

Chapter 1

INTRODUCTION: A POST-DUHEMIAN THERMODYNAMICS

The “irreversibility” of many processes arises because they are so complex that adequate description is impossible, for the practical attitude of thermodynamics toward such complicated processes will be merely to have anything to do with them, which is also its attitude towards irreversible processes.

P. W. Bridgman, *The Nature of Thermodynamics*, 1943, p. 134.

Perhaps, after all, the wise man’s attitude towards thermodynamics should be to have *nothing to do with it*. To deal with thermodynamics is to look for trouble. This is not the citation of a famous scientist, but the result of a deep cogitation following mere observations. Why do we need to get involved in a field of knowledge which, within the last hundred years, has exhibited the largest number of schizophrenics and megalomaniacs, imbalanced scientists, paranoiacs, egocentrists, and probably insomniacs and sleepwalkers? Is there any other field of scientific activity such as this one where, apparently, each of the bricklayers has unhesitatingly revindicated an originality that, to our eyes, and looking through the mirror dear to St. Paul (but also to *Alice*), we may see but with confusion. The intimate relationship between psychoanalysis and the behavior of more than one thermodynamicist may be due to the fact that Ludwig Boltzman (1844–1906) — may his soul rest in peace — both studied and dramatically ended his life in a city that saw the birth and burgeoning of Freud’s theory.

In introducing our subject we shall have to deal with hard-headed scientists and uncompromising characters, among them Pierre Duhem (1861–1916), Percy W. Bridgman (1882–1965), Joseph Kestin (1913–1993), and Clifford

A. Truesdell (born 1919), all kind and affable personalities but sharp, witty, and somewhat aggressive and vivacious critics of the scientific scene who, willingly or not, belong to the above-sketched out “medical” landscape and who, like the author, are not exempt from apriorisms and idiosyncrasies.

For some thermodynamicists and for their enemies as well, *thermodynamics* is the science of everything, so that for the second category of individuals, it is, by mere logic, the science of *nothing*, and thus not a science at all; and the *everything* is naturally seen as a sign of megalomania from which some have not escaped. Let us admit that *megalomania* in a moderate dose is an admissible behavior (after all, sometimes it *does* help in science). What is then the purpose of such a “science”? Is it to *explain* or to *classify* phenomena? Here we touch on the whole problem of the significance of *physical theory*. Should we try to explain essentially through *models* or are we to be satisfied with a mere *natural* classification of phenomena, i.e. *saving the phenomena*. It is not by chance that one of those epistemologists who most impressively pondered this question in a remarkable book full of hindsight was indeed Pierre Duhem (*The Aim and Structure of Physical Theory*, 1906a) who was so active in defending the cause of *thermodynamics* and who produced the longest treatise so far published in *energetics* or, as he says, *general thermodynamics* (Duhem, 1911).¹

Nobody can deny the urge to explain things, whether physical or belonging to other categories. That is, if it is true that a good classification, such as Carl Linnaeus’ in natural history, helps one to describe the variety of life, it does not explain it, so that we easily imagine the relief first brought by the Holy scriptures, and then by a solidly documented theory of evolution. The same applies in physics to which *thermodynamics* belongs. A natural classification dear to P. Duhem² helps us in organizing our knowledge and presenting to our students a neat logico-deductive framework. But this does not disqualify

¹To the few who have read it in the original French, this imposing treatise sounds like an unfinished program of “rational thermomechanics”, simultaneously a declaration of faith in a type of approach to field theory that was later to blossom, and a course on the pedagogy of logico-deductive science where “no hypotheses are framed”. Some of it sounds prematurely Truesdellian in tune, and parts have obviously inspired B. D. Coleman and J. L. Ericksen in some of their approaches to the *stability of continua*.

²In a *secrete*, (at the time) document (report in my French Doctoral Thesis in Mathematics), a well-known French mathematician classified my approach to thermomechanics as *neo-Duhemian* (I had *not* yet read Duhem in those times). When I could read that document after a law was passed giving access to all such personal papers, I felt that this was intended to be derogatory by its author, who could not figure out how much I later became pleased with such a classification.

before hand the use of *ingenious models*³ and, obviously, the call to microscopic descriptions. This is to specify our credo without ambiguity from the outset: we shall be *pragmatic*, and like Henri Poincaré and Percy Bridgman, somewhat *conventionalist* and *operationalist*. That is, like the Romans regarding religion, we would like to take the best out of each contribution while keeping a down-to-earth attitude. We shall accept objects and definitions which can be observed or realized through well-defined *operations*, but we shall not hesitate to have recourse to *pencil and paper* operations (versus *instrumental* operations), and to *gedankenexperiment(s)*, often the deepest and certainly the least costly ones. This “mixed salad” is welcomed as it should avoid fanaticism, dogmatism and sectarianism, as a matter of fact, any spirit of chapel (so much religious wording which tells a lot!) and it should bring some tranquility of mind, some *felicità*.⁴

