THE PHYSICS AND MATHEMATICS OF THE SECOND LAW OF THERMODYNAMICS

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Abstract: The essential postulates of classical thermodynamics are formulated, from which the second law is deduced as the principle of increase of entropy in irreversible adiabatic processes that take one equilibrium state to another. The entropy constructed here is defined only for equilibrium states and no attempt is made to define it otherwise. Statistical mechanics does not enter these considerations. One of the main concepts that makes everything work is the comparison principle (which, in essence, states that given any two states of the same chemical composition at least one is adiabatically accessible from the other) and we show that it can be derived from some assumptions about the pressure and thermal equilibrium. Temperature is derived from entropy, but at the start not even the concept of 'hotness' is assumed. Our formulation offers a certain clarity and rigor that goes beyond most textbook discussions of the second law.

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I. INTRODUCTION

The second law of thermodynamics is, without a doubt, one of the most perfect laws in physics. Any *reproducible* violation of it, however small, would bring the discoverer great riches as well as a trip to Stockholm. The world's energy problems would be solved at one stroke. It is not possible to find any other law (except, perhaps, for super selection rules such as charge conservation) for which a proposed violation would bring more skepticism than this one. Not even Maxwell's laws of electricity or Newton's law of gravitation are so sacrosanct, for each has measurable corrections coming from quantum effects or general relativity. The law has caught the attention of poets and philosophers and has been called the greatest scientific achievement of the nineteenth century. Engels disliked it, for it supported opposition to dialectical materialism, while Pope Pius XII regarded it as proving the existence of a higher being (Bazarow, 1964, Sect. 20).

A. The basic questions

In this paper we shall attempt to formulate the essential elements of *classical* thermodynamics of equilibrium states and deduce from them the second law as the principle of the increase of entropy. 'Classical' means that there is *no mention of statistical mechanics here* and 'equilibrium' means that we deal only with states of systems in equilibrium and do not attempt to define quantities such as entropy and temperature for systems not in equilibrium. This is not to say that we are concerned only with 'thermostatics' because, as will be explained more fully later, arbitrarily violent processes are allowed to occur in the passage from one equilibrium state to another.

Most students of physics regard the subject as essentially perfectly understood and finished, and concentrate instead on the statistical mechanics from which it ostensibly can be derived. But many will admit, if pressed, that thermodynamics is something that they are sure that someone else understands and they will confess to some misgiving about the logic of the steps in traditional presentations that lead to the formulation of an entropy function. If classical thermodynamics is the most perfect physical theory it surely deserves a solid, unambiguous foundation free of little pictures involving unreal Carnot cycles and the like. [For examples of 'un-ordinary' Carnot cycles see (Truesdell and Bharatha 1977, p. 48).]

There are two aims to our presentation. One is frankly pedagogical, i.e., to formulate the foundations of the theory in a clear and unambiguous way. The second is to formulate equilibrium thermodynamics as an 'ideal physical theory', which is to say a theory in which there are well defined mathematical constructs and well defined rules for translating physical reality into these constructs; having done so the mathematics then grinds out whatever answers it can and these are then translated back into physical statements. The point here is that while 'physical intuition' is a useful guide for formulating the mathematical structure and may even be a source of inspiration for constructing mathematical proofs, it should not be necessary to rely on it once the initial 'translation' into mathematical language has been given. These goals are not new, of course; see e.g., (Duistermaat, 1968), (Giles, 1964, Sect. 1.1) and (Serrin, 1986, Sect. 1.1).

Indeed, it seems to us that many formulations of thermodynamics, including most textbook presentations, suffer from mixing the physics with the mathematics. Physics refers to the real world of experiments and results of measurement, the latter quantified in the form of numbers. Mathematics refers to a logical structure and to rules of calculation; usually these are built around numbers, but not always. Thus, mathematics has two functions: one is to provide a transparent logical structure with which to view physics and inspire experiment. The other is to be like a mill into which the miller pours the grain of experiment and out of which comes the flour of verifiable predictions. It is astonishing that this paradigm works to perfection in thermodynamics. (Another good example is Newtonian mechanics, in which the relevant mathematical structure is the calculus.) Our theory of the second law concerns the mathematical structure, primarily. As such it starts with some axioms and proceeds with rules of logic to uncover some non-trivial theorems about the existence of entropy and some of its properties. We do, however, explain how physics leads us to these particular axioms and we explain the physical applicability of the theorems.

As noted in I.C below, we have a total of 15 axioms, which might seem like a lot. We can assure the reader that any other mathematical structure that derives entropy with minimal assumptions will have at least that many, and usually more. (We could roll several axioms into one, as others often do, by using sub-headings, e.g., our A1-A6 might perfectly well be denoted by A1(i)-(vi).) The point is that we leave nothing to the imagination or to silent agreement; it is all laid out.

It must also be emphasized that our desire to clarify the structure of classical equilibrium thermodynamics is not merely pedagogical and not merely nit-picking. If the law of entropy increase is ever going to be derived from statistical mechanics—a goal that has so far eluded the deepest thinkers—then it is important to be absolutely clear about what it is that one wants to derive.

Many attempts have been made in the last century and a half to formulate the second law precisely and to quantify it by means of an entropy function. Three of these formulations are classic (Kestin, 1976), (see also Clausius (1850), Thomson (1849)) and they can be paraphrased as follows:

Clausius: No process is possible, the sole result of which is that heat is transferred from a body to a hotter one.

Kelvin (and Planck): No process is possible, the sole result of which is that a body is cooled and work is done.

Carathéodory: In any neighborhood of any state there are states that cannot be reached from it by an adiabatic process.

The crowning glory of thermodynamics is the quantification of these statements by means of a precise, measurable quantity called entropy. There are two kinds of problems, however. One is to give a precise meaning to the words above. What is 'heat'? What is 'hot' and 'cold'? What is 'adiabatic'? What is a 'neighborhood'? Just about the only word that is relatively unambiguous is 'work' because it comes from mechanics.

The second sort of problem involves the rules of logic that lead from these statements to an entropy. Is it really necessary to draw pictures, some of which are false, or at least not self evident? What are all the hidden assumptions that enter the derivation of entropy? For instance, we all know that discontinuities can and do occur at phase transitions, but almost every presentation of classical thermodynamics is based on the differential calculus (which presupposes continuous derivatives), especially (Carathéodory, 1925) and (Truesdell-Bharata, 1977, p.xvii).

We note, in passing, that the Clausius, Kelvin-Planck and Carathéodory formulations are all assertions about *impossible* processes. Our formulation will rely, instead, mainly on assertions about *possible* processes and thus is noticeably different. At the end of Section VII, where everything is succintly summarized, the relationship of these approaches is discussed. This discussion is left to the end because it it cannot be done without first presenting our results in some detail. Some readers might wish to start by glancing at Section VII.

Of course we are neither the first nor, presumably, the last to present a derivation of the second law (in the sense of an entropy principle) that pretends to remove all confusion and, at the same time, to achieve an unparalleled precision of logic and structure. Indeed, such attempts have multiplied in the past three or four decades. These other theories, reviewed in Sect. I.B, appeal to their creators as much as ours does to us and we must therefore conclude that ultimately a question of 'taste' is involved.

It is not easy to classify other approaches to the problem that concerns us. We shall attempt to do so briefly, but first let us state the problem clearly. Physical systems have certain states (which always mean equilibrium states in this paper) and, by means of certain actions, called *adiabatic processes*, it is possible to change the state of a system to some other state. (Warning: The word 'adiabatic' is used in several ways in physics. Sometimes it means 'slow and gentle', which might conjure up the idea of a quasi-static process, but this is certainly not our intention. The usage we have in the back of our minds is 'without exchange of heat', but we shall avoid defining the word 'heat'. The operational meaning of 'adiabatic' will be defined later on, but for now the reader should simply accept it as singling out a particular class of processes about which certain physically interesting statements are going to be made.) Adiabatic processes do not have to be very gentle, and they certainly do not have to be describable by a curve in the space of equilibrium states. One is allowed, like the gorilla in a well-known advertisement for luggage, to jump up and down on the system and even dismantle it temporarily, provided the system returns to some equilibrium state at the end of the day. In thermodynamics, unlike mechanics, not all conceivable transitions are adiabatic and it is a nontrivial problem to characterize the allowed transitions. We shall characterize them as transitions that have no *net* effect on other systems except that energy has been exchanged with a mechanical source. The truly remarkable fact, which has many consequences, is that for every system there is a function, S, on the space of its (equilibrium) states, with the property that one can go adiabatically from a state X to a state Y if and only if $S(X) \leq S(Y)$. This, in essence, is the 'entropy principle' (EP) (see subsection II.B).

The S function can clearly be multiplied by an arbitrary constant and still continue to do its job, and thus it is not at all obvious that the function S_1 for system 1 has anything to do with the function S_2 for system 2. The second remarkable fact is that the S functions for all the thermodynamic systems in the universe can be simultaneously calibrated (i.e., the multiplicative constants can be determined) in such a way that the entropies are *additive*, i.e., the S function for a compound system is obtained merely by adding the S functions of the individual systems, $S_{1,2} = S_1 + S_2$. ('Compound' does not mean chemical compound; a compound system is just a collection of several systems.) To appreciate this fact it is necessary to recognize that the systems comprising a compound system can interact with each other in several ways, and therefore the possible adiabatic transitions in a compound are far more numerous than those allowed for separate, isolated systems. Nevertheless, the increase of the function $S_1 + S_2$ continues to describe the adiabatic processes exactly—neither allowing more nor allowing less than actually occur. The statement $S_1(X_1) + S_2(X_2) \leq S_1(X_1') + S_2(X_2')$ does not require $S_1(X_1) \leq S_1(X_1')$.

The main problem, from our point of view, is this: What properties of adiabatic processes permit us to construct such a function? To what extent is it unique? And what properties of the interactions of different systems in a compound system result in additive entropy functions?

The existence of an entropy function can be discussed in principle, as in Section II, without parametrizing the equilibrium states by quantities such as energy, volume, etc.. But it is an additional fact that when states are parametrized in the conventional ways then the derivatives of S exist and contain all the information about the equation of state, e.g., the temperature T is defined by $\partial S(U,V)/\partial U|_V = 1/T$.

In our approach to the second law temperature is never formally invoked until the very end when the differentiability of S is proved—not even the more primitive relative notions of 'hotness' and 'coldness' are used. The priority of entropy is common in statistical mechanics and in some other approaches to thermodynamics such as in (Tisza, 1966) and (Callen, 1985), but the elimination of hotness and coldness is not usual in thermodynamics, as the formulations of Clausius and Kelvin show. The laws of thermal equilibrium (Section V), in particular the zeroth law of thermodynamics, do play a crucial role for us by relating one system to another (and they are ultimately responsible for the fact that entropies can be adjusted to be additive), but thermal equilibrium is only an equivalence relation and, in our form, it is not a statement about hotness. It seems to us that temperature is far from being an 'obvious' physical quantity. It emerges, finally, as a derivative of entropy, and unlike quantities in mechanics or electromagnetism, such as forces and masses, it is not vectorial, i.e., it cannot be added or multiplied by a scalar. Even pressure, while it cannot be 'added' in an unambiguous way, can at least be multiplied by a scalar. (Here, we are not speaking about changing a temperature scale; we mean that once a scale has been fixed, it does not mean very much to multiply a given temperature, e.g., the boiling point of water, by the number 17. Whatever meaning one might attach to this is surely not independent of the chosen scale. Indeed, is T the right variable or is it $1/T$? In relativity theory this question has led to an ongoing debate about the natural quantity to choose as the fourth component of a four-vector. On the other hand, it does mean something unambiguous, to multiply the pressure in the boiler by 17. Mechanics dictates the meaning.)

Another mysterious quantity is 'heat'. No one has ever seen heat, nor will it ever be seen, smelled or touched. Clausius wrote about "the kind of motion we call heat", but thermodynamics—either practical or theoretical—does not rely for its validity on the notion of molecules jumping around. There is no way to measure heat flux directly (other than by its effect on the source and sink) and, while we do not wish to be considered antediluvian, it remains true that 'caloric' accounts for physics at a macroscopic level just as well as 'heat' does. The reader will find no mention of heat in our derivation of entropy, except as a mnemonic guide.

To conclude this very brief outline of the main conceptual points, the concept of *convexity* has to be mentioned. It is well known, as Gibbs (Gibbs 1928), Maxwell and others emphasized, that thermodynamics without convex functions (e.g., free energy per unit volume as a function of density) may lead to unstable systems. (A good discussion of convexity is in (Wightman, 1979).) Despite this fact, convexity is almost invisible in most fundamental approaches to the second law. In our treatment it is *essential* for the description of simple systems in Section III, which are the building blocks of thermodynamics.

The concepts and goals we have just enunciated will be discussed in more detail in the following sections. The reader who impatiently wants a quick survey of our results can jump to Section VII where it can be found in capsule form. We also draw the readers attention to the article (Lieb-Yngvason 1998), where a summary of this work appeared. Let us now turn to a brief discussion of other modes of thought about the questions we have raised.

B. Other approaches

The simplest solution to the problem of the foundation of thermodynamics is perhaps that of Tisza (1966), and expanded by Callen (1985) (see also (Guggenheim, 1933)), who, following the tradition of Gibbs (1928), postulate the existence of an additive entropy function from which all equilibrium properties of a substance are then to be derived. This approach has the advantage of bringing one quickly to the applications of thermodynamics, but it leaves unstated such questions as: What physical assumptions are needed in order to insure the existence of such a function? By no means do we wish to minimize the importance of this approach, for the manifold implications of entropy are well known to be non-trivial and highly important theoretically and practically, as Gibbs was one of the first to show in detail in his great work (Gibbs, 1928).

Among the many foundational works on the existence of entropy, the most relevant for our considerations and aims here are those that we might, for want of a better word, call 'order theoretical' because the emphasis is on the derivation of entropy from postulated properties of adiabatic processes. This line of thought goes back to Carathéodory (1909 and 1925), although there are some precursors (see Planck, 1926) and was particularly advocated by (Born, 1921 and 1964). This basic idea, if not Carathéodory's implementation of it with differential forms, was developed in various mutations in the works of Landsberg (956), Buchdahl (1958, 1960, 1962, 1966), Buchdahl and Greve (1962), Falk and Jung (1959), Bernstein (1960), Giles (964), Cooper (1967), Boyling, (1968, 1972), Roberts and Luce (1968), Duistermaat (1968), Hornix (1968), Rastall (1970), Zeleznik (1975) and Borchers (1981). The work of Boyling (1968, 1972), which takes off from the work of Bernstein (1960) is perhaps the most direct and rigorous expression of the original Carthéodory idea of using differential forms. See also the discussion in Landsberg (1970).

Planck (1926) criticized some of Carathéodory's work for not identifying processes that are not adiabatic. He suggested basing thermodynamics on the fact that 'rubbing' is an adiabatic process that is not reversible, an idea he already had in his 1879 dissertation. From this it follows that while one can undo a rubbing operation by some means, one cannot do so adiabatically. We derive this principle of Planck from our axioms. It is very convenient because it means that in an adiabatic process one can effectively add as much 'heat' (colloquially speaking) as one wishes, but the one thing one cannot do is subtract heat, i.e., use a 'refrigerator'.

Most authors introduce the idea of an 'empirical temperature', and later derive the absolute temperature scale. In the same vein they often also introduce an 'empirical entropy' and later derive a 'metric', or additive, entropy, e.g., (Falk and Jung, 1959) and (Buchdahl, 1958, et seq., 1966), (Buchdahl and Greve, 1962), (Cooper, 1967). We avoid all this; one of our results, as stated above, is the derivation of absolute temperature directly, without ever mentioning even 'hot' and 'cold'.

One of the key concepts that is eventually needed, although it is not obvious at first, is that of the comparison principle (or hypothesis), (CH). It concerns classes of thermodynamic states and asserts that for any two states X and Y within a class one can either go *adiabatically* from X to Y, which we write as

$$X \prec Y,$$

(pronounced "X precedes Y" or "Y follows X") or else one can go from Y to X, i.e., $Y \prec X$. Obviously, this is not always possible (we cannot transmute lead into gold, although we *can* transmute hydrogen plus oxygen into water), so we would like to be able to break up the universe of states into equivalence classes, inside each of which the hypothesis holds. It turns out that the key requirement for an equivalence relation is that if $X \prec Y$ and $Z \prec Y$ then either $X \prec Z$ or $Z \prec X$. Likewise, if $Y \prec X$ and $Y \prec Z$ by then either $X \prec Z$ or $Z \prec X$. We find this first clearly stated in Landsberg (1956) and it is also found in one form or another in many places, see e.g., (Falk and Jung, 1959), (Buchdahl, 1958, 1962), (Giles, 1964). However, all authors, except for Duistermaat (1968), seem to take this postulate for granted and do not feel obliged to obtain it from something else. One of the central points in our work is to *derive* the comparison hypothesis. This is discussed further below.

The formulation of the second law of thermodynamics that is closest to ours is that of Giles (Giles, 1964). His book is full of deep insights and we recommend it highly to the reader. It is a classic that does not appear to be as known and appreciated as it should. His derivation of entropy from a few postulates about adiabatic processes is impressive and was the starting point for a number of further investigations. The overlap of our work with Giles's is only partial (the foundational parts, mainly those in our section II) and where there is overlap there are also differences.

To define the entropy of a state, the starting point in both approaches is to let a process that by itself would be adiabatically impossible work against another one that is possible, so that the total process is adiabatically possible. The processes used by us and by Giles are, however, different; for instance Giles uses a fixed external calibrating system, whereas we define the entropy of a state by letting a system interact with a copy of itself. (According to R. E. Barieau (quoted in (Hornix, 1967-1968)) Giles was unaware of the fact that predecessors of the idea of an external entropy meter can be discerned in (Lewis and Randall, 1923).) To be a bit more precise, Giles uses a standard process as a reference and counts how many times a reference process has to be repeated to counteract some multiple of the process whose entropy (or rather 'irreversibility') is to be determined. In contrast, we construct the entropy function for a single system in terms of the amount of substance in a reference state of 'high entropy' that can be converted into the state under investigation with the help of a reference state of 'low entropy'. (This is reminiscent of an old definition of heat by Laplace and Lavoisier (quoted in (Borchers, 1981)) in terms of the amount of ice that a body can melt.) We give a simple formula for the entropy; Giles's definition is less direct, in our view. However, when we calibrate the entropy functions of different systems with each other, we do find it convenient to use a third system as a 'standard' of comparison.

Giles' work and ours use very little of the calculus. Contrary to almost all treatments, and contrary to the assertion (Truesdell-Bharata, 1977) that the differential calculus is the appropriate tool for thermodynamics, we and he agree that entropy and its essential properties can best be described by maximum principles instead of equations among derivatives. To be sure, real analysis does eventually come into the discussion, but only at an advanced stage (Sections III and V in our treatment).

In Giles, too, temperature appears as a totally derived quantity, but Giles's derivation requires some assumptions, such as differentiability of the entropy. We prove the required differentiability from natural assumptions about the pressure.

Among the differences, it can be mentioned that the 'cancellation law', which plays a key role in our proofs, is taken by Giles to be an axiom, whereas we derive it from the assumption of 'stability', which is common to both approaches (see Section II for definitions).

The most important point of contact, however, and at the same time the most significant difference, concerns the comparison hypothesis which, as we emphasized above, is a concept that plays an essential role, although this may not be apparent at first. This hypothesis serves to divide the universe nicely into equivalence classes of mutually accessible states. Giles takes the comparison property as an axiom and does not attempt to justify it from physical premises. The main part of our work is devoted to just that justification, and to inquire what happens if it is violated. (There is also a discussion of this point in (Giles, 1964, Sect 13.3) in connection with hysteresis.) To get an idea of what is involved, note that we can easily go adiabatically from cold hydrogen plus oxygen to hot water and we can go from ice to hot water, but can we go either from the cold gases to ice or the reverse—as the comparison hypothesis demands? It would appear that the only real possibility, if there is one at all, is to invoke hydrolysis to dissociate the ice, but what if hydrolysis did not exist? In other examples the requisite machinery might not be available to save the comparison hypothesis. For this reason we prefer to derive it, when needed, from properties of 'simple systems' and not to invoke it when considering situations involving variable composition or particle number, as in Section VI.

Another point of difference is the fact that convexity is central to our work. Giles mentions it, but it is not central in his work perhaps because he is considering more general systems than we do. To a large extent convexity eliminates the need for explicit topological considerations about state spaces, which otherwise has to be put in 'by hand'.

Further developments of the Giles' approach are in (Cooper, 1967), (Roberts and Luce, 1968) and (Duistermaat, 1968). Cooper assumes the existence of an empirical temperature and introduces topological notions which permits certain simplifications. Roberts and Luce have an elegant formulation of the entropy principle, which is mathematically appealing and is based on axioms about the order relation, $\prec$, (in particular the comparison principle, which they call conditional connectedness), but these axioms are not physically obvious, especially axiom 6 and the comparison hypothesis. Duistermaat is concerned with general statements about morphisms of order relations, thermodynamics being but one application.

A line of thought that is entirely different from the above starts with Carnot (1824) and was amplified in the classics of Clausius and Kelvin (cf. (Kestin, 1976)) and many others. It has dominated most textbook presentations of thermodynamics to this day. The central idea concerns cyclic processes and the efficiency of heat engines; heat and empirical temperature enter as primitive concepts. Some of the modern developments along these lines go well beyond the study of equilibrium states and cyclic processes and use some sophisticated mathematical ideas. A representative list of references is Arens (1963), Coleman and Owen (1974, 1977), Coleman, Owen and Serrin (1981), Dafermos (1979), Day (1987, 1988), Feinberg and Lavine (1983), Green and Naghdi (1978), Gurtin (1975), Man (1989), Owen (1984), Pitteri (1982), Serrin (1979, 1983, 1986), Silhavy (1997), Truesdell and Bharata (1977), Truesdell (1980, 1984). Undoubtedly this approach is important for the practical analysis of many physical systems, but we neither analyze nor take a position on the validity of the claims made by its proponents. Some of these are, quite frankly, highly polemical and are of two kinds: claims of mathematical rigor and physical exactness on the one hand and assertions that these qualities are lacking in other approaches. See, for example, Truesdell's contribution in (Serrin, 1986, Chapter 5). The chief reason we omit discussion of this approach is that it does not directly address the questions we have set for ourselves. Namely, using only the existence of equilibrium states and the existence of certain processes that take one into another, when can it be said that the list of allowed processes is characterized *exactly* by the increase of an entropy function?

Finally, we mention an interesting recent paper by Macdonald (1995) that falls in neither of the two categories described above. In this paper 'heat' and 'reversible processes' are among the primitive concepts and the existence of reversible processes linking any two states of a system is taken as a postulate. Macdonald gives a simple definition of entropy of a state in terms of the maximal amount of heat, extracted from an infinite reservoir, that the system absorbs in processes terminating in the given state. The reservoir thus plays the role of an entropy meter.

The further development of the theory along these lines, however, relies on unstated assumptions about differentiability of the so defined entropy that are not entirely obvious.

C. Outline of the paper

In Section II we formally introduce the relation $\prec$ and explain it more fully, but it is to be emphasized, in connection with what was said above about an ideal physical theory, that $\prec$ has a well defined mathematical meaning independent of the physical context in which it may be used. The concept of an entropy function, which characterizes this accessibility relation, is introduced next; at the end of the section it will be shown to be unique up to a trivial affine transformation of scale. We show that the existence of such a function is *equivalent* to certain simple properties of the relation $\prec$, which we call axioms A1 to A6 and the 'hypothesis' CH. Any formulation of thermodynamics must implicitly contain these axioms, since they are equivalent to the entropy principle, and it is not surprising that they can be found in Giles, for example. We do believe that our presentation has the virtue of directness and clarity, however. We give a simple formula for the entropy, entirely in terms of the relation $\prec$ without invoking Carnot cycles or any other gedanken experiment. Axioms A1 to A6 are highly plausible; it is CH (the comparison hypothesis) that is not obvious but is *crucial* for the existence of entropy. We call it a hypothesis rather than an axiom because our ultimate goal is to derive it from some additional axioms. In a certain sense it can be said that the rest of the paper is devoted to *deriving* the comparison hypothesis from plausible assumptions. The content of Section II, i.e., the derivation of an entropy function, stands on its own feet; the implementation of it via CH is an independent question and we feel it is pedagogically significant to isolate the main input in the derivation from the derivation itself.

Section III introduces one of our most novel contributions. We *prove* that comparison holds for the states inside certain systems which we call *simple systems.* To obtain it we need a few new axioms, S1 to S3. These axioms are mainly about *mechanical* processes, and not about the entropy. In short, our most important assumptions concern the continuity of the generalized pressure and the existence of irreversible processes. Given the other axioms, the latter is equivalent to Carathéodory's principle.

The comparison hypothesis, CH, does not concern simple systems alone, but also their products, i.e., compound systems composed of possibly interacting simple systems. In order to compare states in different simple systems (and, in particular, to calibrate the various entropies so that they can be added together) the notion of a *thermal join* is introduced in Section IV. This concerns states that are usually said to be in thermal equilibrium, but we emphasize that temperature is not mentioned. The thermal join is, by assumption, a simple system and, using the zeroth law and three other axioms about the thermal join, we reduce the comparison hypothesis among states of *compound systems* to the previously derived result for simple systems. This derivation is another novel contribution. With the aid of the thermal join we can prove that the multiplicative constants of the entropies of all systems can be chosen so that entropy is additive, i.e., the sum of the entropies of simple systems gives a correct entropy function for compound systems. This entropy correctly describes all adiabatic processes in which there is no change of the constituents of compound systems. What remains elusive are the additive constants, discussed in Section VI. These are important when changes (due to mixing and chemical reactions) occur.

Section V establishes the continuous differentiability of the entropy and defines inverse temperature as the derivative of the entropy with respect to the energy—in the usual way. No new assumptions are needed here. The fact that the entropy of a simple system is determined uniquely by its adiabats and isotherms is also proved here.

In Section VI we discuss the vexed question of comparing states of systems that differ in constitution or in quantity of matter. How can the entropy of a bottle of water be compared with the sum of the entropies of a container of hydrogen and a container of oxygen? To do so requires being able to transform one into the other, but this may not be easy to do reversibly. The usual theoretical underpinning here is the use of semi-permeable membranes in a 'van't Hoff box' but such membranes are usually far from perfect physical objects, if they exist at all. We examine in detail just how far one can go in determining the *additive* constants for the entropies of different systems in the the real world in which perfect semi-permeable membranes do not exist.

In Section VII we collect all our axioms together and summarize our results briefly.

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II. ADIABATIC ACCESSIBILITY AND CONSTRUCTION OF ENTROPY

Thermodynamics concerns systems, their states and an order relation among these states. The order relation is that of **adiabatic accessibility**, which, physically, is defined by processes whose only net effect on the surroundings is exchange of energy with a mechanical source. The glory of classical thermodynamics is that there always is an *additive* function, called **entropy**, on the state space of any system, that *exactly* describes the order relation in terms of the increase of entropy.

Additivity is very important physically and is certainly not obvious; it tells us that the entropy of a compound system composed of two systems that can interact and exchange energy with each other is the sum of the individual entropies. This means that the pairs of states accessible from a given pair of states, which is a far larger set than merely the pairs individually accessible by the systems in isolation, is given by studying the sum of the individual entropy functions. This is even more surprising when we consider that the individual entropies each have undetermined multiplicative constants; there is a way to adjust, or calibrate the constants in such a way that the sum gives the correct result for the accessible states—and this can be done once and for all so that the same calibration works for all possible pairs of systems. Were additivity to fail we would have to rewrite the steam tables every time a new steam engine is invented.

The other important point about entropy, which is often overlooked, is that entropy not only increases, but entropy also tells us exactly which processes are adiabatically possible in any given system; states of high entropy in a system are *always* accessible from states of lower entropy. As we shall see this is generally true but it could conceivably fail when there are chemical reactions or mixing, as discussed in Section VI.

In this section we begin by defining these basic concepts more precisely, and then we present the entropy principle. Next, we introduce certain axioms, A1-A6, relating the concepts. All these axioms are completely intuitive. However, one other assumption—which we call the *comparison hypothesis*—is needed for the construction of entropy. It is not at all obvious physically, but it is an essential part of conventional thermodynamics. Eventually, in Sections III and IV, this hypothesis will be *derived* from some more detailed physical considerations. For the present, however, this hypothesis will be assumed and, using it, the existence of an entropy function will be proved. We also discuss the extent to which the entropy function is uniquely determined by the order relation; the comparison hypothesis plays a key role here.

The existence of an entropy function is equivalent to axioms A1-A6 in conjunction with CH, neither more nor less is required. The state space need not have any structure besides the one implied by the order relation. However, state spaces parametrized by the energy and work coordinates have an additional, convex structure, which implies concavity of the entropy, provided that the formation of convex combination of states is an adiabatic process. We add this requirement as axiom A7 to our list of general axioms about the order relation.

The axioms in this section are so general that they encompass situations where *all* states in a whole neighborhood of a given state are adiabatically accessible from it. **Carathéodory's principle** is the statement that this does *not* happen for physical thermodynamic systems. In contrast, ideal mechanical systems have the property that every state is accessible from every other one (by mechanical means alone), and thus the world of mechanical systems will trivially obey the entropy principle in the sense that every state has the same entropy. In the last subsection we discuss the connection between Carathéodory's principle and the existence of irreversible processes starting from a given state. This principle will again be invoked when, in Section III, we derive the comparison hypothesis for simple thermodynamic systems.

Temperature will not be used in this section, not even the notion of 'hot' and 'cold'. There will be no cycles, Carnot or otherwise. The entropy only depends on, and is defined by the order relation. Thus, while the approach given here is not the only path to the second law, it has the advantage of a certain simplicity and clarity that at least has pedagogic and conceptual value. We ask the reader's patience with our syllogisms, the point being that everything is here clearly spread out in full view. There are no hidden assumptions, as often occur in many textbook presentations.

Finally, we hope that the reader will not be confused by our sometimes lengthy asides about the motivation and heuristic meaning of our various definitions and theorems. We also hope these remarks will not be construed as part of the structure of the second law. The definitions and theorems are self-contained, as we state them, and the remarks that surround them are intended only as a helpful guide.

A. Basic concepts

1. Systems and their state spaces

Physically speaking a thermodynamic *system* consists of certain specified amounts of different kinds of matter; it might be divisible into parts that can interact with each other in a specified way. A special class of systems called simple systems will be discussed in the next chapter. In any case the possible interaction of the system with its surroundings is specified. It is a "black box" in the sense that we do not need to know what is in the box, but only its response to exchanging energy, volume, etc. with other systems. The states of a system to be considered here are *always* equilibrium states, but the equilibrium may depend upon the existence of internal barriers in the system. Intermediate, non-equilibrium states that a system passes through when changing from one equilibrium state to another will not be considered. The entropy of a system not in equilibrium may, like the temperature of such a system, have a meaning as an approximate and useful concept, but this is not our concern in this treatment.

Our systems can be quite complicated and the outside world can act on them in several ways, e.g., by changing the volume and magnetization, or removing barriers. Indeed, we are allowed to chop a system into pieces violently and reassemble them in several ways, each time waiting for the eventual establishment of equilibrium.

Our systems must be macroscopic, i.e, not too small. Tiny systems (atoms, molecules, DNA) exist, to be sure, but we cannot describe their equilibria thermodynamically, i.e., their equilibrium states cannot be described in terms of the simple coordinates we use later on. There is a gradual shift from tiny systems to macroscopic ones, and the empirical fact is that large enough systems conform to the axioms given below. At some stage a system becomes 'macroscopic'; we do not attempt to explain this phenomenon or to give an exact rule about which systems are 'macroscopic'.

On the other hand, systems that are too large are also ruled out because gravitational forces become important. Two suns cannot unite to form one bigger sun with the same properties (the way two glasses of water can unite to become one large glass of water). A star with two solar masses is intrinsically different from a sun of one solar mass. In principle, the two suns could be kept apart and regarded as one system, but then this would only be a 'constrained' equilibrium because of the gravitational attraction. In other words the conventional notions of 'extensivity' and 'intensivity' fail for cosmic bodies. Nevertheless, it is possible to define an entropy for such systems by measuring its effect on some standard body. Giles' method is applicable, and our formula (2.20) in Section II.E (which, in the context of our development, is used only for calibrating the entropies defined by (2.14) in Section II.D, but which could be taken as an independent definition) would allow it, too. (The 'nice' systems that do satisfy size-scaling are called 'perfect' by Giles.) The entropy, so defined, would satisfy additivity but not extensivity, in the 'entropy principle' of Section II.B. However, to prove this would requires a significant enhancement of the basic axioms. In particular, we would have to take the comparison hypothesis, CH, for all systems as an axiom — as Giles does. It is left to the interested reader to carry out such an extension of our scheme.

A basic operation is **composition** of two or more systems to form a new system. Physically, this simply means putting the individual systems side by side and regarding them as one system. We then speak of each system in the union as a **subsystem**. The subsystems may or may not interact for a while, by exchanging heat or volume for instance, but the important point is that a state of the total system (when in equilibrium) is described completely by the states of the subsystems.

From the mathematical point of view a system is just a collection of points called a **state space**, usually denoted by Γ. The individual points of a state space are called **states** and are denoted here by capital Roman letters, X, Y, Z, etc. From the next section on we shall build up our collection of states satisfying our axioms from the states of certain special systems, called *simple systems.* (To jump ahead for the moment, these are systems with one or more work coordinates but with only one energy coordinate.) In the present section, however, the manner in which states are described (i.e., the coordinates one uses, such as energy and volume, etc.) are of no importance. Not even topological properties are assumed here about our systems, as is often done. In a sense it is amazing that much of the second law follows from certain abstract properties of the relation among states, independent of physical details (and hence of concepts such as Carnot cycles). In approaches like Giles', where it is taken as an axiom that comparable states fall into equivalence classes, it is even possible to do without the system concept altogether, or define it simply as an equivalence class of states. In our approach, however, one of the main goals is to derive the property which Giles takes as an axiom, and systems are basic objects in our axiomatic scheme.

Mathematically, the composition of two spaces, Γ_1 and Γ_2 is simply the Cartesian product of the state spaces $\Gamma_1 \times \Gamma_2$. In other words, the states in $\Gamma_1 \times \Gamma_2$ are pairs (X_1, X_2) with $X_1 \in \Gamma_1$ and $X_2 \in \Gamma_2$. From the physical interpretation of the composition it is clear that the two spaces $\Gamma_1 \times \Gamma_2$ and $\Gamma_2 \times \Gamma_1$ are to be identified. Likewise, when forming multiple compositions of state spaces, the order and the grouping of the spaces is immaterial. Thus $(\Gamma_1 \times \Gamma_2) \times \Gamma_3$, $\Gamma_1 \times (\Gamma_2 \times \Gamma_3)$ and $\Gamma_1 \times \Gamma_2 \times \Gamma_3$ are to be identified as far as composition of state spaces is concerned. Strictly speaking, a symbol like $(X_1, \dots, X_N)$ with states X_i in state spaces Γ_i, $i = 1, \dots, N$ thus stands for an equivalence class of n-tuples, corresponding to the different groupings and permutations of the state spaces. Identifications of this type are not uncommon in mathematics (the formation of direct sums of vector spaces is an example).

A further operation we shall assume is the formation of **scaled copies** of a given system whose state space is Γ. If $t > 0$ is some fixed number (the scaling parameter) the state space $\Gamma^{(t)}$ consists of points denoted tX with $X \in \Gamma$. On the abstract level tX is merely a symbol, or mnemonic, to define points in $\Gamma^{(t)}$, but the symbol acquires meaning through the axioms given later in Sect. II.C. In the physical world, and from Sect. III onward, the state spaces will always be subsets of some $\mathbf{R}^n$ (parametrized by energy, volume, etc.). In this case tX has the concrete representation as the product of the real number t and the vector $X \in \mathbf{R}^n$. Thus in this case $\Gamma^{(t)}$ is simply the image of the set $\Gamma \subset \mathbf{R}^n$ under scaling by the real parameter t. Hence, we shall sometimes denote $\Gamma^{(t)}$ by $t\Gamma$.

Physically, $\Gamma^{(t)}$ is interpreted as the state space of a system that has the same properties as the system with state space Γ, except that the amount of each chemical substance in the system has been scaled by the factor t and the range of extensive variables like energy, volume etc. has been scaled accordingly. Likewise, tX is obtained from X by scaling energy, volume etc., but also the matter content of a state X is scaled by the parameter t. From this physical interpretation it is clear that $s(tX) = (st)X$ and $(\Gamma^{(t)})^{(s)} = \Gamma^{(st)}$ and we take these relations also for granted on the abstract level. The same apples to the identifications $\Gamma^{(1)} = \Gamma$ and $1X = X$, and also $(\Gamma_1 \times \Gamma_2)^{(t)} = \Gamma_1^{(t)} \times \Gamma_2^{(t)}$ and $t(X, Y) = (tX, tY)$.

The operation of forming compound states is thus an associative and commutative binary operation on the set of all states, and the group of positive real numbers acts by the scaling operation on this set in a way compatible with the binary operation and the multiplicative structure of the real numbers. The same is true for the set of all state spaces. From an algebraic point of view the simple systems, to be discussed in Section III, are a basis for this algebraic structure.

While the relation between Γ and $\Gamma^{(t)}$ is physically and intuitively fairly obvious, there can be surprises. Electromagnetic radiation in a cavity ('photon gas'), which is mentioned after (2.6), is an interesting case; the two state spaces Γ and $\Gamma^{(t)}$ and the thermodynamic functions on these spaces are identical in this case! Moreover, the two spaces are physically indistinguishable. This will be explained in more detail in Section II.B.

The formation of scaled copies involves a certain physical idealization because it ignores the molecular structure of matter. Scaling to arbitrarily small sizes brings quantum effects to the fore and macroscopic thermodynamics is no longer applicable. At the other extreme, scaling to arbitrarily large sizes brings in unwanted gravitational effects as discussed above. In spite of these well known limitations the idealization of continuous scaling is common practice in thermodynamics and simplifies things considerably. (In the statistical mechanics literature this goes under the rubric of the 'thermodynamic limit'.) It should be noted that scaling is quite compatible with the inclusion of 'surface effects' in thermodynamics. This will be discussed in Section III. A.

By composing scaled copies of N systems with state spaces $\Gamma_1, \ldots, \Gamma_N$, one can form, for $t_1, \ldots, t_N > 0$, their **scaled product** $\Gamma_1^{(t_1)} \times \cdots \times \Gamma_N^{(t_N)}$ whose points are $(t_1X_1, t_2X_2, \ldots, t_NX_N)$. In the particular case that the Γ_j's are identical, i.e., $\Gamma_1 = \Gamma_2 = \cdots = \Gamma$, we shall call any space of the the form $\Gamma^{(t_1)} \times \cdots \times \Gamma^{(t_N)}$ a **multiple scaled copy** of Γ. As will be explained later in connection with Eq. (2.11), it is sometimes convenient in calculations to allow $t = 0$ as scaling parameter (and even negative values). For the moment let us just note that if $\Gamma^{(0)}$ occurs the reader is asked to regard it as the empty set or 'nosystem'. In other words, ignore it.

Some examples may help clarify the concepts of systems and state spaces.

(a) Γ_a: 1 mole of hydrogen, H_2. The state space can be identified with a subset of $\mathbf{R}^2$ with coordinates U (= energy), V(= volume).

