X_1, \dots, X_n)$, $\mathbf{x} = (x_1, \dots, x_n)$ and the dot denotes the scalar product over \mathbb{R}^n . If one writes (2.13) in the homogeneous form, $dF = 0$, it becomes clear that \mathbf{X} defines a normal field which is orthogonal to the hypersurfaces on which the value of F does not change. Solutions of the equation $dF = \mathbf{X} \cdot d\mathbf{x} = 0$ are surfaces (or curves according to dimension) $\mathbf{x} = \mathbf{x}(\sigma, \tau, \dots)$ on which F is constant. Locally such a solution can always be constructed, however, this surface may possibly not have the largest dimension ($n - 1$). If the local solutions possess the maximal possible dimension, one says that equation (2.12) is *completely integrable* (see also HEIL [53]). In this case it is possible, starting at a particular point, to construct a hypersurface – the mentioned manifold of dimension ($n - 1$) – within which any arbitrary integration of the right-hand side of (2.12) delivers the result zero. In this way one achieves the result to fill the entire phase space with ‘onion shells’ on which the equation $dF = 0$ holds and which never touch or intersect each other. If one imagines that the phase space is ‘partitioned’ in this way, there still remains the problem to assign to each ‘onion shell’ a value for the potential F and to guarantee that an integration of the differential between the various shells delivers always the same difference between these values, irrespective of where this integration is performed. For even if the construction of the surfaces of constant F -values is successful, this does not yet guarantee that the ‘distance’ between the surfaces does not depend on the position at the surface. However, once the ‘onion shells’ are constructed and appropriate potential values assigned to them, these facts then define in a unique way a scalar valued function – the above mentioned *integrating factor* by which the right-hand side of (2.12) must be multiplied to create everywhere the correct ‘distance’ between the

² Configuration space is the space of the independent variables x_j ($j = 1, \dots, n$).

³ In the classical thermodynamic literature, authors often use a different notation for a differential form depending on whether it is total (dF) or not (dF). So, dF is total, but dF is not. The modern mathematical literature does not distinguish the two cases and omits the differential symbol on the left-hand side of (2.12) (see (5.13) and (5.14)).

potential surfaces, respectively to create the desired connection between the differential and potential, provided it is not a priori given.

As we will see, a certain arbitrariness or possibility of choice remains unresolved because the ‘labeling’ of the ‘onion shells’ with potential values is not unique. Except for this freedom, it is, however, possible in this way to construct an integrating function for a vector field or a differential which locally allows in each point in phase space the construction of an equi-potential surface. With the aid of this function the vector field can be derived from a scalar potential or, alternatively, the differential form becomes total so that integrals between two points along arbitrary paths have all the same value. The above qualification of such a differential as being completely integrable is to be understood in this way.

In the following the conditions will be studied which formally must be satisfied in order that a differential form which by itself is not total can be made total by multiplying it with a scalar function, respectively to see whether a differential form is total already ab initio. Generally, the advantage of such a reduction of a vector valued function to a single scalar valued function is that mathematical operations are generally easier to perform with scalars than with vectors or tensors.

In what follows the differential dF will define the entropy (and in a second case the entropy flux) which must in all circumstances be a potential. This requirement allows inferences to be deduced for the coefficients of the differential form, X_i , which must be compatible with the potential properties.

2.2.2 Requirements to be imposed on the ‘normal fields’

Recall that a vector field $\mathbf{v}(x, y, z)$ over \mathbb{R}^3 is a gradient field of a scalar potential field P , $\mathbf{v} = \text{grad } P$, if the vector field $\mathbf{v}(x, y, z)$ is irrotational,

$$\nabla \times \mathbf{v} = \mathbf{0} . \quad (2.14)$$

If this property is not fulfilled, one may try to enforce it by multiplication of \mathbf{v} with a scalar function $f(x, y, z)$. This would make f an integrating factor. Instead of requiring the vanishing of $\nabla \times \mathbf{v}$, one will then request

$$\nabla \times (f\mathbf{v}) = f\nabla \times \mathbf{v} + (\nabla f) \times \mathbf{v} = \mathbf{0} . \quad (2.15)$$