At this point it is customary to make a historical digression which should span some hundred and fifty years.⁵ But we shall do this in gigantic (in Greek *megalo* — again!) steps, following in the footsteps of C. A. Truesdell (1984, “Historical Introit”) but not advocating the entirety of his standpoint.⁶ Apart from an *axiomatic foundation line* and kinetic-theoretical arguments and the recent “*extended*” thermodynamics to be discussed later on in this book, one easily recognizes two main lines, which concurred at some time and then coalesced to our modern view (see Fig. 1.1). On the one hand, we obviously have the line inaugurated by Sadi Carnot (1796–1832) and B. Clapeyron (1799–1864) which built on notions of *thermometry* and *calorimetry* and emphasized to start with the notion of *work*, and then took its most fruitful form with R. Clausius (1822–1888) and the statements of the *first law* (energy conservation) and the *second law* (*nondecrease* of entropy). Regarding the *second law*, one must recall that if energy is to be conserved at all [this is the *first law* whose

³To Duhem, W. Thomson (Lord Kelvin) in England and J. Boussinesq (1842–1929) in France epitomize the class of those who cannot do without (mechanical) models. As to J. C. Maxwell, Duhem criticizes him not for his achievements, which nobody can deny, but for his *inconsistencies* and, finally, for his enlightened amateurism.

⁴We are indebted to Paul Germain for this wise and serene approach to the thermomechanics of continua.

⁵This attitude is exemplified by J. L. Lagrange who, in his classical “*Mécanique Analytique*” of 1788, indeed introduces each part with a long historical quest which, in his opinion, gives the essentials of a somewhat linear development. This is *not* “history of science” in this more mythological, fairy-tale-like *success story* — and not history — which has been fruitful and bears pedagogical value.

⁶“*Tradutore, traditore*”.

FAMILY TREE OF THERMOMECHANICS

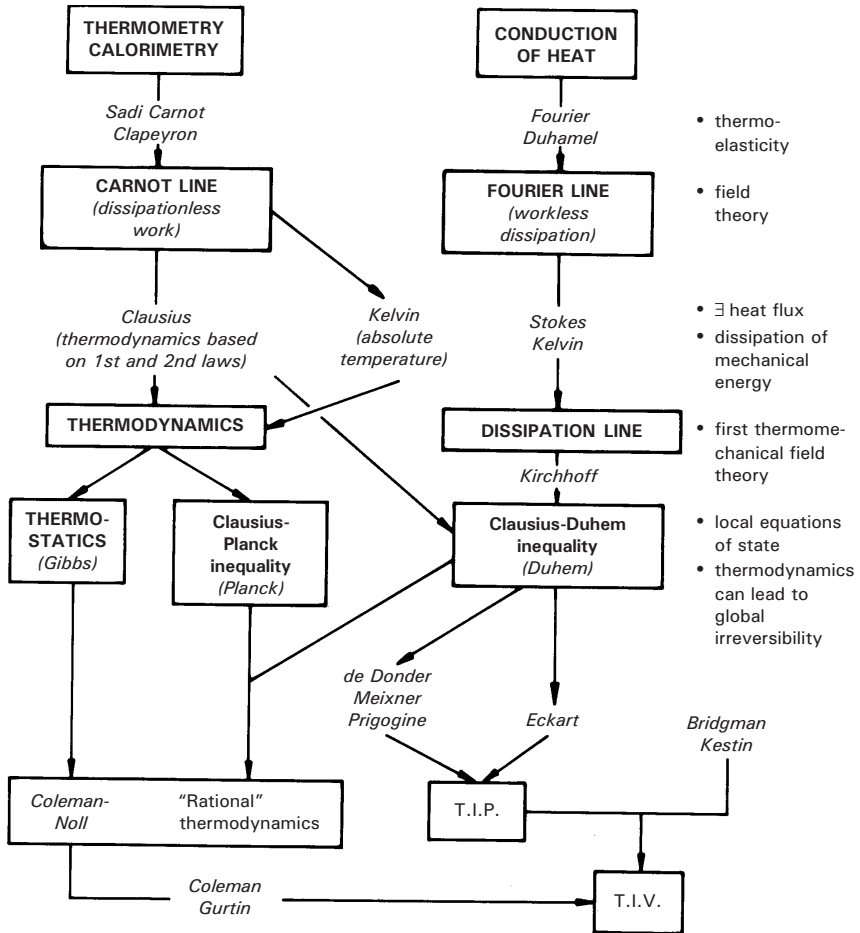


Fig. 1.1. Family tree of thermomechanics.