(b) Γ_b: $\frac{1}{2}$ mole of H_2. If Γ_a and Γ_b are regarded as subsets of $\mathbf{R}^2$ then $\Gamma_b = \Gamma_a^{(1/2)} = \{(\frac{1}{2}U, \frac{1}{2}V) : (U, V) \in \Gamma_a\}$.

(c) Γ_c: 1 mole of H_2 and $\frac{1}{2}$ mole of O_2 (unmixed). $\Gamma_c = \Gamma_a \times \Gamma_{(\frac{1}{2}\text{ mole } O_2)}$. This is a compound system.

(d) Γ_d: 1 mole of H_2O.

(e) Γ_e: 1 mole of $H_2 + \frac{1}{2}$ mole of O_2 (mixed). Note that $\Gamma_e \neq \Gamma_d$ and $\Gamma_e \neq \Gamma_c$. This system shows the perils inherent in the concept of equilibrium. The system Γ_e makes sense as long as one does not drop in a piece of platinum or walk across the laboratory floor too briskly. Real world thermodynamics requires that we admit such quasi-equilibrium systems, although perhaps not quite as dramatic as this one.

(f) Γ_f: All the equilibrium states of one mole of H_2 and half a mole of O_2 (plus a tiny bit of platinum to speed up the reactions) in a container. A typical state will have some fraction of H_2O, some fraction of H_2 and some O_2. Moreover, these fractions can exist in several phases.

2. The order relation

The basic ingredient of thermodynamics is the relation

$$\prec$$

of **adiabatic accessibility** among states of a system— or even different systems. The statement $X \prec Y$, when X and Y are points in some (possibly different) state spaces, means that there is an adiabatic transition, in the sense explained below, that takes the point X into the point Y.

Mathematically, we do not have to ask the meaning of 'adiabatic'. All that matters is that a list of all possible pairs of states X's and Y's such that $X \prec Y$ is regarded as given. This list has to satisfy certain axioms that we prescribe below in subsection C. Among other things it must be reflexive, i.e., $X \prec X$, and transitive, i.e., $X \prec Y$ and $Y \prec Z$ implies $X \prec Z$. (Technically, in standard mathematical terminology this is called a *pre*order relation because we can have both $X \prec Y$ and $Y \prec X$ without $X = Y$.) Of course, in order to have an interesting thermodynamics result from our $\prec$ relation it is essential that there are pairs of points X, Y for which $X \prec Y$ is *not* true.

Although the physical interpretation of the relation $\prec$ is not needed for the mathematical development, for applications it is essential to have a clear understanding of its meaning. It is difficult to avoid some circularity when defining the concept of adiabatic accessibility. The following version (which is in the spirit of Planck's formulation of the second law (Planck, 1926)) appears to be sufficiently general and precise and appeals to us. It has the great virtue (as discovered by Planck) that it avoids having to distinguish between work and heat—or even having to define the concept of heat; heat, in the intuitive sense, can always be generated by rubbing—in accordance with Count Rumford's famous discovery while boring cannons! We emphasize, however, that other definitions are certainly possible. Our physical definition is the following:

Adiabatic accessibility: *A state Y is adiabatically accessible from a state X, in symbols $X \prec Y$, if it is possible to change the state from X to Y by means of an interaction with some device (which may consist of mechanical and electrical parts as well as auxiliary thermodynamic systems) and a weight, in such a way that the device returns to its initial state at the end of the process whereas the weight may have changed its position in a gravitational field.*

Let us write

$$X \prec\prec Y \quad \text{if} \quad X \prec Y \quad \text{but} \quad Y \not\prec X. \tag{2.1}$$

In the real world Y is adiabatically accessible from X only if $X \prec\prec Y$. When $X \prec Y$ and also $Y \prec X$ then the state change can only be realized in an idealized sense, for it will take infinitely long time to achieve it in the manner decribed. An alternative way is to say that the 'device' that appears in the definition of accessibility has to return to within 'ε' of its original state (whatever that may mean) and we take the limit $\varepsilon \to 0$. To avoid this kind of discussion we have taken the definition as given above, but we emphasize that it is certainly possible to redo the whole theory using only the notion of $\prec\prec$. An emphasis on $\prec\prec$ appears in Lewis and Randall's discussion of the second law (Lewis and Randall, 1923, page 116).

Remark: It should be noted that the operational definition above is a definition of the concept of 'adiabatic accessibility' and not the concept of an 'adiabatic process'. A state change leading from X to Y can be achieved in many different ways (usually infinitely many), and not all of them will be 'adiabatic processes' in the usual terminology. Our concern is not the temporal development of the state change which, in real processes, always leads out of the space of equilibrium states. Only the end result for the system and for the rest of the world interests us. However, it is important to clarify the relation between our definition of adiabatic accessiblity and the usual textbook definition of an adiabatic process. This will be discussed in Section C after Theorem 2.1 and again in Sec. III; cf. Theorem 3.8. There it will be shown that our definition indeed coincides with the usual notion based on processes taking place within an 'adiabatic enclosure'. A further point to notice is that the word 'adiabatic' is sometimes used to mean "slow" or quasi-static, but nothing of the sort is meant here. Indeed, an adiabatic process can be quite violent. The explosion of a bomb in a closed container is an adiabatic process.

Here are some further examples of adiabatic processes:

1. Expansion or compression of a gas, with or without the help of a weight being raised or lowered.
2. Rubbing or stirring.
3. Electrical heating. (Note that the concept of 'heat' is not needed here.)
4. Natural processes that occur within an isolated compound system after some barriers have been removed. This includes mixing and chemical or nuclear processes.
5. Breaking a system into pieces with a hammer and reassembling (Fig. 1).
6. Combinations of such changes.

In the usual parlance, rubbing would be an adiabatic process, but not electrical 'heating', because the latter requires the introduction of a pair of wires through the 'adiabatic enclosure'. For us, both processes are adiabatic because what is required is that apart from the change of the system itself, nothing more than the displacement of a weight occurs. To achieve electrical heating, one drills a hole in the container, passes a heater wire through it, connects the wires to a generator which, in turn, is connected to a weight. After the heating the generator is removed along with the wires, the hole is plugged, and the system is observed to be in a new state. The generator, etc. is in its old state and the weight is lower.

—- (Insert Figure 1 here) —-

We shall use the following terminology concerning any two states X and Y. These states are said to be **comparable** (with respect to the relation $\prec$, of course) if either $X \prec Y$ or $Y \prec X$. If both relations hold we say that X and Y are **adiabatically equivalent** and write

$$X \overset{\mathrm{A}}{\sim} Y. \tag{2.2}$$

The comparison hypothesis referred to above is the statement that any two states in the *same* state space are comparable. In the examples of systems (a) to (f) above, all satisfy the comparison hypothesis. Moreover, every point in Γ_c is in the relation $\prec$ to many (but not all) points in Γ_d.

States in different systems may or may not be comparable. An example of non-comparable systems is one mole of H_2 and one mole of O_2. Another is one mole of H_2 and two moles of H_2.

One might think that if the comparison hypothesis, which will be discussed further in Sects. II.C and II.E, were to fail for some state space then the situation could easily be remedied by breaking up the state space into smaller pieces inside each of which the hypothesis holds. This, generally, is false. What is needed to accomplish this is the extra requirement that *comparability is an equivalence relation;* this, in turn, amounts to saying that the condition $X \prec Z$ and $Y \prec Z$ implies that X and Y are comparable and, likewise, the condition $Z \prec X$ and $Z \prec Y$ implies that X and Y are comparable. (This axiom can be found in (Giles, 1964), see axiom 2.1.2, and similar requirements were made earlier by Landsberg (1956), Falk and Jung (1959) and Buchdahl (1962, 1966).) While these two conditions are logically independent, they can be shown to be equivalent if the axiom A3 in Section II. C is adopted. In any case, we do not adopt the comparison hypothesis as an axiom because we find it hard to regard it as a physical necessity. In the same vein, we do not assume that comparability is an equivalence relation (which would then lead to the validity of the comparison hypothesis for suitably defined subsystems). Our goal is to prove the comparison hypothesis starting from axioms that we find more appealing physically.

B. The entropy principle

Given the relation $\prec$ for all possible states of all possible systems, we can ask whether this relation can be encoded in an entropy function according to the following principle, which expresses the **second law of thermodynamics** in a precise and quantitative way:

Entropy principle: *There is a real-valued function on all states of all systems (including compound systems), called* **entropy** *and denoted by S such that*

a) `Monotonicity:` *When X and Y are comparable states then*

$$X \prec Y \quad \text{if and only if} \quad S(X) \leq S(Y). \tag{2.3}$$

(See (2.6) below.)

b) `Additivity and extensivity:` *If X and Y are states of some (possibly different) systems and if (X, Y) denotes the corresponding state in the composition of the two systems, then the entropy is additive for these states, i.e.,*

$$S((X, Y)) = S(X) + S(Y). \tag{2.4}$$

S is also extensive, i.e., for each $t > 0$ and each state X and its scaled copy tX,

$$S(tX) = tS(X). \tag{2.5}$$

[Note: From now on we shall omit the double parenthesis and write simply $S(X, Y)$ in place of $S((X, Y))$.]

A logically equivalent formulation of (2.3), that does not use the word 'comparable' is the following pair of statements:

$$\begin{aligned} X \stackrel{A}{\sim} Y &\Longrightarrow S(X) = S(Y) \quad \text{and} \\ X \prec\prec Y &\Longrightarrow S(X) < S(Y). \end{aligned} \tag{2.6}$$

The last line is especially noteworthy. It says that entropy must increase in an irreversible process.

Our goal is to construct an entropy function that satisfies the criteria (2.3)-(2,5), and to show that it is essentially unique. We shall proceed in stages, the first being to construct an entropy function for a single system, Γ, and its multiple scaled copies (in which comparability is assumed to hold). Having done this, the problem of relating different systems will then arise, i.e., the comparison question for compound systems. In the present Section II (and *only* in this section) we shall simply complete the project by *assuming* what we need by way of comparability. In Section IV, the thermal axioms (the *zeroth law of thermodynamics*, in particular) will be invoked to verify our assumptions about comparability in compound systems. In the remainder of this subsection we discuss he significance of conditions (2.3)-(2.5).

The physical content of (2.3) was already commented on; adiabatic processes not only increase entropy but an increase of entropy also dictates which adiabatic processes are possible (between comparable states, of course).

The content of additivity, (2.4), is considerably more far reaching than one might think from the simplicity of the notation—as we mentioned earlier. Consider four states X, X', Y, Y' and suppose that $X \prec Y$ and $X' \prec Y'$. Then (and this will be one of our axioms) $(X, X') \prec (Y, Y')$, and (2.4) contains nothing new in this case. On the other hand, the compound system can well have an adiabatic process in which $(X, X') \prec (Y, Y')$ but $X \not\prec Y$. In this case, (2.4) conveys much information. Indeed, by monotonicity, there will be many cases of this kind because the inequality $S(X) + S(X') \leq S(Y) + S(Y')$ certainly does not imply that $S(X) \leq S(Y)$. The fact that the inequality $S(X) + S(X') \leq S(Y) + S(Y')$ tells us *exactly* which adiabatic processes are allowed in the compound system (assuming comparability), independent of any detailed knowledge of the manner in which the two systems interact, is astonishing and is at the *heart of thermodynamics.*

Extensivity, (2.5), is *almost* a consequence of (2.4) alone—but logically it is independent. Indeed, (2.4) implies that (2.5) holds for *rational* numbers t provided one accepts the notion of recombination as given in Axiom A5 below, i.e., one can combine two samples of a system in the same state into a bigger system in a state with the same intensive properties. (For systems, such as cosmic bodies, that do not obey this axiom, extensivity and additivity are truly independent concepts.) On the other hand, using the axiom of choice, one may always change a given entropy function satisfying (2.3) and (2.4) in such a way that (2.5) is violated for some irrational t, but then the function $t \mapsto S(tX)$ would end up being unbounded in every t interval. Such pathological cases could be excluded by supplementing (2.3) and (2.4) with the requirement that $S(tX)$ should locally be a bounded function of t, either from below or above. This requirement, plus (2.4), would then imply (2.5). For a discussion related to this point see (Giles, 1964), who effectively considers *only* rational t. See also (Hardy, Littlewood, Polya 1934) for a discussion of the concept of Hamel bases which is relevant in this context.

The extensivity condition can sometimes have surprising results, as in the case of electromagnetic radiation (the 'photon gas'). As is well known (Landau and Lifschitz, 1969, Sect. 60), the phase space of such a gas (which we imagine to reside in a box with a piston that can be used to change the volume) is the quadrant $\Gamma = \{(U, V) \ : \ 0 < U < \infty, \ 0 < V < \infty\}$. Thus,

$$\Gamma^{(t)} = \Gamma$$

as *sets*, which is not surprising or even exceptional. What is exceptional is that S_Γ, which gives the entropy of the states in Γ, satisfies

$$S_\Gamma(U, V) = (\text{const.}) \ V^{1/4} U^{3/4}.$$

It is homogeneous of first degree in the coordinates and, therefore, the extensivity law tells us that the entropy function on the scaled copy $\Gamma^{(t)}$ is

$$S_{\Gamma^{(t)}}(U,V) = tS_{\Gamma}(U/t, V/t) = S_{\Gamma}(U,V).$$

Thus, all the thermodynamic functions on the two state spaces are the same! This unusual situation could, in principle, happen for an ordinary material system, but we know of no example besides the photon gas. Here, the result can be traced to the fact that particle number is not conserved, as it is for material systems, but it does show that one should not jump to conclusions. There is, however, a further conceptual point about the photon gas which is physical rather than mathematical. If a material system had a homogeneous entropy (e.g., $S(U,V) = (\text{const.})V^{1/2}U^{1/2}$)we should still be able to distinguish $\Gamma^{(t)}$ from Γ, even though the coordinates and entropy were indistinguishable. This could be done by weighing the two systems and finding out that one weighs t times as much as the other. But the photon gas is different: no experiment can tell the two apart. However, weight *per se* plays no role in thermodynamics, so the difference between the material and photon systems is not thermodynamically significant.

There are two points of view one could take about this anomalous situation. One is to continue to use the state spaces $\Gamma^{(t)}$, even though they happen to represent identical systems. This is not really a problem because no one said that $\Gamma^{(t)}$ had to be different from Γ. The only concern is to check the axioms, and in this regard there is no problem. We could even allow the additive entropy constant to depend on t, provided it satisfies the extensivity condition (2.5). The second point of view is to say that there is only one Γ and no $\Gamma^{(t)}$'s at all. This would cause us to consider the photon gas as outside our formalism and to require special handling from time to time. The first alternative is more attractive to us for obvious reasons. The photon gas will be mentioned again in connection with Theorem 2.5.

C. Assumptions about the order relation

We now list our assumptions for the order relation $\prec$. As always, X, Y, etc. will denote states (that may belong to different systems), and if X is a state in some state space Γ, then tX with $t > 0$ is the corresponding state in the scaled state space $\Gamma^{(t)}$.

A1) Reflexivity. $X \overset{\mathrm{A}}{\sim} X$.

A2) Transitivity. *$X \prec Y$ and $Y \prec Z$ implies $X \prec Z$.*

A3) Consistency. *$X \prec X'$ and $Y \prec Y'$ implies $(X,Y) \prec (X',Y')$.*

A4) Scaling invariance. *If $X \prec Y$, then $tX \prec tY$ for all $t > 0$.*

A5) Splitting and recombination. *For $0 < t < 1$*

$$X \overset{\mathrm{A}}{\sim} (tX, (1-t)X). \tag{2.7}$$

(If $X \in \Gamma$, then the right side is in the scaled product $\Gamma^{(t)} \times \Gamma^{(1-t)}$, of course.)

A6) Stability. *If, for some pair of states, X and Y,*

$$(X, \varepsilon Z_0) \prec (Y, \varepsilon Z_1)$$

holds for a sequence of ε's tending to zero and some states Z_0, Z_1, then

$$X \prec Y.$$

Remark: 'Stability' means simply that one cannot increase the set of accessible states with an infinitesimal grain of dust.

Besides these axioms the following property of state spaces, the 'comparison hypothesis', plays a crucial role in our analysis in this section. It will eventually be established for all state spaces after we have introduced some more specific axioms in later sections.

CH) Definition: *We say the* **comparison hypothesis** *(CH) holds for a state space if any two states X and Y in the space are comparable, i.e., $X \prec Y$ or $Y \prec X$.*

In the next subsection we shall show that, for every state space, Γ, assumptions A1-A6, and CH for all two-fold scaled products, $(1-\lambda)\Gamma \times \lambda\Gamma$, not just Γ itself, are in fact *equivalent* to the existence of an additive and extensive entropy function that characterizes the order relation on the states in *all* scaled products of Γ. Moreover, for each Γ, this function is unique, up to an affine transformation of scale, $S(X) \to aS(X) + B$. Before we proceed to the construction of entropy we derive a simple property of the order relation from assumptions A1-A6, which is clearly necessary if the relation is to be characterized by an additive entropy function.

THEOREM 2.1 (Stability implies cancellation law). *Assume properties A1-A6, especially A6—the stability law. Then the* **cancellation law** *holds as follows. If X, Y and Z are states of three (possibly distinct) systems then*

$$(X, Z) \prec (Y, Z) \quad \text{implies} \quad X \prec Y \qquad \text{(Cancellation Law).}$$

Proof: Let $\varepsilon = 1/n$ with $n = 1, 2, 3, \ldots$. Then we have

$$\begin{aligned}
(X, \varepsilon Z) &\stackrel{\text{A}}{\sim} ((1-\varepsilon)X, \varepsilon X, \varepsilon Z) && \text{(by A5)} \\
&\prec ((1-\varepsilon)X, \varepsilon Y, \varepsilon Z) && \text{(by A1, A3 and A4)} \\
&\stackrel{\text{A}}{\sim} ((1-2\varepsilon)X, \varepsilon X, \varepsilon Y, \varepsilon Z) && \text{(by A5)} \\
&\prec ((1-2\varepsilon)X, 2\varepsilon Y, \varepsilon Z) && \text{(by A1, A3, A4 and A5).}
\end{aligned}$$

By doing this $n = 1/\varepsilon$ times we find that $(X, \varepsilon Z) \prec (Y, \varepsilon Z)$. By the stability axiom A6 we then have $X \prec Y$. ■

Remark: Under the additional assumption that Y and Z are comparable states (e.g., if they are in the same state space for which CH holds), the cancellation law is logically equivalent to the following statement (using the consistency axiom A3):

If $X \prec\prec Y$ then $(X, Z) \prec\prec (Y, Z)$ for all Z.

The cancellation law looks innocent enough, but it is really rather strong. It is a partial converse of the consistency condition A3 and it says that although the ordering in $\Gamma_1 \times \Gamma_2$ is *not* determined simply by the order in Γ_1 and Γ_2, there are limits to how much the ordering can vary beyond the minimal requirements of A3. It should also be noted that the cancellation law is in accord with our physical interpretation of the order relation in Subsection II.A.2.; a "spectator", namely Z, cannot change the states that are adiabatically accessible from X.

Remark about 'Adiabatic Processes': With the aid of the cancellation law we can now discuss the connection between our notion of adiabatic accessibility and the textbook concept of an 'adiabatic process'. One problem we face is that this latter concept is hard to make precise (this was our reason for avoiding it in our operational definition) and therefore the discussion must necssearily be somewhat informal. The general idea of an adiabatic process, however, is that the system of interest is locked in a thermally isolating enclosure that prevents 'heat' from flowing into or out of our system. Hence, as far as the system is concerned, all the interaction it has with the external world during an adiabatic process can be thought of as being accomplished by means of some mechanical or electrical devices. Our operational definition of the relation $\prec$ appears at first sight to be based on more general processes, since we allow an auxilary thermodynamical system as part of the device. We shall now show that, despite appearances, our definition coincides with the conventional one.

Let us temporarily denote by $\prec^*$ the relation between states based on adiabatic processes, i.e., $X \prec^* Y$ if and only if there is a mechanical/electrical device that starts in a state M and ends up in a state M' while the system changes from X to Y. We now assume that the mechanical/electrical device can be restored to the initial state M from the final state M' by adding or substracting mechanical energy, and this latter process can be reduced to the raising or lowering of a weight in a gravitational field. (This can be taken as a definition of what we mean by a 'mechanical/electrical device'. Note that devices with 'dissipation' do not have this property.) Thus, $X \prec^* Y$ means there is a process in which the mechanical/electrical device starts in some state M and ends up in the same state, a weight moves from height h to height h', while the state of our system changes from X to Y. In symbols,

$$(X, M, h) \longrightarrow (Y, M, h'). \tag{2.8}$$

In our definition of adiabatic accessibility, on the other hand, we have some *arbitrary* device, which interacts with our system and which can generate or remove heat if desired. There is no thermal enclosure. The important constraint is that the device starts in some state D and ends up in the same state D. As before a weight moves from height h to height h', while our system starts in state X and ends up in state Y. In symbols,

$$(X, D, h) \longrightarrow (Y, D, h') \qquad (2.9).$$

It is clear that (2.8) is a special case of (2.9), so we conclude that $X \prec^* Y$ implies $X \prec Y$. The device in (2.9) may consist of a thermal part in some state Z and electrical and mechanical parts in some state M. Thus $D = (Z, M)$, and (2.9) clearly implies that $(X, Z) \prec^* (Y, Z)$.

It is natural to assume that $\prec^*$ satisfies axioms A1-A6, just as $\prec$ does. In that case we can infer the cancellation law for $\prec^*$, i.e., $(X, Z) \prec^* (Y, Z,)$ implies $X \prec^* Y$. Hence, $X \prec Y$ (which is what (2.9) says) implies $X \prec^* Y$. Altogether we have thus shown that $\prec$ and $\prec^*$ are really the same relation. In words: *adiabatic accessibility can always be achieved by an adiabatic process applied to the system plus a device and, furthermore, the adiabatic process can be simplified (although this may not be easy to do experimentally) by eliminating all thermodynamic parts of the device, thus making the process an adiabatic one for the system alone.*

D. The construction of entropy for a single system

Given a state space Γ we may, as discussed in Subsection I.A.1., construct its *multiple scaled copies*, i.e., states of the form

$$Y = (t_1Y_1, \dots, t_NY_N)$$

with $t_i > 0$, $Y_i \in \Gamma$. It follows from our assumption A5 that if CH (comparison hypothesis) holds in the state space $\Gamma^{(t_1)} \times \cdots \times \Gamma^{(t_N)}$ with $t_1, ..., t_N$ fixed, then any other state of the same form, $Y' = (t'_1Y'_1, \dots, t'_MY'_M)$ with $Y'_i \in \Gamma$, is comparable to Y provided $\sum_i t_i = \sum_j t'_j$ (but not, in general, if the sums are not equal). This is proved as follows for $N = M = 2$; the easy extension to the general case is left to the reader. Since $t_1 + t_2 = t'_1 + t'_2$ we can assume, without loss of generality, that $t_1 - t'_1 = t'_2 - t_2 > 0$, because the case $t_1 - t'_1 = 0$ is already covered by CH (which was assumed) for $\Gamma^{(t_1)} \times \Gamma^{(t_2)}$. By the splitting axiom, A5, we have $(t_1Y_1, t_2Y_2) \overset{A}{\sim} (t'_1Y_1, (t_1 - t'_1)Y_1, t_2Y_2)$ and $(t'_1Y'_1, t'_2Y'_2) \overset{A}{\sim} (t'_1Y'_1, (t_1 - t'_1)Y'_2, t_2Y'_2)$. The comparability now follows from CH on the space $\Gamma^{(t'_1)} \times \Gamma^{(t_1 - t'_1)} \times \Gamma^{(t_2)}$.

The entropy principle for the states in the multiple scaled copies of a single system will now be derived. More precisely, we shall prove the following theorem:

THEOREM 2.2 (Equivalence of entropy and assumptions A1–A6, CH). *Let Γ be a state space and let $\prec$ be a relation on the multiple scaled copies of Γ. The following statements are equivalent.*

(1) The relation $\prec$ satisfies axioms A1–A6, and CH holds for all multiple scaled copies of Γ.

(2) There is a function, S_Γ on Γ that characterizes the relation in the sense that if $t_1 + \cdots + t_N = t'_1 + \cdots + t'_M$, (for all $N \geq 1$ and $M \geq 1$) then

$$(t_1Y_1, ..., t_NY_N) \ \prec \ (t'_1Y'_1, ..., t'_MY'_M)$$

holds if and only if

$$\sum_{i=1}^{N} t_i S_\Gamma(Y_i) \ \leq \ \sum_{j=1}^{M} t'_j S_\Gamma(Y'_j) \ . \tag{2.10}$$

The function S_Γ is uniquely determined on Γ, up to an affine transformation, i.e., any other function S^*_Γ on Γ satisfying (2.10) is of the form $S^*_\Gamma(X) = aS_\Gamma(X) + B$ with constants $a > 0$ and B.

Definition. A function S_Γ on Γ that characterizes the relation $\prec$ on the multiple scaled copies of Γ in the sense stated in the theorem is called an **entropy function on** Γ.

We shall split the proof of Theorem 2.2 into Lemmas 2.1, 2.2, 2.3 and Theorem 2.3 below.

At this point it is convenient to introduce the following notion of **generalized ordering**. While $(a_1X_1, a_2X_2, \dots, a_NX_N)$ has so far only been defined when all $a_i > 0$, we can *define* the meaning of the relation

$$(a_1X_1, \dots, a_NX_N) \prec (a'_1X'_1, \dots, a'_MX'_M) \tag{2.11}$$

for arbitrary $a_i \in \mathbf{R}$, $a'_i \in \mathbf{R}$, N and M positive integers and $X_i \in \Gamma_i$, $X'_i \in \Gamma'_i$ as follows. If any a_i (or a'_i) is zero we just ignore the corresponding term. Example: $(0X_1, X_2) \prec (2X_3, 0X_4)$ means the same thing as $X_2 \prec 2X_3$. If any a_i (or a'_i) is negative, just move a_iX_i (or $a'_iX'_i$) to the other side and change the sign of a_i (or a'_i). Example:

$$(2X_1, X_2) \prec (X_3, -5X_4, 2X_5, X_6)$$

means that

$$(2X_1, 5X_4, X_2) \prec (X_3, 2X_5, X_6)$$

in $\Gamma_1^{(2)} \times \Gamma_4^{(5)} \times \Gamma_2$ and $\Gamma_3 \times \Gamma_5^{(2)} \times \Gamma_6$. (Recall that $\Gamma_a \times \Gamma_b = \Gamma_b \times \Gamma_a$). It is easy to check, using the cancellation law, that *the splitting and recombination axiom A5 extends to nonpositive scaling parameters*, i.e., axioms A1-A6 imply that $X \stackrel{A}{\sim} (aX, bX)$ for all $a, b \in \mathbf{R}$ with $a + b = 1$, if the relation $\prec$ for nonpositive a and b is understood in the sense just decribed.

For the definition of the entropy function we need the following lemma, which depends crucially on the stability assumption A6 and on the comparison hypothesis CH for the state spaces $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$.

LEMMA 2.1 *Suppose X_0 and X_1 are two points in Γ with $X_0 \prec\prec X_1$. For $\lambda \in \mathbf{R}$ define*

$$\mathcal{S}_\lambda = \{X \in \Gamma : ((1-\lambda)X_0, \lambda X_1) \prec X\}. \tag{2.12}$$

Then

(i) For every $X \in \Gamma$ there is a $\lambda \in \mathbf{R}$ such that $X \in \mathcal{S}_\lambda$.

(ii) For every $X \in \Gamma$, $\sup\{\lambda : X \in \mathcal{S}_\lambda\} < \infty$.

Remark. Since $X \stackrel{A}{\sim} ((1-\lambda)X, \lambda X)$ by assumption A5, the definition of $\mathcal{S}_\lambda$ really involves the order relation on double scaled copies of Γ (or on Γ itself, if $\lambda = 0$ or 1.)

Proof of Lemma 2.1. (i) If $X_0 \prec X$ then obviously $X \in \mathcal{S}_0$ by axiom A2. For general X we claim that

$$(1+\alpha)X_0 \prec (\alpha X_1, X) \tag{2.13}$$

for some $\alpha \geq 0$ and hence $((1-\lambda)X_0, \lambda X_1) \prec X$ with $\lambda = -\alpha$. The proof relies on stability, A6, and the comparison hypothesis CH (which comes into play for the first time): If (2.13) were not true, then by CH we would have

$$(\alpha X_1, X) \prec (1+\alpha)X_0$$

for all $\alpha > 0$ and so, by scaling, A4, and A5

$$\left(X_1, \frac{1}{\alpha}X\right) \prec \left(X_0, \frac{1}{\alpha}X_0\right).$$

By the stability axiom A6 this would imply $X_1 \prec X_0$ in contradiction to $X_0 \prec\prec X_1$.

(ii) If $\sup\{\lambda : X \in \mathcal{S}_\lambda\} = \infty$, then for some sequence of λ's tending to infinity we would have $((1-\lambda)X_0, \lambda X) \prec X$ and hence $(X_0, \lambda X_1) \prec (X, \lambda X_0)$ by A3 and A5. By A4 this implies $\left(\frac{1}{\lambda}X_0, X_1\right) \prec \left(\frac{1}{\lambda}X, X_0\right)$ and hence $X_1 \prec X_0$ by stability, A6. ■

We can now state our **formula for the entropy function**. If all points in Γ are adiabatically equivalent there is nothing to prove (the entropy is constant), so we may assume that there are points X_0, $X_1 \in \Gamma$ with $X_0 \prec\prec X_1$. We then define for $X \in \Gamma$

$$S_\Gamma(X) := \sup\{\lambda : \ ((1-\lambda)X_0, \lambda X_1) \prec X\}. \tag{2.14}$$

(The symbol $a := b$ means that a is defined by b.) This S_Γ will be referred to as the **canonical entropy** on Γ with **reference points** X_0 and X_1. This definition is illustrated in Figure 2.

—- Insert Figure 2 here —-

By Lemma 2.1 $S_\Gamma(X)$ is well defined and $S_\Gamma(X) < \infty$ for all X. (Note that by stability we could replace $\prec$ by $\prec\prec$ in (2.14).) We shall now show that this S_Γ has all the right properties. The first step is the following simple lemma, which does not depend on the comparison hypothesis.

LEMMA 2.2 ($\prec$ is equivalent to $\leq$). *Suppose $X_0 \prec\prec X_1$ are states and a_0, a_1, a_0', a_1' are real numbers with $a_0 + a_1 = a_0' + a_1'$. Then the following are equivalent.*
(i) $(a_0 X_0, a_1 X_1) \prec (a_0' X_0, a_1' X_1)$
(ii) $a_1 \leq a_1'$ *(and hence $a_0 \geq a_0'$).*
In particular, $\stackrel{A}{\sim}$ holds in (i) if and only if $a_1 = a_1'$ and $a_0 = a_0'$.

Proof: We give the proof assuming that the numbers a_0, a_1, a_0', a_1' are all positive and $a_0 + a_1 = a_0' + a_1' = 1$. The other cases are similar. We write $a_1 = \lambda$ and $a_1' = \lambda'$.

(i) $\Rightarrow$ (ii). If $\lambda > \lambda'$ then, by A5 and A3, $((1-\lambda)X_0, \lambda' X_1, (\lambda - \lambda')X_1) \prec ((1-\lambda)X_0, (\lambda - \lambda')X_0, \lambda' X_1)$. By the cancellation law, Theorem 2.1, $((\lambda - \lambda')X_1) \prec ((\lambda - \lambda')X_0)$. By scaling invariance, A5, $X_1 \prec X_0$, which contradicts $X_0 \prec\prec X_1$.
(ii) $\Rightarrow$ (i). This follows from the following computation.

$$\begin{aligned}
((1-\lambda)X_0, \lambda X_1) &\stackrel{A}{\sim} ((1-\lambda')X_0, (\lambda' - \lambda)X_0, \lambda X_1) &&\text{(by axioms A3 and A5)}\\
&\prec ((1-\lambda')X_0, (\lambda' - \lambda)X_1, \lambda X_1) &&\text{(by axioms A3 and A4)}\\
&\stackrel{A}{\sim} ((1-\lambda')X_0, \lambda' X_1) &&\text{(by axioms A3 and A5).}
\end{aligned}$$

■

The next lemma will imply, among other things, that entropy is unique, up to an affine transformation.

LEMMA 2.3 (Characterization of entropy). *Let S_Γ denote the canonical entropy (2.14) on Γ with respect to the reference points $X_0 \prec\prec X_1$. If $X \in \Gamma$ then the equality*

$$\lambda = S_\Gamma(X)$$

is equivalent to

$$X \stackrel{A}{\sim} ((1-\lambda)X_0, \lambda X_1).$$

Proof: First, if $\lambda = S_\Gamma(X)$ then, by the definition of supremum, there is a sequence $\varepsilon_1 \geq \varepsilon_2 \geq \ldots \geq 0$ converging to zero, such that

$$((1-(\lambda - \varepsilon_n))X_0, (\lambda - \varepsilon_n)X_1) \prec X$$

for each n. Hence, by A5,

$$((1-\lambda)X_0, \lambda X_1, \varepsilon_n X_0) \stackrel{A}{\sim} ((1-\lambda+\varepsilon_n)X_0, (\lambda - \varepsilon_n)X_1, \varepsilon_n X_1) \prec (X, \varepsilon_n X_1),$$

and thus $((1-\lambda)X_0, \lambda X_1) \prec X$ by the stability property A6. On the other hand, since λ is the supremum we have

$$X \prec ((1-(\lambda+\varepsilon)X_0, (\lambda+\varepsilon)X_1)$$

for all $\varepsilon > 0$ by the comparison hypothesis CH. Thus,

$$(X, \varepsilon X_0) \prec ((1-\lambda)X_0, \lambda X_1, \varepsilon X_1),$$

so, by A6, $X \prec ((1-\lambda)X_0, \lambda X_1)$. This shows that $X \stackrel{\rm A}{\sim} ((1-\lambda)X_0, \lambda X_1)$ when $\lambda = S_\Gamma(X)$.

Conversely, if $\lambda' \in [0,1]$ is such that $X \stackrel{\rm A}{\sim} ((1-\lambda')X_0, \lambda' X_1)$, then $((1-\lambda')X_0, \lambda' X_1) \stackrel{\rm A}{\sim} ((1-\lambda)X_0, \lambda X_1)$ by transitivity. Thus, $\lambda = \lambda'$ by Lemma 2.2. ■

Remark 1: Without the comparison hypothesis we could find that $S_\Gamma(X_0) = 0$ and $S_\Gamma(X) = 1$ for all X such that $X_0 \prec X$.

Remark 2: From Lemma 2.3 and the cancellation law it follows that the canonical entropy with reference points $X_0 \prec\prec X_1$ satisfies $0 \leq S_\Gamma(X) \leq 1$ if and only if X belongs to the **strip** $\Sigma(X_0, X_1)$ defined by

$$\Sigma(X_0, X_1) := \{X \in \Gamma : X_0 \prec X \prec X_1\} \subset \Gamma.$$

Let us make the dependence of the canonical entropy on X_0 and X_1 explicit by writing

$$S_\Gamma(X) = S_\Gamma(X|X_0, X_1)\ . \tag{2.15}$$

For X outside the strip we can then write

$$S_\Gamma(X|X_0, X_1) = S_\Gamma(X_1|X_0, X)^{-1} \qquad \text{if } X_1 \prec X$$

and

$$S_\Gamma(X|X_0, X_1) = -\frac{S_\Gamma(X_0|X, X_1)}{1 - S_\Gamma(X_0|X, X_1)} \qquad \text{if } X \prec X_0.$$

`Proof of Theorem 2.2:`

(1) $\Longrightarrow$ (2): Put $\lambda_i = S_\Gamma(Y_i)$, $\lambda_i' = S_\Gamma(Y_i')$. By Lemma 2.3 we know that $Y_i \stackrel{\rm A}{\sim} ((1-\lambda_i)X_0, \lambda_i X_1)$ and $Y_i' \stackrel{\rm A}{\sim} ((1-\lambda_i')X_0, \lambda_i' X_1)$. By the consistency axiom A3 and the recombination axiom A5 it follows that

$$(t_1 Y_1, \ldots, t_N Y_N) \stackrel{\rm A}{\sim} (\sum_i t_i(1-\lambda_i)X_0, \sum_i t_i \lambda_i X_1)$$

and

$$(t_1' Y_1', \ldots, t_N' Y_N') \stackrel{\rm A}{\sim} (\sum_i t_i'(1-\lambda_i')X_0, \sum_i t_i' \lambda_i' X_1)\ .$$

Statement (2) now follows from Lemma 2.2. The implication (2) $\Longrightarrow$ (1) is obvious.

The proof of Theorem 2.2 is now complete except for the uniqueness part. We formulate this part separately in Theorem 2.3 below, which is slightly stronger than the last assertion in Theorem 2.2. It implies that an entropy function for the multiple scaled copies of Γ is already uniquely determined, up to an affine transformation, by the relation on states of the form $((1-\lambda)X, \lambda Y)$, i.e., it requires only the case $N = M = 2$, in the notation of Theorem 2.2.

THEOREM 2.3 (Uniqueness of entropy) *If S_Γ^* is a function on Γ that satisfies*

$$((1-\lambda)X, \lambda Y) \prec ((1-\lambda)X', \lambda Y')$$

if and only if

$$(1-\lambda)S_\Gamma^*(X) + \lambda S_\Gamma^*(Y) \leq (1-\lambda)S_\Gamma^*(X') + \lambda S_\Gamma^*(Y'),$$

for all $\lambda \in \mathbf{R}$ and $X, Y, X', Y' \in \Gamma$, then

$$S_\Gamma^*(X) = aS_\Gamma(X) + B$$

with

$$a = S_\Gamma^*(X_1) - S_\Gamma^*(X_0) > 0, \qquad B = S_\Gamma^*(X_0).$$

Here S_Γ is the canonical entropy on Γ with reference points $X_0 \prec\prec X_1$.

Proof: This follows immediately from Lemma 2.3, which says that for every X there is a unique λ, namely $\lambda = S_\Gamma(X)$, such that

$$X \overset{\text{A}}{\sim} ((1-\lambda)X, \lambda X) \overset{\text{A}}{\sim} ((1-\lambda)X_0, \lambda X_1).$$

Hence, by the hypothesis on S_Γ^*, and $\lambda = S_\Gamma(X)$, we have

$$S_\Gamma^*(X) = (1-\lambda)S_\Gamma^*(X_0) + \lambda S_\Gamma^*(X_1) = [S_\Gamma^*(X_1) - S_\Gamma^*(X_0)]S_\Gamma(X) + S_\Gamma^*(X_0).$$

The hypothesis on S_Γ^* also implies that $a := S_\Gamma^*(X_1) - S_\Gamma^*(X_0) > 0$, because $X_0 \prec\prec X_1$. ■

Remark: Note that S_Γ^* is defined on Γ and satisfies $S_\Gamma^*(X) = aS_\Gamma(X) + B$ there. On the space $\Gamma^{(t)}$ a corresponding entropy is, *by definition*, given by $S_{\Gamma^{(t)}}^*(tX) = tS_\Gamma^*(X) = atS_\Gamma(X) + tB = aS_\Gamma^{(t)}(tX) + tB$, where $S_\Gamma^{(t)}(tX)$ is the canonical entropy on $\Gamma^{(t)}$ with reference points tX_0, tX_1. Thus, $S_{\Gamma^{(t)}}^*(tX) \neq aS_\Gamma^{(t)}(tX) + B$ (unless $B = 0$, of course).