Scalar multiplication of this equation with \mathbf{v} yields, since only $f \neq 0$ is reasonable,

$$(\nabla \times \mathbf{v}) \cdot \mathbf{v} = 0 , \quad (2.16)$$

which is a necessary condition that a non-trivial function can exist by which (2.15) can be fulfilled. However, that (2.16) is also a sufficient condition for

the existence of a non-trivial f is not easy to prove. Rather than to pursue this restricted case for $\mathbf{v} \in \mathbb{R}^3$ it is advantageous here to address the generalization of this theorem of differential forms for arbitrary dimensions. This proposition is known in the theory of differential forms or in exterior calculus as the *Frobenius condition* and is well known. Its derivation is somewhat complicated and requires algebraic techniques of exterior calculus, see CARTAN [18], [19], EDELEN [35]. Just as the FROBENIUS condition generalizes equation (2.16), so condition (2.14), which is a statement restricted to a vector field over \mathbb{R}^3 to make it derivable from a potential, can be generalized to POINCARÉ'S *theorem*, valid in a space of arbitrary dimension, see CARTAN [18], [19], EDELEN [35]. We shall state these propositions without proof.

a) POINCARÉ'S theorem:

The formal mathematical statement is as follows:⁴

To a differential form ω of given order p there exists a differential form Ω of order $p - 1$, from which ω ensues via an exterior derivative according to $d\Omega = \omega$, provided ω is closed, (that is, if $d\omega = 0$).

If this statement is translated into the common language of this book, it means that a differential form $dF = \sum_i X_i dx_i$ is total or exact and therefore derivable from a potential, if and only if after a further differentiation the coefficients are crosswise equal, viz.,

$$\frac{\partial X_i}{\partial x_j} = \frac{\partial X_j}{\partial x_i} . \quad (2.17)$$

When the vector space is \mathbb{R}^3 , (2.17) states that the vector field over \mathbb{R}^3 must be irrotational in order to be derivable from a potential. If the conditions of POINCARÉ'S theorem are not fulfilled, then one is confronted with the question whether introduction of an integrating factor may lead to a success. In this regard the theory of exterior calculus or differential forms makes the following statement.

b) The condition of FROBENIUS:

Let the differential form ω not be closed, that is, let $d\omega \neq 0$. Under such a condition the differential form is completely integrable, if $\omega \wedge d\omega = 0$, where ' \wedge ' is the exterior or 'veck' product defined as

$$\mathbf{w}_1 \wedge \mathbf{w}_2 := \mathbf{w}_1 \otimes \mathbf{w}_2 - \mathbf{w}_2 \otimes \mathbf{w}_1, \quad \mathbf{w}_1, \mathbf{w}_2 \in \mathbb{R}^3 \quad (2.18)$$

⁴ For the formal presentation of the terminology used in this theorem, see Appendix A.

In the simpler notation used in this book the FROBENIUS condition means the following: consider that for the differential form $dF = \sum_i X_i dx_i$ the condition (2.17) is not satisfied. Then, this differential can be transformed with an integrating factor into a total differential, if the condition

$$\sum_{ijk} e_{ijk} \left(\frac{\partial X_i}{\partial x_j} \right) X_k = 0 \quad (2.19)$$

holds, in which the sum stretches over all possible combinations of the indices i, j, k ; moreover, e_{ijk} is the alternating symbol defined in (2.7). The indices $\{i, j, k\}$ can be arbitrarily selected from the set of available indices in any initial order. This is so since all permutations of an initially selected order are contained in the sum (2.19). In \mathbb{R}^3 the FROBENIUS condition is equivalent to the satisfaction of the requirement (2.16) that the curl of a vector field must be perpendicular to the field itself. In \mathbb{R}^2 the curl of a vector field, interpreted as a field in \mathbb{R}^3 is trivially perpendicular to the field (if the vector field lies in the $x - y$ -plane, the curl points into the z -direction), and in \mathbb{R}^1 , there is only a single route along which a function can be integrated between two points, making every differential a total one. In spaces $\mathbb{R}^n, n > 3$, the condition of FROBENIUS can be interpreted as follows:

If the mixed derivatives of a differential form with respect to x_i and x_j with different sequences differ from one another (and this only holds for this single pair of variables) i. e., if

$$\frac{\partial X_i}{\partial x_j} \neq \frac{\partial X_j}{\partial x_i} \quad (2.20)$$

then in points where (2.20) is valid all other coefficient functions X_k of the differential dF with $k \notin (i, j)$ must vanish. The FROBENIUS condition (2.19) then reduces to

$$\sum_k e_{ijk} \left(\frac{\partial X_i}{\partial x_j} \right) X_k = 0, \quad \text{for fixed } i \neq j. \quad (2.21)$$

In the geometric language of \mathbf{X} as vector in \mathbb{R}^n ($n > 3$) this means, if two mixed derivatives are not equal (as in (2.21)), that the normal vector \mathbf{X} , formed by the components X_i ($i = 1, \dots, n$) must lie in the plane spanned by the coordinates belonging to these derivatives (otherwise (2.21) does not hold). Only in this case a hypersurface can locally and consistently be defined, which is perpendicular to the normal vectors and thereby guarantees the existence of an adequate integrating factor. Hence, the problem must essentially be 'locally two-dimensional'. The larger the dimension of the configuration space is, the more restrictive will be the constraints which correspond to the conditions of FROBENIUS.

Let us briefly summarize what the POINCARÉ theorem and condition of FROBENIUS imply for different dimensions n .

- $n = 1$ In the one-dimensional case each differential is total. There is no choice between different integration paths to reach point b from point a ; every integral along a ‘closed path’ vanishes trivially.
- $n = 2$ In two dimensions, there are infinitely many non-trivial possibilities to vary the path of integration between two given points. Not every field satisfies by itself the condition that the result of this integration will be independent of the choice of the path of integration. Where this is a priori not the case, an integrating factor can always be found which establishes this property and makes the differential form of the vector field a total one.
- $n \geq 3$ Not every vector field is so structured that it could be derived from a potential. Neither can it be guaranteed that for such an ‘unpleasant’ field an integrating factor could always be found that makes the corresponding differential a total one. Thus, there are ‘pathological’ differentials which are neither total nor would be transformable with an integrating factor into total differentials. The question under which circumstances a differential form can be made total, is equivalent to the question whether the FROBENIUS condition is satisfied. In \mathbb{R}^3 satisfaction of the FROBENIUS condition is tantamount to stating that the vector field is perpendicular to its vorticity field. In higher dimensions a good interpretation in terms of geometry is not available. In these cases one is left with the algebraic requirement (2.19) that must formally be verified or required for vector fields to be potential fields.

In this book the differential forms which are encountered are those of the entropy and its flux and arise first in (5.13) and (5.14) as scalar and vector valued one-forms. The variables x_i ($i = 1, \dots, n$) here are the independent constitutive variables there. Moreover, dF here is written as \mathcal{P} and \mathcal{F} , depending on whether the entropy \mathcal{P} or the entropy flux \mathcal{F} is in focus. The explicit forms of the coefficient functions X_i ($i = 1, \dots, n$) follow from the exploitation of the entropy principle (Second Law of Thermodynamics). Since the number of independent constitutive variables for the mixture theory of this book is much greater than three, the question of \mathcal{P} and \mathcal{F} to be total or not is crucial. The requirement that the entropy is meaningfully defined as a potential then corresponds to the requirement that the FROBENIUS condition is satisfied. This then implies restrictions to the constitutive variables which constitute necessary constraints for the satisfaction of the Second Law of Thermodynamics.

2.2.3 On the non-uniqueness of the integrating factors

As already explained, the single requirement that a differential form be total does not lead to the determination of a unique integrating factor. As an example, simply imagine that a successfully determined integrating function is globally multiplied with an arbitrary non-vanishing constant factor, then it is clear that a new integrating function is obtained; however, this factor f stretches ($f > 1$) or compresses ($0 < f < 1$) or mirrors ($f = -1$) the scale of the assumed potential values relative to the first function with the chosen factor. A mirroring operation will generally be excluded because with it a significant different interpretation of the related quantity would go along with such a change; alternatively, stretches or compressions are relatively harmless and only correspond to a change in the employed unit for the potential. More precisely, a given integrating factor g (here written as an integrating denominator) of an arbitrary non-total differential df ,

$$dF = \frac{df}{g}, \quad (2.22)$$

can always be multiplied with an arbitrary non-trivial differentiable function G of F , $G(F)$, without destroying the integrability properties. Indeed, by multiplication with G a new differential form dH is obtained which is given by

$$dH = \frac{G(F)}{g} df = \frac{G(F)}{g} \sum_i \frac{\partial f}{\partial x_i} dx_i. \quad (2.23)$$