statement is due in essence to J. R. Mayer (1814–1878) and Kelvin (1824–1907)], energy in most physical situations *changes its nature*. This change of quality, according to Clausius, goes only in one way, either there is *no change* or energy is *degraded*. But this last word had no meaning in Clausius’ time, the 1840s–1850s. By analogy with the word *en-ergy*, Clausius then invented a

neologism, *en-tropy*, a word specially designed to qualify what changes when energy is conserved, a word which has a meaning only to physicists or this was what expected.⁷ Thus a quantity other than energy evolves only in *one direction*, later called the *Arrow of time* — and is witness to the irresistible *degradation* of energy (see the book by Brunhes, 1909). In practice, heat is the ultimate form of energy, in some sense the *worst* one, the one that we feel when an intense electric current passes through a resistive wire or when friction occurs between two parts of materials in contact in relative motion. Two general *laws of Nature*, i.e. *principles*, have thus emerged, the *conservation of energy* and the *necessary non-decrease of entropy*, of which the first developed at length in the works in *thermostatistics* of W. Gibbs (1839–1905) (book, 1928), while the second gave rise to the *Clausius-Planck inequality* in the expert hands of Max Planck (1858–1947).

On the other hand, J.-B. Fourier (1768–1830) and later J.-M.-C. Duhamel (1797–1872) are the founding fathers of the *Fourier line*, a true *mathematical physics*, which gave rise to a paragon of *field theory* (first, *thermal conduction* and then *thermoelasticity* in isotropic bodies and anisotropic crystals — see Bachelard, 1927) with its paraphernalia of partial differential equations and “mathematical methods for physics and engineering”, among them the celebrated Fourier series and integrals. This line would emphasize the role of *dissipation* with the recognition of the existence of the *heat flux vector* by G. G. Stokes (1819–1903) and of the *dissipation of mechanical energy* by Kelvin. This line, via G. Kirchhoff (1824–1887) who completed the first *thermomechanical field theory*, would lead to the essential formulation of the *Clausius-Duhem inequality* by P. Duhem who also clearly introduced *local equations of state* while recognizing that thermo-dynamics can lead to *global irreversibility*. With Gibbs, Planck and Duhem we enter the twentieth century. The Belgian school of thermodynamics, under the leadership of Th. de Donder (1872–1957) was then to create the *standard* theory of thermodynamics, the *theory of irreversible processes*, referred to as *T.I.P.* for short. At this point we need to pause as some of the ingredients introduced become our daily bread and the main actors our contemporaries.

What is the situation with thermodynamics on the eve of World War I? Along the kinetic-theoretical line which was also inaugurated by Clausius and

⁷ “τροπή” (*tropé*) means change, transformation; “tropism” in fact relates to changes in orientation. But in modern Greek “entropy” means something like “pudeur” or “sense of decency”, a virtue seldom exhibited by thermodynamicists!

much improved by J. C. Maxwell (1831–1879) with the introduction of his equilibrium distribution function, Ludwig Boltzmann (1844–1906), in breakthrough studies, has definitely shown that the notion of *entropy*, whether of Clausius’ or Gibbs’ origin,⁸ coincides with his definition (essentially a number) that is attributed, via a statistical theory of time-asymmetric irreversible non-equilibrium behavior, to each *microscopic* state of a *macroscopic* system be it solid, liquid, gas or otherwise. But contrary to Gibbs’ entropy which does not change in time even for ensembles describing isolated systems not in equilibrium, Boltzmann’s entropy *increases* in a way that explains the evolution toward equilibrium of such systems. Unlike Gibbs’ entropy, Boltzmann’s one captures the separation between *microscopic* and *mesoscopic* scales (see Lebowitz, 1993). More practically, Lord Rayleigh (J. W. Strutt, 1842–1919) has already introduced his *dissipation function* to deal with some macroscopic systems — essentially Newtonian–Stokesian viscosity — (Rayleigh, 1945; originally 1877, 1894), and this has already been used by Maxwell in some problems of electrodynamics (electric conduction currents, Maxwell, 1873). But apart from this, researchers are stocked as far as phenomenology is concerned. This is illustrated by P. Duhem who, in a rather famous literary review of the state of the Art, entitled “*The Evolution of Mechanics*” (Duhem, 1903), identifies several branches of applied physics that seem to resist a thermodynamical unification and are therefore called *nonsensical*. These branches are *friction*, *hysteresis* (such as in the plasticity of metals, or magnetic hysteresis), and *electromagnetic fields*. This was very well explored by Manville (1927) who wrote a masterly review of Duhem’s scientific achievements. Three essential ingredients which are still lacking at that moment (1910s) are: (i) the expression of a *balance law for entropy*, (ii) the formal expression of the *production of entropy as a bilinear form*, and (iii) the *nonquadratic nature* of the assumed dissipation potential (truly *nonlinear* dissipative processes). The first of these is clarified in Bridgman (1943, pp. 142, 143) who speaks (at the time) of the “not very much used”⁹ equation of balance that, parodying Bridgman, we can state as:

$$\text{“(net entropy leaving a close region) = (entropy created within the region) – (increase of entropy localized in this region)”},$$

⁸In Clausius’ case entropy is that of a system at equilibrium. In Gibbs’ case, it is defined for a *statistical ensemble* (a collection of independent systems, all with the same Hamiltonian, distributed in different microscopic states consistent with some specified macroscopic constraints). This quantity does *not* change in time even for systems not in equilibrium.

⁹An exception seems to be in discussions by Paul Ehrenfest (Bridgman, 1943, p. 146).

or in mathematical modern terms, where S is the entropy per unit volume, \mathbf{S} is the entropy flux (also called entropy flow vector), and C is the body source of entropy:

$$\operatorname{div} \mathbf{S} = -\frac{\partial S}{\partial t} + C. \quad (1.0.1)$$

The last quantity C is at first a pure convention. The problem resides in its expression. Bridgman shows in the case of pure heat conduction that for heat passing through a bridge between two reservoirs, one has

$$C = -\theta^{-2} \mathbf{q} \cdot \nabla \theta, \quad (1.0.2)$$

if $\mathbf{S} = \mathbf{q}/\theta$, where \mathbf{q} is the heat current and θ is the absolute temperature, the introduction of which is due to Lord Kelvin. He shows by the same token that the “final location of *entropy change* may be different from the location of the irreversible processes which generates it . . . There need be *no* irreversible process occurring at the place where the flow of entropy occurs”. For pure thermal processes, the second law of thermodynamics results then in the non-negativeness of the C term in the form of a *dissipation inequality*:

$$C = \theta^{-1} \Phi_{\text{th}} = \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0, \quad (1.0.3)$$

where Φ_{th} is the *thermal dissipation* that we shall meet later on on several occasions.

The second ingredient (ii) was reached by Carl Eckart (1902–1980) who, in a beautiful series of papers (Eckart, 1940, 1948), laid out part of the mathematical framework for describing the phenomenon of *diffusion*, a fully *thermo-mechanical* phenomenon as it is associated not only with mass transport but also with thermal influences and flow of heat. In the same papers Eckart introduces a consistent formulation of relativistic continuum thermodynamics and, last but not least, he remarks that the density of production of entropy (the C term above) is a *bilinear form in certain variables*, all of which vanish in equilibrium. This *bilinearity* property was also noticed by Josef Meixner (1908–1994) who, in addition, brought the support of the kinetic theory (of monatomic gases) and of Lars Onsager’s 1931 statistical treatment of small fluctuations about equilibrium (the celebrated *Onsager symmetry relations* between coefficients of the bilinear form in the presence of coupled dissipative phenomena). With this *T.I.P.* was born and it would take a definite, almost dogmatic, form in the famous treatise of S. R. de Groot and P. Mazur (1962), still probably

the most reliable and best available on the market. This, however, did not fully give satisfactory answers to the questions raised by the third point (iii). One had to await for the 1970s–1980s for its fulfillment.

It is probably at this point that Bridgman’s thorough analysis of the bases of thermodynamics — *its nature* — plays a most important role, the main question being: *What are the independent variables of thermo-mechanics?* (this is Truesdell’s language, 1960, p. 100). In other words, what are the most relevant *variables of state* in a true thermo-dynamical description of irreversible phenomena, i.e. those that may make the entropy grow? The answer to this question is clearly related to matters of time and space *scales*, perhaps *frequencies* (for periodic processes), and a *threshold value* of some characteristic fields, a matter that shall be recurrent in the remainder of this book.