It is apparent from formula (2.14) that the definition of the canonical entropy function on Γ involves only the relation $\prec$ on the double scaled products $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ besides the reference points X_0 and X_1. Moreover, the canonical entropy uniquely characterizes the relation on all multiple scaled copies of Γ, which implies in particular that CH holds for all multiple scaled copies. Theorem 2.3 may therefore be rephrased as follows:

THEOREM 2.4 (The relation on double scaled copies determines the relation everywhere). *Let $\prec$ and $\prec^*$ be two relations on the multiple scaled copies of Γ satisfying axioms A1-A6, and also CH for $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ for each fixed $\lambda \in [0,1]$. If $\prec$ and $\prec^*$ coincide on $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ for each $\lambda \in [0,1]$, then $\prec$ and $\prec^*$ coincide on all multiple scaled copies of Γ, and CH holds on all the multiple scaled copies.*

The proof of Theorem 2.2 is now complete.

E. Construction of a universal entropy in the absence of mixing

In the previous subsection we showed how to construct an entropy for a single system, Γ, that exactly describes the relation $\prec$ within the states obtained by forming multiple scaled copies of Γ. It is unique up to a multiplicative constant $a > 0$ and an additive constant B, i.e., to within an affine transformation. We remind the reader that this entropy was constructed by considering just the product of two scaled copies of Γ, but our axioms implied that it automatically worked for *all* multiple scaled copies of Γ. We shall refer to a and B as **entropy constants** for the system Γ.

Our goal is to put these entropies together and show that they behave in the right way on products of arbitrarily many copies of *different* systems. Moreover, this 'universal' entropy will be unique up to *one* multiplicative constant—but still many additive constants. The central question here is one of *'calibration'*, which is to say that the multiplicative constant in front of each elementary entropy has to be chosen in such a way that the additivity rule (2.4) holds. It is not even obvious yet that the additivity can be made to hold at all, whatever the choice of constants.

Let us note that the number of additive constants depends heavily on the kinds of adiabatic processes available. The system consisting of one mole of hydrogen mixed with one mole of helium and the system consisting of one mole of hydrogen mixed with two moles of helium are different. The additive constants are independent *unless* a process exists in which both systems can be unmixed, and thereby making the constants comparable. In nature we expect only 92 constants, one for each element of the periodic table, unless we allow nuclear processes as well, in which case there are only two constants (for neutrons and for hydrogen). On the other hand, if un-mixing is not allowed uncountably many constants are undetermined. In Section VI we address the question of adiabatic processes that unmix mixtures and reverse chemical reactions. That such processes exist is not so obvious.

To be precise, the principal goal of this subsection is the proof of the following Theorem 2.5, which is a case of the entropy principle that is special in that it is restricted to processes that do not involve mixing or chemical reactions. It is a generalization of Theorem 2.2.

THEOREM 2.5 (Consistent entropy scales). *Consider a family of systems fulfilling the following requirements:*

(i) The state spaces of any two systems in the family are disjoint sets, i.e., every state of a system in the family belongs to exactly one state space.

(ii) All multiple scaled products of systems in the family belong also to the family.

(iii) Every system in the family satisfies the comparison hypothesis.

For each state space Γ of a system in the family let S_Γ be some d efinite entropy function on Γ. Then there are constants a_Γ and B_Γ such that the function S, defined for all states in all Γ's by

$$S(X) = a_\Gamma S_\Gamma(X) + B_\Gamma$$

for $X \in \Gamma$, has the following properties:

a). If X and Y are in the same state space then

$$X \prec Y \qquad \text{if and only if} \qquad S(X) \leq S(Y).$$

b). S is additive and extensive, i.e.,

$$S(X, Y) = S(X) + S(Y). \tag{2.4}$$

and, for $t > 0$,

$$S(tX) = tS(X). \tag{2.5}$$

Remark. Note that Γ_1 and $\Gamma_1 \times \Gamma_2$ are disjoint as sets for any (nonempty) state spaces Γ_1 and Γ_2.

Proof: Fix some system Γ_0 and two points $Z_0 \prec\prec Z_1$ in Γ_0. In each state space Γ choose some fixed point $X_\Gamma \in \Gamma$ in such a way that the identities

$$X_{\Gamma_1 \times \Gamma_2} = (X_{\Gamma_1}, X_{\Gamma_2}) \tag{2.16}$$

$$X_{t\Gamma} = tX_\Gamma \tag{2.17}$$

hold. With the aid or the axiom of choice this can be achieved by considering the formal vector space spanned by all systems and choosing a Hamel basis of systems $\{\Gamma_\alpha\}$ in this space such that every system can be written uniquely as a scaled product of a finite number of the Γ_α's. (See Hardy, Littlewood and Polya, 1934). The choice of an arbitrary state X_{Γ_α} in each of these 'elementary' systems Γ_α then defines for each Γ a unique X_Γ such that (2.17) holds. (If the reader does not wish to invoke the axiom of choice then an alternative is to hypothesize that every system has a unique decomposition into elementary systems; the simple systems considered in the next section obviously qualify as the elementary systems.)

For $X \in \Gamma$ we consider the space $\Gamma \times \Gamma_0$ with its canonical entropy as defined in (2.14), (2.15) relative to the points (X_Γ, Z_0) and (X_Γ, Z_1). Using this function we define

$$S(X) = S_{\Gamma\times\Gamma_0}((X, Z_0) \mid (X_\Gamma, Z_0), (X_\Gamma, Z_1)). \tag{2.18}$$

Note: Equation (2.18) fixes the entropy of X_Γ to be zero.

Let us denote $S(X)$ by λ which, by Lemma 2.3, is characterized by

$$(X, Z_0) \overset{\text{A}}{\sim} ((1-\lambda)(X_\Gamma, Z_0), \lambda(X_\Gamma, Z_1)).$$

By the cancellation law this is equivalent to

$$(X, \lambda Z_0) \overset{\text{A}}{\sim} (X_\Gamma, \lambda Z_1)). \tag{2.19}$$

By (2.16) and (2.17) this immediately implies the additivity and extensivity of S. Moreover, since $X \prec Y$ holds if and only if $(X, Z_0) \prec (Y, Z_0)$ it is also clear that S is an entropy function on any Γ. Hence S and S_Γ are related by an affine transformation, according to Theorem 2.3. ■

Definition (Consistent entropies). A collection of entropy functions S_Γ on state spaces Γ is called *consistent* if the appropriate linear combination of the functions is an entropy function on all multiple scaled products of these state spaces. In other words, the set is consistent if the multiplicative constants a_Γ, referred to in Theorem 2.5, can all be chosen equal to 1.

Important Remark: From the definition, (2.14), of the canonical entropy and (2.19) it follows that the entropy (2.18) is given by the formula

$$S(X) = \sup\{\lambda \ : \ (X_\Gamma, \lambda Z_1) \prec (X, \lambda Z_0)\} \tag{2.20}$$

for $X \in \Gamma$. The auxiliary system Γ_0 can thus be regarded as an 'entropy meter' in the spirit of (Lewis and Randall, 1923) and (Giles, 1964). Since we have chosen to define the entropy for each system independently, by equation (2.14), the role of Γ_0 in our approach is solely to calibrate the entropy of different systems in order to make them consistent.

Remark about the photon gas: As we discussed in Section II.B the photon gas is special and there are two ways to view it. One way is to regard the scaled copies $\Gamma^{(t)}$ as distinct systems and the other is to say that there is only one Γ and the scaled copies are identical to it and, in particular, must have exactly the same entropy function. We shall now see how the first point of view can be reconciled with the latter requirement. Note, first, that in our construction above we cannot take the point $(U, V) = (0, 0)$ to be the fiducial point X_Γ because $(0, 0)$ is not in our state space which, according to the discussion in Section III below, has to be an open set and hence cannot contain any of its boundary points such as $(0, 0)$. Therefore, we have to make another choice, so let us take $X_\Gamma = (1,1)$. But the construction in the proof above sets $S_\Gamma(1,1) = 0$ and therefore $S_\Gamma(U,V)$ will not have the homogeneous form $S^{\rm hom}(U,V) = V^{1/4}U^{3/4}$. Nevertheless, the entropies of the scaled copies will be extensive, as required by the theorem. If one feels that all scaled copies should have the same entropy (because they represent the same physical system) then the situation can be remedied in the following way: With $S_\Gamma(U,V)$ being the entropy constructed as in the proof using $(1,1)$, we note that $S_\Gamma(U,V) = S^{\rm hom}(U,V) + B_\Gamma$ with the constant B_Γ given by $B_\Gamma = -S_\Gamma(2,2)$. This follows from simple algebra and the fact that we know that the entropy of the photon gas constructed in our proof must equal $S^{\rm hom}$ to within an additive constant. (The reader might ask how we know this and the answer is that the entropy of the 'gas' is unique up to additive and multiplicative constants, the latter being determined by the system of units employed. Thus, the entropy determined by our construction must be the 'correct entropy', up to an additive constant, and this 'correct entropy' is what it is, as determined by physical measurement. Hopefully it agrees with the function deduced in (Landau and Lifschitz, 1969).) Let us use our freedom to alter the additive constants as we please, provided we maintain the extensivity condition (2.5). It will not be until Section VI that we have to worry about the additive constants *per se* because it is only there that mixing and chemical reactions are treated. Therefore, we redefine the entropy of the state space Γ of the photon gas to be $S^*(U,V) := S_\Gamma(U,V) + S_\Gamma(2,2)$. which is the same as $S^{\rm hom}(U,V)$. We also have to alter the entropy of the scaled copies according to the rule that preserves extensivity, namely $S_{\Gamma^{(t)}}(U,V) \to S_{\Gamma^{(t)}}(U,V) + tS_\Gamma(2,2) = S_{\Gamma^{(t)}}(U,V) + S_{\Gamma^{(t)}}(2t,2t) = S^{\rm hom}(U,V)$. In this way, all the scaled copies now have the same (homogeneous) entropy, but we remind the reader that the same construction could be carried out for any material system with a homogeneous (or, more exactly an affine) entropy function—if one existed. From the thermodynamic viewpoint, the photon gas is unusual but not special.

F. Concavity of entropy

Up to now we have not used, or assumed, any geometric property of a state space Γ. It is an important stability property of thermodynamical systems, however, that the entropy function is a *concave* function of the state variables —a requirement that was emphasized by Maxwell, Gibbs, Callen and many others. Concavity also plays an important role in the definition of temperature, as in section V.

In order to have this concavity it is first necessary to make the state space on which entropy is defined into a convex set, and for this purpose the choice of coordinates is important. Here, we begin the discussion of concavity by discussing this geometric property of the underlying state space and some of the consequences of the *convex combination axiom* A7 for the relation $\prec$, to be given after the following definition.

Definition: By a **state space with a convex structure**, or simply a **convex state space**, we mean a state space Γ, that is a convex subset of some linear space, e.g., $\mathbf{R}^n$. That is, if X and Y are any two points in Γ and if $0 \le t \le 1$, then the point $tX + (1-t)Y$ is a well-defined point in Γ. A *concave function*, S, on Γ is one satisfying the inequality

$$S(tX + (1-t)Y) \ge tS(X) + (1-t)S(Y). \tag{2.21}$$

Our basic convex combination axiom for the relation $\prec$ is the following.

A7) Convex combination. Assume X and Y are states in the same *convex* state space, Γ. For $t \in [0,1]$ let tX and $(1-t)Y$ be the corresponding states of their t scaled and $(1-t)$ scaled copies, respectively. Then the point $(tX,(1-t)Y)$ in the product space $\Gamma^{(t)} \times \Gamma^{(1-t)}$ satisfies

$$(tX,(1-t)Y) \prec tX + (1-t)Y \ . \tag{2.22}$$

Note that the right side of (2.22) is in Γ and is defined by ordinary convex combination of points in the convex set Γ.

The physical meaning of A7 is more or less evident, but it is essential to note that the convex structure depends heavily on the choice of coordinates for Γ. A7 means that if we take a bottle containing 1/4 moles of nitrogen and one containing 3/4 moles (with possibly different pressures and densities), and if we mix them together, then among the states of one mole of nitrogen that can be reached adiabatically there is one in which the energy is the sum of the two energies and, likewise, the volume is the sum of the two volumes. Again, we emphasize that the choice of energy and volume as the (mechanical) variables with which we can make this statement is an important assumption. If, for example, temperature and pressure were used instead, the statement would not only not hold, it would not even make much sense.

The physical example above seems not exceptionable for liquids and gases. On the other hand it is not entirely clear how to ascribe an operational meaning to a convex combination in the state space of a solid, and the physical meaning of axiom A7 is not as obvious in this case. Note, however, that although convexity is a global property, it can often be inferred from a local property of the boundary. (A connected set with a smooth boundary, for instance, is convex if every point on the boundary has a neighbourhood, whose intersection with the set is convex.) In such cases it suffices to consider convex combinations of points that are close together and close to the boundary. For small deformation of an isotropic solid the six strain coordinates, multiplied by the volume, can be taken as work coordinates. Thus, A7 amounts to assuming that a convex combination of these coordinates can always be achieved adiabatically. See, e.g., (Callen, 1985).

If $X \in \Gamma$ we denote by A_X the set $\{Y \in \Gamma : X \prec Y\}$. A_X is called the **forward sector** of X in Γ. More generally, if Γ' is another system, we call the set

$$\{Y \in \Gamma' : X \prec Y\},$$

the forward sector of X in Γ'.

Usually this concept is applied to the case in which Γ and Γ' are identical, but it can also be useful in cases in which one system is changed into another; an example is the mixing of two liquids in two containers (in which case Γ is a compound system) into a third vessel containing the mixture (in which case Γ' is simple).

The main effect of A7 is that forward sectors are convex sets.

THEOREM 2.6 (Forward sectors are convex). *Let Γ and Γ' be state spaces of two systems, with Γ' a convex state space. Assume that A1–A5 hold for Γ and Γ' and, in addition, A7 holds for Γ'. Then the forward sector of X in Γ', defined above, is a convex subset of Γ' for each $X \in \Gamma$.*

Proof: Suppose $X \prec Y_1$ and $X \prec Y_2$ and that $0 < t < 1$. We want to show that $X \prec tY_1 + (1-t)Y_2$. (The right side defines, by ordinary vector addition, a point in the convex set Γ'.) First, $X \prec (tX,(1-t)X) \in \Gamma^{(t)} \times \Gamma^{(1-t)}$, by axiom A5. Next, $(tX,(1-t)X) \prec (tY_1,(1-t)Y_2)$ by the consistency axiom A3 and the scaling invariance axiom A4. Finally, $(tY_1,(1-t)Y_2) \prec tY_1+(1-t)Y_2$ by the convex combination axiom A7. ■

Figure 3 illustrates this theorem in the case $\Gamma = \Gamma'$.

—- Insert Figure 3 here —-

THEOREM 2.7 (Convexity of $\mathcal{S}_\lambda$). *Let the sets $\mathcal{S}_\lambda \subset \Gamma$ be defined as in (2.12) and assume the state space Γ satisfies the convex combination axiom A7 in addition to A1-A5. Then:*

(i) $\mathcal{S}_\lambda$ is convex.

(ii) If $X \in \mathcal{S}_{\lambda_1}$, $Y \in \mathcal{S}_{\lambda_2}$ and $0 \le t \le 1$, then $tX + (1-t)Y \in \mathcal{S}_{t\lambda_1+(1-t)\lambda_2}$.

Proof. (i) This follows immediately from the scaling, splitting and convex combination axioms A4, A5 and A7.

(ii) This is proved by splitting, moving the states of the subsystems into forward sectors and bringing the subsystems together at the end. More precisely, defining $\lambda = t\lambda_1 + (1-t)\lambda_2$ we have to show that $((1-\lambda)X_0, \lambda X_1) \prec tX + (1-t)Y$. Starting with $((1-\lambda)X_0, \lambda X_1)$ we split $(1-\lambda)X_0$ into $(t(1-\lambda_1)X_0, (1-t)(1-\lambda_2)X_0)$ and λX_1 into $(t\lambda_1 X_1, (1-t)\lambda_2 X_1)$. Next we consider the states $(t(1-\lambda_1)X_0, t\lambda_1 X_1)$ and $((1-t)(1-\lambda_2)X_0, (1-t)\lambda_2 X_1)$. By scaling invariance A4 and the splitting property A5 we can pass from the former to $(t(1-\lambda_1)X, t\lambda_1 X)$ and from the latter to $((1-t)(1-\lambda_2)Y, (1-t)\lambda_2 Y)$. Now we combine the parts of $(t(1-\lambda_1)X, t\lambda_1 X)$ to obtain tX and the parts of $((1-t)(1-\lambda_2)Y, (1-t)\lambda_2 Y)$ to obtain $(1-t)Y$, and finally we use the convex combination property A7 to reach $tX + (1-t)Y$. ■

THEOREM 2.8 (Concavity of entropy). *Let Γ be a convex state space. Assume axiom A7 in addition to A1-A6, and CH for multiple scaled copies of Γ. Then the entropy S_Γ defined by (2.14) is a concave function on Γ. Conversely, if S_Γ is concave, then axiom A7 necessarily holds a-fortiori.*

Proof: If $X \in \mathcal{S}_{\lambda_1}, Y \in \mathcal{S}_{\lambda_2}$, then by Theorem 2.7, (ii), $tX + (1-t)Y \in \mathcal{S}_{t\lambda_1+(1-t)\lambda_2}$, for $t, \lambda_1, \lambda_2 \in [0,1]$. By definition, this implies $S_\Gamma(tX+(1-t)Y) \ge t\lambda_1+(1-t)\lambda_2$. Taking the supremum over all λ_1 and λ_2 such that $X \in \mathcal{S}_{\lambda_1}, Y \in \mathcal{S}_{\lambda_2}$, then gives $S_\Gamma(tX+(1-t)Y) \ge tS_\Gamma(X)+(1-t)S_\Gamma(Y)$. The converse is obvious. ■

G. Irreversibility and Carathéodory's principle

One of the milestones in the history of the second law is Carathéodory's attempt to formulate the second law in terms of purely local properties of the equivalence relation $\stackrel{A}{\sim}$. The disadvantage of the purely local formulation is, as we said earlier, the difficulty of deriving a globally defined concave entropy function. Additionally, Carathéodory relies on differentiability (differential forms), and we would like to avoid this, if possible, because physical systems do have points (e.g., phase transitions) in their state spaces where differentiability fails. Nevertheless, Carathéodory's idea remains a powerful one and it does play an important role in the story. We shall replace it by a seemingly more natural idea, namely the existence of irreversible processes. *The existence of many such processes lies at the heart of thermodynamics.* If they did not exist, it would mean that nothing is forbidden, and hence there would be no second law. We now show the relation between the two concepts. There will be no mention of differentiability, however.

Carathéodory's principle has been criticized (see, for example, the remark attributed to Walter in Truesdell's paper in (Serrin, 1986, Chapter 5)) on the ground that this principle does not tell us where to look for a non adiabatic process that is supposed, by the principle, to exist in every neighborhood of every state. In Sect. III and V we show that this criticism is too severe because the principle, when properly interpreted, shows exactly where to look and, in conjunction with the other axioms, it leads to the Kelvin-Planck version of the second law.

THEOREM 2.9 (Carathéodory's principle and irreversible processes). *Let Γ be a state space that is a convex subset of $\mathbf{R}^n$ and assume that axioms A1–A7 hold on Γ. Consider the following two statements.*

(1) **Existence of irreversible processes:** *For every point $X \in \Gamma$ there is a $Y \in \Gamma$ such that $X \prec\prec Y$.*

(2) **Carathéodory's principle:** *In every neighborhood of every $X \in \Gamma$ there is a point $Z \in \Gamma$ such that $X \stackrel{\text{A}}{\sim} Z$ is false.*

Then (1) always implies (2). Indeed, (1) implies the stronger statement that there is a Z such that $X \prec Z$ is false. On the other hand, if all the forward sectors in Γ have non-empty interiors (i.e., they are not contained in lower dimensional hyperplanes) then (2) implies (1).

Proof: Suppose that for some $X \in \Gamma$ there is a neighborhood, $\mathcal{N}_X$ of X such that $\mathcal{N}_X$ is contained in A_X, the forward sector of X. (This is the negation of the statement that in every neighbourhood of every X there is a Z such that $X \prec Z$ is false.) Let $Y \in A_X$ be arbitrary. By the convexity of A_X (which is implied by the axioms), X is an interior point of a line segment joining Y and some point $Z \in \mathcal{N}_X$. By axiom A7, we thus have

$$((1-\lambda)Z, \lambda Y) \prec X \stackrel{\text{A}}{\sim} ((1-\lambda)X, \lambda X)$$

for some $\lambda \in (0,1)$. But we also have that $((1-\lambda)X, \lambda Y) \prec ((1-\lambda)Z, \lambda Y)$ since $Z \in A_X$. This implies, by the cancellation law, that $Y \prec X$. Thus we conclude that for some X, we have that $X \prec Y$ implies $X \stackrel{\text{A}}{\sim} Y$. This contradicts (1). In particular, we have shown that (1) $\Rightarrow$(2).

Conversely, assuming that (1) is false, there is a point X_0 whose forward sector is given by $A_{X_0} = \{Y : Y \stackrel{\text{A}}{\sim} X_0\}$. Let X be an interior point of A_{X_0}, i.e., there is a neighborhood of X, $\mathcal{N}_X$, which is entirely contained in A_{X_0}. All points in $\mathcal{N}_X$ are adiabatically equivalent to X_0, however, and hence to X, since $X \in \mathcal{N}_X$. Thus, (2) is false. ∎

H. Some further results on uniqueness

As stated in Theorem 2.2, the existence of an entropy function on a state space Γ is equivalent to the axioms A1-A6 and CH for the multiple scaled copies of Γ. The entropy function is unique, up to an affine change of scale, and according to formula (2.14) it is even sufficient to know the relation on the double scaled copies $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ in order to compute the entropy. This was the observation behind the uniqueness Theorem 2.4 which stated that the restriction of the relation $\prec$ to the double scaled copies determines the relation everywhere.

The following very general result shows that it is in fact not necessary to know $\prec$ on all $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ to determine the entropy, provided the relation is such that the range of the entropy is connected. In this case $\lambda = 1/2$ suffices. By Theorem 2.8 the range of the entropy is necessarily connected if the convex combination axiom A7 holds.

THEOREM 2.10 (The relation on $\Gamma \times \Gamma$ determines entropy). *Let Γ be a set and $\prec$ a relation on $\Gamma \times \Gamma$. Let S be a real valued function on Γ satisfying the following conditions:*

(i) S characterizes the relation on $\Gamma\times\Gamma$ in the sense that

$$(X,Y)\prec(X',Y') \qquad \textit{if and only if} \qquad S(X)+S(Y)\leq S(X')+S(Y')$$

(ii) The range of S is an interval (bounded or unbounded and which could even be a point).

Let S^* be another function on Γ satisfying condition (i). Then S and S^* are affinely related, i.e., there are numbers $a>0$ and B such that $S^*(X)=aS(X)+B$ for all $X\in\Gamma$. In particular, S^* must satisfy condition (ii).

Proof: In general, if F and G are any two real valued functions on $\Gamma\times\Gamma$, such that $F(X,Y)\leq F(X',Y')$ if and only if $G(X,Y)\leq G(X',Y')$, it is an easy logical exercise to show that there is a monotone increasing function K (i.e., $x\leq y$ implies $K(x)\leq K(y)$) defined on the range of F, so that $G=K\circ F$. In our case $F(X,Y)=S(X)+S(Y)$. If the range of S is the interval L then the range of F is $2L$. Thus K, which is defined on $2L$, satisfies

$$K(S(X)+S(Y))=S^*(X)+S^*(Y) \tag{2.23}$$

for all X and Y in Γ because both S and S^* satisfy condition (i). For convenience, define M on L by $M(t)=\frac{1}{2}K(2t)$. If we now set $Y=X$ in (1) we obtain

$$S^*(X)=M(S(X)),\quad X\in\Gamma \tag{2.24}$$

and (2.23) becomes, in general,

$$M\left(\frac{x+y}{2}\right)=\tfrac{1}{2}M(x)+\tfrac{1}{2}M(y) \tag{2.25}$$

for all x and y in L. Since M is monotone, it is bounded on all finite subintervals of L. Hence (Hardy, Littlewood, Polya 1934) M is both concave and convex in the usual sense, i.e.,

$$M(tx+(1-t)y)=tM(x)+(1-t)M(y)$$

for all $0\leq t\leq 1$ and $x,y\in L$. From this it follows that $M(x)=ax+B$ with $a\geq 0$. If a were zero then S^* would be constant on Γ which would imply that S is constant as well. In that case we could always replace a by 1 and replace B by $B-S(X)$. ∎

Remark: It should be noted that Theorem 2.10 does not rely on any structural property of Γ, which could be any abstract set. In particular, continuity plays no role; indeed it cannot be defined because no topology on Γ is assumed. The only residue of "continuity" is the requirement that the range of S be an interval.

That condition (ii) is not superfluous for the uniqueness theorem may be seen from the following simple counterexample.

EXAMPLE: Suppose the state space Γ consists of 3 points, X_0, X_1 and X_2, and let S and S^* be defined by $S(X_0)=S^*(X_0)=0$, $S(X_1)=S^*(X_1)=1$, $S(X_2)$=3, $S^*(X_2)$=4. These functions correspond to the same order relation on $\Gamma\times\Gamma$, but they are not related by an affine transformation.

The following sharpening of Theorem 2.4 is an immediate corollary of Theorem 2.10 in the case that the convexity axiom A7 holds, so that the range of the entropy is connected.

THEOREM 2.11 (The relation on $\Gamma \times \Gamma$ determines the relation everywhere) *Let $\prec$ and $\prec^*$ be two relations on the multiple scaled copies of Γ satisfying axioms A1-A7, and CH for $\Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}$ for each fixed $\lambda \in [0,1]$. If $\prec$ and $\prec^*$ coincide on $\Gamma \times \Gamma$, i.e.,*

$$(X,Y) \prec (X',Y') \quad \textit{if and only if} \quad (X,Y) \prec^* (X',Y')$$

for $X, X', Y, Y' \in \Gamma$, then $\prec$ and $\prec^*$ coincide on all multiple scaled copies of Γ.

As a last variation on the theme of this subsection let us note that uniqueness of entropy does even not require knowledge of the order relation $\prec$ on all of $\Gamma \times \Gamma$. The knowledge of $\prec$ on a relatively thin "diagonal" set will suffice, as Theorem 2.12 shows.

THEOREM 2.12 (Diagonal sets determine entropy). *Let $\prec$ be an order relation on $\Gamma \times \Gamma$ and let S be a function on Γ satisfying conditions (i) and (ii) of Theorem 2.10. Let $\mathcal{D}$ be a subset of $\Gamma \times \Gamma$ with the following properties:*
(i) *$(X,X) \in \mathcal{D}$ for every $X \in \Gamma$.*
(ii) *The set $D = \{(S(X), S(Y)) \in \mathbf{R}^2 : (X,Y) \in \mathcal{D}\}$ contains an open subset of $\mathbf{R}^2$ (which necessarily contains the set $\{(x,x) : x \in \mathrm{Range}\, S\}$).*

Suppose now that $\prec^*$ is another order relation on $\Gamma \times \Gamma$ and that S^* is a function on Γ satisfying condition (i) of Theorem 2.10 with respect to $\prec^*$ on $\Gamma \times \Gamma$. Suppose further, that $\prec$ and $\prec^*$ agree on $\mathcal{D}$, i.e.,

$$(X,Y) \prec (X',Y') \quad \textit{if and only if} \quad (X,Y) \prec^* (X',Y')$$

whenever (X,Y) and (X',Y') are both in $\mathcal{D}$. Then $\prec$ and $\prec^*$ agree on all of $\Gamma \times \Gamma$ and hence, by Theorem 2.10, S and S^* are related by an affine transformation.

Proof: By considering points $(X,X) \in \mathcal{D}$, the consistency of S and S^* implies that $S^*(X) = M(S(X))$ for all $X \in \Gamma$, where M is some monotone increasing function on $L \subset \mathbf{R}$. Again, as in the proof of Theorem 2.10,

$$\tfrac{1}{2}M(S(X)) + \tfrac{1}{2}M(S(Y)) = M\Big(\frac{S(X)) + S(Y)}{2}\Big) \tag{2.26}$$

for all $(X,Y) \in \mathcal{D}$. (Note: In deriving Eq. (2.25) we did not use the fact that $\Gamma \times \Gamma$ was the Cartesian product of two spaces; the only thing that was used was the fact that $S(X) + S(Y)$ characterized the level sets of $\Gamma \times \Gamma$. Thus, the same argument holds with $\Gamma \times \Gamma$ replaced by $\mathcal{D}$.)

Now fix $X \in \Gamma$ and let $x = S(X)$. Since D contains an open set that contains the point $(x,x) \in \mathbf{R}^2$, there is an open square

$$Q = (x-\epsilon, x+\epsilon) \times (x-\epsilon, x+\epsilon)$$

in D. Eqn. (1) holds on Q and so we conclude, as in the proof of Theorem 2.10, that, for $y \in (x-\epsilon, x+\epsilon)$ $M(y) = ay + B$ for some a, B, which could depend on Q, a-priori.

The diagonal $\{(x,x) : x \in L\}$ is covered by these open squares and, by the Heine-Borel theorem, any closed, finite section of the diagonal can be covered by finitely many squares $Q_1, Q_2, ..., Q_N$, which we order according to their "diagonal point" (x_i, x_i). They are not disjoint and, in fact, we can assume that $T_i := Q_i \cap Q_{i+1}$ is never empty. In each interval $(x_i - \epsilon, x_i + \epsilon)$, $M(x) = a_i x + B_i$ but agreement in the overlap region T_i requires that a_1 and B_i be independent of i. Thus, $S^*(X) = aS(X) + B$ for all $X \in \Gamma$, as claimed. ■

III. SIMPLE SYSTEMS

Simple systems are the building blocks of thermodynamics. In general, the *equilibrium* state of a (simple or complex) system is described by certain coordinates called *work coordinates* and certain coordinates called *energy coordinates.* Physically, the work coordinates are the parameters one can adjust by mechanical (or electric or magnetic) actions. We denote work coordinates collectively by V because the volume is a typical one. A simple system is characterized by the fact that it has exactly one energy coordinate, denoted by U.

The meaning of these words will be made precise; as always there is a physical interpretation and a mathematical one. The remark we made in the beginning of Section II is especially apt here; the mathematical axioms and theorems should be regarded as independent of the numerous asides and physical discussions that surround them and which are not intrinsic to the logical structure, even though they are very important for the physical interpretation. The mathematical description of simple systems will require three new assumptions, S1–S3. *In our axiomatics simple systems with their energy and work coordinates are basic (primitive) concepts that are related to the other concepts by the axioms.* The statement that they are the building blocks of thermodynamics has in our approach the precise meaning that from this section on, *all systems under consideration are assumed to be scaled products of simple systems.*

From the physical point of view, a simple system is a *fixed* quantity of matter with a *fixed* amount of each element of the periodic table. The content of a simple system can be quite complicated. It can consist of a mixture of several chemical species, even reactive ones, in which case the amount of the different components might change as the external parameters (e.g., the volume) change. A simple system need not be spatially homogeneous. For example a system consisting of two vessels, each with a piston, but joined by a heat conducting thread, is simple; it has two work coordinates (the volumes of the two vessels), but only one energy coordinate since the two vessels are always in thermal equilibrium when the total system is in equilibrium. This example is meant to be informal and there is no need to define the words 'piston', 'thread' and 'heat conducting'. It is placed here as an attempt at clarification and also to emphasize that our definition of 'simple system' is not necessarily the same as that used by other authors.

An example of a compound, i.e., non-simple system is provided by two simple systems placed side by side and not interacting with each other. In this case the state space is just the Cartesian product of the individual state spaces. In particular, two energies are needed to describe the state of the system, one for each subsystem.

Some examples of simple systems are:

(a) One mole of water in a container with a piston (one work coordinate).

(b) A half mole of oxygen in a container with a piston and in a magnetic field (two work coordinates, the volume and the magnetization).

(c) Systems (a) and (b) joined by a copper thread (three work coordinates).

(d) A mixture consisting of 7 moles of hydrogen and one mole of oxygen (one work coordinate). Such a mixture is capable of explosively reacting to form water, of course, but for certain purposes (e.g., in chemistry, material science and in astrophysics) we can regard a non-reacting, metastable mixture as capable of being in an equilibrium state, as long as one is careful not to bump the container with one's elbow.

To a certain extent, the question of which physical states are to be regarded as equilibrium states is a matter of practical convention. The introduction of a small piece of platinum in (d) will soon show us that this system is not truly in equilibrium, although it can be considered to be in equilibrium for practical purposes if no catalyst is present.

A few more remarks will be made in the following about the physics of simple systems, especially the meaning of the distinguished energy coordinate. In the real world, it is up to the experimenter to decide when a system is in equilibrium and when it is simple. If the system satisfies the mathematical assumptions of a simple system—which we present next—then our analysis applies and the second law holds for it. Otherwise, we cannot be sure.

Our main goal in this section is to show that the forward sectors in the state space Γ of a simple system form a *nested* family of closed sets, i.e., two sectors are either identical or one is contained in the interior of the other (Theorem 3.7). Fig. 5 illustrates this true state of affairs, and also what could go wrong *a priori* in the arrangement of the forward sectors, but is excluded by our additional axioms S1-S3. Nestedness of forward sectors means that the comparison principle holds within the state space Γ. The comparison principle for multiple scaled copies of Γ, which is needed for the definition of an entropy function on Γ, will be derived in the next section from additional assumptions about thermal equilibrium.

A. Coordinates for simple systems

A (equilibrium) state of a simple system is parametrized uniquely (for thermodynamic purposes) by a point in $\mathbf{R}^{n+1}$, for some $n > 0$ depending on the system (but not on the state).

A point in $\mathbf{R}^{n+1}$ is written as $X = (U, V)$ with U a distinguished coordinate called the **internal energy** and with $V = (V_1, \dots, V_n) \in \mathbf{R}^n$. The coordinates V_i are called the **work coordinates**.

We could, if we wished, consider the case $n = 0$, in which case we would have a system whose states are parametrized by the energy alone. Such a system is called a **thermometer** or a **degenerate simple system.** These systems must be (and will be in Section IV) treated separately because they will fail to satisfy the transversality axiom T4, introduced in Section IV. From the point of view of the convexity analysis in the present section, degenerate simple systems can be regarded as trivial.

The energy is special, both mathematically and physically. The fact that it can be defined as a physical coordinate really goes back to the **first law of thermodynamics**, which says that the amount of work done by the outside world in going adiabatically from one state of the system to another is independent of the manner in which this transition is carried out. This amount of work is the amount by which a weight was raised or lowered in the physical definition given earlier of an adiabatic process. (At the risk of being tiresomely repetitive, we remind the reader that 'adiabatic, means neither 'slow' nor 'isolated' nor any restriction other than the requirement that the external machinery returns to its original state while a weight may have risen or fallen.) Repeatedly, authors have discussed the question of exactly what has to be assumed in order that this fact lead to a *unique* (up to an additive constant) energy coordinate for all states in a system with the property that the difference in the value of the parameter at two points equals the work done by the outside world in going adiabatically from one point to the other. See e.g., (Buchdahl, 1966), (Rastall, 1970), and (Boyling, 1972). These discussions are interesting, but for us the question lies outside the scope of our inquiry, namely the second law. We simply take it for granted that the state space of a simple system can be parametrized by a subset of some $\mathbf{R}^{n+1}$ and that there is one special coordinate, which we call 'energy' and which we label by U. Whether or not this parametrization is unique is of no particular importance for us. The way in which U is special will become clear presently when we discuss the tangent planes that define the pressure function.

Mathematically, we just have coordinates. The question of which physical variables to attach to them is important in making the transition from physics to mathematics and back again. Certainly, the coordinates have to be chosen so that we are capable of specifying states in a one-to-one manner. Thus, U = energy and V = volume are better coordinates for water than, e.g., $H = U + PV$ and P, because U and V are capable of uniquely specifying the division of a multi-phase system into phases, while H and P do not have this property. For example, the triple point of water corresponds to a triangle in the U, V plane (see Fig. 8), but in the H, P plane the triple point corresponds to a line, in which case one cannot know the amount of the three phases merely by specifying a point on the line. The fundamental nature of energy and volume as coordinates was well understood by Gibbs and others, but seems to have gotten lost in many textbooks. Not only do these coordinates have the property of uniquely specifying a state but they also have the advantage of being directly tied to the fundamental classical mechanical variables, energy and length. We do not mean to imply that energy and volume always suffice. Additional work coordinates, such as magnetization, components of the strain tensor, etc., might be needed.

Associated with a simple system is its **state space**, which is a non-empty *convex* and *open* subset $\Gamma \subset \mathbf{R}^{n+1}$. This Γ constitutes all values of the coordinates that the system can reach. Γ is open because points on the boundary of Γ are regarded as not reachable physically in a finite time, but there could be exceptions.

The reason that Γ is convex was discussed at length in Section II.F. We assume axioms A1–A7. In particular, a state space Γ, scaled by $t > 0$, is the convex set

$$\Gamma^{(t)} = t\Gamma := \{tX : X \in \Gamma\} \ . \tag{3.1}$$

Thus, what was formerly the abstract symbol tX is now concretely realized as the point $(tU, tV) \in \mathbf{R}^{n+1}$ when $X = (U, V) \in \mathbf{R}^{n+1}$.

Remark. Even if $\Gamma^{(t)}$ happens to coincide with Γ as a subset of $\mathbf{R}^{n+1}$ (as it does, e.g., if Γ is the orthant $\Gamma = \mathbf{R}^n_+$) it is important to keep in mind that the mole numbers that specify the material content of the states in $\Gamma^{(t)}$ are t-times the mole numbers for the states in Γ. Hence the state spaces must be regarded as different. The photon gas, mentioned in Sect. II.B. is an exception: Particle number is not conserved, and 'material content' is not an independent variable. Hence the state spaces $\Gamma^{(t)}$ are all *physically* identical in this case, i.e., no physical measurement can tell them apart. Nevertheless it is a convenient fiction to regard them as mathematically distinguishable; in the end, of course, they must all have the same properties, e.g., entropy, as a function of the coordinates—up to an additive constant, which can always be adjusted to be zero, as discussed after Theorem 2.5.

Usually, a forward sector, A_X, with $X = (U^0, V^0)$, contains the 'half-lines' $\{(U, V^0) : U \geq U^0\}$ and $\{(U^0, V) : V_i \geq V_i^0, i = 1, \ldots, n\}$ but, theoretically, at least, it might not do so. In other words, Γ might be a bounded subset of $\mathbf{R}^n$. This happens, e.g., for a quantum spin system. Such a system is a theoretical abstraction from the real world because real systems always contain modes, other than spin modes, capable of having arbitrarily high energy. We can include such systems with bounded state spaces in our theory, however, but then we have to be a bit careful about our definitions of state spaces and the forward sectors that lie in them. This partially accounts for what might appear to be the complicated nature of the theorems in this section.