POINCARÉ's theorem can now be employed to verify whether the conditions for a total differential are also fulfilled for H : With condition (2.17) one obtains

$$\text{for } k = i \quad : \quad \frac{\partial^2 H}{\partial x_j \partial x_i} = \frac{dG}{dF} \frac{\partial F}{\partial x_j} \frac{1}{g} \frac{\partial f}{\partial x_i} + G \frac{\partial}{\partial x_j} \left(\frac{1}{g} \frac{\partial f}{\partial x_i} \right), \quad (2.24)$$

$$\text{for } k = j \quad : \quad \frac{\partial^2 H}{\partial x_i \partial x_j} = \frac{dG}{dF} \frac{\partial F}{\partial x_i} \frac{1}{g} \frac{\partial f}{\partial x_j} + G \frac{\partial}{\partial x_i} \left(\frac{1}{g} \frac{\partial f}{\partial x_j} \right) \quad (2.25)$$

for $\{i, j\} \in (1, \dots, n)$. In (2.24) and (2.25) the last terms on the right-hand sides are equal, since g is an integrating factor by assumption; the first terms on the right-hand side of (2.24) and (2.25) are also identical, since $F = \int dF/g$. Indeed, the two expressions

$$\begin{aligned} \frac{dG}{dF} \frac{\partial F}{\partial x_j} \left(\frac{1}{g} \frac{\partial f}{\partial x_i} \right) &= \frac{dG}{dF} \frac{\partial F}{\partial x_j} \frac{\partial F}{\partial x_i}, \\ \frac{dG}{dF} \frac{\partial F}{\partial x_i} \left(\frac{1}{g} \frac{\partial f}{\partial x_j} \right) &= \frac{dG}{dF} \frac{\partial F}{\partial x_i} \frac{\partial F}{\partial x_j}, \end{aligned} \quad (2.26)$$

are equal. Therefore, it is ascertained that

$$dH = G(F) \frac{df}{g} \quad (2.27)$$

is a total differential of a function H , which, however, is not identical to F . Rather, if $\Delta_{a \rightarrow b} F$ denotes the value of the integral $\int_a^b dF$ between the states a and b in phase space of the considered system, then

$$\Delta_{a \rightarrow b} H = \Delta_{a \rightarrow b}(GF) - \int_a^b F \left(\frac{dG}{dF} \right) dF . \quad (2.28)$$

Depending upon the properties of G , different total differentials can be formed from the original differential df . This arbitrariness holds for each integrating factor of any differential form and is not particularly surprising either. Such an operation, as it leads here from F to another potential, H , is also somewhat irrelevant. True, the values of the original potential are stretched and moved, but the equi-potential surfaces remain unchanged thereby. This can easily be seen by looking at equation (2.13) or its homogeneous variant

$$dF = \mathbf{X} \cdot d\mathbf{x} = 0 \quad (2.29)$$

which defines the hypersurfaces of constant values of the potential. If the normal vector \mathbf{X} is stretched by a certain factor, then this process does not change any property of the surface whatsoever that is defined by (2.29). Since the vector can not vanish if both F and H are well defined and the integrating factor must also be continuous, the function G must be only of one sign; avoiding mirror transformation this requires G to be positive valued. Applied to the entropy, this requirement guarantees that all entropies which can be defined this way maintain the ‘ordering’ of their values. Indeed, if equation (2.28) is written for an infinitesimal process, it takes the form

$$\Delta_{a \rightarrow b} H = \Delta_{a \rightarrow b}(GF) - F \Delta_{a \rightarrow b} G = G \Delta_{a \rightarrow b} F \quad (2.30)$$