Bridgman first admits that thermodynamics (1943, p. 6) is “a subject not yet complete or at least, . . . , one whose ultimate possibilities have not yet been explored, so that perhaps there may still be further generalizations awaiting discovery. . .” (he writes in the early 1940s). Then he emphasizes the notion of thermodynamical *state* and that of parameters of state (p. 17). Classical thermodynamics — to fix ideas, at the human scale of experience, and *not* the *quantum* scale — presupposes *large-scale* instrumental operations (p. 135) and this, in turn, provides a framework for the relevant parameters of state (p. 152). These are the parameters which *completely* define a state, in the way we can present specific values to the properties of a body (if God knows what is meant by that).¹⁰ In any case, this demonstrates the “macroscopic attack” of thermodynamics whose main function is *not* to explain (p. 222) in agreement with P. Duhem’s vision of the physical theory. “Thermodynamics smells more of its human origin than other branches of physics” (p. 214).¹¹ Relating to characteristic scales Bridgman rightfully mentions that in some “situations the irreversible aspects could be made to vanish in comparison with the reversible aspects by a suitable choice of the *dimension* of the apparatus and the *time*¹² of the experiments, or of some other parameters” (p. 138). Along the same line he points out to the possibility of “measurements on systems which are not *too* inhomogeneous” (p. 75).

¹⁰Bridgman will be very instrumental in the clear-cut selection of state variables in elastoplasticity (cf. Kestin, 1966, p. 369; Bridgman, 1950).

¹¹This may explain the practically neurotic behavior of more than one thermodynamicist; see first paragraph of this chapter.

¹²The Deborah number will be introduced for that purpose.

Although simple cases of irreversible processes exist which include “heat conduction, Joulean heat, diffusion, laminar flow of a viscous fluid” (p. 134), there are also obvious complex cases of which *hysteresis* (one of Duhem’s nonsensical examples) is paradigmatic. His feeling towards such cases is reflected by the difficulty in writing the functional dependence of the energy function (pp. 65, 66) — this is essential to write down the expression of the first law of thermodynamics or Gibbs’ equation — and he already alludes to “one or more new parameters that would effect the desired reduction to states of these complex cases” (p. 64). Perhaps in those complicated cases “the expression of the flow vector of entropy has to be modified” (p. 146)¹³ — remember that $\mathbf{S} = \mathbf{q}/\theta$ in Eq. (1.0.1) — and, in any case, “a more detailed study and classification of irreversible processes than any yet attempted would doubtless be rewarding” (p. 135). The present monograph is just about that, relying heavily on the notion of *internal variables of state*. This notion, some sharp observers believe to have spotted it in Bridgman’s writings,¹⁴ at least this is what the above quotation about additional parameters allowing for the definition of a “state” hints at. Other writers see the germ of this notion in some of Duhem’s works (Truesdell, 1984, p. 39, citing Duhem’s 1911 treatise). As it happened, this notion and presently no other one, allows one to construct a true *post-Duhemian* thermomechanics which does bring the nonsensical branches of mechanics of P. Duhem under the unifying, but also constraining, umbrella of *irreversible thermodynamics*. This has materialized through the works of many contributors, not the least among them, Kluitenberg (1962a, b; 1963), Coleman and Gurtin (1967a), Rice (1971), Sidoroff (1976), Nguyen Quoc Son (1973) and several others whom we shall discover as we proceed from one chapter to the next. Other developments such as the so-called “*rational*” thermodynamics of Coleman, Noll and Truesdell which may be considered an offspring of Gibbs’

¹³This remark is of far reaching insight when we consider what happens in *diffusive systems involving gradients* (see below).

¹⁴J. Kestin (1992, p. 1830; also in Muschik and Maugin, 1992, p. 44, the last publication of the late Prof. Kestin) cites Bridgman (1943):

“I believe that in general the analysis of such systems will be furthered by the recognition of a new type of large-scale thermodynamic parameter of state, namely the parameter of state which can be measured but not controlled... These parameters are measurable, but they are not controllable, which means that they are coupled to no external force variable which might provide the means of control. And not being coupled to a force variable, they cannot take part in mechanical work.”

thermodynamics and Duhem's grand program, and "extended" thermodynamics whose bases are rooted in the kinetic-theoretical program, are part of the present study, and we shall deal with them in due course, although briefly.