Scaling and convexity might at first sight appear to be requirements that exclude from the outset the treatment of 'surface effects' in our framework. In fact, a system like a drop of a liquid, where volume and surface effects are coupled, is not a simple system. But as we shall now argue, the state space of such a system can be regarded as a subset of the convex state space of a simple system that contains all the relevant thermodynamic information. The independent work coordinates of this system are the volume V and the surface area A. Such a system could, at least in principle, be realized by putting the liquid in a rectangular pan made out of such a material that the adhesive energy between the walls of the pan and the liquid exactly matches the cohesive energy of the liquid. I.e., there is no surface energy associated with the boundary beween liquid and walls, only between liquid and air. (Alternatively, one can think of an 'ocean' of liquid and separate a fixed amount of it (a 'system') from the rest by a purely fictitious boundary.) By making the pan (or the fictuous boundary) longer at fixed breadth and depth and, by pouring in the necessary amount of liquid, one can scale the system as one pleases. Convex combination of states also has an obvious operational meaning. By varying breadth and depth at fixed length the surface area A can be varied independently of the volume V. Lack of scaling and convexity enter only when we restrict ourselves to non-convex submanifolds of the state space, defined by subsidiary conditions like $A = (4\pi)^{1/3}3^{2/3}V^{2/3}$ that are appropriate for a drop of liquid. But such coupling of work coordinates is not special to surface effects; by suitable devices one can do similar things for any system with more than one work coordinate. *The important point is that the thermodynamic properties of the constrained system are derivable from those of the unconstrained one, for which our axioms hold.*

It should be remarked that the experimental realization of the simple system with volume and surface as independent work coordinates described above might not be easy in practice. In fact, the usual procedure would be to compare measurments on the liquid in bulk and on drops of liquid, and then, by inverting the data, infer the properties of the system where volume and surface are independent variables. The claim that scaling and convexity are compatible with the inclusion of surface effects amounts to saying that these properties hold after such a 'disentanglement' of the coordinates.

B. Assumptions about simple systems

As was already stated, we assume the general axioms A1–A7 of Section II. Since the state space Γ of a simple system has a convex structure, we recall from Theorem 2.6 that the forward sector of a point $X \in \Gamma$, namely $A_X = \{Y \in \Gamma : X \prec Y\}$ is a convex subset of $\Gamma \subset \mathbf{R}^{n+1}$. We now introduce three new axioms. It is also to be noted that the comparison hypothesis, CH, is *not* used here—indeed, *our chief goal in this section and the next is to derive CH from the other axioms.*

The new axioms are:

S1) Irreversibility. For each $X \in \Gamma$ there is a point $Y \in \Gamma$ such that $X \prec\prec Y$. In other words, each forward sector, A_X, consists of *more* than merely points that, like X itself, are adiabatically equivalent to X.

We remark that axiom S1 is implied by the thermal transversality axiom T4 in Section IV. This fact deserves to be noted in any count of the total number of axioms in our formulation of the second law, and it explains why we gave the number of our axioms as 15 in Section I. Axiom S1 is listed here as a separate axiom because it is basic to the analysis of simple systems and is conceptually independent of the notion of thermal equilibrium presented in Section IV.

By Theorem 2.9 Carathéodory's principle holds. This principle implies that

$$X \in \partial A_X \ , \tag{3.2}$$

where ∂A_X denotes the **boundary** of A_X. By 'boundary' we mean, of course, the *relative* boundary, i.e., the part of the usual boundary of A_X, (considered as a subset of $\mathbf{R}^{n+1}$) that lies in Γ.

Since X lies on the boundary of the convex set A_X we can draw at least one support plane to A_X that passes through X, i. e., a plane with the property that A_X lies entirely on one side of the plane. Convexity alone does not imply that this plane is unique, or that this plane intersects the energy axis of Γ. The next axiom deals with these matters.

S2) Lipschitz tangent planes. For each $X \in \Gamma$ the forward sector A_X has a *unique* support plane at X (i.e., A_X has a *tangent plane* at X), denoted by Π_X . The tangent plane Π_X is assumed to have a finite slope with respect to the work coordinates and the slope is moreover assumed to be a *locally Lipschitz continuous* function of X.

We emphasize that this tangent plane to A_X is initially assumed to exist only at X itself. In principle, ∂A_X could have 'cusps' at points other than X, but Theorem 3.5 will state that this does not occur.

The precise meaning of the statements in axiom S2 is the following: The tangent plane at $X = (U^0, V^0)$ is, like any plane in $\mathbf{R}^{n+1}$, defined by a linear equation. The finiteness of the slope with respect to the work coordinates means that this equation can be written as

$$U - U^0 + \sum_{i=1}^{n} P_i(X)(V_i - V_i^0) = 0, \tag{3.3}$$

in which the X dependent numbers $P_i(X)$ are the parameters that define the slope of the plane passing through X. (The slope is thus in general a vector.) The assumption that $P_i(X)$ is *finite* means that the plane is never 'vertical', i.e., it never contains the line $\{(U, V^0) : U \in \mathbf{R}\}$.

The assumption that Π_X is the unique supporting hyperplane of A_X at X means that the linear expression, with coefficients g_i,

$$U - U^0 + \sum_{i=1}^{n} g_i(V_i - V_i^0) \tag{3.4}$$

has one sign for all $(U, V) \in A_X$ (i.e., it is ≥ 0 or ≤ 0 for all points in A_X) if and only if $g_i = P_i(X)$ for all $i = 1, \dots, n$. The assumption that the slope of the tangent plane is locally Lipschitz continuous means that each P_i is a locally Lipschitz continuous function on Γ. This, in turn, means that for any closed ball $B \subset \Gamma$ with finite radius there is a constant $c = c(B)$ such that for all X and $Y \in B$

$$|P_i(X) - P_i(Y)| \leq c|X - Y|_{\mathbf{R}^{n+1}}. \tag{3.5}$$

The function $X \mapsto P(X) = (P_1(X), \dots, P_n(X))$ from Γ to $\mathbf{R}^n$ is called the **pressure**. *Note:* We do *not* need to assume that $P_i \geq 0$.

Physical motivation: The uniqueness of the support plane comes from the following physical consideration. We interpret the pressure as realized by a force on a spring that is so adjusted that the system is in equilibrium at some point (U^0, V^0). By turning the screw on the spring we can change the volume infinitesimally to $V^0 + \delta V$, all the while remaining in equilibrium. In so doing we change U^0 to $U^0 + \delta U$. The physical idea is that a slow reversal of the screw can take the system to $(U^0 - \delta U, V^0 - \delta V)$, infinitesimally. The energy change is the same, apart from a sign, in both directions.

The Lipschitz continuity assumption is weaker than, and is implied by, the assumption that P_i is continuously differentiable. By Rademacher's theorem, however, a locally Lipschitz continuous function is differentiable almost everywhere, but the relatively rare points of discontinuity of a derivative are particularly interesting.

The fact that we do *not* require the pressure to be a differentiable function of X is important for real physics because phase transitions occur in the real world, and the pressure need not be differentiable at such transition points. Some kind of continuity seems to be needed, however, and local Lipschitz continuity does accord with physical reality, as far as we know. It plays an important role here because it guarantees the uniqueness of the solution of the differential equation given in Theorem 3.5 below. It is also important in Section V when we prove the differentiability of the entropy, and hence the uniqueness of temperature. This is really the only reason we invoke continuity of the pressure and this assumption could, in principle, be dropped if we could be sure about the uniqueness and differentiablity just mentioned. There are, in fact statistical mechanical models with special forces that display discontinuous pressures (see e.g., (Fisher and Milton, 1983)) and temperatures (which then makes temperature into an 'interval-valued' function, as we explain in Section V) (see e.g., (Thirring, 1983)). These models are not claimed to be realistic; indeed, there are some theorems in statistical mechanics that prove the Lipschitz continuity of the pressure under some assumptions on the interaction potentials, e.g., (Dobrushin and Minlos, 1967). See (Griffiths, 1972).

There is another crucial fact about the pressure functions that will finally be proved in Section V, Theorem 5.4. The surfaces ∂A_X will turn out to be the surfaces of constant entropy, $S(U,V)$, and evidently, from the definition of the tangent plane (3.3), the functions $P_i(X)$ are truly the pressures in the sense that

$$P_i(X) = \frac{\partial U}{\partial V_i}(X) \tag{3.6}$$

along the (constant entropy) surface ∂A_X. However, one would also like to know the following two facts, which are at the basis of Maxwell's relations, and which are the fundamental defining relations in many treatments.

$$\frac{1}{T(X)} := \frac{\partial S}{\partial U}(X) \tag{3.7}$$

and

$$\frac{P_i(X)}{T(X)} = \frac{\partial S}{\partial V_i}(X), \tag{3.8}$$

where $T(X)$ is the temperature in the state X. Equation (3.7) constitutes, for us, the *definition* of temperature, but we must first prove that $S(U,V)$ is sufficiently smooth in order to make sense of (3.7). Basically, this is what Section V is all about.

In Theorems 3.1 and 3.2 we shall show that A_X is closed and has a non-empty interior, Interior(A_X). Physically, the points in Interior(A_X) represent the states that can be reached from X, by some adiabatic means, in a finite time. (Of course, the re-establishment of equilibrium usually requires an infinite time but, practically speaking, a finite time suffices.) On the other hand, the points in ∂A_X require a truly infinite time to reach from X. In the usual parlance they are reached from X only by 'quasi-static reversible processes'. However, these boundary points can be reached in a finite time with the aid of a tiny bit of cold matter—according to the stability assumption. If we wish to be pedantically 'physical' we should exclude ∂A_X from A_X. This amounts to replacing $\prec$ by $\prec\prec$, and we would still be able to carry out our theory, with the help of the stability assumption and some unilluminating epsilons and deltas. Thus, the seemingly innocuous, but important stability axiom permits us to regard certain infinitely slow processes as physically valid processes.

Our third axiom about simple systems is technical but important.

S3) Connectedness of the boundary. We assume that ∂A_X is arcwise connected.

Without this assumption counterexamples to the comparison hypothesis, CH, can be constructed, even ones satisfying all the other axioms.

Physical motivation: If $Y \in \partial A_X$, we think of Y as physically and adiabatically reachable from X by a continuous curve in ∂A_X whose endpoints are X and Y. (It is not possible to go from X to Y by a curve that traverses the interior of A_X because such a process could not be adiabatic.) Given this conventional interpretation, it follows trivially that $Y, Z \in \partial A_X$ implies the existence of a continuous curve in ∂A_X from Y to Z. Therefore ∂A_X must be a connected set.

We call the family of relatively closed sets $\{\partial A_X\}_{X\in\Gamma}$ the **adiabats** of our system. As we shall see later in Theorem 3.6, $Y \in \partial A_X$ implies that $X \in \partial A_Y$. Thus, all the points on any given adiabat are equivalent and it is immaterial which one is chosen to specify the adiabat.

C. The geometry of forward sectors

In this subsection all points are in the state space of the same fixed, simple system Γ, if not otherwise stated. Γ is, of course, regarded here as a subset of some $\mathbf{R}^{n+1}$.

We begin with an interesting geometric fact that complements convexity, in some sense. Suppose that X, Y, Z are three collinear points, with Y in the middle, i.e., $Y = tX + (1-t)Z$ with $0 < t < 1$. The convexity axiom A7 tells us that

$$X \prec Z \qquad \text{implies that} \qquad X \prec Y \tag{3.9}$$

because $X \prec ((1-t)X, tX) \prec (1-t)Z, tX) \prec Y$. The next lemma is geometrically related to this, but its origins are different. We shall use this lemma in the proof of Theorems 3.3 and 3.7 below.

LEMMA 3.1 (Collinear points). *Let $Y = tX + (1-t)Z$ with $0 < t < 1$ as above and suppose that $Y \prec Z$. Then $X \prec Y$ (and hence $X \prec Z$).*

Remark: Equation (3.9) and Lemma 3.1 rely only on the convexity of Γ and on axioms A1-A7. The same properties hold for compounds of simple systems (note that the Cartesian product of two convex sets is convex) and hence (3.9) and Lemma 3.1 hold for compounds as well.

Proof: By A7, A5, our hypothesis, and A3

$$(tX, (1-t)Z)) \prec Y \stackrel{\text{A}}{\sim} (tY, (1-t)Y) \prec (tY, (1-t)Z).$$

By transitivity, A2, and the cancellation law, Theorem 2.1, $tX \prec tY$. By scaling, A4, $X \prec Y$. ∎

Our first theorem in this section, about closedness, is crucial because it lies behind many of the more complex theorems. Once again, the seemingly innocuous stability axiom A6 plays a central role. As we said in Section II, this axiom amounts to some kind of continuity in a setting in which, at first, there is not even any topology on the state spaces. Now that we are in $\mathbf{R}^{n+1}$, the topology is evident and stability reveals its true character in the statement of closedness in the usual topological sense. The following proof has some of the spirit of the proof of Lemma 3.1.

THEOREM 3.1 (Forward sectors are closed). *The forward sector, A_X, of each point $X \in \Gamma$ is a relatively closed subset of Γ, i.e., $Closure(A_X) \cap \Gamma = A_X$.*

Proof: The proof uses only axioms A1-A7, in particular stability, A6, and convexity, A7, but not S1-S3. What we have to prove is that if $Y \in \Gamma$ is on the boundary of A_X then Y is in A_X. For this purpose we can assume that the set A_X has full dimension, i.e., the interior of A_X is not empty. If, on the contrary, A_X lay in some lower dimensional hyperplane then the following proof would work, without any changes, simply by replacing Γ by the intersection of Γ with this hyperplane.

Let W be any point in the interior of A_X. Since A_X is convex, and Y is on the boundary of A_X, the half-open line segment joining W to Y (call it $[W, Y)$, bearing in mind that $Y \notin [W, Y)$) lies in A_X. The prolongation of this line beyond Y lies in the complement of A_X and has at least one point (call it Z) in Γ. (This follows from the fact that Γ is open and $Y \in \Gamma$.) For all sufficiently large integers n the point Y_n defined by

$$\frac{n}{(n+1)} Y_n + \frac{1}{(n+1)} Z = Y \tag{3.10}$$

belongs to $[W, Y)$. We claim that $(X, \frac{1}{n}Z) \prec (Y, \frac{1}{n}Y)$. If this is so then we are done because, by the stability axiom, $X \prec Y$.

To prove the last claim, first note that $(X, \frac{1}{n}Z) \prec (Y_n, \frac{1}{n}Z)$ because $X \prec Y_n$ and by axiom A3. By scaling, A4, the convex combination axiom A7, and (3.10)

$$\left(Y_n, \frac{1}{n}Z\right) = \frac{n+1}{n}\left(\frac{n}{(n+1)}Y_n, \frac{1}{(n+1)}Z\right) \prec \frac{n+1}{n}Y \ . \tag{3.11}$$

But this last equals $(Y, \frac{1}{n}Y)$ by the splitting axiom, A5. Hence $(X, \frac{1}{n}Z) \prec (Y, \frac{1}{n}Y)$. ■

The following theorem uses Theorem 3.1 in an essential way.

THEOREM 3.2 (Forward sectors have interiors). *For all X, the forward sector A_X has a non empty interior.*

Proof. The proof uses the transitivity axiom, A2, convexity, A7, the existence of irreversible processes, S1, and the tangent plane axiom S2, but neither local Lipschitz continuity of the pressure nor the connectedness of the boundary, S3, are required for our proof here.

We start by remarking that a convex set in $\mathbf{R}^{n+1}$ either has a non empty interior, or it is contained in a hyperplane. We therefore assume that A_X is contained in a hyperplane and show that this contradicts the axioms. [An illustrative picture to keep in mind here is that A_X is a closed, (two-dimensional) disc in $\mathbf{R}^3$ and X is some point inside this disc and not on its perimeter. This disc is a closed subset of $\mathbf{R}^3$ and X is on its boundary (when the disc is viewed as a subset of $\mathbf{R}^3$). The hyperplane is the plane in $\mathbf{R}^3$ that contains the disc.]

Any hyperplane containing A_X is a support plane to A_X at X, and by axiom S2 the support plane is unique, so $A_X \subset \Pi_X$. If $Y \in A_X$, then $A_Y \subset A_X \subset \Pi_X$ by transitivity, A2. By the irreversibility axiom S1, there exists a $Y \in A_X$ such that $A_Y \neq A_X$, which implies that the convex set $A_Y \subset \Pi_X$, regarded as a subset of Π_X, has a boundary point in Π_X. If $Z \in \Pi_X$ is such a boundary point of A_Y, then $Z \in A_Y$ because A_Y is closed. By transitivity, $A_Z \subset A_Y \subset \Pi_X$, and $A_Z \neq \Pi_X$ because $A_Y \neq A_X$.

Now A_Y, considered as a subset of Π_X, has an $(n-1)$-dimensional supporting hyperplane at Z (because Z is a boundary point). Call this hyperplane Π'_Z. Since $A_Z \subset A_Y$, Π'_Z is a supporting hyperplane for A_Z, regarded as a subset of Π_X. Any n-dimensional hyperplane in $\mathbf{R}^{n+1}$ that contains the $(n-1)$-dimensional hyperplane $\Pi'_Z \subset \Pi_X$ clearly supports A_Z at Z, where A_Z is now considered as a convex subset of $\mathbf{R}^{n+1}$. Since there are infinitely many such n-dimensional hyperplanes in $\mathbf{R}^{n+1}$, we have a contradiction to the uniqueness axiom S2. ■

Thanks to this last theorem it makes sense to talk about the direction of the normal to the tangent plane Π_X (with respect to the canonical scalar product on $\mathbf{R}^{(n+1)}$) pointing to the interior of A_X. The part of axiom S2, that requires the tangent plane to have finite slope with respect to the work coordinates, means that the normal is never orthogonal to the energy axis. It appears natural to extend the continuity requirement of axiom S2 by requiring not only that the slope but also the direction of the normal depends continuously on X. Since Γ is connected it then follows immediately that forward sectors are on the 'same side' of the tangent plane, i.e., the projection of the normal on the energy axis is either positive for all sectors or negative for all sectors.

In fact, it is not necessary to invoke this strengthened continuity requirement to prove that forward sectors all point the same way. It is already a consequence of axioms A1-A7, S1 and the finite slope part of axiom S2. We shall prove this below as Theorem 3.3, but leave the reader the option to accept it simply as a part of the continuity requirement for tangent planes if preferred.

As far as our axiomatic framework is concerned the direction of the energy coordinate and hence of the forward sectors is purely conventional, except for the proviso that once it has been set for one system it is set for all systems. (This follows from Theorem 4.2 in the next section.) *We shall adopt the convention that they are on the positive energy side.* From a physical point of view there is more at stake, however. In fact, our operational interpretation of adiabatic processes in Sect. II involves either the raising or lowering of a weight in a gravitational field and these two cases are physically distinct. Our convention, together with the usual convention for the sign of energy for mechanical systems and energy conservation, means that we are concerned with a world where adiabatic process at fixed work coordinate can never result in the raising of a weight, only in the lowering of a weight. The opposite possibility differs from the former in a mathematically trivial way, namely by an overall sign of the energy, but given the physical interpretation of the energy direction in terms of raising and lowering of weights, such a world would be different from the one we are used to.

Note that (3.7) tells us that the fact that forward sectors point upward is equivalent to the temperature being everywhere positive. To illustrate what is involved here, let us consider a system of N independent spins in a magnetic field, so that each spin has energy either 0 or e. In the thermodynamic limit N, $U \to \infty$ with $X = U/(Ne)$ fixed, the entropy per spin is easily calculated according to the rules of statistical mechanics to be $S/N = -X \ln X - (1-X)\ln(1-X)$. The first half of the energy range, $0 < U/(Ne) < 1/2$ has positive temperature while the second half $1/2 < U/(Ne) < 1$ has negative temperature, according to (3.7). How can we reconcile this with our formulation of simple systems? That is to say, we insist that the state space Γ of our spin system consists only of the region $0 < U/(Ne) < 1/2$, and we ask what feature of our axioms has ruled out the complementary region. The answer is that if we included the second half then convexity would require that we also include the maximum entropy point $X = 1/2$. But the forward sector of X contains only X itself and this violates axiom S1.

This example captures the essential feature that lies behind the following general fact.

LEMMA 3.2 (Range of energy in forward sectors). *Let* $X = (U^0, V^0) \in \Gamma$ *and assume that its forward sector* A_X *is on the positive energy side of* Π_X*. Then*

$$A_X \cap \{(U, V^0) : U \in \mathbf{R}\} = \{(U, V^0) : U \geq U^0\} \cap \Gamma. \tag{3.12}$$

(If A_X is on the negative energy side, then (3.12) holds with '$\geq$' replaced by '$\leq$'.)

Proof: The left side of (3.12), denoted J_X, is convex and relatively closed in Γ by Theorem 3.1. It is not larger than the right side because A_X lies above the tangent plane that cuts the line $L = \{(U, V^0) : U \in \mathbf{R}\}$ at X. If it is strictly smaller than the right side of (3.12), then J_X is a compact interval. Let X_1 denote its mid point. Then J_{X_1}, the intersection of A_{X_1} with the line L, is a closed subinterval of J_X and its length is at most half the length of J_X. (Here we have used transitivity, closedness, and that X_1 is on the boundary of J_{X_1}.) Repeating this procedure we obtain a convergent sequence, X_n, $n = 1, 2, \ldots$ of points in J_X, such that the forward sector of its limit point X_∞ contains only X_∞ itself in violation of S1. ■

The 'same sidedness' of forward sectors follows from Lemmas 3.1 and 3.2 together with the finite slope of tangent planes.

THEOREM 3.3 (Forward sectors point the same way). *If* Γ *is the state space of a simple system, and if the forward sector* A_X *for one* $X \in \Gamma$ *is on the positive energy side of the tangent plane* Π_X*, then the same holds for all states in* Γ*.*

Proof: For brevity, let us say that a state $X \in \Gamma$ is 'positive' if A_X is on the positive energy side of Π_X, and that X is 'negative' otherwise. Let I be the intersection of Γ with a line parallel to the U-axis, i.e., $I = \{(U, V) \in \Gamma, U \in \mathbf{R}\}$ for some $V \in \mathbf{R}^n$. If I contains a positive point, Y, then it follows immediately from Lemma 3.2 that all points, Z, that lie above it on I (i.e., have higher energy) are also positive. In fact, one can pass from Y to Z, and if Z were negative, then, using Lemma 3.2 again, one could pass from Z to a state X below Y, violating the positivity of Y. Lemma 3.1, on the other hand, immediately implies that all points X below Y are positive, for $Y \prec Z$ for some Z strictly above Y, by S1. By the analogous argument for negative Y we conclude that all points on I have the same 'sign'.

Since Γ is convex, and therefore connected, the coexistence of positive and negative points would mean that there are pairs of points of different sign, arbitrarily close together. Now if X and Y are sufficiently close, then the line I_Y through Y parallel to the U axis intersects both A_X and its complement. (This follows easily from the finite slope of the tangent plane, cf. the proof of Theorem 3.5 (ii) below.) Transitivity and Lemma 3.2 imply that any point in $\partial A_X \cap I_Y$ has the same sign as X, and since all points on I_Y have the same sign, this applies also to Y. ■

From now on we adopt the convention that the forward sectors in Γ are on the *positive energy side* of all the tangent planes. The mathematical and physical aspects of this choice were already discussed above.

Since negative states are thus excluded (the possibility to do so is the content of Theorem 3.3), we may restate Lemma 3.2 in the following way, which we call *Planck's principle* because Planck emphasized the importance for thermodynamics of the fact that 'rubbing' (i.e., increasing the energy at fixed work coordinate) is an irreversible process (Planck, 1926, 1954).

THEOREM 3.4 (Planck's principle). *If two states,* X *and* Y*, of a simple system have the same work coordinates, then* $X \prec Y$ *if and only if the energy of* Y *is no less than the energy of* X*.*

Taking our operational definition of the relation $\prec$ in Sect. II into account, the 'only if' part of this theorem is essentially a paraphrasing of the Kelvin-Planck statement in Section I.A., but avoiding the concept of 'cooling':

'No process is possible, the sole result of which is a change in the energy of a simple system (without changing the work coordinates) and the raising of a weight.'

This statement is clearly stronger than Carathéodory's principle, for it explicitly identifies states that are arbitrarily close to a given state, but not adiabatically accessible from it.

It is worth remarking that Planck's principle, and hence this version of the Kelvin-Planck statement, already follows from axioms A1-A7, S1 and a part of S2, namely the requirement that the tangent planes to the forward sectors have finite slope with respect to the work coordinates. Neither Lipschitz continuity of the slope, nor the connectedness axiom S3, are needed for this. However, although Planck's principle puts severe restrictions on the geometry of forward sectors, it alone does not suffice to establish the comparison principle. For instance, the forward sector A_Y of a point Y on the boundary ∂A_X of another forward sector could be properly contained in A_X. In such a situation the relation $\prec$ could not be characterized by an entropy function. In order to exclude pathological cases like this we shall now study the boundary ∂A_X of a forward sectors in more detail, making full use of the axioms S2 and S3.

We denote by ρ_X the projection of ∂A_X on $\mathbf{R}^n$, i.e.,

$$\rho_X = \{V \in \mathbf{R}^n : (U,V) \in \partial A_X \text{ for some } U \in \mathbf{R}\}. \tag{3.13}$$

Clearly, ρ_X is a *connected subset* of $\mathbf{R}^n$ because of assumption S3. Note that ρ_X might be strictly smaller than the projection of A_X. See Figure 4.

—- Insert Figure 4 here —-

THEOREM 3.5 (Definition and properties of the function u_X). *Fix $X = (U^0, V^0)$ in Γ.*

(i). Let $Y \in \partial A_X$. Then A_X has a tangent plane at Y and it is Π_Y.

(ii). ρ_X is an open, connected subset of $\mathbf{R}^n$.

(iii). For each $V \in \rho_X$ there is exactly one number, $u_X(V)$, such that $(u_X(V), V) \in \partial A_X$. I.e.,

$$\partial A_X = \{(u_X(V), V) : V \in \rho_X\}. \tag{3.14}$$

This $u_X(V)$ is given by

$$u_X(V) = \inf\{u : (u,V) \in A_X\}. \tag{3.15}$$

The function u_X is continuous on ρ_X and locally convex, i.e., u_X is convex on any convex subset of ρ_X. (Note that ρ_X need not be convex—or even contractible to a point.) Moreover,

$$A_X \supset \{(U,V) : U \geq u_X(V), \quad V \in \rho_X\} \bigcap \Gamma. \tag{3.16}$$

(iv). The function u_X is a differentiable function on ρ_X with a locally Lipschitz continuous derivative and satisfies the system of partial differential equations

$$\frac{\partial u_X}{\partial V_j}(V) = -P_j(u_X(V), V) \quad \text{for } j = 1, \ldots, n\ . \tag{3.17}$$

(v). The function u_X is the only continuous function defined on ρ_X that satisfies the differential equation, (3.17)*, in the sense of distributions, and that satisfies $u_X(V^0) = U^0$.*

Remark: A solution to (3.17) is not guaranteed *a priori*; an integrability condition on P is needed. However, our assumption S2 implies that P describes the boundary of A_X (cf. (i) above), so the integrability condition is automatically fulfilled. Thus, a solution exists. It is the Lipschitz continuity that yields uniqueness; indeed, it was precisely our desire to have a unique solution to (3.17) that motivated axiom S2.

Proof: (i). Since $Y \in \partial A_X$, A_X has some support plane, Π, at Y. Since A_X is closed by Theorem 3.1 we have $Y \in A_X$ and hence $A_Y \subset A_X$ by transitivity, A2. Thus Π also supports A_Y at Y. By assumption S2, A_Y has a *unique* support plane at Y, namely Π_Y. Therefore, $\Pi = \Pi_Y$.

(ii). Connectedness of ρ_X follows immediately from assumption S3, i.e., ∂A_X is connected. The following proof that ρ_X is open does not use assumption S3. The key fact is that by (i) and S2 the tangent plane to the convex set A_X has finite slope at any $Y \in \partial A_X$. Pick a $Y = (U, V) \in \partial A_X$. Since Γ is open, the closed cylinder $C = \{(U', V') : |V' - V| \leq \varepsilon,\ |U' - U| \leq \sqrt{\varepsilon}\}$ with Y at its center lies in Γ for $\varepsilon > 0$ small enough. Since the tangent plane through Y has finite slope, the bottom 'disc' $D_- = \{(U - \sqrt{\varepsilon}, V') : |V' - V| < \varepsilon\}$ lies below the tangent plane for ε small enough and thus belongs to the complement of A_X. Consider the intersection of A_X with the top disc, $D_+ = \{(U + \sqrt{\varepsilon}, V') : |V' - V| < \varepsilon\}$. This intersection is compact, convex and contains the point $(U + \sqrt{\varepsilon}, V)$ by Lemma 3.2 and A2 (the latter implies that $A_Y \subset A_X$). Its boundary is also compact and thus contains a point with minimal distance δ from the cylinder axis (i.e, from the point $(U + \sqrt{\varepsilon}, V)$). We are obviously done if we show that $\delta > 0$, for then all lines parallel to the cylinder axis with distance $< \delta$ from the axis intersect both A_X and its complement, and hence the boundary ∂A_X. Now, if $\delta = 0$, it follows from Lemma 3.2 and transitivity that the vertical line joining $(U + \sqrt{\varepsilon}, V)$ and (U, V) has an empty intersection with the interior of A_X. But then A_X has a vertical support plane (because it is a convex set), contradicting S2.

(iii). The proof of (3.14)-(3.16) is already contained in Lemma 3.2, bearing in mind that $A_Y \subset A_X$ for all $Y \in \partial A_X$. The local convexity of u_X follows from its definition: Let $C \subset \rho_X$ be convex, let V^1 and V^2 be in C and let $0 \leq \lambda \leq 1$. Then the point $V := \lambda V^1 + (1 - \lambda)V^2$ is in C (by definition) and, by axiom A7, $(\lambda u_X(V^1) + (1 - \lambda)u_X(V^2), V)$ is in A_X. Hence, by (3.15), $u_X(V) \leq \lambda u_X(V^1) + (1 - \lambda)u_X(V^2)$. Finally, every convex function defined on an open, convex subset of $\mathbf{R}^n$ is continuous.

(iv). Fix $V \in \rho_X$, let $B \subset \rho_X$ be an open ball centered at V and let $Y := (u_X(V), V) \in \partial A_X$. By (i) above and (3.4) we have

$$u_X(V') - u_X(V) + \sum_i P_i(Y)(V_i' - V_i) \geq 0 \tag{3.18}$$

for all $V' \in B$. Likewise, applying (i) above and (3.4) to the point $Y' := (u_X(V'), V')$ we have

$$u_X(V) - u_X(V') + \sum_i P_i(Y')(V_i - V_i') \geq 0\ . \tag{3.19}$$

As $V' \to V, P(Y') \to P(Y)$, since u_X is continuous and P is continuous. Thus, if $1 \leq j \leq n$ is fixed and if $V_i' := V_i$ for $i \neq j$, $V_j' = V_j + \varepsilon$ then, taking limits $\varepsilon \to 0$ in the two inequalities above, we have that

$$\frac{u_X(V') - u_X(V)}{\varepsilon} \to -P_j(Y)\ , \tag{3.20}$$

which is precisely (3.17).

By assumption $P(Y)$ is continuous, so u_X is continuously differentiable, and hence locally Lipschitz continuous. But then $P(u_X(V), V)$ is locally Lipschitz continuous in V.

(v). The uniqueness is a standard application of Banach's contraction mapping principle, given the important hypothesis that P is locally Lipschitz continuous and the connectedness of the open set ρ_X. ρ_X. ■

According to the last theorem the boundary of a forward sector is described by the unique solution of a system of differential equations. As a corollary it follows that all points on the boundary are adiabatically equivalent and thus have the same forward sectors:

THEOREM 3.6 (Reversibility on the boundary). *If $Y \in \partial A_X$, then $X \in \partial A_Y$ and hence $A_Y = A_X$.*

Proof: Assume $Y = (U^1, V^1) \in \partial A_X$. The boundary ∂A_Y is described by the function u_Y which solves Eqs. (3.17) with the condition $u_Y(V^1) = U^1$. But u_X , which describes the boundary ∂A_X, solves the same equation with the same initial condition. This solution is unique on ρ_Y by Theorem 3.5(v), so we conclude that $\partial A_Y \subset \partial A_X$ and hence $\rho_Y \subset \rho_X$. The theorem will be proved if we show that $\rho_X = \rho_Y$. Suppose, on the contrary, that ρ_Y is strictly smaller than ρ_X. Then, since ρ_X is open, there is some point $V \in \rho_X$ that is in the boundary of ρ_Y, and hence $V \notin \rho_Y$ since ρ_Y is open. We claim that ∂A_Y is not relatively closed in Γ, which is a contradiction since A_Y must be relatively closed. To see this, let V^j, for $j = 1, 2, 3, \ldots$ be in ρ_Y and $V^j \to V$ as $j \to \infty$. Then $u_X(V^j) \to u_X(V)$ since u_X is continuous. But $u_Y(V^j) = u_X(V^j)$, so the sequence of points $(u_Y(V^j), V)$ in A_X converges to $Z := (u_X(V), V) \in \Gamma$. Thus, Z is in the relative closure of ∂A_Y but $Z \notin \partial A_Y$ because $V \notin \rho_Y$, thereby establishing a contradiction. ■

We are now in a position to prove the main result in this section. It shows that Γ is foliated by the adiabatic surfaces ∂A_X, and that the points of Γ are all comparable. More precisely, $X \prec\prec Y$ if and only if A_Y is contained in the interior of A_X, and $X \stackrel{A}{\sim} Y$ if and only if $Y \in \partial A_X$.

THEOREM 3.7 (Forward sectors are nested). *With the above assumptions, i.e., A1-A7 and S1-S3, we have the following. If A_X and A_Y are two forward sectors in the state space, Γ, of a simple system then exactly one of the following holds.*

(a). $A_X = A_Y$, i.e., $X \stackrel{A}{\sim} Y$.

(b). $A_X \subset \mathrm{Interior}(A_Y)$, i.e., $Y \prec\prec X$.

(c). $A_Y \subset \mathrm{Interior}(A_X)$, i.e., $X \prec\prec Y$.

In particular, ∂A_X and ∂A_Y are either identical or disjoint.

Proof: There are three (non-exclusive) cases:

Case 1. $Y \in A_X$

Case 2. $X \in A_Y$

Case 3. $X \notin A_Y$ and $Y \notin A_X$.

By transitivity, case 1 is equivalent to $A_Y \subset A_X$. Then, either $Y \in \partial A_X$ (in which case $A_Y = A_X$ by Theorem 3.6) or $Y \in \mathrm{Interior}(A_X)$. In the latter situation we conclude that $\partial A_Y \subset \mathrm{Interior}(A_X)$, for otherwise $\partial A_Y \cap \partial A_X$ contains a point Z and Theorem 3.6 would tell us that $\partial A_Y = \partial A_Z = \partial A_X$, which would mean that $A_Y = A_X$. Thus, case 1 agrees with the conclusion of our theorem.

Case 2 is identical to case 1, except for interchanging X and Y.

Therefore, we are left with the case that $Y \notin A_X$ and $X \notin A_Y$. This, we claim, is impossible for the following reason.

Let Z be some point in the interior of A_X and consider the line segment L joining Y to Z (which lies in Γ since Γ is convex). If we assume $Y \notin A_X$ then part of L lies outside A_X, and therefore L intersects ∂A_X at some point $W \in \partial A_X$. By Theorem 3.6, A_X and A_W are the same set, so $W \prec Z$ (because $X \prec Z$). By Lemma 3.1, $Y \prec Z$ also. Since Z was arbitrary, we learn that Interior$(A_X) \subset A_Y$. By the same reasoning Interior$(A_Y) \subset A_X$. Since A_X and A_Y are both closed, the assumption that $Y \notin A_X$ and $X \notin A_Y$ has led us to the conclusion that they are identical. ■

Figure 5 illustrates the content of Theorem 3.7. The end result is that the forward sectors are nicely nested and thereby establishes the comparison hypothesis for simple systems, among other things.

—- Insert Figure 5 here —-

The adiabats ∂A_X foliate Γ and using Theorem 3.5 it may be shown that there is always a continuous function σ that has exactly these adiabats as level sets. (Such a function is usually referred to as an 'empirical entropy'.) But although the sets A_X are convex, the results established so far do not suffice to show that there is a *concave* function with the adiabats as level sets. For this and further properties of entropy we shall rely on the axioms about *thermal equilibrium* discussed in the next section.

As a last topic in this section we would like to come back to the claim made in Section II.A.2. that our operational definition of the relation $\prec$ coincides with definitions in textbooks based on the concept of 'adiabatic process', i.e., a process taking place in an 'adiabatic enclosure'. We already discussed the connection from a general point of view in Section II.C, and showed that both definitions coincide. However, there is also another point of view that relates the two, and which we now present. It is based on the idea that, quite generally , if one relation is included in another then the two relations must coincide for simple systems. This very general result is Theorem 3.8 below.

Whatever 'adiabatic process' means, we consider it a minimal requirement that the relation based on it is a subrelation of our $\prec$, according to the operational definition in Sect. II.A. More precisely, denoting this hypothetical relation based on 'adiabatic process' by $\prec^*$, it should be true that $X \prec^* Y$ implies $X \prec Y$. Moreover, our motivations for the axioms A1-A6 and S1-S3 for $\prec$ apply equally well to $\prec^*$, so we may assume that $\prec^*$ also satisfies these axioms. In particular, the forward sector A^*_X of X with respect to $\prec^*$ is convex and closed with a nonempty interior and with X on its boundary. The following simple result shows that $\prec$ and $\prec^*$ must then necessarily coincide.

THEOREM 3.8 (There are no proper inclusions). *Suppose that $\prec^{(1)}$ and $\prec^{(2)}$ are two relations on multiple scaled products of a simple system Γ satisfying axioms A1-A7 as well as S1-S3. If*

$$X \prec^{(1)} Y \qquad \text{implies} \qquad X \prec^{(2)} Y$$

for all $X, Y \in \Gamma$, then $\prec^{(1)} = \prec^{(2)}$.

Proof: We use superscripts (1) and (2) to denote the two cases. Clearly, the hypothesis is equivalent to $A^{(1)}_X \subset A^{(2)}_X$ for all $X \in \Gamma$. We have to prove $A^{(2)}_X \subset A^{(1)}_X$. Suppose not. Then there is a Y such that $X \prec^{(2)} Y$ but $X \not\prec^{(1)} Y$. By Theorem 3.7 for $\prec^{(1)}$ we have that $Y \prec^{(1)} X$. By our hypothesis, $Y \prec^{(2)} X$, and thus we have $X \overset{\mathrm{A}}{\sim}^{(2)} Y$.

Now we use what we know about the forward sectors of simple systems. $A_X^{(2)}$ has a non-empty interior, so the complement of $A_X^{(1)}$ in $A_X^{(2)}$ contains a point Y that is *not* on the boundary of $A_X^{(2)}$. On the other hand, we just proved that $X \overset{\mathrm{A}}{\sim}^{(2)} Y$, which implies that $Y \in \partial A_X^{(2)}$. This is a contradiction. ■

IV. THERMAL EQUILIBRIUM

In this section we introduce our axioms about thermal contact of simple systems. We then use these assumptions to derive the comparison hypothesis for products of such systems. This will be done in two steps. First we consider scaled copies of a single simple system and then products of different systems. The key idea is that two simple systems in thermal equilibrium can be regarded as a new simple system, to which Theorem 3.7 applies. We emphasize that the word 'thermal' has nothing to do with temperature—at this point in the discussion. Temperature will be introduced in the next section, and its existence will rely on the properties of thermal contact, but thermal equilibrium, which is governed by the zeroth law, is only a statement about mutual equilibrium of systems and not a statement about temperature.