A positive entropy difference remains in such a transformation positive, if G is selected according to the above description. If this holds true for every infinitesimal partial transformation, so it will hold also for the entire finite process. This then also guarantees that a configuration which in one formulation possesses minimum entropy and thus corresponds to a thermodynamic equilibrium state also possesses minimum entropy in every other such formulation. There remains the question whether with the functions $G(F)$ of the potential F all possible transformations have been found. That this is so can be seen, if one recalls that neighbouring equi-potential surfaces must have ‘the same distance’ everywhere. This, alternatively, implies that the normal vectors \mathbf{X} on such a surface must everywhere on this surface be stretched with the same value. Consequently, the transformation factor G must at most be

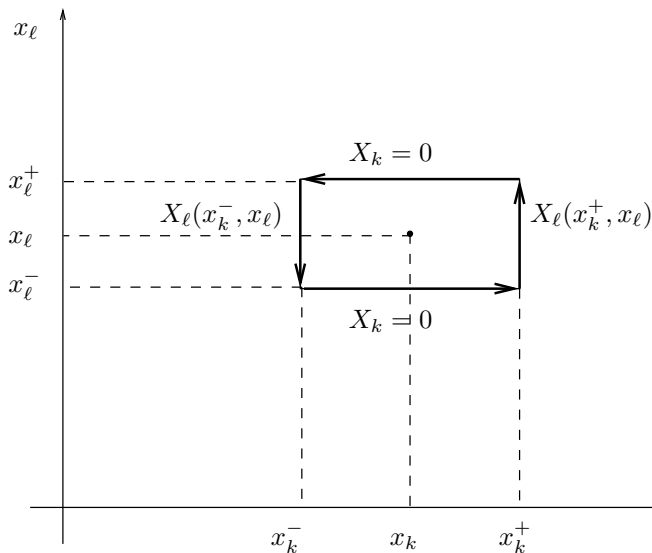


Fig. 2.1 Infinitesimal rectangle centered at (x_k, x_ℓ) with coefficient functions X_k and X_ℓ along the four sides of the infinitesimal rectangle.

a function of F for this is the only quantity which does not change on the equi-potential surfaces.

A further property in the context of functional dependences of integrating functions and coefficients in differential forms ensues if a given total differential only involves some but not all of the variables of the configuration space, i. e., if

$$dF = \sum_{i=1}^n X_i dx_i \quad \text{with} \quad X_k = 0 \quad \forall k \in (k_1, k_2, \dots, k_m), \quad m < n. \quad (2.31)$$

In this case one can prove the following

Proposition regarding the dependence of the coefficients X_i on the x_j : If a total differential of the form (2.31) has coefficients which vanish identically, then those coefficients which do not vanish equally only depend functionally on those variables x_i which belong to them (that is, they do not depend on x_k , $k \in (k_1, k_2, \dots, k_m)$, $m < n$ in (2.31)).

The proof follows by contradiction of the opposite assumption. So, let X_ℓ with $\ell \neq k$ depend on x_k , and assume X_k to vanish identically. Consider, moreover, the closed infinitesimal rectangular integration path shown in Fig.

2.1, centered at x_k, x_ℓ . It is now clear that the integrals $X_k dx_k$ along the horizontal edges vanish because $X_k = 0$; analogously, the integrals along the left and right sides of the rectangle of $X_\ell dx_\ell$ differ in absolute value from one another since by assumption $\partial X_\ell / \partial x_k \neq 0$. Therefore, the integral along the closed path composed of all four contributions, $\oint dF$, does not vanish. This result is in conflict with the assumption that dF is a total differential; consequently, X_ℓ cannot depend on x_k as was assumed above. This statement holds locally or globally, depending upon whether the respective coefficients of the differential form vanish locally or globally.

This result is particularly important because, later, it will imply non-trivial consequences for the differential of the entropy via the so-called GIBBS relation, which connects it with the internal energy and additional variables with an integrating denominator which in classical thermostatics of CARATHEODORY [17] is proved to agree with the KELVIN temperature. An analogous result should also hold here. As we shall see, it will follow in this mixture theory from a judicious application of the POINCARÉ theorem, the FROBENIUS condition and ad hoc assumptions which are plausible on the basis of physical or mathematical arguments.



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