The above-developed ideas, brief as they are, are just to preach to the already convinced the usefulness of a general thermodynamical view. But 80 years after Duhem's writings there are still groups of scientists working at the *human* scale of experience, who do not recognize this evidence. For instance, some very active rheologists still completely ignore thermodynamical constraints (e.g. Larson, 1988, in an otherwise well-documented work). The same holds true in elastoplasticity and its generalizations with the Russian and English engineering schools. If it is true that thermodynamics amounted only to the consideration of Rayleigh's dissipation function for the Newtonian–Stokesian fluids, and could thus be dispensed with, this is no longer a tenable position with more involved behaviors that, according to others (e.g. Sidoroff, 1976; Luillier and Ouibrahim, 1980; Maugin and Drouot, 1983a; Jou *et al.*, 1993; Grmela, 1990, 1995), clearly necessitate, and practically fit, a thermodynamical background. The wealth of theoretically *dissipative* constitutive behaviors certainly needs to be restrained by the second law which then does provide some information. Likewise in elastoplasticity, fracture, and their generalizations where first the American and French, and now the German and North-European (Denmark, Holland) schools of theoretical mechanics have shown that the strict thermomechanical framework was the one which also corresponds to the best numerical one in so far as implementation is concerned (treatment of mathematical systems of evolution, use of convexity properties, exhibition of good stability properties, problems analogous to those handled in nonlinear programming techniques such as in econometry). Thus the "national style"¹⁵ in science, often originally propounded by only a few creative individuals, has some importance here because, like Newton's and Leibniz's notations for calculus, it may either hinder or foster a fruitful and rapid development. Furthermore, while the Art of cooking gains through the continuous aggregation of new recipes, the main purpose of Science — an economical one — is to *reduce* the number of *recipes*.¹⁶ General thermodynamics or *energetics à la Duhem*, or *thermomechanics* as we shall say, is just such a scientific framework

¹⁵No "nationalistic" connotation, obviously; pre-World War I Duhem's times are gone.

¹⁶Think of the endless collection of rheological models which discard *invariance* rules and thermodynamical constraints!

that gathers under the same umbrella so many phenomena while singularizing an evolution in a definite sense, the *Arrow of time*.

Now in attacking such a program we face the problem of the degree of abstractness and mathematical formalism that we should work with. Again, we shall stick to our pragmatic attitude. Is it reasonable, following thinkers like Auguste Comte, Nicolas Bourbaki (a famous collective author in mathematics), and some disciples of C. A. Truesdell, to assume previous knowledge of all of mathematics, to start studying a specialized, although vast, domain of physics? The answer is definitely *no*, because one should not expect so much from both our readers and ourselves. This would be both cheating and supererogatory pedantry. We shall rather be satisfied with a basic knowledge of college mathematics for physics and engineering.¹⁷ If the message does not go through, then we, alone, shall be considered responsible for this failure.

The contents of this book:

Following the general arguments expanded in following sections, we shall spend some time on introducing the basic elements of thermodynamics, that is, thermo-*statics* and the various approaches to thermo-*dynamics*, i.e. outside (even-though just slightly outside) equilibrium. In order to introduce thermodynamics in its thermo-*static* background (this is our approach which contrasts with “rational” thermodynamics), we must, it is clear, carefully define the notions of *system*, *state*, and *variable of state*. This is done in Chapter 2, where the Born–Caratheodory formulation of the *second law* has been followed. This is where the trouble starts. While we practically all agree on the statement of the *first law of thermodynamics*, the second law can be formulated in different more or less mathematical, formal, or physical ways. The *Born–Caratheodory* formulation of the second law was proposed by C. Caratheodory (1873–1950) on a suggestion by Max Born (1882–1970). Achieving elegance and generality in exposition, this is the mathematical formulation which is based on a common characteristic of all irreversible processes, the *inaccessibility of states*. The question boils down to whether some states can be reached from other neighboring ones in an *adiabatic* process (no exchange of heat in the bulk or

¹⁷We are referring to a good college where analysis and algebra are cultivated in a modern fashion, but without unnecessary symbolism. This does not exclude elements of topology, matrix algebra, vector analysis, tensor analysis, convex analysis, and functional analysis, all things which have become a necessity for a competitive engineer of high standard.

per unit area) taking place in a *closed* system (all terms are precisely defined in Chapter 2). This is a convincing formulation which supersedes the more classical ones derived from the Clausius and Kelvin–Planck statements found in classical college books (e.g. Kestin, 1966); Truesdell (1986, p. 114 on), however, strongly criticized the Born–Caratheodory formulation, claiming, with some controversial exaggeration, that in Caratheodory one finds “both mathematical gaps and errors”. It was supposedly shown by Cooper (1967) that Caratheodory failed to prove that his “absolute temperature” deserves the name of temperature. But this was proved false by Walter (1976). According to Bernstein (1960), the problem with Caratheodory’s absolute temperature is that its existence is established only *locally*, while the scale of such a temperature should be *global*. But then J. Serrin has also claimed (cf. Truesdell, 1986, p. 117) “that all ‘flaws’ [quotation marks mine, G.A.M.], whether mathematical or physical, can be overcome by a thorough reformulation and recasting”. Walter (1978) has indeed provided some reconciliation of the classical method (Carnot, Gibbs) with that of Caratheodory. Walter’s development, it is true, like Caratheodory’s, makes the second law contingent on the first. We shall be satisfied with the “modest” formulation of Caratheodory while referring the reader to Truesdell’s writing for a flavor of scandal and a touch of excitement. Whether Caratheodory distracted us from Carnot and Gibbs (cf. Truesdell and Bharatha, 1977; Pitteri, 1982) is somewhat peripheral and a disputable subject.