A. Assumptions about thermal contact

We assume that a relation $\prec$ satisfying axioms A1–A6 is given, but A7 and CH are *not* assumed here. We shall make five assumptions about thermal equilibrium, T1-T5. Our first axiom says that one can form new simple systems by bringing two simple systems into thermal equilibrium and that this operation is adiabatic (for the compound system, not for each system individually).

T1) Thermal contact. Given any two simple systems with state spaces Γ_1 and Γ_2, there is another simple system, called the **the thermal join of Γ_1 and Γ_2**, whose state space is denoted by Δ_{12}. The work coordinates in Δ_{12} are (V_1, V_2) with V_1 the work coordinates of Γ_1 and V_2 the work coordinates of Γ_2. The range of the (single) energy coordinate of Δ_{12} is the *sum* of all possible energies in Γ_1 and Γ_2 for the given values of the work coordinates. In symbols:

$$\Delta_{12} = \{(U, V_1, V_2) : U = U_1 + U_2 \text{ with } (U_1, V_1) \in \Gamma_1, (U_2, V_2) \in \Gamma_2\}. \tag{4.1}$$

By assumption, there is always an adiabatic process, called **thermal equilibration** that takes a state in the compound system, $\Gamma_1 \times \Gamma_2$, into a state in Δ_{12} which is given by the following formula:

$$\Gamma_1 \times \Gamma_2 \ni ((U_1, V_1), (U_2, V_2)) \prec (U_1 + U_2, V_1, V_2) \in \Delta_{12}.$$

From the physical point of view, a state in Δ_{12} is a "black box" containing the two systems, with energies U_1 and U_2, respectively, such that $U_1 + U_2 = U$. The values of U_1 and U_2 need not be unique, and we regard all such pairs (if there is more than one) as being equivalent since, by T2 below, they are adiabatically equivalent. This state in Δ_{12} can be pictured, physically, as having the two systems side by side (each with its own pistons, etc.) and linked by a copper thread that allows 'heat' to flow from one to the other until thermal equilibrium is attained. The total energy $U = U_1 + U_2$ can be selected at will (within the range permitted by V_1 and V_2), but the individual energies U_1 and U_2 will be determined by the properties of the two systems. Note that Δ_{12} is convex—a fact that follows easily from the convexity of Γ_1 and Γ_2.

The next axiom simply declares the 'obvious' fact that we can disconnect the copper thread, once equilibrium has been reached, and restore the original two systems.

T2) Thermal splitting. For any point $(U, V_1, V_2) \in \Delta_{12}$ there is at least one pair of states, $(U_1, V_1) \in \Gamma_1$, $(U_2, V_2)) \in \Gamma_2$, with $U = U_1 + U_2$, such that

$$\Delta_{12} \ni (U, V_1, V_2) \stackrel{A}{\sim} ((U_1, V_1), (U_2, V_2)) \in \Gamma_1 \times \Gamma_2.$$

In particular, the following is assumed to hold: If (U,V) is a state of a simple system Γ and $\lambda \in [0,1]$ then

$$(U,(1-\lambda)V,\lambda V) \overset{\text{A}}{\sim} (((1-\lambda)U,(1-\lambda)V),(\lambda U,\lambda V)) \in \Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}.$$

We are now in a position to introduce another kind of equivalence relation among states, in addition to $\overset{\text{A}}{\sim}$.

Definition. If $((U_1,V_1),(U_2,V_2)) \overset{\text{A}}{\sim} (U_1+U_2,V_1,V_2)$ we say that the states $X=(U_1,V_1)$ and $Y=(U_2,V_2)$ are in **thermal equilibrium** and write

$$X \overset{\text{T}}{\sim} Y.$$

It is clear that $X \overset{\text{T}}{\sim} Y$ implies $Y \overset{\text{T}}{\sim} X$. Moreover, by axiom T2 and axioms A4 and A5 we always have $X \overset{\text{T}}{\sim} X$.

The next axiom implies that $\overset{\text{T}}{\sim}$ is, indeed, an equivalence relation. It is difficult to overstate its importance since it is the key to eventually establishing the fact that *entropy is additive not only with respect to scaled copies of one system but also with respect to different kinds of systems.*

T3) Zeroth law of thermodynamics. If $X \overset{\text{T}}{\sim} Y$ and if $Y \overset{\text{T}}{\sim} Z$ then $X \overset{\text{T}}{\sim} Z$.

The equivalence classes w.r.t. the relation $\overset{\text{T}}{\sim}$ are called **isotherms**.

The question whether the zeroth law is really needed as an independent postulate or can be derived from other assumptions is the subject of some controversy, see e.g., (Buchdahl, 1986), (Walter, 1989), (Buchdahl, 1989). Buchdahl (1986) derives it from his analysis of the second law for *three* systems in thermal equilibrium. However, it is not clear whether the zeroth law comes for free; if we really pursued this idea in our framework we should probably find it necessary to invoke some sort of assumption about the three-system equilibria.

Before proceeding further let us point out a simple consequences of T1-T3.

THEOREM 4.1 (Scaling invariance of thermal equilibrium.) *If X and Y are two states of two simple systems (possibly the same or possibly different systems) and if $\lambda,\mu>0$ then the relation $X \overset{\text{T}}{\sim} Y$ implies $\lambda X \overset{\text{T}}{\sim} \mu Y$.*

Proof: $(X,\lambda X) = ((U_X,V_X),(\lambda U_X,\lambda V_X)) \overset{\text{A}}{\sim} ((1+\lambda)U_X,V_X,\lambda V_X)$ by axiom T2. But this means, by the above definition of thermal equilibrium, that $X \overset{\text{T}}{\sim} \lambda X$. In the same way, $Y \overset{\text{T}}{\sim} \mu Y$. By the zeroth law, axiom T3, this implies $\lambda X \overset{\text{T}}{\sim} \mu Y$. ■

Another simple consequence of the axioms for thermal contact concerns the orientation of forward sectors with respect to the energy. In Theorem 3.3 in the previous section we had already showed that in a simple system the forward sectors are either all on the positive energy side or all on the negative energy side of the tangent planes to the sectors, but the possibility that the direction is different for different systems was still open. The coexistence of systems belonging to both cases, however, would violate our axioms T1 and T2. The different orientations of the sectors with respect to the energy correspond to different signs for the temperature as defined in Section V. Our axioms are only compatible with systems of one sign.

THEOREM 4.2 (Direction of forward sectors). *The forward sectors of all simple systems point the same way, i.e., they are either all on the positive energy side of their tangent planes or all on the negative energy side.*

Proof: This follows directly from T1 and T2, because a system with sectors on the positive energy side of the tangent planes can never come to thermal equilibrium with a system whose sectors are on the negative side of the tangent planes. To be precise, suppose that Γ_1 has positive sectors, Γ_2 has negative sectors and that there are states $X = (U_1, V_1) \in \Gamma_1$ and $Y = (U_2, V_2) \in \Gamma_2$ such that $X \stackrel{\mathrm{T}}{\sim} Y$. (Such states exist by T2.) Then, for any sufficiently small $\delta > 0$,

$$(U_1, V_1) \prec (U_1 + \delta, V_1) \qquad \text{and} \qquad (U_2, V_2) \prec (U_2 - \delta, V_2)$$

by Theorem 3.4 (Planck's principle). With $U := U_1 + U_2$ we then have the two relations

$$(U, V_1, V_2) \stackrel{\mathrm{A}}{\sim} ((U_1, V_1),\ (U_2, V_2)) \prec ((U_1 + \delta, V_1),\ (U_2, V_2)) \prec (U + \delta, V_1, V_2)$$
$$(U, V_1, V_2) \stackrel{\mathrm{A}}{\sim} ((U_1, V_1),\ (U_2, V_2)) \prec ((U_1, V_1),\ (U_2 - \delta, V_2)) \prec (U - \delta, V_1, V_2).$$

This means that starting from $(U, V_1, V_2) \in \Delta_{12}$ we can move adiabatically both upwards and downwards in energy (at fixed work coordinates), but this is impossible (by Theorem 3.3) because Δ_{12} is a simple system, by Axiom T1. ■

For the next theorem we recall that an entropy function on Γ is a function that exactly characterizes the relation $\prec$ on multiple scaled copies of Γ, in the sense of Theorem 2.2. As defined in Section II, entropy functions S_1 on Γ_1 and S_2 on Γ_2 are said to be *consistent* if together they characterize the relation $\prec$ on multiple scaled products of Γ_1 and Γ_2 in the sense of Theorem 2.5. The comparison hypothesis guarantees the existence of such consistent entropy functions, by Theorem 2.5, but our present goal is to derive the comparison hypothesis for compound systems by using the notion of thermal equilibrium. In doing so, and also in Section V, we shall make use of the following consequence of consistent entropy functions.

THEOREM 4.3 (Thermal equilibrium is characterized by maximum entropy). *If S is an entropy function on the state space of a simple system, then S is a concave function of U for fixed V. If S_1 and S_2 are consistent entropy functions on the state spaces Γ_1 and Γ_2 of two simple systems and $(U_i, V_i) \in \Gamma_i$, $i = 1, 2$, then $(U_1, V_1) \stackrel{\mathrm{T}}{\sim} (U_2, V_2)$ holds if and only if the sum of the entropies takes its maximum value at $((U_1, V_1), (U_2, V_2))$ for fixed total energy and fixed work coordinates, i.e.,*

$$\max_W [S_1(W, V_1) + S_2((U_1 + U_2) - W), V_2)] = S_1(U_1, V_1) + S_2(U_2, V_2). \tag{4.2}$$

Proof: The concavity of S is true for any simple system by Theorem 2.8, which uses the convex combination axiom A7. It is interesting to note, however, that concavity in U for fixed V follows from axioms T1, T2 and A5 alone, even if A7 is *not* assumed. In fact, by axiom T1 we have, for states (U, V) and (U', V) of a simple system with the same work coordinates,

$$(((1-\lambda)U, (1-\lambda)V), (\lambda U', \lambda V)) \prec ((1-\lambda)U + \lambda U', (1-\lambda)V, \lambda V).$$

By T2, and with $U'' := (1-\lambda)U + \lambda U'$, this latter state is $\stackrel{\mathrm{A}}{\sim}$ equivalent to

$$((1-\lambda)U'', (1-\lambda)V), (\lambda U'', \lambda V)),$$

which, by A5, is $\stackrel{\mathrm{A}}{\sim}$ equivalent to (U'', V). Since S is additive and non decreasing under $\prec$ this implies

$$(1-\lambda)S(U, V) + \lambda S(U', V) \le S((1-\lambda)U + \lambda U', V).$$

For the second part of our theorem, let (U_1, V_1) and (U_2, V_2) be states of two simple systems. Then T1 says that for any W such that $(W, V_1) \in \Gamma_1$ and $((U_1 + U_2 - W), V_2) \in \Gamma_2$ one has

$$((W, V_1), ((U_1 + U_2) - W), V_2)) \prec (U_1 + U_2, V_1, V_2).$$

The definition of thermal equilibrium says that $(U_1 + U_2, V_1, V_2) \stackrel{A}{\sim} ((U_1, V_1)(U_2, V_2))$ if and only if $(U_1, V_1) \stackrel{T}{\sim} (U_2, V_2)$. Since the sum of consistent entropies characterizes the order relation on the product space the assertion of the lemma follows. ■

We come now to what we call the *transversality axiom*, which is crucial for establishing the comparison hypothesis, CH, for products of simple systems.

T4) Transversality. If Γ is the state space of a simple system and if $X \in \Gamma$, then there exist states $X_0 \stackrel{T}{\sim} X_1$ with $X_0 \prec\prec X \prec\prec X_1$.

To put this in words, the axiom requires that for every adiabat there exists at least one isotherm (i.e., an equivalence class w.r.t. $\stackrel{T}{\sim}$), containing points on both sides of the adiabat. Note that, for each given X, only two points in the entire state space Γ are required to have the stated property. See Figure 6.

—- Insert Figure 6 here —-

We remark that the condition $X \prec\prec X_1$ obviously implies axiom S1. However, as far as the needs of this Section IV are concerned, the weaker condition $X_0 \prec X \prec X_1$ together with $X_0 \prec\prec X_1$ would suffice, and this would *not* imply S1. The strong version of transversality, stated above, will be needed in Section V, however.

At the end of this section we shall illustrate, by the example of 'thermometers', the significance of axiom T4 for the existence of an entropy function. There we shall also show how an entropy function can be defined for a system that violates T4, *provided* its thermal combination with some other system (that itself satisfies T4) does satisfy T4.

The final thermal axiom states, essentially, that the range of temperatures that a simple system can have is the same for all simple systems under consideration and is independent of the work coordinates. In this section axiom T5 will be needed only for Theorem 4.9. It will also be used again in the next section when we establish the existence and properties of temperature. (We repeat that the word 'temperature' is used in this section solely as a mnemonic.)

T5) Universal temperature range. If Γ_1 and Γ_2 are state spaces of simple systems then, for every $X \in \Gamma_1$ and every $V \in \rho(\Gamma_2)$, where ρ denotes the projection on the work coordinates, $\rho(U', V') := V'$, there is a $Y \in \Gamma_2$ with $\rho(Y) = V$, such that $X \stackrel{T}{\sim} Y$.

The physical motivation for T5 is the following. A sufficiently large copy of the first system in the state $X \in \Gamma_1$ can act as a heat bath for the second, i.e., when the second system is brought into thermal contact with the first at fixed work coordinates, V, it is always possible to reach thermal equilibrium, but the change of X will be very small since X is so large.

This axiom is inserted mainly for convenience and one might weaken it and require it to hold only within a group of systems that can be placed in thermal contact with each other. However, within such a group this axiom is really necessary if one wants to have a consistent theory.

B. The comparison principle in compound systems

1. Scaled copies of a single simple system

We shall now apply the thermal axioms, T4 in particular, to derive the comparison hypothesis, CH, for multiple scaled copies of simple systems.

THEOREM 4.4 (Comparison in multiple scaled copies of a simple system). *Let Γ be the state space of a simple system and let $a_1, \dots, a_M, a_1', \dots, a_M'$ be positive real numbers with $a_1 + \dots + a_N = a_1' + \dots + a_M'$. Then all points in $a_1\Gamma \times \dots \times a_N\Gamma$ are comparable to all points in $a_1'\Gamma \times \dots \times a_M'\Gamma$.*

Proof: We may suppose that $a_1 + \dots + a_N = a_1' + \dots + a_M' = 1$. We shall show that for any points $Y_1, \dots, Y_N, Y_1', \dots, Y_M' \in \Gamma$ there exist points $X_0 \prec\prec X_1$ in Γ such that $(a_1Y_1, \dots, a_NY_N) \stackrel{A}{\sim} ((1-\alpha)X_0, \alpha X_1)$ and $(a_1'Y_1', \dots, a_N'Y_N') \stackrel{A}{\sim} ((1-\alpha')X_0, \alpha' X_1)$ with $\alpha, \alpha' \in \mathbf{R}$. This will prove the statement because of Lemma 2.2.

By Theorem 3.7, the points in Γ are comparable, and hence there are points $X_0 \prec X_1$ such that all the points $Y_1, \dots, Y_N, Y_1', \dots, Y_M'$ are contained in the strip $\Sigma(X_0, X_1) = \{X \in \Gamma : X_0 \prec X \prec X_1\}$; in particular, these $N+M$ points can be linearly ordered and X_0 and X_1 can be chosen from this set. If $X_0 \stackrel{A}{\sim} X_1$ then all the points in the strip would be equivalent and the assertion would hold trivially. Hence we may assume that $X_0 \prec\prec X_1$. Moreover, it is clearly sufficient to prove that for each $Y \in \Sigma(X_0, X_1)$ one has $Y \stackrel{A}{\sim} ((1-\lambda)X_0, \lambda X_1)$ for some $\lambda \in [0,1]$, because the general case then follows by the splitting and recombination axiom A5 and Lemma 2.2.

If $X_0 \stackrel{T}{\sim} X_1$ (or, if there exist $X_0' \stackrel{A}{\sim} X_0$ and $X_1' \stackrel{A}{\sim} X_1$ with $X_0' \stackrel{T}{\sim} X_1'$, which is just as good for the present purpose) the existence of such a λ for a given Y can be seen as follows. For any $\lambda' \in [0,1]$ the states $((1-\lambda')X_0, \lambda' X_1)$ and $((1-\lambda')Y, \lambda' Y)$ are adiabatically equivalent to certain states in the state space of a simple system, thanks to thermal axiom T2. Hence $((1-\lambda')X_0, \lambda' X_1)$ and $Y \stackrel{A}{\sim} ((1-\lambda')Y, \lambda' Y)$ are comparable. We define

$$\lambda = \sup\{\lambda' \in [0,1] : ((1-\lambda')X_0, \lambda' X_1) \prec Y\}. \tag{4.3}$$

Since $X_0 \prec Y$ the set on the right of (4.3) is not empty (it contains 0) and therefore λ is well defined and $0 \le \lambda \le 1$. Next, one shows that $((1-\lambda)X_0, \lambda X_1) \stackrel{A}{\sim} Y$ by exactly the same argument as in Lemma 2.3. (Note that this argument only uses that Y and $((1-\lambda')X_0, \lambda' X')$ are comparable.) Thus, our theorem is established under the hypothesis that $X_0 \stackrel{T}{\sim} X_1$.

The following Lemma 4.1 will be needed to show that we can, indeed, always choose X_0 and X_1 so that $X_0 \stackrel{T}{\sim} X_1$.

LEMMA 4.1 (Extension of strips). *For any state space (of a simple or a compund system), if $X_0 \prec\prec X_1, X_0' \prec\prec X_1'$ and if*

$$X \stackrel{A}{\sim} ((1-\lambda)X_0, \lambda X_1) \tag{4.4}$$

$$X_1 \stackrel{A}{\sim} ((1-\lambda_1)X_0', \lambda_1 X_1') \tag{4.5}$$

$$X_0' \stackrel{A}{\sim} ((1-\lambda_0)X_0, \lambda_0 X_1) \tag{4.6}$$

then

$$X \stackrel{A}{\sim} ((1-\mu)X_0, \mu X_1') \tag{4.7}$$

with

$$\mu = \frac{\lambda\lambda_1}{1-\lambda_0+\lambda_0\lambda_1}.$$

Proof: We first consider the special case $X = X_1$, i.e., $\lambda = 1$. By simple arithmetic, using the cancellation law, one obtains (4.7) from (4.5) and (4.6) with $\mu = \mu_1 = \frac{\lambda_1}{1-\lambda_0+\lambda_0\lambda_1}$. The general case now follows by inserting the splitting of X_1 into (4.4) and recombining.

■

Proof of Theorem 4.4 continued: By the transversality property, each point X lies in some strip $\Sigma(X_0, X_1)$ with $X_0 \prec\prec X_1$ and $X_0 \overset{\mathrm{T}}{\sim} X_1$. Hence the whole state space can be covered by strips $\sum(X_0^{(i)}, X_1^{(i)})$ with $X_0^{(i)} \prec\prec X_0^{(i)}$ and $X_0^{(i)} \overset{\mathrm{T}}{\sim} X_1^{(i)}$. Here i belongs to some index set. Since all adiabats ∂A_X with $X \in \Gamma$ are relatively closed in Γ by axiom S3 we can even cover each X (and hence Γ) with *open* strips $\overset{o}{\sum}_i := \overset{o}{\sum}(X_0^{(i)}, X_1^{(i)}) = \{X : X_0^{(i)} \prec\prec X \prec\prec X_0^{(i)}\}$ with $X_0^{(i)} \overset{\mathrm{T}}{\sim} X_1^{(i)}$. Moreover, any compact subset, C, of Γ is covered by a finite number of such strips $\overset{o}{\sum}_i, i = 1, \ldots, K$, and if C is connected we may assume that $\overset{o}{\sum}_i \cap \overset{o}{\sum}_{i+1} \neq \emptyset$. If $\bar{X}_0$ denotes the smallest of the elements $X_0^{(i)}$ (with respect to the relation $\prec$) and $\bar{X}_1$ the largest, it follows from Lemma 2.3 that for any $X \in C$ we have $X \overset{\mathrm{A}}{\sim} ((1-\mu)\bar{X}_0, \mu\bar{X}_1)$ for some μ. If a finite number of points, $Y_1, \ldots, Y_N, Y_1', \ldots, Y_M'$ is given, we take C to be a polygon connecting the points, which exists because Γ is convex. Hence each of the points $Y_1, \ldots, Y_N, Y_1', \ldots, Y_M'$ is equivalent to $((1-\lambda)\bar{X}_0, \lambda\bar{X}_1)$ for some λ, and the proof is complete. ■

The comparison hypothesis, CH, has thus been established for multiple scaled copies of a single simple system. From Theorem 2.2 we then know that for such a system the relation $\prec$ is characterized by an entropy function, which is unique up to an affine transformation $S \to aS + B$.

2. Products of different simple systems

Our next goal is to verify the comparison hypothesis for products of different simple systems. For this task we shall appeal to the following:

THEOREM 4.5 (Criterion for comparison in product spaces). *Let Γ_1 and Γ_2 be two (possibly unrelated) state spaces. Assume there is a relation $\prec$ satisfying axioms A1-A6 that holds for Γ_1, Γ_2 and their scaled products. Additionally, $\prec$ satisfies the comparison hypothesis CH on Γ_1 and its multiple scaled copies and on Γ_2 and its multiple scaled copies but, a-priori, not necessarily on $\Gamma_1 \times \Gamma_2$ or any other products involving both Γ_1 and Γ_2*

If there are points $X_0, X_1 \in \Gamma_1$ and $Y_0, Y_1 \in \Gamma_2$ such that

$$X_0 \prec\prec X_1, \quad Y_0 \prec\prec Y_1 \tag{4.8}$$

$$(X_0, Y_1) \overset{\mathrm{A}}{\sim} (X_1, Y_0), \tag{4.9}$$

then the comparison hypothesis CH holds on products of any number of scaled copies of Γ_1 and Γ_2.

Proof: Since the comparison principle holds for Γ_1 and Γ_2 these spaces have canonical entropy functions corresponding, respectively, to the reference points X_0, X_1 and Y_0, Y_1. If $X \in \Gamma_1$ and $\lambda_1 = S_1(X|X_0, X_1)$ (in the notation of eq. (2.15)) then, by Lemma 2.3,

$$X \overset{\mathrm{A}}{\sim} ((1-\lambda_1)X_0, \lambda_1 X_1)$$

and similarly, for $Y \in \Gamma_2$ and $\lambda_2 = S_2(Y|Y_0, Y_1)$,

$$Y \overset{A}{\sim} ((1-\lambda_2)Y_0, \lambda_2 Y_1).$$

Set $\lambda = \frac{1}{2}(\lambda_1 + \lambda_2)$ and $\delta = \frac{1}{2}(\lambda_1 - \lambda_2)$. We then have

$$\begin{aligned}
(X,Y) &\overset{A}{\sim} ((1-\lambda_1)X_0, \lambda_1 X_1, (1-\lambda_2)Y_0, \lambda_2 Y_1) && \text{by A3}\\
&\overset{A}{\sim} ((1-\lambda)X_0, -\delta X_0, \lambda X_1, \delta X_1, (1-\lambda)Y_0, \delta Y_0, \lambda Y_1, -\delta Y_1) && \text{by A5}\\
&\overset{A}{\sim} ((1-\lambda)X_0, -\delta X_0, \lambda X_1, \delta X_0, (1-\lambda)Y_0, \delta Y_1, \lambda Y_1, -\delta Y_1) && \text{by (4.9), A3, A4}\\
&\overset{A}{\sim} ((1-\lambda)(X_0, Y_0), \lambda(X_1, Y_1)) && \text{by A5.}
\end{aligned}$$

Thus, every point in $\Gamma_1 \times \Gamma_2 =: \Gamma_{12}$ is equivalent to a point of the form $((1-\lambda)Z_0, \lambda Z_1)$ in $(1-\lambda)\Gamma_{12} \times \lambda\Gamma_{12}$ with $Z_0 = (X_0, Y_0)$ and $Z_1 = (X_1, Y_1)$ fixed and $\lambda \in \mathbf{R}$. But any two points of this form (with the same Z_0, Z_1, but variable λ) are comparable by Lemma 2.2.

A similar argument extends CH to multiple scaled copies of Γ_{12}. Finally, by induction, CH extends to scaled products of Γ_{12} and Γ_1 and Γ_2, i.e., to scaled products of arbitrarily many copies of Γ_1 and Γ_2. ■

We shall refer to a quadruple of points satisfying (4.8) and (4.9) as an **entropy calibrator**. To establish the existence of such calibrators we need the following result.

THEOREM 4.6 (Transversality and location of isotherms). *Let Γ be the state space of a simple system that satisfies the thermal axioms T1-T4. Then either*
(i) All points in Γ are in thermal equilibrium, i.e., $X \overset{T}{\sim} Y$ for all $X, Y \in \Gamma$.

or

(ii) There is at least one adiabat in Γ (i.e., at least one ∂A_X) that has at least two points that are not in thermal equilibrium, i.e., $Z \overset{T}{\sim} Y$ is false for some pair of points Z and Y in ∂A_X.

Proof: Our proof will be somewhat indirect because it will use the fact—which we already proved—that there is a concave entropy function, S, on Γ which satisfies the maximum principle, Theorem 4.3 (for $\Gamma_1 = \Gamma_2 = \Gamma$). This means that if $\mathcal{R} \subset \mathbf{R}$ denotes the range of S on Γ then the sets

$$E_\sigma = \{X \in \Gamma : S(X) = \sigma\}, \qquad \sigma \in \mathcal{R}$$

are precisely the adiabats of Γ and, moreover, $X = (U_1, V_1)$, $Y = (U_2, V_2)$ in Γ satisfy $X \overset{T}{\sim} Y$ if and only if $W = U_2$, maximizes $S(U_1 + U_2 - W, V_1) + S(W, V_2)$ over all choices of W such that $(U_1 + U_2 - W, V_1) \in \Gamma$ and $(W, V_2) \in \Gamma$. Furthermore, the concavity of S — and hence its continuity on the connected open set Γ — implies that $\mathcal{R}$ is connected, i.e., $\mathcal{R}$ is an interval.

Let us assume now that (ii) is false. By the zeroth law, T3, $\overset{T}{\sim}$ is an equivalence relation that divides Γ into disjoint equivalence classes. Since (ii) is false, each such equivalence class must be a union of adiabats, which means that the equivalence classes are represented by a family of disjoint subsets of $\mathcal{R}$. Thus

$$\mathcal{R} = \bigcup_{\alpha \in \mathcal{I}} \mathcal{R}_\alpha$$

where $\mathcal{I}$ is some index set, $\mathcal{R}_\alpha$ is a subset of $\mathcal{R}$, $\mathcal{R}_\alpha \cap \mathcal{R}_\beta = 0$ for $\alpha \neq \beta$, and $E_\sigma \overset{T}{\sim} E_\tau$ if and only if σ and τ are in some common $\mathcal{R}_\alpha$.

We will now prove that each $\mathcal{R}_\alpha$ is an open set. It is then an elementary topological fact (using the connectedness of Γ) that there can be only one non-empty $\mathcal{R}_\alpha$, i.e., (i) holds, and our proof is complete.

The concavity of $S(U,V)$ with respect to U for each fixed V implies the existence of an upper and lower U-derivative at each point, which we denote by $1/T_+$ and $1/T_-$, i.e.,

$$(1/T_\pm)(U,V) = \pm \lim_{\varepsilon \searrow 0} \varepsilon^{-1}[S(U \pm \varepsilon, V) - S(U,V)].$$

Theorem 4.3 implies that $X \stackrel{\mathrm{T}}{\sim} Y$ if and only if the closed intervals $[T_-(X), T_+(X)]$ and $[T_-(Y), T_+(Y)]$ are not disjoint. Suppose that some $\mathcal{R}_\alpha$ is not open, i.e., there is $\sigma \in \mathcal{R}_\alpha$ and either a sequence $\sigma_1 > \sigma_2 > \sigma_3 \cdots$, converging to σ or a sequence $\sigma_1 < \sigma_2 < \sigma_3 < \cdots$ converging to σ with $\sigma_i \notin \mathcal{R}_\alpha$. Suppose the former (the other case is similar). Then (since $T_\pm$ are monotone increasing in U by the concavity of S) we can conclude that for *every* $Y \in E_{\sigma_i}$ and *every* $X \in E_\sigma$

$$T_-(Y) > T_+(X). \tag{4.10}$$

We also note, by the monotonicity of $T_\pm$ in U, that (4.10) necessarily holds if $Y \in E_\mu$ and $\mu \geq \sigma_i$; hence (1) holds for all $Y \in E_\mu$ for *any* $\mu > \sigma$ (because $\sigma_i \searrow \sigma$). On the other hand, if $\tau \leq \sigma$

$$T_+(Z) \leq T_-(X)$$

for $Z \in E_\tau$ and $X \in E_\sigma$. This contradicts transversality, namely the hypothesis that there is $\tau < \sigma < \mu$, $Z \in E_\tau, Y \in E_\mu$ such that $[T_-(Z), T_+(Z)] \cap [T_-(Y), T_+(Y)]$ is not empty. ■

THEOREM 4.7 (Existence of calibrators). *Let Γ_1 and Γ_2 be state spaces of simple systems and assume the thermal axioms, T1-T4, in particular the transversality property T4. Then there exist states $X_0, X_1 \in \Gamma_1$ and $Y_0, Y_1 \in \Gamma_2$ such that*

$$X_0 \prec\prec X_1 \qquad \textit{and} \qquad Y_0 \prec\prec Y_1\ , \tag{4.11}$$

$$(X_0, Y_1) \stackrel{\mathrm{A}}{\sim} (X_1, Y_0). \tag{4.12}$$

Proof: Consider the simple system Δ_{12} obtained by thermally coupling Γ_1 and Γ_2. Fix some $\bar{X} = (U_{\bar{X}}, V_{\bar{X}}) \in \Gamma_1$ and $\bar{Y} = (U_{\bar{Y}}, V_{\bar{Y}}) \in \Gamma_2$ with $\bar{X} \stackrel{\mathrm{T}}{\sim} \bar{Y}$. We form the combined state $\phi(\bar{X}, \bar{Y}) = (U_{\bar{X}} + U_{\bar{Y}}, V_{\bar{X}}, V_{\bar{Y}}) \in \Delta_{12}$ and consider the adiabat $\partial A_{\phi(\bar{X},\bar{Y})} \subset \Delta_{12}$. By axiom T2 every point $Z \in \partial A_{\phi(\bar{X},\bar{Y})}$ can be split in at least one way as

$$\psi(Z) = ((U_X, V_X), (U_Y, V_Y)) \in \Gamma_1 \times \Gamma_2, \tag{4.13}$$

where (V_X, V_Y) are the work coordinates of Z with $U_X + U_Y = U_Z$ and where $X = (U_X, V_X), Y = (U_Y, V_Y)$ are in thermal equilibrium, i.e., $X \stackrel{\mathrm{T}}{\sim} Y$. If the splitting in (4.13) is *not* unique, i.e., there exist $X^{(1)}, Y^{(1)}$ and $X^{(2)}, Y^{(2)}$ satisfying these conditions, then we are done for the following reason: First, $(X^{(1)}, Y^{(1)}) \stackrel{\mathrm{A}}{\sim} (X^{(2)}, Y^{(2)})$ (by axiom T2). Second, since $U_{X^{(1)}} + U_{Y^{(1)}} = U_{X^{(2)}} + U_{Y^{(2)}}$ we have either $U_{X^{(1)}} < U_{X^{(2)}}, U_{Y^{(1)}} > U_{Y^{(2)}}$ or $U_{X^{(1)}} > U_{X^{(1)}}, U_{Y^{(1)}} < U_{Y^{(2)}}$. This implies, by Theorem 3.4, that either $X^{(1)} \prec\prec X^{(2)}$ and $Y^{(2)} \prec\prec Y^{(1)}$ or $X^{(2)} \prec\prec X^{(1)}$ and $Y^{(1)} \prec\prec Y^{(2)}$.

Let us assume, therefore, that the thermal splitting (4.13) of each $Z \in \partial A_{\phi(\bar{X},\bar{Y})}$ is unique so we can write $\psi(Z) = (X, Y)$ with uniquely determined $X \stackrel{\mathrm{T}}{\sim} Y$. (This means, in particular, that alternative (i) in Theorem 4.6 is excluded.) If some pair (X,Y) obtained in this way does not satisfy $X \stackrel{\mathrm{A}}{\sim} \bar{X}$ and $Y \stackrel{\mathrm{A}}{\sim} \bar{Y}$, e.g., $X \prec\prec \bar{X}$ holds, then it follows from axiom A3 and the cancellation law that $\bar{Y} \prec\prec Y$, and thus we have obtained points with the desired properties.

So let us suppose that $X \stackrel{\mathrm{A}}{\sim} \bar{X}$ and $Y \stackrel{\mathrm{A}}{\sim} \bar{Y}$ whenever $(X,Y) = \psi(Z)$ and $Z \in \partial A_{\phi(\bar{X},\bar{Y})}$. In other words, $\psi(\partial A_{\phi(\bar{X},\bar{Y})}) \subset \partial A_{\bar{X}} \times \partial A_{\bar{Y}}$. We then claim that all $Z \in \partial A_{\phi(\bar{X},\bar{Y})}$ are in thermal equilibrium with each other. By the zeroth law, T3, (and since $\rho(\partial A_{\phi(\bar{X}\bar{Y})})$ is open and connected, by the definition of a simple systems) it suffices to show that all points (U,V_1,V_2) in $\partial A_{\phi(\bar{X},\bar{Y})}$ with V_1 fixed are in thermal equilibrium with each other and, likewise, all points (U,V_1,V_2) in $\partial A_{\phi(\bar{X},\bar{Y})}$ with V_2 fixed are in thermal equilibrium with each other. Now each fixed V_1 in $\rho(A_{\bar{X}})$ determines a unique point $(U_1,V_1) \in \partial A_{\bar{X}}$ (by Theorem 3.5 (iii)). Since, by assumption, $\psi(U,V_1,V_2) \subset \partial A_{\bar{X}} \times \partial A_{\bar{Y}}$ we must then have

$$\psi(U,V_1,V_2) = ((U_1,V_1)),(U_2,V_2)) \tag{4.14}$$

with $U_2 = U - U_1$. But (4.14), together with the zeroth law, implies that all points $(U,V_1,V_2) \in \partial A_{\phi(\bar{X},\bar{Y})}$ with V_1 fixed are in thermal equilibrium with (U_1,V_1) (because (4.14) shows that they all have the same Γ_1 component) and hence they are in thermal equilibrium with each other. The same argument shows that all points with fixed V_2 are in thermal equilibrium.

We have demonstrated that the hypothesis $X \stackrel{\mathrm{A}}{\sim} \bar{X}$ and $Y \stackrel{\mathrm{A}}{\sim} \bar{Y}$ for all $(X,Y) \in \psi(\partial A_{\phi(\bar{X},\bar{Y})})$ implies that all points in $\partial A_{\phi(\bar{X},\bar{Y}}$ are in thermal equilibrium. Since, by Theorem 4.6, at least one adiabat in Δ_{12} contains at least two points not in thermal equilibrium, the existence of points satisfying (1) and (2) is established. ■

Having established the entropy calibrators we may now appeal to Theorem 4.5 and summarize the discussion so far in the following theorem.

Theorem 4.8 (Entropy principle in products of simple systems) *Assume Axioms A1-A7, S1-S3 and T1-T4. Then the comparison hypothesis CH is valid in arbitrary scaled products of simple systems. Hence, by Theorem 2.5, the relation $\prec$ among states in such state spaces is characterized by an entropy function S. The entropy function is unique, up to an overall multiplicative constant and one additive constant for each simple system under consideration.*

C. The role of transversality

It is conceptually important to give an example of a state space Γ of a simple system and a relation $\prec$ on its multiple scaled copies, so that all our axioms *except T4* are satisfied. In this example the comparison hypothesis CH is violated for the spaces $\Gamma \times \Gamma$ and hence the relation can *not* be characterized by an entropy function. This shows that the transversality axiom T4 is essential for the proof of Theorem 4.8. The example we give is not entirely academic; it is based on the physics of thermometers. See the discussion in the beginning of Section III.

For simplicity, we choose our system to be a degenerate simple system, i.e., its state space is one-dimensional. (It can be interpreted as a system with a work coordinate V in a trivial way, by simply declaring that everything is independent of V and the pressure function is identically zero). A hypothetical universe consisting only of scaled copies of such a system (in addition to mechanical devices) might be referred to as a 'world of thermometers'. The relation $\prec$ is generated, physically speaking, by two operations: "rubbing", which increases the energy, and thermal equilibration of two scaled copies of the system.

To describe this in a more formal way we take as our state space $\Gamma = \mathbf{R}_+ = \{U : U > 0\}$. Rubbing the system increases U and we accordingly define $\prec$ on Γ simply by the relation $\leq$ on the real numbers U. On $\Gamma^{(\lambda_1)} \times \Gamma^{(\lambda_2)}$ we define the forward sector of $(\lambda_1 U_1, \lambda_2 U_2)$ as the convex hull of the union $A \cup B$ of two sets of points,

$$A = \{(\lambda_1 U_1', \lambda_2 U_2') : U_1 \leq U_1',\ U_2 \leq U_2'\}$$

and

$$B = \{(\lambda_1 U_1'', \lambda_2 U_2'') : \bar{U} \leq U_1'', \bar{U} \leq U_2''\}$$

with

$$\bar{U} = (\lambda_1 + \lambda_2)^{-1}(\lambda_1 U_1 + \lambda_2 U_2).$$

This choice of forward sector is minimally consistent with our axioms. The set A corresponds to rubbing the individual thermometers while B corresponds to thermal equilibration followed by rubbing.

The forward sector of a point $(\lambda_1 U_1, \dots, \lambda_n U_n)$ in the product of more than two scaled copies of Γ is then defined as the convex hull of all points of the form

$$(\lambda_1 U_1, \dots, \lambda_i U_i', \dots \lambda_j U_j', \dots \lambda_n U_n) \quad \text{with} \quad (\lambda_i U_i, \lambda_j U_j) \prec (\lambda_i U_i', \lambda_j U_j').$$

The thermal join of $\Gamma^{(\lambda_1)}$ and $\Gamma^{(\lambda_2)}$ is identified with $\Gamma^{(\lambda_1+\lambda_2)}$. Thermal equilibration is simply addition of the energies, and $\lambda_1 U_1$ is in thermal equilibrium with $\lambda_2 U_2$ if and only if $U_1 = U_2$.

Since the adiabats and isotherms in Γ coincide (both consist only of single points) axiom T4 is violated in this example. The forward sectors in $\Gamma \times \Gamma$ are shown in Figure 7. It is evident that these sectors are not nested and hence *cannot be characterized by an entropy function.* This example thus illustrates how violation of the transversality axiom T4 can prevent the existence of an entropy function for a relation $\prec$ that is well behaved in other ways.

—- Insert Figure 7 here —-

On the other hand we may recall the usual entropy function for a body with constant heat capacity, namely

$$S(U) = \ln U. \tag{4.15}$$

In the above example this function defines, by simple addition of entropies in the obvious way, another relation, $\prec^*$, on the multiple scaled copies of Γ which extends the relation $\prec$ previously defined. On Γ the two relations coincide (since S is a monotonous function of U), but on $\Gamma \times \Gamma$ this is no longer the case: The inequality $S(U_1) + S(U_2) \leq S(U_1') + S(U_2')$, i.e., $U_1 U_2 \leq U_1' U_2'$, is only a necessary but not a sufficient condition for $(U_1, U_2) \prec (U_1', U_2')$ to hold. The passage from (U_1, U_2) to (U_1', U_2') in the sense of the relation $\prec^*$ (but not $\prec$) may, however, be accomplished by coupling each copy of Γ to another system, e.g., to a Carnot machine that uses the two copies of Γ as heat reservoirs. From the relation $\prec^*$ one could then reconstruct S in (4.15) by the method of Section II. The lesson drawn is that even if T4 fails to hold for a system, it may be possible to construct an entropy function for that system, provided its thermal join with some other system behaves normally.

A precise version of this idea is given in the following theorem.

THEOREM 4.9 (Entropy without transversality). *Suppose Γ_1 and Γ_2 are normal or degenerate simple systems and assume that axioms A1–A5, T1–T3 and T5 hold for the relation*

$\prec$ on scaled products of Γ_1 and Γ_2. (They already hold for Γ_1 and Γ_2 separately—by definition.) Let Δ_{12} be the thermal join of Γ_1 and Γ_2 and suppose that Δ_{12} and Γ_2 have consistent entropy functions S_{12} and S_2, which holds, in particular, if T4 is valid for Δ_{12} and Γ_2. Then Γ_1 has an entropy function S_1 that is consistent with S_2 and satisfies

$$S_{12}(\phi(X,Y)) = S_1(X) + S_2(Y)$$

if $X \stackrel{\mathrm{T}}{\sim} Y$, where ϕ is the canonical map $\Gamma_1 \times \Gamma_2 \to \Delta_{12}$, given by $\phi(X,Y) = (U_X + U_Y, V_X, V_Y)$ if $X = (U_X, V_X)$ and $Y = (U_Y, V_Y)$.

Proof: Given $X \in \Gamma_1$ we can, by axiom T5, find a $Y \in \Gamma_2$ with $X \stackrel{\mathrm{T}}{\sim} Y$, and hence $Z := \phi(X,Y) \stackrel{\mathrm{A}}{\sim} (X,Y)$ by axiom T2. If $Y' \in \Gamma_2$ is another point with $X \stackrel{\mathrm{T}}{\sim} Y'$ and $Z' := \phi(X,Y')$ then, by axiom T2, $(Y',Z) \stackrel{\mathrm{A}}{\sim} (Y',X,Y) \stackrel{\mathrm{A}}{\sim} (Y,(X,Y')) \stackrel{\mathrm{A}}{\sim} (Y,Z')$. Since S_2 and S_{12} are consistent entropies, this means that

$$S_2(Y') + S_{12}(Z) = S_2(Y) + S_{12}(Z'),$$

or

$$S_{12}(Z) - S_2(Y) = S_{12}(Z') - S_2(Y'). \tag{4.16}$$

We can thus *define* S_1 on Γ_1 by

$$S_1(X) := S_{12}(\phi(X,Y)) - S_2(Y) \tag{4.17}$$

for each $X \in \Gamma$ and for any Y satisfying $Y \stackrel{\mathrm{T}}{\sim} X$, because, according to (4.16), the right side of (4.17) is independent of Y, as long as $Y \stackrel{\mathrm{T}}{\sim} X$.

To check that S_1 is an entropy on Γ_1 we show first that the relation

$$(X_1, X_2) \prec (X_1', X_2')$$

with $X_1, X_2, X_1', X_2' \in \Gamma_1$ is equivalent to

$$S_1(X_1) + S_2(X_2) \leq S_1(X_1') + S_2(X_2'). \tag{4.18}$$

We pick $Y_1, Y_2, Y_1', Y_2' \in \Gamma_2$ with $Y_1 \stackrel{\mathrm{T}}{\sim} X_1, Y_2 \stackrel{\mathrm{T}}{\sim} X_2$, etc. and insert the definition (4.17) of S_1 into (4.18). We then see that (4.16) is equivalent to

$$\begin{aligned} &S_{12}(\phi(X_1,Y_1)) + S_2(Y_1') + S_{12}(\phi(X_2,Y_2)) + S_2(Y_2') \\ &\leq S_{12}(\phi(X_1',Y_1')) + S_2(Y_1) + S_{12}(\phi(X_2',Y_2')) + S_2(Y_2). \end{aligned}$$

Since S_{12} and S_2 are consistent entropies, this is equivalent to

$$(\phi(X_1,Y_1), Y_1', \phi(X_2,Y_2), Y_2') \prec (\phi(X_1',Y_1'), Y_1, \phi(X_2',Y_2'), Y_2).$$

By the splitting axiom T2 this is equivalent to

$$(X_1, Y_1, Y_1', X_2, Y_2, Y_2') \prec (X_1', Y_1', Y_1, X_2', Y_2', Y_2).$$

The cancellation law then tells us that this holds if and only if $(X_1, X_2) \prec (X_1', X_2')$.

To verify more generally that S_1 characterizes the relation on all multiple scaled copies of Γ_1 one may proceed in exactly the same way, using the scale invariance of thermal equilibrium (Theorem 4.1) and the hypothesis that S_{12} and S_2 are entropy functions, which means that they characterize the relation on all products of scaled copies of Δ_{12} and Γ_2. ∎

V. TEMPERATURE AND ITS PROPERTIES

Up to now we have succeeded in proving the existence of entropy functions that do everything they should do, namely specify exactly the adiabatic processes that can occur among systems, both simple and compound. The thermal join was needed in order to relate different systems, or copies of the same system to each other, but temperature, as a numerical quantifier of thermal equilibrium, was never used. Not even the concept of 'hot and cold' was used. In the present section we shall define temperature and show that it has all the properties it is normally expected to have. Temperature, then, is a corollary of entropy; it is epilogue rather than prologue.

One of our main results here is equation (5.3): Thermal equilibrium and equality of temperature are the same thing. Another one is Theorem 5.3 which gives the differentiability of the entropy and which leads to Maxwell's equations and other manipulations of derivatives that are to be found in the usual textbook treatment of thermodynamics.

Temperature will be defined *only* for simple systems (because 1/(temperature) is the variable dual to energy and it is only the simple systems that have only one energy variable).

A. Differentiability of entropy and the existence of temperature

The entropy function, S, defined on the (open, convex) state space, Γ, of a simple system is concave (Theorem 2.8). Therefore (as already mentioned in the proof of Theorem 4.5) the upper and lower partial derivatives of S with respect to U (and also with respect to V) exist at every point $X \in \Gamma$, i.e., the limits

$$1/T_+(X) = \lim_{\varepsilon \downarrow 0} \frac{1}{\varepsilon}[S(U+\varepsilon, V) - S(U,V)]$$
$$1/T_-(X) = \lim_{\varepsilon \downarrow 0} \frac{1}{\varepsilon}[S(U,V) - S(U-\varepsilon, V)]$$

exist for every $X = (U,V) \in \Gamma$. The functions $T_+(X)$ (resp. $T_-(X)$) are finite *and positive* everywhere (since S is strictly monotone increasing in U for each fixed V (by Planck's principle, Theorem 3.4). These functions are called, respectively, the **upper** and **lower temperatures**. Evidently, concavity implies that if $U_1 < U_2$

$$T_-(U_1, V) \le T_+(U_1, V) \le T_-(U_2, V) \le T_+(U_2, V) \tag{5.1}$$

for all V. The concavity of S *alone* does not imply continuity of these functions. Our goal here is to prove continuity by invoking some of our earlier axioms.

First, we prove a limited kind of continuity.

LEMMA 5.1 (Continuity of upper and lower temperatures on adiabats). *The temperatures T_+ and T_- are locally Lipschitz continuous along each adiabat ∂A_X. I.e., for each $X \in \Gamma$ and each closed ball $B_{X,r} \subset \Gamma$ of radius r and centered at X there is a constant $c(X,r)$ such that*

$$|T_+(X) - T_+(Y)| \le c(X,r)|X - Y|$$

for all $Y \in \partial A_X$ with $|X - Y| < r$. The same inequality holds for $T_-(X)$. Furthermore, $c(X,r)$ is a continuous function of X in any domain $D \subset \Gamma$ such that $B_{X,2r} \subset \Gamma$ for all $X \in D$.

Proof: Recall that the pressure $P(X)$ is assumed to be locally Lipschitz continuous and that $\partial U/\partial V_i = P_i$ on adiabats. Write $X = (U_0, V_0)$ and let the adiabatic surface through X be denoted by $(W_0(V), V)$ where $W_0(V)$ is the unique solution to the system of equations

$$\frac{\partial W_0(V)}{\partial V_i} = P_i(W_0(V), V)$$

with $W_0(V_0) = U_0$. (Thus W_0 is the function u_X of Theorem 3.5.) Similarly, for $\varepsilon > 0$ we let $W_\varepsilon(V)$ be the solution to

$$\frac{\partial W_\varepsilon(V)}{\partial V_i} = P_i(W_\varepsilon(V), V)$$

with $W_\varepsilon(V_0) = U_0 + \varepsilon$. Of course all this makes sense only if $|V - V_0|$ and ε are sufficiently small so that the points $(W_\varepsilon(V), V)$ lie in Γ. In this region (which we can take to be bounded) we let C denote the Lipschitz constant for P, i.e. $|P(Z) - P(Z')| \leq C|Z - Z'|$ for all Z, Z' in the region.

Let S_ε denote the entropy on $(W_\varepsilon(V), V)$; it is constant on this surface by assumption. By definition

$$\frac{1}{T_+(U_0, V_0)} = \lim_{\varepsilon \downarrow 0} \frac{S_\varepsilon - S_0}{\varepsilon},$$

and

$$T_+(W_0(V), V) = \lim_{\varepsilon \downarrow 0} \frac{W_\varepsilon(V) - W_0(V)}{S_\varepsilon - S_0} = T_+(U_0, V_0)\big[\lim_{\varepsilon \downarrow 0} G_\varepsilon(V) + 1\big],$$

where $G_\varepsilon(V) := \frac{1}{\varepsilon}[W_\varepsilon(V) - W_0(V) - \varepsilon]$. The lemma will be proved if we can show that there is a number D and a radius $R > 0$ such that $G_\varepsilon(V) \leq D|V - V_0|$ for all $|V - V_0| < R$.

Let v be a unit vector in the direction of $V - V_0$ and set $V(t) = V_0 + tv$, so that $V(0) = V_0, V(t) = V$ for $t = |V - V_0|$. Set $W_\varepsilon(t) := W_\varepsilon(V(t))$ and $\Pi(U, t) := v \cdot P(U, V(t))$. Fix $T > 0$ so that $CT \leq \frac{1}{2}$ and so that the ball $B_{X,2T}$ with center X and radius $2T$ satisfies $B_{X,2T} \subset \Gamma$. Then, for $0 \leq t \leq T$ and ε small enough

$$\begin{aligned} W_0(t) &= U_0 + \int_0^t \Pi(W_0(t'), t')\mathrm{d}t' \\ W_\varepsilon(t) - \varepsilon &= U_0 + \int_0^t \Pi(W_\varepsilon(t') - \varepsilon + \varepsilon, t')\mathrm{d}t'. \end{aligned}$$

Define

$$g_\varepsilon = \sup_{0 \leq t \leq T} \frac{1}{\varepsilon}[W_\varepsilon(t) - \varepsilon - W_0(t)] = \sup_{0 \leq t \leq T} G_\varepsilon(V(t)).$$

By subtracting the equation for W_0 from that of W_ε we have that

$$|G_\varepsilon(V(t))| \leq \int_0^t C[1 + g_\varepsilon]\mathrm{d}t' \leq tC[1 + g_\varepsilon].$$

By taking the supremum of the left side over $0 \leq t \leq T$ we obtain $g_\varepsilon \leq TC[1 + g_\varepsilon]$, from which we see that $g_\varepsilon \leq 1$ (because $TC \leq 1/2$). But then $|G_\varepsilon(V(t)| \leq 2tC$ or, in other words, $|G_\varepsilon(V)| \leq 2|V - V_0|C$ whenever $|V - V_0| < T$, which was to be proved. ■

Before addressing our next goal—the equality of T_+ and T_-—let us note the maximum entropy principle, Theorem 4.2, and its relation to $T_\pm$. The principle states that if $X_1 = (U_1, V_1)$ and $X_2 = (U_2, V_2)$ are in Γ then $X_1 \stackrel{\mathrm{T}}{\sim} X_2$ if and only if the following is true:

$$S(X_1)+S(X_2) = \sup_W\{S(U_1+U_2-W, V_1)+S(W, V_2) : (U_1+U_2-W, V_1) \in \Gamma \text{ and } (W, V_2) \in \Gamma\}. \quad (5.2)$$

Since S is concave, at every point $X \in \Gamma$ there is an upper temperature and lower temperature, as given in (5.1). This gives us an "*interval-valued*" function on Γ which assigns to each X the interval

$$T(X) = [T_-(X), T_+(X)].$$

If S is differentiable at X then $T_-(X) = T_+(X)$ and the closed interval $T(X)$ is then merely the single number $\left(\frac{\partial S}{\partial U}\right)(X)$. If $T_-(X) = T_+(X)$ we shall abuse the notation slightly by thinking of $T(X)$ as a number, i.e., $T(X) = T_-(X) = T_+(X)$.

The significance of the interval $T(X)$ is that (5.2) is equivalent to:

$$X_1 \stackrel{\mathrm{T}}{\sim} X_2 \quad \text{if and only if} \quad T(X_1) \cap T(X_2) \neq \emptyset.$$

In other words, if $\partial S/\partial U$ makes a jump at X then one should think of X as having *all* the temperatures in the closed interval $T(X)$.

In Theorem 5.1 we shall prove that the temperature is single-valued, i.e., $T_-(X) = T_+(X)$. Thus, we have the following fact relating **thermal equilibrium and temperature:**

$$X_1 \stackrel{\mathrm{T}}{\sim} X_2 \quad \text{if and only if} \quad T(X_1) = T(X_2). \quad (5.3)$$

THEOREM 5.1 (Uniqueness of temperature). *At every point X in the state space of a simple system, Γ, we have*

$$T_+(X) = T_-(X),$$

i.e., $T(X)$ is the number $\left[\left(\frac{\partial S}{\partial U}\right)(X)\right]^{-1}$.

Proof: The proof will rely heavily on the zeroth law, on the continuity of $T_\pm$ on adiabats, on transversality, on axiom T5 and on the maximum entropy principle for thermal equilibrium, Theorem 4.2.

Assume that $Z \in \Gamma$ is a point for which $T_+(Z) > T_-(Z)$. We shall obtain a contradiction from this.

Part 1: We claim that for every $Y \in \partial A_Z$, $T_+(Y) = T_+(Z)$ and $T_-(Y) = T_-(Z)$. To this end define the (conceivably empty) set $K \subset \Gamma$ by $K = \{X \in \Gamma : T_+(X) = T_-(X) \in T(Z)\}$. If $X_1 \in K$ and $X_2 \in K$ then $T(X_1) = T(X_2) \in T(Z)$ by the zeroth law (since $X_1 \stackrel{\mathrm{T}}{\sim} Z$ and $X_2 \stackrel{\mathrm{T}}{\sim} Z$, and thus $X_1 \stackrel{\mathrm{T}}{\sim} X_2$). Therefore, there is a single number $T^* \in T(Z)$ such that $T(X) = T^*$ for all $X \in K$.

Now suppose that $Y \in \partial A_Z$ and that $T_+(Y) < T_+(Z)$. By the continuity of T_+ on ∂A_Z (Lemma 5.1) there is then another point $W \in \partial A_Z$ such that $T_-(Z) \leq T_+(W) < T_+(Z)$, which implies that $W \stackrel{\mathrm{T}}{\sim} Z$. We write $W = (U_W, V_W)$ and consider $f_W(U) = S(U, V_W)$, which is a concave function of one variable (namely U) defined on some open interval containing U_W. It is a general fact about concave functions that the set of points at which f_W is differentiable (i.e., $T_+ = T_-$) is dense and that if $U_1 > U_2 > U_3 > \ldots > U_W$ is a decreasing sequence of such points converging to U_W then $T(U_i)$ converges to $T_+(U_W)$. We denote the corresponding points (U_i, V_W) by W_i and note that, for large i, $T(W_i) \in T(Z)$. Therefore $T(W_i) = T^*$ for all large i and hence $T_+(W) = T^*$.

Now use continuity again to find a point $R \in \partial A_Z$ such that $T^* = T_+(W) < T_+(R) < T_+(Z)$. Again there is a sequence $R_i = (U^i, V_R)$ with $T_+(R_i) = T_-(R_i) = T(R_i)$ converging downward to R and such that $T(R_i) \to T_+(R) > T^*$. But for large i, $T(R_i) \in T(Z)$ so $T(R_i) = T^*$. This is a contradiction, and we thus conclude that

$$T_+(Y) = T_+(Z)$$

for all $Y \in \partial A_Z$ when $T_+(Z) > T_-(Z)$.

Likewise $T_-(Y) = T_-(Z)$ under the same conditions.

Part 2: Now we study $\rho_Z \subset \mathbf{R}^n$, which is the projection of ∂A_Z on $\mathbf{R}^n$. By Theorem 3.3, ρ_Z is open and connected. It is necessary to consider two cases.

Case 1: ρ_Z is the projection of Γ, i.e., $\rho_Z = \{V \in \mathbf{R}^n : (U, V) \in \Gamma \text{ for some } U \in \mathbf{R}\} = \rho(\Gamma)$. In this case we use the *transversality axiom* T4, according to which there are points X and Y in Γ with $X \prec\prec Z \prec\prec Y$, (and hence $S(X) < S(Z) < S(Y)$), but with $X \overset{\mathrm{T}}{\sim} Y$. We claim that every X with $S(X) < S(Z)$ has $T_+(X) \leq T_-(Z)$. Likewise, we claim that $S(Y) > S(Z)$ implies that $T_-(Y) \geq T_+(Z)$. These two facts will contradict the assumption that $T(Y) \cap T(X)$ is not empty. To prove that $T_+(X) \leq T_-(Z)$ we consider the line $(U, V_X) \cap \Gamma$. As U increases from the value U_X, the temperature $T_+(U, V_X)$ also cannot decrease (by the concavity of S). Furthermore, $(U_X, V_X) \prec (U, V_X)$ if and only if $U \geq U_X$ by Theorem 3.4. Since $\rho_Z = \rho(\Gamma)$ there is (by Theorem 3.4) some $U_0 > U_X$ such that $(U_0, V_X) \in \partial A_Z$. But $T_-(U_0, V_X) = T_-(Z)$ as we proved above. However, $T_+(X) \leq T_-(U_0, V_X)$ by (5.1). A similar proof shows that $T_-(Y) \geq T_+(Z)$ when $S(Y) > S(Z)$.

Case 2: $\rho_Z \neq \rho(\Gamma)$. Here we use T5. Both ρ_Z and $\rho(\Gamma)$ are open sets and $\rho_Z \subset \rho(\Gamma)$. Hence, there is a point V in $\bar{\rho}_Z$, the closure of ρ_Z, such that $V \in \rho(\Gamma)$. Let $l_V := L_V \cap \Gamma = \{(U, V) : U \in \mathbf{R}$ and $(U, V) \in \Gamma\}$. If $X \in l_V$ then either $Z \prec\prec X$ or $X \prec\prec Z$. (This is so because we are dealing with a simple system, which implies that $X \succ Z$ or $X \prec Z$, but we cannot have $X \overset{\mathrm{A}}{\sim} Z$ because then $X \in \partial A_Z$, which is impossible since $l_V \cap \partial A_Z$ is empty.) Suppose, for example, that $Z \prec\prec X$ or, equivalently, $S(X) > S(Z)$. Then $S(Y) > S(Z)$ for all $Y \in l_V$ (by continuity of S, and by the fact that $S(Y) \neq S(Z)$ on l_V).

Now A_X has a tangent plane Π_X at X, which implies that $\rho_X \cap \rho_Z$ is *not* empty. Thus there is a point

$$W_1 = (U_1, V_1) \in \partial A_X \text{ with } V_1 \in \rho_X \cap \rho_Z \text{ and } S(W_1) = S(X) > S(Z).$$

By definition, there is a point $(U_0, V_1) \in \partial A_Z$ with $U_0 < U_1$. By concavity of $U \mapsto S(U, V_1)$ we have that $T_-(W_1) \geq T_+(U_0, V_1) = T_+(Z)$. By continuity of T_- along the adiabat ∂A_X we conclude that $T_-(X) \geq T_+(Z)$. The same conclusion holds for every $Y \in l_V$ and thus the range of temperature on the line l_V is an interval (t_1, t_2) with $t_1 \geq T_+(Z)$.

By similar reasoning, if R is in the set $\{(U, V) : V \in \rho_Z, S(U, V) < S(Z)\}$ then $T_+(R) \leq T_-(Z)$. Hence the temperature range on any line $l_{\widehat{V}}$ with $\widehat{V} \in \rho_Z$ satisfies $t_1 \leq T_-(Z)$. This contradicts T5 since $T_-(Z) < T_+(Z)$. A similar proof works if $X \prec\prec Z$. ∎

Having shown that the temperature is uniquely defined at each point of Γ we are now in a position to establish our goal.

THEOREM 5.2 (Continuity of temperature). *The temperature $T(X) = T_+(X) = T_-(X)$ is a continuous function on the state space, $\Gamma \subset \mathbf{R}^{n+1}$, of a simple system.*

Proof: Let $X_\infty, X_1, X_2, \ldots$ be points in Γ such that $X_j \to X_\infty$ as $j \to \infty$. We write $X_j = (U_j, V_j)$, we let A_j denote the adiabat ∂A_{X_j}, we let $T_j = T(X_j)$ and we set $l_j = \{(U, V_j) : (U, V_j) \in \Gamma\}$. We know that T is continuous and monotone along each l_j because $T_+ = T_-$ everywhere by Theorem 5.1. We also know that T is continuous on each A_j by Lemma 5.1. In fact, if we assume that all the X_j's are in some sufficiently small ball, B centered at X_∞, then by Lemma 5.1 we can also assume that for some $c < \infty$

$$|T(X) - T(Y)| \leq c|X - Y|$$

whenever X and Y are in B and X and Y are on the same adiabat, A_j. Lemma 5.1 also states that c can be taken to be independent of X and Y in the ball B.

By assumption, the slope of the tangent plane Π_X is locally Lipschitz continuous, i.e., the pressure $P(X)$ is locally Lipschitz continuous. Therefore (again, assuming that B is taken small enough) we can assume that each adiabat A_j intersects l_∞ in some point, which we denote by Y_j. Since $|X_j - X_\infty| \to 0$ as $j \to \infty$, we have that $Y_j \to X_\infty$ as well. Thus,

$$|T(X_j) - T(X_\infty)| \leq |T(X_j) - T(Y_j)| + |T(Y_j) - T(X_\infty)|.$$

As $j \to \infty$, $T(Y_j) - T(X_\infty) \to 0$ because Y_j and X_∞ are in l_∞. Also, $T(X_j) - T(Y_j) \to 0$ because $|T(X_j) - T(Y_j)| < c|X_j - Y_j| \leq c|X_j - X_\infty| + c|Y_j - X_\infty|$. ∎

THEOREM 5.3 (Differentiability of S). *The entropy, S, is a continuously differentiable function on the state space Γ of a simple system.*

Proof: The adiabat through a point $X \in \Gamma$ is characterized by the once continuously differentiable function, $u_X(V)$, on $\mathbf{R}^n$. Thus, $S(u_X(V), V)$ is constant, so (in the sense of distributions)

$$0 = \left(\frac{\partial S}{\partial U}\right)\left(\frac{\partial u_X}{\partial V_j}\right) + \frac{\partial S}{\partial V_j}.$$

Since $1/T = \partial S/\partial U$ is continuous, and $\partial u_X/\partial V_j = -P_j$ is Lipschitz continuous, we see that $\partial S/\partial V_j$ is a continuous function and we have the well known formula

$$\frac{\partial S}{\partial V_j} = \frac{P_j}{T}$$ ∎

We are now in a position to give a simple proof of the most important property of temperature, namely its role in determining the direction of energy transfer, and hence, ultimately, the linear ordering of systems with respect to heat transfer (even though we have not defined 'heat' and have no intention of doing so). The fact that energy only flows 'downhill' without the intervention of extra machinery was taken by Clausius as the foundation of the second law of thermodynamics, as we said in Section I.

THEOREM 5.4 (Energy flows from hot to cold). *Let (U_1, V_1) be a point in a state space Γ_1 of a simple system and let (U_2, V_2) be a point in a state space Γ_2 of another simple system. Let T_1 and T_2 be their respective temperatures and assume that $T_1 > T_2$. If (U_1', V_1) and (U_2', V_2) are two points with the same respective work coordinates as the original points, with the same total* *energy $U_1 + U_2 = U_1' + U_2'$, and for which the temperatures are equal to a common value, T (the existence of such points is guaranteed by axioms T1 and T2), then*

$$U_1' < U_1 \text{ and } U_2' > U_2.$$

Proof: By assumption $T_1 > T_2$ and we claim that

$$T_1 \geq T \geq T_2. \tag{5.4}$$

(At least one of these inequalities is strict because of the uniqueness of temperature for each state.) Suppose that inequality (5.4) failed, e.g., $T > T_1 > T_2$. Then we would have that $U_1' > U_1$ and $U_2' > U_2$ and at least one of these would be strict (by the strict monotonicity of U with respect to T, which follows from the concavity and differentiability of S). This pair of inequalities is impossible in view of the condition $U_1 + U_2 = U_1' + U_2'$.

Since T satisfies (5.4), the theorem now follows from the monotonicity of U with respect to T. ■

From the entropy principle and the relation

$$1/T = (\partial S/\partial U)^{-1}$$

between temperature and entropy we can now derive the usual formula for the **Carnot efficiency**

$$\eta_{\mathrm{C}} := 1 - (T_0/T_1) \tag{5.5}$$

as an upper bound for the efficiency of a 'heat engine' that undergoes a cyclic process. Let us define a **thermal reservoir** to be a simple system whose work coordinates remains unchanged during some process (or which has no work coordinates, i.e. is a degenerate simple system). Consider a combined system consisting of a thermal reservoir and some machine, and an adiabatic process for this combined system. The entropy principle says that the total entropy change in this process is

$$\Delta S_{\text{machine}} + \Delta S_{\text{reservoir}} \geq 0. \tag{5.6}$$

Let $-Q$ be the energy change of the reservoir, i.e., if $Q \geq 0$, then the reservoir delivers energy, otherwise it absorbs energy. If T denotes the temperature of the reservoir *at the end of the process*, then, by the convexity of $S_{\text{reservoir}}$ in U, we have

$$\Delta S_{\text{reservoir}} \leq -\frac{Q}{T}. \tag{5.7}$$

Hence

$$\Delta S_{\text{machine}} - \frac{Q}{T} \geq 0. \tag{5.8}$$

Let us now couple the machine first to a 'high temperature reservoir' which delivers energy Q_1 and reaches a final temperature T_1, and later to a "low temperature reservoir" which absorbs energy $-Q_0$ and reaches a final temperature T_0. The whole process is assumed to be cyclic for the machine so the entropy changes for the machine in both steps cancel. (It returns to its initial state.) Combining (5.6), (5.7) and (5.8) we obtain

$$Q_1/T_1 + Q_0/T_0 \leq 0 \tag{5.9}$$

which gives the usual inequality for the efficiency $\eta := (Q_1 + Q_0)/Q_1$:

$$\eta \leq 1 - (T_0/T_1) = \eta_C. \tag{5.10}$$

In text book presentations it is usually assumed that the reservoirs are infinitely large, so that their temperature remains unchanged, but formula (5.10) remains valid for finite reservoirs, provided T_1 and T_0 are properly interpreted, as above.

B. Geometry of isotherms and adiabats

Each adiabat in a simple system is the boundary of a convex set and hence has a simple geometric shape, like a 'bowl'. It must be an object of dimension n when the state space in question is a subset of $\mathbf{R}^{n+1}$. In contrast, an isotherm, i.e., the set on which the temperature assumes a given value T, can be more complicated. When $n = 1$ (with energy and volume as coordinates) and when the system has a triple point, a portion of an isotherm (namely the isotherm through the triple point) can be two-dimensional. See Figure 8 where this isotherm is described graphically.

—- Insert Figure 8 here —-

One can ask whether isotherms can have other peculiar properties. Axiom T4 and Theorem 4.5 already told us that an isotherm cannot coincide completely with an adiabat (although they could coincide over some region). If this were to happen then, in effect, our state space would be cut into two non-communicating pieces, and we have ruled out this pathology by fiat. However, another possible pathology would be that an isotherm consists of several disconnected pieces, in which case we could not pass from one side of an adiabat to another except by changing the temperature. Were this to happen then the pictures in the textbooks would really be suspect, but fortunately, this perversity does not occur, as we prove next.

There is one technical point that must first be noted. By concavity and differentiability of the entropy, the range of the temperature function over Γ is always an interval. There are no gaps. But the range need not go from 0 to ∞ —in principle. (Since we defined the state spaces of simple systems to be open sets, the point 0 can never belong to the range.) Physical systems ideally always cover the entire range $(0, \infty)$, but there is no harm, and perhaps even a whiff of physical reality, in supposing that the temperature range of the world is bounded. Recall that in axiom T5 we said that the range must be the same for all systems and, indeed, for each choice of work coordinate within a simple system. Thus, for an arbitrary simple system, Γ, and $V \in \rho(\Gamma)$

$$T_{\min} := \inf\{T(X) : X \in \Gamma\} = \inf\{T(U,V) : U \in \mathbf{R} \text{ such that } (U,V) \in \Gamma\}$$

and

$$T_{\max} := \sup\{T(X) : X \in \Gamma\} = \sup\{T(U,V) : U \in \mathbf{R} \text{ such that } (U,V) \in \Gamma\}.$$

THEOREM 5.5 (Isotherms cut adiabats) *Suppose $X_0 \prec X \prec X_1$ and X_0 and X_1 have equal temperatures, $T(X_0) = T(X_1) = T_0$.*

(1). If $T_{\min} < T_0 < T_{\max}$ then there is a point $X' \overset{\mathrm{A}}{\sim} X$ with $T(X') = T_0$. In other words: The isotherm through X_0 cuts every adiabat between X_0 and X_1.

(2). If $T_0 = T_{\max}$, then either there is an $X' \overset{\mathrm{A}}{\sim} X$ with $T(X') = T_0$, or, for any $T_0' < T_0$ there exist points X_0', X' and X_1' with $X_0' \prec X' \overset{\mathrm{A}}{\sim} X \prec X_1'$ and $T(X_0') = T(X') = T(X_1') = T_0'$.

(3). If $T_0 = T_{\min}$, then either there is an $X' \overset{\mathrm{A}}{\sim} X$ with $T(X') = T_0$, or, for any $T_0' > T_0$ there exist points X_0', X' and X_1' with $X_0' \prec X' \overset{\mathrm{A}}{\sim} X \prec X_1'$ and $T(X_0') = T(X') = T(X_1') = T_0'$.

Proof: Step 1. First we show that for every T_0 with $T_{\min} < T_0 < T_{\max}$ the sets $\Omega_> := \{Y : T(Y) > T_0\}$ and $\Omega_< := \{Y : T(Y) < T_0\}$ are open and connected. The openness follows from the continuity of T. Suppose that Ω_1 and Ω_2 are non empty, open sets satisfying $\Omega_> = \Omega_1 \cup \Omega_2$. We shall show that $\Omega_1 \cap \Omega_2$ is not empty, thereby showing that $\Omega_>$ is connected. By axiom T5, the range of T, restricted to points $(U,V) \in \Gamma$, with V fixed, is independent of V, and hence $\rho(\Omega_>) = \rho(\Gamma)$, where ρ denotes the projection $(U,V) \mapsto V$. It follows that $\rho(\Omega_1) \cup \rho(\Omega_2) = \rho(\Gamma)$ and, since ρ is an open mapping and $\rho(\Gamma)$ is connected, we have that $\rho(\Omega_1) \cap \rho(\Omega_2)$ is not empty. Now if $(U_1,V) \in \Omega_1 \subset \Omega_>$ and if $(U_2,V) \in \Omega_2 \subset \Omega_>$, then, by the monotonicity of $T(U,V)$ in U for fixed V, it follows that the line joining $(U_1,V) \in \Omega_1$ and $(U_2,V) \in \Omega_2$ lies entirely in $\Omega_> = \Omega_1 \cup \Omega_2$. Since Ω_1 and Ω_2 are open, $\Omega_1 \cap \Omega_2$ is not empty and $\Omega_>$ is connected. Similarly, $\Omega_<$ is connected.

Step 2. We show that if $T_{\min} < T_0 < T_{\max}$, then there exist points $X_>$, $X_<$, with $X_> \overset{\mathrm{A}}{\sim} X \overset{\mathrm{A}}{\sim} X_<$ and $T(X_<) \le T_0 \le T(X_>)$. We write the proof for $X_>$, the existence of $X_<$ is shown in the same way. In the case that $V_{X_0} \in \rho(A_X)$ the existence of $X_>$ follows immediately from the monotonicity of $T(U,V)$ in U for fixed V. If $V_{X_0} \notin \rho(A_X)$ we first remark that by axiom T5 and because $T_0 < T_{\max}$ there exists $X_0' \prec X$ with $T_0 < T(X_0')$. Also, by monotonicity of T in U there exists X_1' with $X \prec X_1 \prec X_1'$ and $T(X_1') > T_0$. Hence X_0' and X_1' both belong to $\Omega_>$, and $X_0' \prec X \prec X_1'$. Now $\Omega_>$ is nonempty, open and connected, and ∂A_X splits $\Gamma \setminus \partial A_X$ into disjoint, open sets. Hence $\Omega_>$ must cut ∂A_X, i.e., there exists an $X_> \in \Omega_> \cap \partial A_X$.

Having established the existence of $X_>$ and $X_<$ we now appeal to continuity of T and connectedness of ∂A_X (axiom S4) to conclude that there is an $X' \in \partial A_X$ with $T(X') = T_0$. This completes the proof of assertion (1).

Step 3. If $T_0 = T_{\max}$ and $V_{X_0} \in \rho(A_X)$, then the existence of $X' \in \partial A_X$ with $T(X') = T_0$ follows from monotonicity of T in U. Let us now assume that all points on ∂A_X have temperatures strictly less than $T_{\max}$. By axiom A5 and by continuity and monotonicity of T in U, there is for every $T_0' < T_0$ an $X_0' \prec X_0$ with $T(X_0') = T_0'$. For the same reasons there is an X_1' with $X \prec X_1' \prec X_1$ and $T(X_1') = T_0'$. By the argument of step 2 there is thus an $X' \in \partial A_X$ with $T(X') = T_0'$. Thus assertion (2) is established. The case $T_0 = T_{\min}$ (assertion (3)) is treated analogously. ∎

C. Thermal equilibrium and uniqueness of entropy

In Section II we have encountered two general uniqueness theorems for entropy. The first, Theorem 2.4, relies only on axioms A1-A6, and CH for the double scaled copies of Γ, and states that an entropy function on Γ is uniquely determined, up to an affine transformation of scale, by the relation $\prec$ on the double scaled copies. In the second, Theorem 2.10, it is further assumed that the range of the entropy is connected which, in particular, is the case if the convex combination axiom A7 holds. Under this condition the relation $\prec$ on $\Gamma \times \Gamma$ determines the entropy. Both these uniqueness results are of a very general nature and rely only on the structure introduced in Section

II. The properties of entropy and temperature that we have now established on the basis of axioms A1–A7, S1–S3 and T1–T5, allow us to supplement these results now with a uniqueness theorem of a different kind.

THEOREM 5.6 (Adiabats and isotherms in Γ determine the entropy). *Let $\prec$ and $\prec^*$ be two relations on the multiple scaled copies of a simple system Γ satisfying axioms A1–A7, S1–S3 and T1–T5. Let $\overset{\mathrm{T}}{\sim}$ and $\overset{\mathrm{T}^*}{\sim}$ denote the corresponding relations of thermal equilibrium between states in Γ. If $\prec$ and $\prec^*$ coincide on Γ and the same holds for the relations $\overset{\mathrm{T}}{\sim}$ and $\overset{\mathrm{T}^*}{\sim}$, then $\prec$ and $\prec^*$ coincide everywhere. In other words: The adiabats in Γ together with the isotherms determine the relation $\prec$ on all multiple scaled copies of Γ and hence the entropy is uniquely determined up to an affine transformation of scale.*

Proof: Let S and S^* be (concave and continuously differentiable) entropies characterizing respectively the relations $\prec$ and $\prec^*$. (The existence follows from axioms A1-A7, S1-S3, and T1-T4, as shown in the previous sections.) For points $X, Y \in \Gamma$ we have $S(X) = S(Y)$ if and only if $X \overset{\mathrm{A}}{\sim} Y$, which holds if and only if $S^*(X) = S^*(Y)$, because $\prec$ and $\prec^*$ coincide on Γ by assumption. Hence S and S^* have the same level sets, namely the adiabats of the simple system. Thus, we can write

$$S^*(X) = f(S(X))$$

for some strictly monotone function, f, defined on the range of S—which is some interval $I \subset \mathbf{R}$. We claim that f is differentiable on I and therefore

$$\frac{\partial S^*}{\partial U}(X) = f'(S(X))\frac{\partial S}{\partial U}(X). \tag{5.11}$$

To prove the differentiability note that $\partial S/\partial U$ is never zero (since S is strictly monotonic in U by Planck's principle, Theorem 3.4). This implies that for each fixed V in $\rho(\Gamma)$ the function $U \mapsto S(U,V)$ has a continuous inverse $K(S,V)$. (This, in turn, implies that I is open.) Thus, if $X = (U,V)$ and $S(U,V) = \sigma$ and if $\sigma_1, \sigma_2, \dots$ is *any* sequence of numbers converging to σ, the sequence of numbers $U_j := K(\sigma_j, V)$ converges to U. Hence

$$\frac{S^*(U_j,V) - S^*(U,V)}{U_j - U} = \left[\frac{f(\sigma_j) - f(\sigma)}{\sigma_j - \sigma}\right]\left[\frac{S(U_j,V) - S(U_j,V)}{U_j - U}\right],$$

from which we deduce the differentiability of f and the formula (5.11).

Now consider the function

$$G(X) = \left(\frac{\partial S^*}{\partial U}\right) \Big/ \left(\frac{\partial S}{\partial U}\right),$$

which is continuous because S and S^* are continuously differentiable and $\left(\frac{\partial S}{\partial U}\right) \neq 0$. By Eq. (5.11), with $g = f'$,

$$G(X) = g(S(X)),$$

and we now wish to prove that $g: I \to \mathbf{R}$ is a constant function (call it a). This will prove our theorem because it implies that

$$S^*(U,V) = aS(U,V) + B(V),$$

This, in turn, implies that $B(V)$ is constant on adiabats. However, the projection of an adiabat, ∂A_X, on $\mathbf{R}^n$ is an open set (because the pressure, which defines the tangent planes, is finite everywhere). Thus, the projection $\rho(\Gamma)$ is covered by open sets on each of which $B(V)$ is constant. But $\rho(\Gamma)$ is connected (indeed, it is convex) and therefore $B(V)$ is constant on all of $\rho(\Gamma)$.