Chapter 3 has for declared purpose to present in a nutshell the essential *theories* of irreversible thermodynamics. We have already mentioned *T.I.P.* as the “successful” one. It indeed provides the core for further developments as we shall exploit a direct extension of it, leaving aside the *linearity* of constitutive equations while enlarging the set of *state variables*. “Rational thermodynamics”, of which the credo and dogma are cognizably expanded in Truesdell (1969, 1984), offers the elegance and temptations of all formal logico-deductive approaches: *it is very attractive!* P. Germain (1975) has thoroughly analyzed its biases, shortcomings and audacity. “Extended thermodynamics”, of much more recent extraction [although early works by R. E. Nettleton (e.g. 1960) should not be discarded], and well expanded in two monographs by its most ardent proponents (Müller and Ruggieri, 1993; Jou *et al.*, 1993), lends itself to few manageable applications and suffers from its intrinsic limitations to the set of fluxes considered. Thus the essential of our efforts will naturally be

placed on the *thermodynamics with internal variables*, for short, *T.I.V.*, i.e. the thermodynamics which introduces additional *variables of state*, say along the timid but farsighted proposal of P. W. Bridgman, that are *not controllable*.

Thermodynamics with internal variables is formally examined in Chapter 4. The main problems there are the proper selection of such internal variables, the relationship of the resulting theory with other thermodynamics, the way entropy can be defined in spite of the lack of equilibrium, and how does one generalize the notion of dissipation potential initially introduced by Rayleigh. Furthermore, there exist some relationships between the notions of *internal variables* and *internal degrees of freedom*, as also with the *order parameter* of phase-transition theory. What are we to do when the bodies subject of our thermodynamical analysis are highly heterogeneous, i.e. when length-scales enter the stage? This is complemented in Chapter 5 by the statement of the general rules of application of *T.I.V.*

Chapter 6 outlines the numerous applications which will allow the reader to grasp the flexibility of the method and the profusion of applications in all domains of physical science, especially in *materials science*, in the sense granted nowadays to this term. Many of these successful applications have been developed by the author and co-workers during the last two decades. These applications are presented in order, following a somewhat traditional classification of the behavior of materials (recall Duhem's vision of the *physical theory*). Thus Chapter 6 discusses the problem of the representation of *viscosity* in fluids of all kinds, with an emphasis on dilute solutions of polymers, liquid crystals, and turbulence. This representation varies within a large spectrum, depending markedly on the *internal variables* introduced as new "Bridgmanian" variables of state. This provides a true *thermodynamically admissible* approach to *rheology* (the science of what flows).

T.I.V. applied to solid-like materials is probably the most successful of its application as its acceptance in this domain has practically become universal. Our previous (specialized) textbook on the *Thermomechanics of Plasticity and Fracture* (Maugin, 1992a) is witness of this trend. This also holds true of the book on the *Mechanics of Materials* by J. Lemaitre and J.-L. Chaboche (1990) which, in a different style, has been instrumental in spreading the gospel of *Thermomechanics*. *Viscoelasticity*, *Viscoplasticity*, at both small and large strains, together with *damage* and *creep* are obviously covered, although rather briefly in order to avoid duplication, in Chapter 7. *Mechanical hysteresis* and *friction* (two of the Duhem's *nonsensical* branches of mechanics) are thus

incorporated in the thermodynamical framework, at the price, however, of some mathematical complication (use of convex analysis, potential which are homogeneous functions of degree one, and thus somewhat singular). The debt to the original views of Ziegler in Switzerland, to J. R. Rice and J. Kestin (in the USA) and to the French school of analysis and theoretical mechanics, especially with J. Mandel, P. Germain, J.-J. Moreau, Nguyen Quoc Son, and P. Suquet, in these developments need to be emphasized.

With *fracture*, we enter a different domain of application in Chapter 8. That is, the global thermodynamical behavior of a specimen may be *dissipative*, while the local constitutive equations in the bulk do not manifest any dissipation. This is the case in *brittle fracture* where the irreversibility clearly stems from the fact that we cannot solder back the faces of the growing crack; the latter progresses irreversibly, if it progresses at all. Here the expression of the laws of thermodynamics in global form plays a fundamental role. But the originality is that the *domain of integration of these laws evolves with the progress of the crack*. It is possible to construct the corresponding *global irreversible thermodynamics* and to devise thermodynamically based criteria of progress. This in fact is an example of thermodynamics of *material forces* (see our book on “*Material Inhomogeneities in Elasticity*”, Maugin, 1993a) of which other examples are exhibited in further chapters. The role of Griffith (energy concept of fracture, 1920), Eshelby (force on an elastic singularity, 1951), Cherepanov (Γ -integral in many phenomena, 1967), Rice (path-independent integral of fracture, 1968), Freund (dynamical fracture, 1972, 1990), Bui (fracture of different types, 1978) and Nguyen Quoc Son (1980) must be recognized as decisive. In our own works with co-workers to be cited in due course we have placed the fracture of solids under the umbrella of the general *theory of material forces* on a material manifold and *not* in physical space, as the non-linear deformation theory of material demands. Brittle, dynamic, and ductile fractures can be treated thus, as well as the fracture of electromagnetic solids (see below).

Electromagnetic theory was conceived by Duhem as the most difficult branch of continuum physics to incorporate into the thermodynamical framework. This is certainly true if one considers the full electrodynamics of continua, i.e. the theory of moving media which are magnetized, electrically polarized, and possibly conductors of current. The problem remains at first view inextricable even though we satisfy ourselves with an approximate Galilean invariant theory to start with (which is sufficient in all cases of engineering

interest). For the general aspects of the electrodynamics of nonlinear continua, whether solids or fluids, for the time being we can find no better references in the existing literature than our own books (Maugin, 1988; Eringen and Maugin, 1990). Thus only a sketch of this theory is given in the first sections of Chapter 9. Rather than duplicating existing books, after a brief review we show how the simplest irreversible behaviors follow from a more or less standard use of *T.I.P.* once the appropriately invariant fields have been introduced. Of greater interest is the application of *T.I.V.* which answers Duhem's worries about this *nonsensical branch of mechanics*. Dielectric relaxation, electro- and magneto-hysteresis, and their coupling with temperature and mechanical effects can be incorporated in the thermodynamical framework which *does* provide rules and constraints to select the most comprehensive and satisfactory representations of these somewhat singular behaviors. As in the case of viscoplasticity, the identification of the relevant *internal variables* is the most formidable problem, requiring physical insight. A prime example from this viewpoint is the identification of the unexpected variable in the magnetic-hysteresis theory developed by Motogi and Maugin (1993a, b): the area of magnetic domains oriented at 90° to the direction of the magnetizing field. Other sensible applications concern *deformable superconductors* where the internal variable of interest is a function which intervenes at a lower degree of description (the complex-valued wave function of Cooper's pairs), polyelectrolyte solutions (Drouot and Maugin, 1985), ferrofluidic solutions, elastic semiconductors, and the mechanical fracture and electric breakdown of electromagnetic structures. Most of the examples presented have been devised by the author and co-workers in a long series of memoirs and collated here for the first time. Some of the aspects concerning *nonlinear dissipative electromechanical behaviors, per se*, have been examined in a different monograph (Maugin, Pouget *et al.*, 1992).

We have gathered in Chapter 10 problems relating to the *reaction-diffusion systems* which abound in physics and which have played historically an important role in the inception of *T.I.V.* (think of reaction advancement rates and the associated thermodynamics). Nowadays such systems are exemplary of some typical problems of *progress* of some signals (like in nerve-pulse dynamics) or some phase-transition fronts. The latter problem can also be viewed as one of *thermodynamic material forces* (see above) but which relates to moving jumps in properties of the material. Coherent phase-transition fronts in elastic crystals enter this framework. In this respect we must underline the contributions

of Jü. Engelbrecht, C. Trimarco, M. E. Gurtin and coworkers (e.g., Gurtin, 1993a, b), M. Grinfeld (1991), and L. Truskinowski (1987, 1991), the first two in collaboration with the author (see bibliography).

Notation. As a rule we use the standard notation of vector analysis (with the nabla symbol ∇) without indices. For tensors the intrinsic (no index) notation is in general preferred over the indexed Cartesian tensor notation commonly used by engineers, but, in harmony with our opened declaration of pragmatism, indices may be called for in case of ambiguity. Because of the wealth of material expanded in this book, we may have to use several different types of fonts (including German Gothic ones!), but these are used in a consistent manner which the reader will identify as we proceed, especially when dealing with electromagnetic fields in various frameworks.