To show that g is constant, it suffices to show this locally. We know that $X \mapsto G(X) = g(S(X))$ is constant on adiabats, and it is also constant on isotherms because the level sets of $\partial S/\partial U$ and $\partial S^*/\partial U$ both coincide with the isotherms. We now invoke the transversality property and Theorem 5.5. Let $\widehat{\sigma}$ be any fixed point in the range I of S, i.e., $\widehat{\sigma} = S(\widehat{X})$ for some $\widehat{X} \in \Gamma$. By the transversality property there are points X_0, X_1 such that

$$\sigma_0 = S(X_0) < \widehat{\sigma} < S(X_1) = \sigma_1$$

and $X_0 \overset{\mathrm{T}}{\sim} X_1$. Now let $\sigma = S(X)$ be any other point in the open interval (σ_0, σ_1). By Theorem 5.5 there are points $\widehat{X}' \overset{\mathrm{A}}{\sim} \widehat{X}$ and $X' \overset{\mathrm{A}}{\sim} X$ such that $\widehat{X}'$ and X' both lie on the same isotherm (namely the isotherm through X_0 and X_1). But this means that $g(\sigma) = G(S(X')) = G(S(\widehat{X}') = g(\widehat{\sigma})$, so g is constant. ∎

Remark: The transversality property is essential for this uniqueness theorem. As a counterexample, suppose that every isotherm is an adiabat. Then *any* concave S that has the adiabats as its level sets would be an acceptable entropy.

VI. MIXING AND CHEMICAL REACTIONS

A. The difficulty of fixing entropy constants

We have seen in Sections II and IV that the entropies of all simple systems can be calibrated once and for all so that the entropy of any compound system made up of any combination of the basic simple systems is exactly the sum of the individual entropies. This global entropy works (i.e., it satisfies the entropy principle of Sect. II B and tells us *exactly* which processes can occur) in those cases in which the 'masses' of the individual systems are conserved. That is, splitting and recombination of simple systems is allowed, but not mixing of different systems or (chemical or nuclear) reactions.

Nature does allow us to mix the contents of different simple systems, however, (which is not to be confused with the formation of a compound system). Thus, we can mix one mole of water and one mole of alcohol to form two moles of whiskey. The entropy of the mixture is certainly not the sum of the individual entropies, as would be the case if we were forming a compound system. Nevertheless, our previous analysis, namely Theorem 2.5, does tell us the entropy of the mixture—*up to an additive constant ! The multiplicative constant can be, and will be henceforth, fixed by the entropy function of one standard system*, e.g., one mole of mercury. The reason that the multiplicative constant is fixed for the mixture is, as we have stressed, the notion of thermal equilibrium. Another way to say this is that once the unit of energy (say Joules) and of temperature (say Kelvin) have been fixed, then the entropy of every system, simple and compound, is fixed up to an additive constant. Our assumptions A1-A7, S1-S3 and T1-T5 guarantee this.

A similar discussion applies to chemical reaction products. After all, the solution of alcohol in water can be considered a chemical reaction if one wishes. It requires a certain amount of chemical sophistication, which was not available before the enlightenment, to distinguish a mixture from a chemical compound.

The question addressed in this section is this: to what extent can the *additive constants* (denoted by the letter B, in conformity with Theorems 2.3 and 2.5) be determined so that whenever a mixture or reaction occurs adiabatically we can say that the entropy has not decreased? To what extent is this determination unique?

One thing that conceivably might have to be discarded, partially at least, is the idea that comparability is an equivalence relation. As stated in Section I, to have an equivalence relation would require that whenever $X \prec Z$ and $Y \prec Z$ then $X \prec Y$ or $Y \prec X$ (and similarly for $Z \prec X$ and $Z \prec Y$). If one were to resort to the standard devices of semi-permeable membranes and van t'Hofft boxes, as in the usual textbooks, then it would be possible to maintain this hypothesis, even for mixing and chemical reactions. In that case, one would be able to prove that the additive entropy constants are uniquely determined for all matter, once they have been chosen for the 92 chemical elements.

Alas, van t'Hofft boxes do not exist in nature, except in imperfect form. For example, Fermi (1956, p. 101), in a discussion of the van t'Hofft box, writes that "The equilibria of gaseous reactions can be treated thermodynamically by assuming the existence of ideal semi-permeable membranes", but then goes on to state that "We should notice, finally, that in reality no ideal semi-permeable membranes exist. The best approximation of such a membrane is a hot palladium foil, which behaves like a semi-permeable membrane for hydrogen." Nevertheless, the rest of Fermi's discussion is based on the existence of such membranes!

We are the not saying that the comparison hypothesis *must* be discarded for chemical reactions and mixtures; we are only raising the logical possibility. As a result, we shall try to organize our discussion without using this hypothesis.

Therefore, we shall have to allow the possibility that if a certain kind of process is theoretically possible then entropy increase *alone* does not determine whether it will actually occur; in particular cases it *might* conceivably be necessary to have a certain minimum amount of entropy increase before a reaction can take place. Moreover, the entropy principle of Section II. B conceivably might not hold in full generality in the sense that there could be irreversible processes for which entropy does not strictly increase. What we do show in this section is that it is possible, nevertheless, to fix the entropy constants of all substances in such a way, that the entropy never decreases in an adiabatic process. This weak form of the entropy principle is stated in Theorem 6.2. However, it is only because of a technicality concerned with uncountably many dimensions that we cannot prove the entropy principle in the strong form and there is no doubt that the 'good case' mentioned at the end of this section actually holds in the real world. For all practical purposes we do have the strong form because the construction of the constants is done inductively in such a way that at each stage it is not necessary to revise the constants previously obtained; this means that in the finite world in which we live we are actually dealing, at any given moment, with the countable case.

A significant point to notice about the additive constants, B, is that they must scale correctly when the system scales; a somewhat subtler point is that they must also obey the additivity law under composition of two or more systems, $\Gamma_1 \times \Gamma_2$, in order that (2.4) holds. As we shall see in Sect. B, this latter requirement will not be met automatically and it will take a bit of effort to achieve it.

As a final introductory remark let us mention a computational device that is often used, and which seems to eliminate the need for any special discussion about mixing, reactions or other variations in the amount of matter. This device is simply to regard the amount of a substance (often called the 'particle number' because of our statistical mechanical heritage) as just one more work coordinate. The corresponding 'pressure' is called the *chemical potential* in this case. Why does this not solve our problems? The answer, equally simply, is that the comparison hypothesis will not hold within a state space since the extended state space will 'foliate' into sheets, in each of which the particle number is fixed. Axiom S2 will fail to hold. *If particle number is introduced as a work coordinate then the price we will have to pay is that there will be no simple systems.* Nothing will have been gained. The question we address here is a true physical question and cannot be eliminated by introducing a mathematical definition.

B. Determination of additive entropy constants

Let us consider a collection of systems (more precisely, state spaces), containing simple and/or compound systems. Certain adiabatic state changes are possible, and we shall be mainly interested in those that take us from one specified system to another, e.g., $X \prec Y$ with $X \in \Gamma$ and $Y \in \Gamma'$. Although there are uncountably many systems (since, in our convention, changing the amount of any component means changing the system), we shall always deal in the following with processes involving only finitely many systems at one time. In our notation the process of making one mole of water from hydrogen and oxygen is carried out by letting X be a state in the compound system Γ consisting of one mole of H_2 and one half mole of O_2 and by taking Y to be a state in the simple system, Γ', consisting of one mole of water.

Each system has a well defined entropy function, e.g., for Γ there is S_Γ, and we know from Section IV that these can be determined in such a way that the sum of the entropies increases in any adiabatic process in any compound space $\Gamma_1 \times \Gamma_2 \times ....$ Thus, if $X_i \in \Gamma_i$ and $Y_i \in \Gamma_i$ then

$$(X_1, X_2, ...) \prec (Y_1, Y_2, ...) \quad \text{if and only if} \quad S_1(X_1) + S_2(X_2) + \cdots \leq S_1(Y_1) + S_2(Y_2) + \cdots \ . \tag{6.1}$$

where we have denoted S_{Γ_i} by S_i for short. The additive entropy constants do not matter here since each function S_i appears on both sides of this inequality.

Now we consider relations of the type

$$X \prec Y \qquad \text{with} \qquad X \in \Gamma,\ Y \in \Gamma'. \tag{6.2}$$

Our goal is to find constants $B(\Gamma)$, one for each state space Γ, in such a way that the entropy defined by

$$S(X) := S_\Gamma(X) + B(\Gamma) \qquad \text{for} \qquad X \in \Gamma \tag{6.3}$$

satisfies

$$S(X) \leq S(Y) \tag{6.4}$$

whenever (6.2) holds.

Additionally, we require that the newly defined entropy satisfies scaling and additivity under composition. Since the initial entropies $S_\Gamma(X)$ already satisfy them, these requirements become conditions on the additive constants $B(\Gamma)$:

$$B(t_1\Gamma_1 \times t_2\Gamma_2) = t_1 B(\Gamma_1) + t_2 B(\Gamma_2) \tag{6.5}$$

for all state spaces Γ_1, Γ_2 under consideration and $t_1, t_2 > 0$.

As we shall see, the additivity requirement is not trivial to satisfy, the reason being that a given substance, say hydrogen, can appear in many different compound systems with many different ratios of the mole numbers of the constituents of the compound system.

The condition (6.4) means that

$$B(\Gamma) - B(\Gamma') \leq S_{\Gamma'}(Y) - S_\Gamma(X)$$

whenever $X \prec Y$. Let us denote by $D(\Gamma, \Gamma')$ the minimal entropy difference for all adiabatic processes that can take us from Γ to Γ', i.e.,

$$D(\Gamma, \Gamma') := \inf\{S_{\Gamma'}(Y) - S_\Gamma(X) \ : \ X \prec Y\}. \tag{6.6}$$

It is to be noted that $D(\Gamma, \Gamma')$ can be positive or negative and $D(\Gamma, \Gamma') \neq D(\Gamma', \Gamma)$ in general. Clearly $D(\Gamma, \Gamma) = 0$. Definition (6.6) makes sense only if there is at least one adiabatic process that goes from Γ to Γ', and it is convenient to define $D(\Gamma, \Gamma') = +\infty$ if there is no such process. In terms of the $D(\Gamma, \Gamma')$'s condition (6.4) means precisely that

$$-D(\Gamma', \Gamma) \leq B(\Gamma) - B(\Gamma') \leq D(\Gamma, \Gamma') \tag{6.7}$$

Although $D(\Gamma, \Gamma')$ has no particular sign, we can assert the crucial fact that

$$-D(\Gamma', \Gamma) \leq D(\Gamma, \Gamma') \tag{6.8}$$

This is trivially true if $D(\Gamma,\Gamma')=+\infty$ or $D(\Gamma',\Gamma)=+\infty$. If both are $<\infty$ the reason (6.8) is true is simply (6.1): By the definition (6.6), there is a pair of states $X\in\Gamma$ and $Y\in\Gamma'$ such that $X\prec Y$ and $S_{\Gamma'}(Y)-S_\Gamma(X)=D(\Gamma,\Gamma')$ (or at least as closely as we please). Likewise, we can find $W\in\Gamma$ and $Z\in\Gamma'$, such that $Z\prec W$ and $S_\Gamma(W)-S_{\Gamma'}(Z)=D(\Gamma',\Gamma)$. Then, in the compound system $\Gamma\times\Gamma'$ we have that $(X,Z)\prec(W,Y)$, and this, by (6.1), implies (6.8). Thus $D(\Gamma,\Gamma')>-\infty$ if there is at least one adiabatic process from Γ' to Γ.

Some reflection shows us that consistency in the definition of the entropy constants $B(\Gamma)$ requires us to consider all possible chains of adiabatic processes leading from one space to another via intermediate steps. Moreover, the additivity requirement leads us to allow the use of a 'catalyst' in these processes, i.e., an auxiliary system, that is recovered at the end, although a state change *within* this system might take place.

For this reason we now define new quantities, $E(\Gamma,\Gamma')$ and $F(\Gamma,\Gamma')$, in the following way. First, for any given Γ and Γ' we consider all finite chains of state spaces, $\Gamma=\Gamma_1,\Gamma_2,\dots,\Gamma_N=\Gamma'$ such that $D(\Gamma_i,\Gamma_{i+1})<\infty$ for all i, and we define

$$E(\Gamma,\Gamma'):=\inf\{D(\Gamma_1,\Gamma_2)+\cdots+D(\Gamma_{N-1},\Gamma_N)\}, \tag{6.9}$$

where the infimum is taken over all such chains linking Γ with Γ'. Note that $E(\Gamma,\Gamma')\le D(\Gamma,\Gamma')$ and $E(\Gamma,\Gamma')$ could be $<\infty$ even if there is no direct adiabatic process linking Γ and Γ', i.e., $D(\Gamma,\Gamma')=\infty$. We then define

$$F(\Gamma,\Gamma'):=\inf\{E(\Gamma\times\Gamma_0,\Gamma'\times\Gamma_0)\}\}, \tag{6.10}$$

where the infimum is taken over all state spaces Γ_0. (These are the 'catalysts'.)

The following properties of $F(\Gamma,\Gamma')$ are easily verified:

$$F(\Gamma,\Gamma)=0 \tag{6.11}$$

$$F(t\Gamma,t\Gamma')=tF(\Gamma,\Gamma')\qquad\text{for } t>0 \tag{6.12}$$

$$F(\Gamma_1\times\Gamma_2,\Gamma_1'\times\Gamma_2')\le F(\Gamma_1,\Gamma_1')+F(\Gamma_2,\Gamma_2') \tag{6.13}$$

$$F(\Gamma\times\Gamma_0,\Gamma'\times\Gamma_0)=F(\Gamma,\Gamma')\qquad\text{for all }\ \Gamma_0. \tag{6.14}$$

In fact, (6.11) and (6.12) are also shared by the D's and the E's. The 'subadditivity' (6.13) holds also for the E's, but the 'translational invariance' (6.14) might only hold for the F's.

From (6.13) and (6.14) it follows that the F's satisfy the 'triangle inequality'

$$F(\Gamma,\Gamma'')\le F(\Gamma,\Gamma')+F(\Gamma',\Gamma'') \tag{6.15}$$

(put $\Gamma=\Gamma_1$, $\Gamma''=\Gamma_1'$, $\Gamma'=\Gamma_2=\Gamma_2'$.) This inequality also holds for the E's as is obvious from the definition (6.9). A special case (using (6.11)) is the analogue of (6.8):

$$-F(\Gamma',\Gamma)\le F(\Gamma,\Gamma') \tag{6.16}$$

(This is trivial if $F(\Gamma',\Gamma)$ or $F(\Gamma',\Gamma)$ is infinite, otherwise use (6.15) with $\Gamma=\Gamma''$.)

Obviously, the following inequalities hold:

$$-D(\Gamma',\Gamma)\le -E(\Gamma',\Gamma)\le -F(\Gamma',\Gamma)\le F(\Gamma,\Gamma')\le E(\Gamma,\Gamma')\le D(\Gamma,\Gamma').$$

The importance of the F's for the determination of the additive constants is made clear in the following theorem:

THEOREM 6.1 (Constant entropy differences). *If Γ and Γ' are two state spaces then for any two points $X \in \Gamma$ and $Y \in \Gamma'$*

$$X \prec Y \quad \text{if and only if} \quad S_\Gamma(X) + F(\Gamma,\Gamma') \leq S_{\Gamma'}(Y). \tag{6.17}$$

Remarks: (1). Since $F(\Gamma,\Gamma') \leq D(\Gamma,\Gamma')$ the theorem is trivially true when $F(\Gamma,\Gamma') = +\infty$, in the sense that there is then no adiabatic process from Γ to Γ'. The reason for the title 'constant entropy differences' is that the minimum jump between the entropies $S_\Gamma(X)$ and $S_{\Gamma'}(Y)$ for $X \prec Y$ to be possible is independent of X.

(2). There is an interesting corollary of Theorem 6.1. We know, from the definition (6.6), that $X \prec Y$ only if $S_\Gamma(X) + D(\Gamma,\Gamma') \leq S_{\Gamma'}(Y)$. Since $D(\Gamma,\Gamma') \leq F(\Gamma,\Gamma')$, Theorem 6.1 tells us two things:

$$X \prec Y \quad \text{if and only if} \quad S_\Gamma(X) + F(\Gamma,\Gamma') \leq S_{\Gamma'}(Y). \tag{6.18}$$

and

$$S_\Gamma(X) + D(\Gamma,\Gamma') \leq S_{\Gamma'}(Y) \quad \text{if and only if} \quad S_\Gamma(X) + F(\Gamma,\Gamma') \leq S_{\Gamma'}(Y). \tag{6.19}$$

We *cannot* conclude from this, however, that $D(\Gamma,\Gamma') = F(\Gamma,\Gamma')$.

Proof: The 'only if' part is obvious because $F(\Gamma,\Gamma') \leq D(\Gamma,\Gamma')$, and thus our goal is to prove the 'if' part. For clarity, we begin by assuming that the infima in (6.6), (6.9) and (6.10) are minima, i.e., there are state spaces Γ_0, Γ_1, Γ_2,..., Γ_N and states $X_i \in \Gamma_i$ and $Y_i \in \Gamma_i$, for $i = 0, ..., N$ and states $\tilde{X} \in \Gamma$ and $\tilde{Y} \in \Gamma'$ such that

$$\begin{aligned}(\tilde{X}, X_0) &\prec Y_1 \\ X_i &\prec Y_{i+1} \qquad \text{for } i = 1, ..., N-1 \\ X_N &\prec (\tilde{Y}, Y_0)\end{aligned} \tag{6.20}$$

and $F(\Gamma,\Gamma')$ is given by

$$\begin{aligned}F(\Gamma,\Gamma') &= D(\Gamma\times\Gamma_0,\Gamma_1) + D(\Gamma_1,\Gamma_2) + \cdots + D(\Gamma_N,\Gamma'\times\Gamma_0) \\ &= S_{\Gamma'}(\tilde{Y}) + \sum_{j=0}^{N} S_j(Y_j) - S_\Gamma(\tilde{X}) - \sum_{j=0}^{N} S_j(X_j).\end{aligned} \tag{6.21}$$

In (6.21) we used the abbreviated notation S_j for S_{Γ_j} and we used the fact that $S_{\Gamma\times\Gamma_0} = S_\Gamma + S_0$.

From the assumed inequality $S_\Gamma(X) + F(\Gamma,\Gamma') \leq S_{\Gamma'}(Y)$ and (6.21) we conclude that

$$S_\Gamma(X) + S_{\Gamma'}(\tilde{Y}) + \sum_{j=0}^{N} S_j(Y_j) \leq S_\Gamma(\tilde{X}) + S_{\Gamma'}(Y) + \sum_{j=0}^{N} S_j(X_j). \tag{6.22}$$

However, both sides of this inequality can be thought of as the entropy of a state in the compound space $\hat{\Gamma} := \Gamma\times\Gamma'\times\Gamma_0\times\Gamma_1\times\cdots\times\Gamma_N$. The entropy principle (6.1) for $\hat{\Gamma}$ then tell us that

$$(X, \tilde{Y}, Y_0, \ldots, Y_N) \prec (\tilde{X}, Y, X_0, \ldots, X_N) \tag{6.23}$$

On the other hand, using (6.20) and the axiom of consistency, we have that

$$(\tilde{X}, X_0, X_1, ..., X_N) \prec (\tilde{Y}, Y_0, Y_1, ..., Y_N). \tag{6.24}$$

By the consistency axiom again, we have from (6.24) that $(\tilde{X}, Y, X_0, \cdots, X_N) \prec (Y, \tilde{Y}, Y_0, Y_1, ..., Y_N)$. From transitivity we then have

$$(X, \tilde{Y}, Y_0, Y_1, ..., Y_N) \prec (Y, \tilde{Y}, Y_0, Y_1, ..., Y_N),$$

and the desired conclusion, $X \prec Y$, follows from the cancellation law.

If $F(\Gamma, \Gamma')$ is not a minimum, then, for every $\varepsilon > 0$, there is a chain of spaces Γ_0, Γ_1, Γ_2,..., Γ_N and corresponding states as in (6.20) such that (6.21) holds to within ε and (6.22) becomes (for simplicity of notation we omit the explicit dependence of the states and N on ε)

$$S_\Gamma(X) + S_{\Gamma'}(\tilde{Y}) + \sum_{j=0}^{N} S_j(Y_j) \le S_\Gamma(\tilde{X}) + S_{\Gamma'}(Y) + \sum_{j=0}^{N} S_j(X_j) + \varepsilon. \tag{6.25}$$

Now choose any auxiliary state space $\widetilde{\Gamma}$, with entropy function $\widetilde{S}$, and two states $Z_0, Z_1 \in \widetilde{\Gamma}$ with $Z_0 \prec\prec Z_1$. The space Γ itself could be used for this purpose, but for clarity we regard $\widetilde{\Gamma}$ as distinct. Define $\delta(\varepsilon) := [\widetilde{S}(Z_1) - \widetilde{S}(Z_0)]^{-1}\varepsilon$. Recalling that $\delta\widetilde{S}(Z) = \widetilde{S}(\delta Z)$ by scaling, we see that (6.25) implies the following analogue of (6.23).

$$(\delta Z_0, X, \tilde{Y}, Y_0, \ldots, Y_N) \prec (\delta Z_1, \tilde{X}, Y, X_0, \ldots, X_N). \tag{6.26}$$

Proceeding as before, we conclude that

$$(\delta Z_0, X, \tilde{Y}, Y_0, Y_1, ..., Y_N) \prec (\delta Z_1, Y, \tilde{Y}, Y_0, Y_1, ..., Y_N),$$

and thus $(X, \delta Z_0) \prec (Y, \delta Z_1)$ by the cancellation law. However, $\delta \to 0$ as $\varepsilon \to 0$ and hence $X \prec Y$ by the stability axiom. ■

According to Theorem 6.1 the determination of the entropy constants $B(\Gamma)$ amounts to satisfying the estimates

$$-F(\Gamma', \Gamma) \le B(\Gamma) - B(\Gamma') \le F(\Gamma, \Gamma') \tag{6.27}$$

together with the linearity condition (6.5). It is clear that (6.27) can only be satisfied with finite constants $B(\Gamma)$ and $B(\Gamma')$, if $F(\Gamma, \Gamma') > -\infty$. While the assumptions made so far do not exclude $F(\Gamma, \Gamma') = -\infty$ as a possibility, it follows from (6.16) that this can only be the case if at the same time $F(\Gamma', \Gamma) = +\infty$, i.e., there is no chain of intermediate adiabatic processes in the sense described above that allows a passage from Γ' back to Γ. For all we know this is not the situation encountered in nature and we exclude it by an additional axiom. Let us write $\Gamma \prec \Gamma'$ and say that Γ is *connected to* Γ' if $F(\Gamma, \Gamma') < \infty$, i.e. if there is a finite chain of state spaces, $\Gamma_0, \Gamma_1, \Gamma_2, \ldots, \Gamma_N$ and states such that (6.20) holds with $\tilde{X} \in \Gamma$ and $\tilde{Y} \in \Gamma'$. Our new axiom is the following:

M) Absence of sinks. If Γ is connected to Γ' then Γ' is connected to Γ, i.e., $\Gamma \prec \Gamma' \Longrightarrow \Gamma' \prec \Gamma$.

The introduction of this axiom may seem a little special, even artificial, but it is not. For one thing, it is not used in Theorem 6.1 which, like the entropy principle itself, states the condition under which adiabatic process from X to Y is possible. Axiom M is only needed for setting the additive entropy constants so that (6.17) can be converted into a statement involving $S(X)$ and $S(Y)$ alone, as in Theorem 6.2. Second, axiom M should not be misread as saying that if we can make water from hydrogen and oxygen then we can make hydrogen and oxygen directly from water (which requires hydrolysis). What it does require is that water can eventually be converted into its chemical elements, but not necessarily in one step and not necessarily reversibly. The intervention of irreversible processes involving other substances is allowed. Were axiom M to fail in this case then all the oxygen in the universe would eventually turn up in water and we should have to rely on supernovae to replenish the supply from time to time.

By axiom M (and the obvious transitivity of the relation $\prec$ for state spaces), connectedness defines an equivalence relation between state spaces, and instead of $\Gamma \prec \Gamma'$ we can write

$$\Gamma \sim \Gamma' \tag{6.28}$$

to indicate that the $\prec$ relation among state spaces goes both ways. As already noted, $\Gamma \sim \Gamma'$ is equivalent to $-\infty < F(\Gamma, \Gamma') < \infty$ and $-\infty < F(\Gamma', \Gamma) < \infty$.

Without further assumptions (note, in particular, that no assumptions about 'semi-permeable membranes' have been made) we can now derive the entropy principle in the following weak version:

THEOREM 6.2 (Weak form of the entropy principle). *Assume axiom M in addition to A1-A7, S1-S3, T1-T5. Then the entropy constants $B(\Gamma)$ can be chosen in such a way that the entropy S, defined on all states of all systems by (6.3), satisfies additivity and extensivity (2.4), (2.5), and moreover*

$$X \prec Y \quad \text{implies} \quad S(X) \leq S(Y). \tag{6.29}$$

Proof: The proof is a simple application of the Hahn-Banach theorem (see, e.g., the appendix to (Giles, 1964) and (Reed and Simon, 1972)). Consider the set $\mathcal{S}$ of all pairs of state spaces (Γ, Γ'). On $\mathcal{S}$ we define an equivalence relation by declaring (Γ, Γ') to be equivalent to $(\Gamma \times \Gamma_0, \Gamma' \times \Gamma_0)$ for all Γ_0. Denote by $[\Gamma, \Gamma']$ the equivalence class of (Γ, Γ') and let $\mathcal{L}$ be the set of all these equivalence classes.

On $\mathcal{L}$ we define multiplication by scalars and addition in the following way:

$$\begin{aligned}
t[\Gamma, \Gamma'] &:= [t\Gamma, t\Gamma'] \qquad \text{for } t > 0 \\
t[\Gamma, \Gamma'] &:= [-t\Gamma', -t\Gamma] \qquad \text{for } t < 0 \\
0[\Gamma, \Gamma'] &:= [\Gamma, \Gamma] = [\Gamma', \Gamma'] \\
[\Gamma_1, \Gamma_1'] + [\Gamma_2, \Gamma_2'] &:= [\Gamma_1 \times \Gamma_2, \Gamma_1' \times \Gamma_2'].
\end{aligned}$$

With these operations $\mathcal{L}$ becomes a vector space, which is infinite dimensional in general. The zero element is the class $[\Gamma, \Gamma]$ for any Γ, because by our definition of the equivalence relation (Γ, Γ) is equivalent to $(\Gamma \times \Gamma', \Gamma \times \Gamma')$, which in turn is equivalent to (Γ', Γ'). Note that for the same reason $[\Gamma', \Gamma]$ is the negative of $[\Gamma, \Gamma']$.

Next, we define a function H on $\mathcal{L}$ by

$$H([\Gamma, \Gamma']) := F(\Gamma, \Gamma')$$

Because of (6.14), this function is well defined and it takes values in $(-\infty, \infty]$. Moreover, it follows from (6.12) and (6.13) that H is homogeneous, i.e., $H(t[\Gamma, \Gamma']) = tH([\Gamma, \Gamma'])$, and subadditive, i.e., $H([\Gamma_1, \Gamma'_1] + [\Gamma_2, \Gamma'_2]) \leq H([\Gamma_1, \Gamma'_1]) + H([\Gamma_2, \Gamma'_2])$. Likewise,

$$G([\Gamma, \Gamma']) := -F(\Gamma', \Gamma)$$

is homogeneous and superadditive, i.e., $G([\Gamma_1, \Gamma'_1] + [\Gamma_2, \Gamma'_2]) \geq G([\Gamma_1, \Gamma'_1]) + G([\Gamma_2, \Gamma'_2])$. By (6.16) we have $G \leq F$ so, by the Hahn-Banach theorem, there exists a real-valued *linear* function L on $\mathcal{L}$ lying between G and H; that is

$$-F(\Gamma', \Gamma) \leq L([\Gamma, \Gamma']) \leq F(\Gamma, \Gamma'). \tag{6.30}$$

Pick any fixed Γ_0 and define

$$B(\Gamma) := L([\Gamma_0 \times \Gamma, \Gamma_0]).$$

By linearity, L satisfies $L([\Gamma, \Gamma']) = -L(-[\Gamma, \Gamma']) = -L([\Gamma', \Gamma])$. We then have

$$B(\Gamma) - B(\Gamma') = L([\Gamma_0 \times \Gamma, \Gamma_0]) + L([\Gamma_0, \Gamma_0 \times \Gamma']) = L([\Gamma, \Gamma'])$$

and hence (6.27) is satisfied. ■

From the proof of Theorem 6.2 it is clear that the indeterminacy of the additive constants $B(\Gamma)$ can be traced back to the non uniqueness of the linear function $L([\Gamma, \Gamma'])$ lying between $G([\Gamma, \Gamma']) = -F(\Gamma', \Gamma)$ and $H([\Gamma, \Gamma']) = F(\Gamma, \Gamma')$. This non uniqueness has two possible sources: One is that some pairs of state spaces Γ and Γ' may not be connected, i.e., $F(\Gamma, \Gamma')$ may be infinite (in which case $F(\Gamma', \Gamma)$ is also infinite by axiom M). The other possibility is that there is a finite, but positive 'gap' between G and H, i.e.,

$$-F(\Gamma', \Gamma) < F(\Gamma, \Gamma') \tag{6.31}$$

might hold for some state spaces, even if both sides are finite.

In nature only states containing the same amount of the chemical elements can be transformed into each other. Hence $F(\Gamma, \Gamma') = +\infty$ for many pairs of state spaces, in particular, for those that contain different amounts of some chemical element. The constants $B(\Gamma)$ are therefore never unique: For each equivalence class of state spaces (with respect to $\sim$) one can define a constant that is arbitrary except for the proviso that the constants should be additive and extensive under composition and scaling of systems. In our world, where there are 92 chemical elements (or, strictly speaking, a somewhat larger number, N, since one should count different isotopes as different elements), and this leaves us with at least 92 free constants that specify the entropy of one mole of each of the chemical elements in some specific state.

The other possible source of non uniqueness, a non zero gap (6.31) is, as far as we know, not realized in nature, although it is a logical possibility. The true situation seems rather to be the following: The equivalence class $[\Gamma]$ (with respect to $\sim$) of every state space Γ contains a distinguished state space

$$\Lambda([\Gamma]) = \lambda_1 \Gamma_1 \times \ldots \times \lambda_N \Gamma_N$$

where the Γ_i are the state spaces of one mole of each of the chemical elements, and the numbers $(\lambda_1, \dots, \lambda_N)$ specify the amount of each chemical element in Γ. We have

$$\Lambda([t\Gamma]) = t\Lambda([\Gamma]) \tag{6.32}$$

and

$$\Lambda([\Gamma \times \Gamma']) = \Lambda([\Gamma]) \times \Lambda([\Gamma']). \tag{6.33}$$

Moreover (and this is the crucial 'experimental fact'),

$$-F(\Lambda([\Gamma]), \Gamma]) = F(\Gamma, \Lambda([\Gamma])) \tag{6.34}$$

for all Γ. Note that (6.34) is subject to experimental verification by measuring on the one hand entropy differences for processes that synthesize chemical compounds from the elements (possibly through many intermediate steps and with the aid of catalysts), and on the other hand for processes where chemical compounds are decomposed into the elements.

It follows from (6.15) (6.16) and (6.34) that

$$F(\Gamma, \Gamma') = F(\Gamma, \Lambda([\Gamma])) + F(\Lambda([\Gamma]), \Gamma') \tag{6.35}$$

and

$$-F(\Gamma', \Gamma) = F(\Gamma, \Gamma') \tag{6.36}$$

for all $\Gamma' \sim \Gamma$. Moreover, an explicit formula for $B(\Gamma)$ can be given in this good case:

$$B(\Gamma) = F(\Gamma, \Lambda([\Gamma]). \tag{6.37}$$

If $F(\Gamma, \Gamma') = \infty$, then (6.27) holds trivially, while for $\Gamma \sim \Gamma'$ we have by (6.35) and(6.36)

$$B(\Gamma) - B(\Gamma') = F(\Gamma, \Gamma') = -F(\Gamma', \Gamma), \tag{6.38}$$

i.e., the inequality (6.27) is saturated. It is also clear that in this case $B(\Gamma)$ is unique up to the choice of arbitrary constants for the fixed systems $\Gamma_1, \dots, \Gamma_N$. The particular choice (6.37) corresponds to putting $B(\Gamma_i) = 0$ for the chemical elements $i = 1, \dots, N$.

From Theorem 6.1 it follows that in the good case just described the comparison principle holds in the sense that *all states belonging to systems in the same equivalence class are comparable*, and the relation $\prec$ is *exactly* characterized by the entropy function, i.e., the *full* entropy principle holds.

If there is a genuine gap, (6.31), then for some pair of state spaces we might have only the weak version of the entropy principle, Theorem 6.2. Moreover, it follows from Theorem 6.1 that in this case there are no states $X \in \Gamma$ and $Y \in \Gamma'$ such that $X \overset{A}{\sim} Y$. Hence, in order for the full entropy principle to hold as far as Γ and Γ' are concerned, it is only necessary to ensure that $X \prec\prec Y$ implies $S(X) < S(Y)$, and this will be the case (again by Theorem 6.1) if and only if

$$-F(\Gamma', \Gamma) < B(\Gamma) - B(\Gamma') < F(\Gamma, \Gamma'). \tag{6.39}$$

In other words, we would have the full entropy principle, gaps notwithstanding, if we could be sure that whenever (6.31) holds then the inequalities in (6.30) are both strict inequalities.

We are not aware of a proof of the Hahn-Banach theorem that will allow us to conclude that (6.30) is strict in all cases where (6.31) holds. If, however, the dimension of the linear space $\mathcal{L}$ considered in the proof of Theorem 6.2 were finite then the Hahn-Banach theorem would allow us to choose the B's in this way. This is a consequence of the following lemma.

LEMMA 6.1 (Strict Hahn-Banach). *Let V be a finite dimensional, real vector space and $p : V \to \mathbf{R}$ subadditive, i.e., $p(x+y) \leq p(x) + p(y)$ for all $x, y \in V$, and homogenous, i.e., $p(\lambda x) = \lambda p(x)$ for all $\lambda \geq 0$, $x \in V$. Then there is a linear functional L on V, such that $-p(-x) \leq L(x) \leq p(x)$ for all $x \in V$. Moreover, for those x for which $-p(-x) < p(x)$ holds we have the strict inequalities $-p(-x) < L(x) < p(x)$.*

Proof: Note first that subadditivity implies that $p(x) - p(-y) \leq p(x+y) \leq p(x) + p(y)$ for all $x, y \in V$. Define $V_0 = \{x : -p(-x) = p(x)\}$. If $x \in V$ and $y \in V_0$, then $p(x) + p(y) = p(x) - p(-y) \leq p(x+y) \leq p(x) + p(y)$ and hence $p(x) + p(y) = p(x+y)$. (Note that x need not belong to V_0.) If $x \in V_0$ and $\lambda \geq 0$, then $p(\lambda x) = \lambda p(x) = \lambda(-p(-x)) = -p(-\lambda x)$, and if $\lambda < 0$ we have, in the same way, $p(\lambda x) = p((-\lambda)(-x)) = (-\lambda)p(-x) = \lambda(-p(-x)) = \lambda p(x)$. Thus V_0 is a linear space, and p is a linear functional on it. We define $L(x) = p(x)$ for $x \in V_0$.

Let V_0' be an algebraic complement of V_0, i.e., all $x \in V$ can be written as $x = y + z$ with $y \in V_0$, $z \in V_0'$ and the decomposition is unique if $x \neq 0$. On V_0' the strict inequality $-p(-x) < p(x)$ holds for all $x \neq 0$. If L can be defined on V_0' such that $-p(-x) < L(x) < p(x)$ for all $V_0' \ni x \neq 0$ we reach our goal by defining $L(x+y) = L(x) + L(y)$ for $x \in V_0'$, $y \in V_0$. Hence it suffices to consider the case that $V_0 = \{0\}$.

Now suppose $V_1 \subset V$ is a linear space and and L has been extended from $\{0\}$ to V_1 such that our requirements are fulfilled on V_1, i.e., $-p(-x) < L(x) < p(x)$ for $x \in V_1$, $x \neq 0$. Define, for $x \in V$

$$\bar{p}(x) = \inf_{y \in V_1} \{p(x+y) - L(y)\}.$$

By subadditivity it is clear that for all x

$$-p(-x) \leq -\bar{p}(-x) \leq \bar{p}(x) \leq p(x).$$

Since V is finite dimensional (by assumption) and p continuous (by convexity) the infimum is, in fact, a minimum for each x, i.e., $\bar{p}(x) = p(x+y) - L(y)$ with some $y \in V_1$, depending on x.

Suppose V_1 is not the whole of V. Pick x_2 linearly independent of V_1. On the space spanned by V_1 and x_2 we define

$$L(\lambda x_2 + x_1) = (\lambda/2)(\bar{p}(x_2) - \bar{p}(-x_2)) + L(x_1).$$

if $x_1 \in V_1$, $\lambda \in \mathbf{R}$.

Then

$$p(\lambda x_2 + x_1) - L(\lambda x_2 + x_1) = p(\lambda x_2 + x_1) - L(x_1) - L(\lambda x_2) \geq \bar{p}(\lambda x_2) - L(\lambda x_2) \geq 0$$

and equality holds in the last inequality if and only if $\bar{p}(\lambda x_2) = -\bar{p}(-\lambda x_2)$, i.e.,

$$p(\lambda x_2 + y) + p(-\lambda x_2 + y') = L(y + y') \leq p(y + y'). \tag{6.40}$$

for some $y,\ y' \in V_1$ (depending on λx_2). On the other hand,

$$p(\lambda x_2 + y) + p(-\lambda x_2 + y') \geq p(y + y')$$

by subadditivity, so (6.40) implies

$$L(y + y') = p(y + y') \tag{6.41}$$

By our assumption about V_1 this hold only if $y + y' = 0$. But then

$$p(-\lambda x_2 + y') = p(-\lambda x_2 - y)$$

and from (6.40) and (6.41) we get $-p(-\lambda x_2 - y) = p(\lambda x_2 + y)$ and hence $\lambda x_2 = -y \in V_1$. Since $x_2 \notin V_1$ this is only possible for $\lambda = 0$, in which case $p(x_1) = L(x_1)$ and hence (by our assumption about V_1), $x_1 = 0$. Thus the statement $L(x) = p(x)$ for some x lying in the span of V_1 and x_2 implies that $x = 0$. In the same way one shows that $L(x) = -p(-x)$ implies $x = 0$. Thus, we have succeeded in extending L from V_1 to the larger space $\mathrm{span}\{V_1, x_2\}$. Proceeding by induction we obtain L satisfying our requirements on all V. ■

Since the proof of the above version of the Hahn-Banach theorem proceeds inductively over subspaces of increasing dimension it generalizes in a straightforward way to spaces of countable algebraic dimension. Morover, in such spaces the condition (6.39) could be fulfilled at any induction step *without modifying the constants previously defined.* Hence, even in cases where (6.36) is violated, this hypothetical weakening of the full entropy principle could never be detected in real experiments involving only finitely many systems.

VII. SUMMARY AND CONCLUSIONS

In this final section we recall our notation for the convenience of the reader and collect all the axioms introduced in Sects. 2, 3, 4 and 6. We then review the logical structure of the paper and the main conclusions.

Our axioms concern equilibrium states, denoted by X, Y etc., and the relation $\prec$ of adiabatic accessibility between them. If $X \prec Y$ and $Y \prec X$ we write $X \stackrel{\text{A}}{\sim} Y$, while $X \prec\prec Y$ means that $X \prec Y$, but not $Y \prec X$. States belong to state spaces $\Gamma, \Gamma', \ldots$ of systems, that may be simple or compound. The composition of two state spaces Γ, Γ' is the Cartesian product $\Gamma \times \Gamma'$ (the order of the factors is unimportant); the composition of $X \in \Gamma$ and $Y \in \Gamma'$ is denoted $(X, Y) \in \Gamma \times \Gamma'$. A state $X \in \Gamma$ may be scaled by a real parameter $t > 0$, leading to a state tX in a scaled state space $\Gamma^{(t)}$, sometimes written $t\Gamma$. For simple systems the states are parametrized by the energy coordinate $U \in \mathbf{R}$ and the work coordinates $V \in \mathbf{R}^n$.

The axioms are grouped as follows:

A. GENERAL AXIOMS

A1) Reflexivity. $X \stackrel{\text{A}}{\sim} X$.

A2) Transitivity. $X \prec Y$ and $Y \prec Z$ implies $X \prec Z$.

A3) Consistency. $X \prec X'$ and $Y \prec Y'$ implies $(X, Y) \prec (X', Y')$.

A4) Scaling invariance. If $X \prec Y$, then $tX \prec tY$ for all $t > 0$.

A5) Splitting and recombination. For $0 < t < 1$, $X \stackrel{\text{A}}{\sim} (tX, (1-t)X)$.

A6) Stability. If $(X, \varepsilon Z_0) \prec (Y, \varepsilon Z_1)$ holds for a sequence of ε's tending to zero and some states Z_0, Z_1, then $X \prec Y$.

A7) Convex combination. Assume X and Y are states in the same state space, Γ, that has a convex structure. If $t \in [0, 1]$ then $(tX, (1-t)Y) \prec tX + (1-t)Y$.

B. AXIOMS FOR SIMPLE SYSTEMS

Let Γ, a convex subset of $\mathbf{R}^{n+1}$ for some $n > 0$, be the state space of a simple system.

S1) Irreversibility. For each $X \in \Gamma$ there is a point $Y \in \Gamma$ such that $X \prec\prec Y$. (Note: This axiom is implied by T4, and hence it is not really independent.)

S2) Lipschitz tangent planes. For each $X \in \Gamma$ the forward sector $A_X = \{Y \in \Gamma : X \prec Y\}$ has a *unique* support plane at X (i.e., A_X has a *tangent plane* at X). The slope of the tangent plane is assumed to be a *locally Lipschitz continuous* function of X.

S3) Connectedness of the boundary. The boundary ∂A_X of a forward sector is connected.

C. AXIOMS FOR THERMAL EQUILIBRIUM

T1) Thermal contact. For any two simple systems with state spaces Γ_1 and Γ_2, there is another simple system, the *thermal join* of Γ_1 and Γ_2, with state space

$$\Delta_{12} = \{(U, V_1, V_2) : U = U_1 + U_2 \text{ with } (U_1, V_1) \in \Gamma_1, (U_2, V_2) \in \Gamma_2\}.$$

Moreover,

$$\Gamma_1 \times \Gamma_2 \ni ((U, V_1),\ (U_2, V_2)) \prec (U_1 + U_2, V_1, V_2) \in \Delta_{12}.$$

T2) Thermal splitting. For any point $(U, V_1, V_2) \in \Delta_{12}$ there is at least one pair of states, $(U_1, V_1) \in \Gamma_1$, $(U_2, V_2)) \in \Gamma_2$, with $U = U_1 + U_2$, such that

$$(U, V_1, V_2) \overset{\text{A}}{\sim} ((U_1, V_1), (U_2, V_2)).$$

In particular, if (U, V) is a state of a simple system Γ and $\lambda \in [0, 1]$ then

$$(U, (1-\lambda)V, \lambda V) \overset{\text{A}}{\sim} (((1-\lambda)U, (1-\lambda)V), (\lambda U, \lambda V)) \in \Gamma^{(1-\lambda)} \times \Gamma^{(\lambda)}.$$

If $(U, V_1, V_2) \overset{\text{A}}{\sim} ((U_1, V_1), (U_2, V_2))$ we write $(U_1, V_1) \overset{\text{T}}{\sim} (U_2, V_2)$.

T3) Zeroth law. If $X \overset{\text{T}}{\sim} Y$ and if $Y \overset{\text{T}}{\sim} Z$ then $X \overset{\text{T}}{\sim} Z$.

T4) Transversality. If Γ is the state space of a simple system and if $X \in \Gamma$, then there exist states $X_0 \overset{\text{T}}{\sim} X_1$ with $X_0 \prec\prec X \prec\prec X_1$.

T5) Universal temperature range. If Γ_1 and Γ_2 are state spaces of simple systems then, for every $X \in \Gamma_1$ and every V in the projection of Γ_2 onto the space of its work coordinates, there is a $Y \in \Gamma_2$ with work coordinates V such that $X \overset{\text{T}}{\sim} Y$.

D. AXIOM FOR MIXTURES AND REACTIONS

Two state spaces, Γ and Γ' are said to be connected, written $\Gamma \prec \Gamma'$, if there are state spaces Γ_0, Γ_1, Γ_2,..., Γ_N and states $X_i \in \Gamma_i$ and $Y_i \in \Gamma_i$, for $i = 1, ..., N$ and states $\tilde{X} \in \Gamma$ and $\tilde{Y} \in \Gamma'$ such that $(\tilde{X}, X_0) \prec Y_1$, $X_i \prec Y_{i+1}$ for $i = 1, ..., N-1$, and $X_N \prec (\tilde{Y}, Y_0)$.

M) Absence of sinks. If Γ is connected to Γ' then Γ' is connected to Γ, i.e., $\Gamma \prec \Gamma' \Longrightarrow \Gamma' \prec \Gamma$.

The main goal of the paper is to derive the **entropy principle** (EP) from these properties of $\prec$:

There is a function, called **entropy** *and denoted by S, on all states of all simple and compound systems, such that*

a) <u>`Monotonicity:`</u> *If $X \prec\prec Y$, then $S(X) < S(Y)$, and if $X \overset{\text{A}}{\sim} Y$, then $S(X) = S(Y)$.*

b) <u>`Additivity and extensivity:`</u> *$S((X, X')) = S(X) + S(X')$ and $S(tX) = tS(X)$.*

Differentiability of S as function of the energy and work coordinates of simple systems is also proved and *temperature* is derived from entropy.

A central result on our road to the EP is a proof, from our axioms, of the *comparison hypothesis* (CH) for simple and compound systems, which says that for any two states X, Y in the *same* state space either $X \prec Y$ or $Y \prec X$ holds. This is stated in Theorem 4.8. The existence of an entropy function is discussed already in Section II on the basis of Axioms A1-A6 alone *assuming* in addition CH. In the subsequent sections CH is *derived* from the other axioms. The main steps involved in this derivation of CH are as follows.

The comparison hypothesis (which, once proved, is more appropriately called the *comparison principle*) is first derived for simple systems in Theorem 3.7 in Sect. III. This proof uses both the special axioms S1-S3 of Sect. III and the general axioms A1-A7 introduced in Sect. II. On the other hand, it should be stressed that Theorem 3.7 is independent of the discussion in Sect. II D-E, where an entropy function is constructed, assuming the validity of CH.

The extension of CH to compound systems relies heavily on the axioms for thermal equilibrium that are discussed in Sect. IV. The key point is that by forming the thermal join of two simple systems we obtain a new simple system to which Theorem 3.7 can be applied. The extension of

CH from simple to compound systems is first carried out for products of scaled copies of the *same* simple system (Theorem 4.4). Here the transversality axiom T4 plays an essential role by reducing the consideration of states of the compound system that are not in thermal equilibrium to states in the thermal join.

The proof of CH for products of *different* simple systems requires more effort. The main step here is to prove the existence of 'entropy calibrators' (Theorem 4.7). This says that for each pair of simple systems Γ_1, Γ_2 there are exist four states, $X_0, X_1 \in \Gamma_1$, $Y_0, Y_1 \in \Gamma_2$ such that $X_0 \prec\prec X_1$, $Y_0 \prec\prec Y_1$, but $(X_0, Y_1) \stackrel{A}{\sim} (X_1, X_0)$. In establishing this property, we find it convenient to make use of the existence of an entropy function for each of the spaces Γ_1 and Γ_2 separately, which, as shown in Sects. II D-E, follows from axioms A1-A6 and the already established property CH for products of scaled copies of the *same* simple system.

Once CH has been established for arbitrary products of simple systems the entropy principle for all adiabatic state changes, except for mixing of different substances and chemical reactions, follows from the considerations of Sects. II D-E. An explicit formula for S is given in Eq. (2.20): We pick a reference system with two states $Z_0 \prec\prec Z_1$, and for each system Γ a reference point $X_\Gamma \in \Gamma$ is chosen in such a way that $X_{t\Gamma} = tX_\Gamma$ and $X_{\Gamma_1 \times \Gamma_2} = (X_{\Gamma_1}, X_{\Gamma_2})$. Then, for $X \in \Gamma$,

$$S(X) = \sup\{\lambda \ : \ (X_\Gamma, \lambda Z_1) \prec (X, \lambda Z_0)\}.$$

(For $\lambda < 0$, $(X_\Gamma, \lambda Z_1) \prec (X, \lambda Z_0)$ means, per definition, that $(X_\Gamma, -\lambda Z_0) \prec (X, -\lambda Z_1)$, and for $\lambda = 0$ that $X_\Gamma \prec X$.)

In Section V we prove that for a simple system the entropy function is a once continuously differentiable function of the energy and the work coordinates. The convexity axiom A7, which leads to concavity of the entropy, and the axiom S2 (Lipschitz tangent planes) are essential here. We prove that the usual thermodynamic relations hold, in particular $T = (\partial S/\partial U)^{-1}$ *defines* the absolute temperature. Up to this point neither temperature nor hotness and coldness have actually been used. In this section we also prove (in Theorem 5.6) that the entropy for every simple system is uniquely determined, up to an affine change of scale, by the level sets of S and T, i.e., by the adiabats and isotherms regarded only as sets, and without numerical values.

In the final Section VI we discuss the problem of fixing the additive entropy constants when processes that change the system by mixing and chemical reactions are taken into account. We show that, even without making any assumptions about the existence of unrealistic semi-permeable membranes, it is always possible to fix the constants in such a way that the entropy remains additive, and never decreases under adiabatic processes. This is not quite the full entropy principle, since there could still be states with $X \prec\prec Y$, but $S(X) = S(Y)$. This abnormal possibility, however, is irrelevant in practice, and we give a necessary and sufficient condition for the situation to occur that seems to be realized in nature: The entropy of every substance is uniquely determined once an arbitrary entropy constant has been fixed for each of the chemical elements, and $X \prec\prec Y$ implies that $S(X) < S(Y)$.

After this summary of the logical structure of the paper we add some remarks on the relation of our treatment of the second law and more conventional formulations, e.g., the classical statements of Kelvin, Clausius and Carathéodory paraphrased in Sect. I.A. What immediately strikes the eye is that these classical formulations are *negative* statements: They claim that certain processes are *not* possible. Thus, the Clausius formulation essentially says that thermal contact leads to an irreversible process. On the other hand, what the founding fathers seem to have taken for granted, is that there also exist *reversible* processes. Thus the Clausius inequality, $\int \delta Q/T \leq 0$, which ostensibly follows from his version of the second law and is the starting point for most textbook discussions of entropy, does not by itself lead to an entropy function. What is needed in this formulation is the existence of reversible processes, where *equality* holds (or at least processes that approximate equality arbitrarily closely). One might even question the possibility of attaching a precise meaning to 'δQ' and 'T' for irreversible processes. (See, however, Eq. (5.8) and the discussion preceding it, where the symbols are given a precise meaning in a concrete situation.)

The basic question we set out to examine is this: Why can adiabatic processes within a system be exactly characterized by the increase (more precisely, non-decrease) of an additive entropy function? In Section II, where the comparison principle CH is *assumed*, an answer is already given: It is because all reasonable notions of adiabatic accessibility should satisfy axioms A1-A6, and these axioms, *together with CH*, are *equivalent* to the existence of an additive entropy function that characterizes the relation. This is expressed in Theorem 2.2. If we now look at axioms A1-A6 and the comparison principle we see that these are all *positive* statements about the relation $\prec$: They all say that certain elementary processes are *possible* (provided some other processes are possible), and none of them says that some processes are *impossible.* In particular, the trivial case, when everything is accessible form everything else, is not in conflict with A1-A6 and the comparison principle: It corresponds to a constant entropy.

From this point of view the existence of an entropy function is an issue that can, to a large extent, be discussed independently of the second law, as originally formulated by the founders (as given in Section I.A). *The existence of entropy has more to do with comparability of states and reversibility than with irreversibility.* In fact, one can conceive of mathematical examples of a relation $\prec$ that is characterized by a function S and satisfies A1-A6 and CH, but S is a constant in a whole neighbourhood of some points—and the Clausius inequality fails. Conversely, the example of the 'world of thermometers', discussed in Sect. IV. D and Fig. 7. is relevant in this context. Here the second law in the sense of Clausius holds, but the Clausius *equality* $\int \delta Q/T = 0$ cannot be achieved and there is no entropy that characterizes the relation for compound systems!

In our formulation the reversibility required for the definition of entropy is a consequence of the comparison principle and the stability axiom A3. (The latter allows us to treat reversible processes as limiting cases of irreversible processes, which are, strictly speaking the only processes realized in nature.) This is seen most directly in Lemma 2.3, which characterizes the entropy of a state in terms of adiabatic *equivalence* of this state with another state in a compound system. This lemma depends crucially on CH (for the compound system) and A3.

So one may ask what, in our formulation, corresponds to the negative statements in the classical versions of the second law. The answer is: It is axiom S1, which says that from every state of a simple system one can start an irreversible adiabatic process. In combination with A1-A6 and the convexity axiom A7, this is *equivalent* to Carathéodory's principle. Moreover, together with the other simple system axioms, in particular the assumption about the pressure, S2, it leads to Planck's principle, Theorem 3.4, which states the impossibility of extracting energy adiabatically from a simple system at fixed work coordinates. Hence, the entropy not only exists, but also *it is nowhere locally constant.* This additional property of entropy is a precise version of the classical statements of the second law. By contrast, an entropy having level sets like the temperature in Fig. 8 would allow the construction of a perpetual motion machine of the second kind.

It would be mistake, however, to underestimate the role played by the axioms other than S1. They are all part of the structure of thermodynamics as presented here, and conspire to produce an entropy function that separates precisely the possible from the impossible and has the convexity and regularity properties required in the practical application of thermodynamics .

LIST OF SYMBOLS

A. Some Standard Mathematical Symbols

$a \in A$ or $A \ni a$	means 'the point a is an element of the set A'.
$a \notin A$	means 'the point a is not an element of the set A'.
$A \subset B$ or $B \supset A$	means 'the set A is in the set B'.
$A \cap B$	is the set of objects that are in the set A and in the set B.
$A \cup B$	is the set of objects that are either in the set A or in the set B or in both sets.
$A \times B$	is the set consisting of pairs (a, b) with $a \in A$ and $b \in B$.
$\{a : P\}$	means the set of objects a having property P.
$a := b$ or $b =: a$	means 'the quantity a is defined by b'.
$P \Rightarrow Q$	means 'P implies Q'.
$\mathbf{R}^n$	is n-dimensional Euclidean space whose points are n-tuples $(x_1, ..., x_n)$ of real numbers.
[s, t]	means the closed interval $s \leq x \leq t$.
∂A	means the boundary of a set A.

B. Special Symbols

$X \prec Y$	('X precedes Y') means that the state Y is adiabatically accessible from the state X.	(Sect. II.A.2)
$X \not\prec Y$	('X does not precede Y') means that Y is *not* adiabatically accessible from X.	(Sect. II.A.2)
$X \prec\prec Y$	('X strictly precedes Y') means that Y is adiabatically accessible from X, but X is not accessible from Y.	(Sect. II.A.2)
$X \overset{A}{\sim} Y$	('X is adiabatically equivalent to Y') means that $X \prec Y$ *and* $Y \prec X$.	(Sect. II.A.2)
$X \overset{T}{\sim} Y$	means that the states X and Y are in thermal equilibrium.	(Sect. IV.A)
A_X	the 'forward sector' of a state $X \in \Gamma$, i.e., $\{Y \in \Gamma : X \prec Y\}$.	(Sect. II.F)
tX	a copy of the state X, but scaled by a factor t.	(Sect. II.A.1)
$\Gamma^{(t)}$	the state space consisting of scaled states tX, with $X \in \Gamma$.	(Sect. II.A.1)
$tX + (1-t)Y$	a convex combination of states X and Y in a state space with a convex structure.	(Sect. II.F)
$\Sigma(X_0, X_1)$	the 'strip' $\{X \in \Gamma : X_0 \prec X \prec X_1\}$ between the adiabats through X_0 and $X_1 \in \Gamma$, $X_0 \prec X_1$.	(Sect. II.D)
ρ_X	the projection of ∂A_X onto the space of work coordinates, for X in the state space of a simple system $\Gamma \subset \mathbf{R}^{n+1}$, i.e., $\rho_X = \{V \in \mathbf{R}^n : (U, V) \in \partial A_X \text{ for some } U \in \mathbf{R}\}$.	(Sect. III.C)
ρ	the projection onto the space of work coordinates of a simple system Γ, i.e., if $X = (U, V) \in \Gamma$, then $\rho(X) = V$.	(Sect. IV.A)

INDEX OF TECHNICAL TERMS

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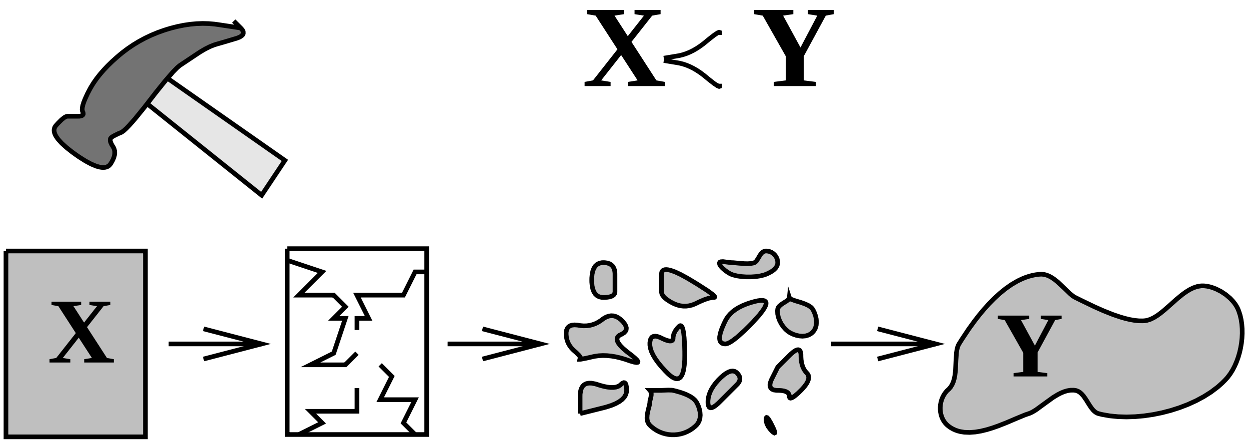

Figure 1. An example of a violent adiabatic process. The system in an equilibrium state X is transformed by mechanical means to another equilibrium state Y.

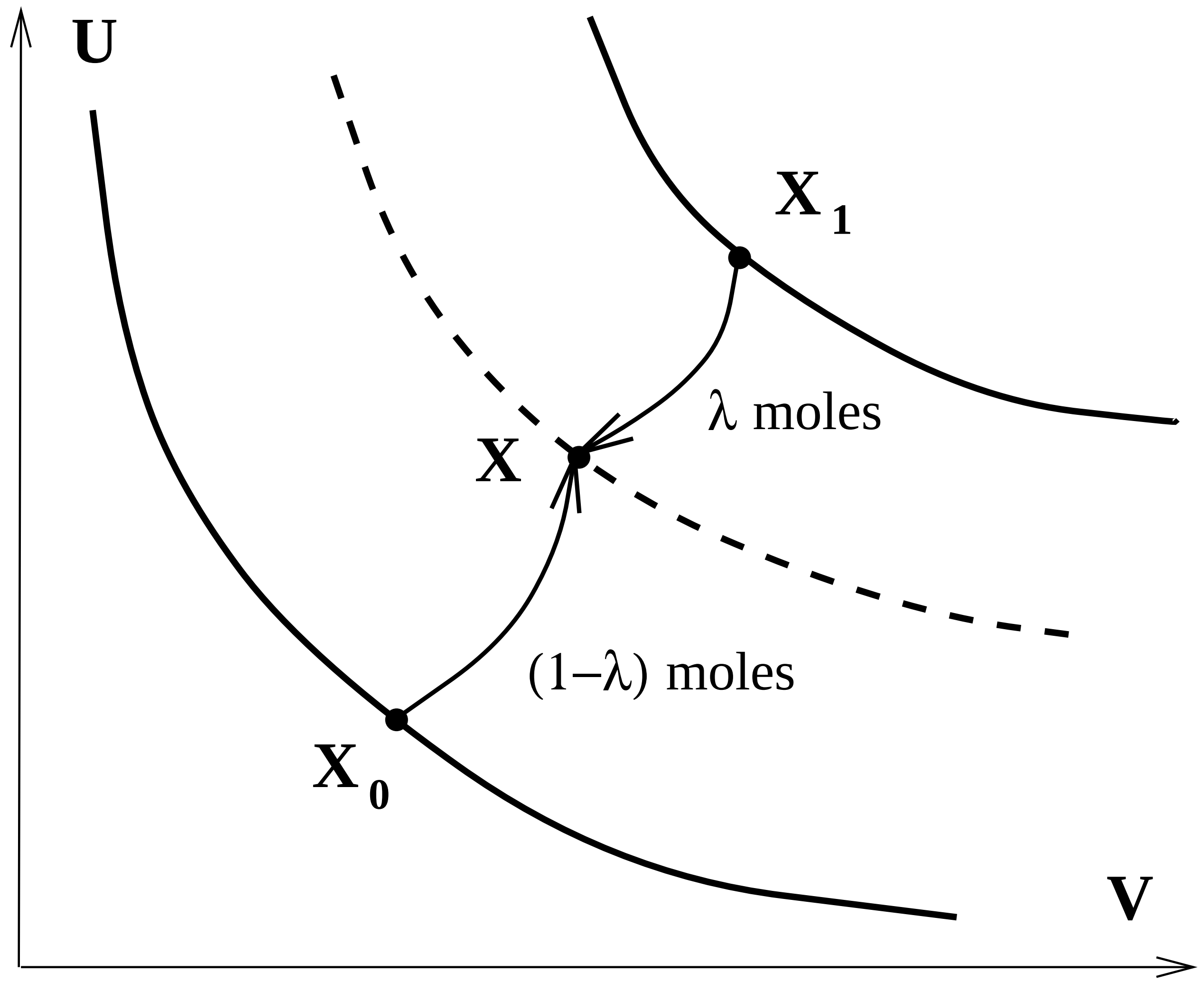

Figure 2. The entropy of a state X is determined, according to formula 2.14, by the amount of substance in state X_1 that can be transformed to X with the aid of a complementary amount of substance in the state X_0.

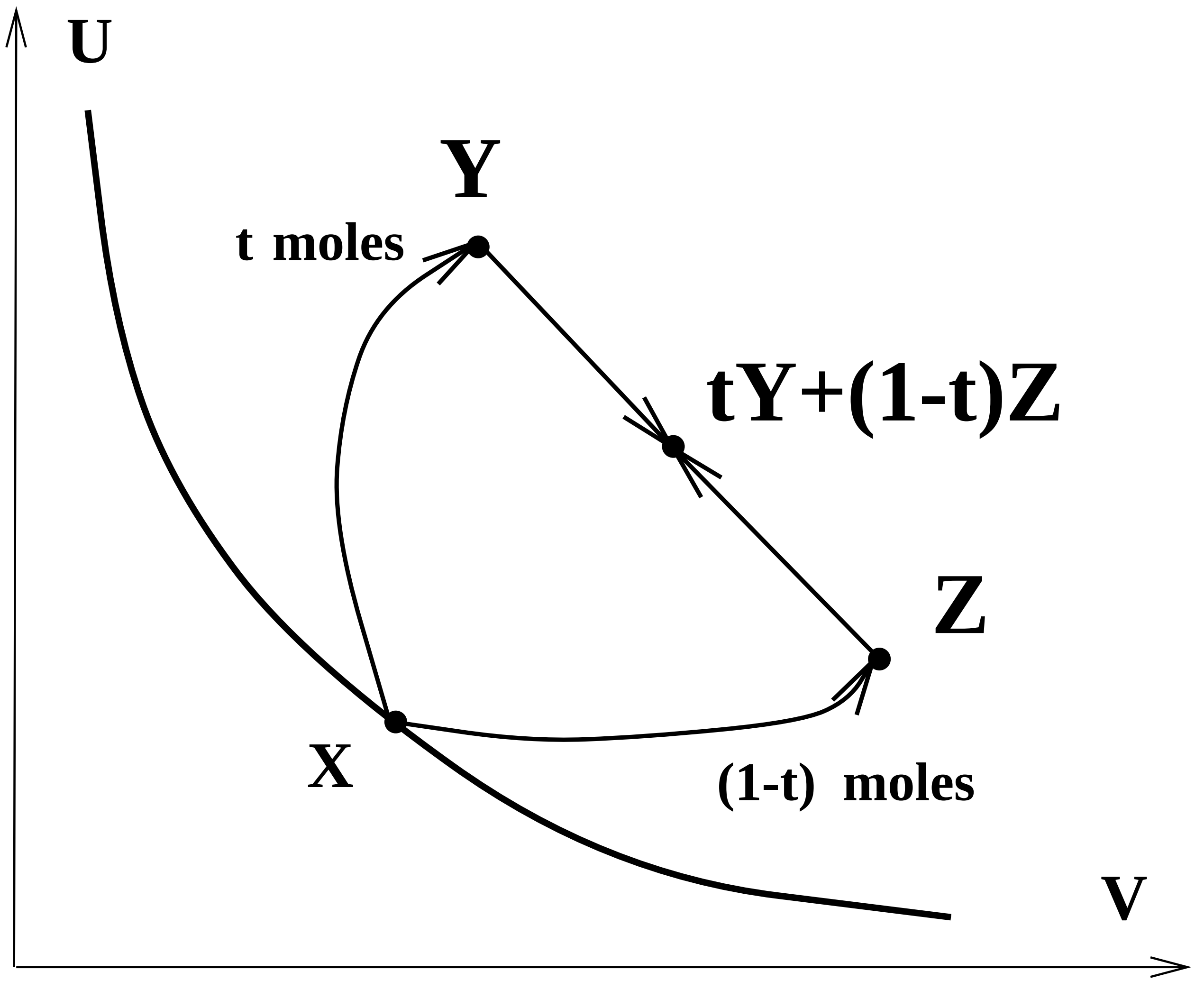

Figure 3. This illustrates axiom A7 and Theorem 2.6 which says that if states Y and Z can be reached adiabatically from a state X and if the state space has a convex structure then convex combinations of Y and Z are also in the forward sector of X.

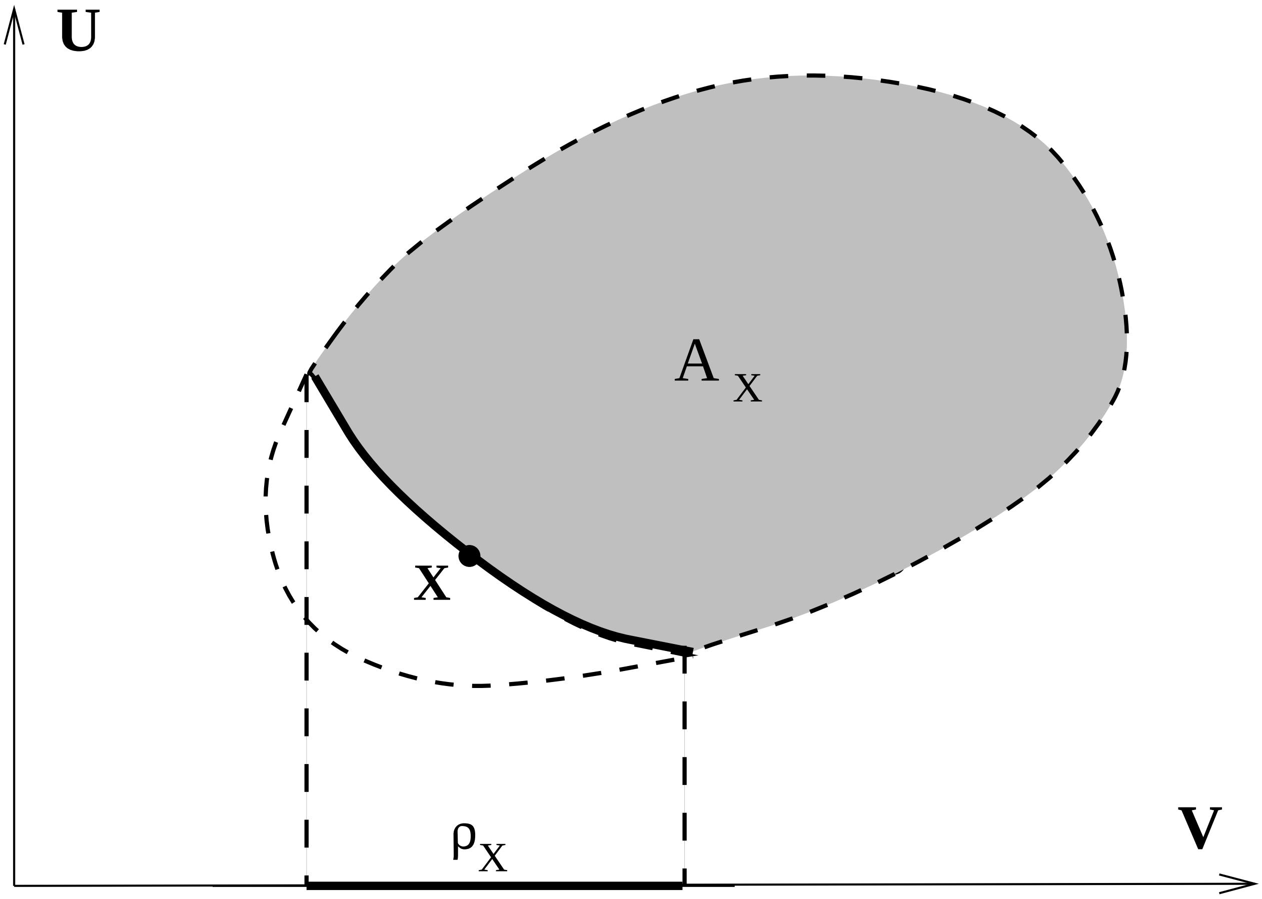

Figure 4. This illustrates the energy U and work coordinates V of a simple system. The state space (dashed line) is always a convex set and the forward sector A_X of any point X is always a convex subset of the state space. The heavy dark curve denotes the boundary ∂A_X of A_X and consists of points that are adiabatically equivalent to X (as Theorem 3.7 states). The projection of this boundary on the work coordinates is ρ_X which can be strictly smaller than the projection of A_X.

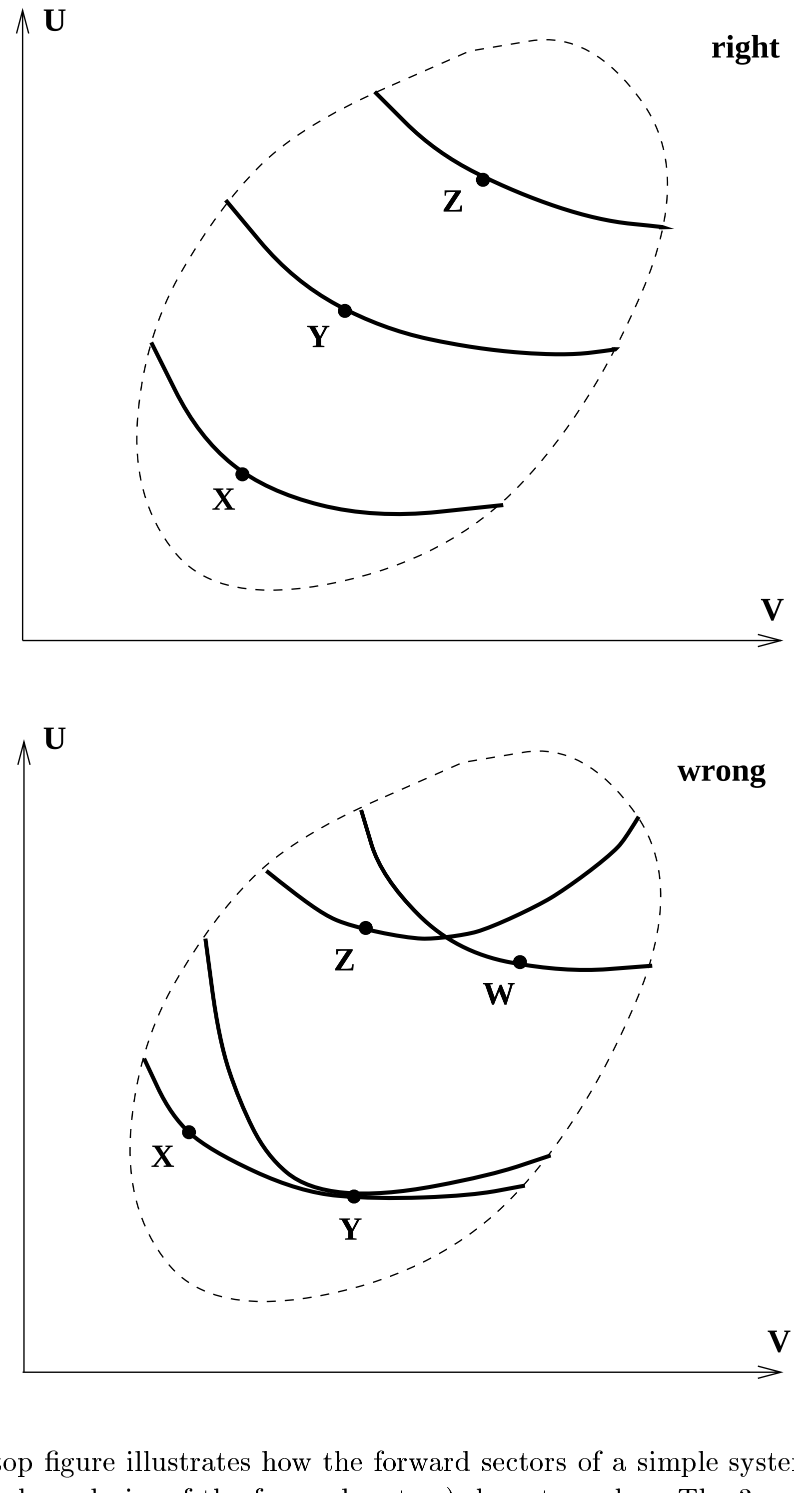

Figure 5. The top figure illustrates how the forward sectors of a simple system are nested. The adiabats (i.e., the boundaries of the forward sectors) do not overlap. The 3 points are related by $X \prec\prec Y \prec\prec Z$. The lower figure shows what, in principle, could go wrong—but doesn't, according to Theorem 3.7. The top pair of adiabats have a point in common but neither $W \prec Z$ nor $Z \prec W$ holds. The bottom pair is a bit more subtle; $X \prec Y$ and Y is on the boundary of the forward sector of X, but X is not in the forward sector of Y.

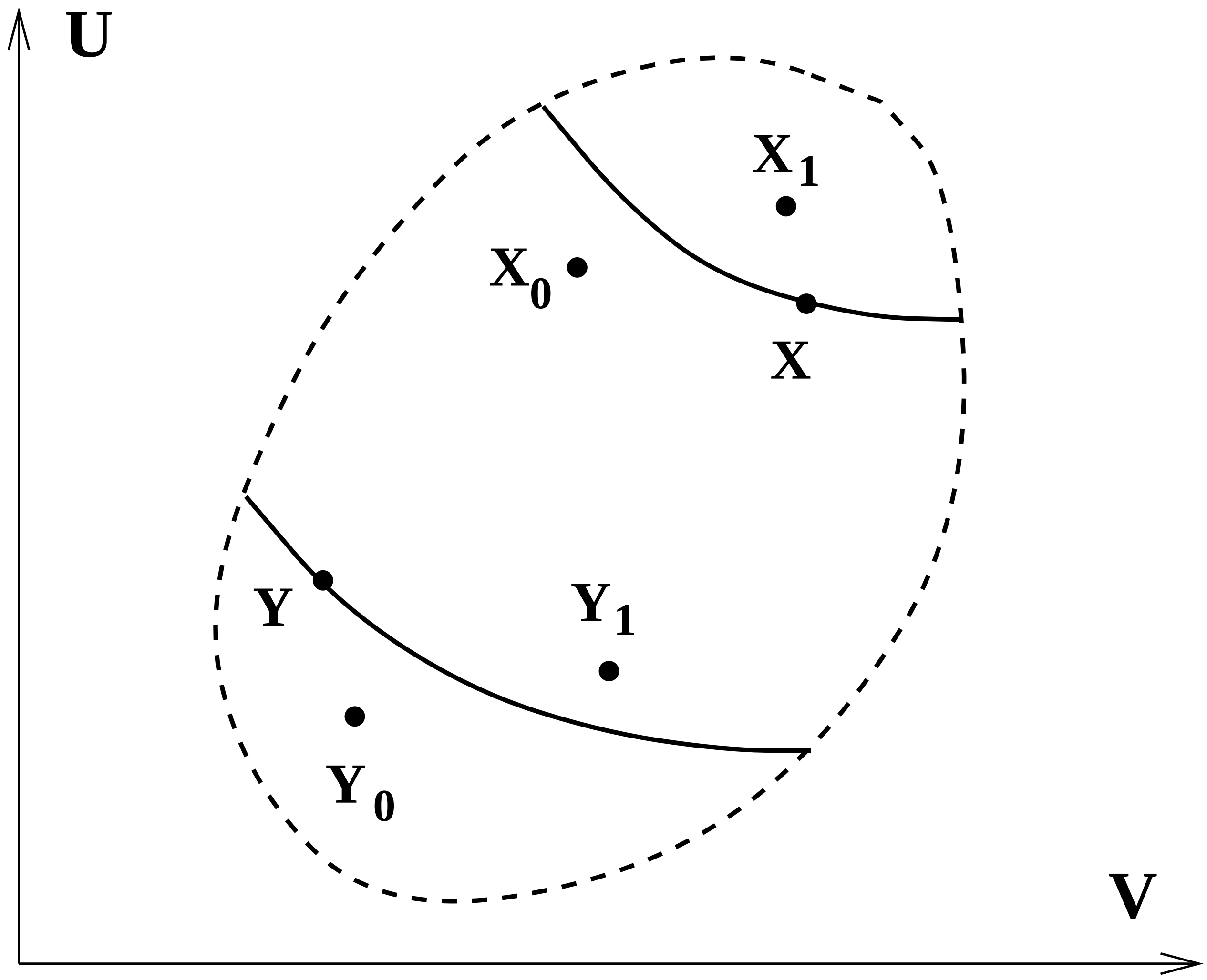

Figure 6. This illustrates the transversality axiom T4. For every state X there are points X_0 and X_1 on both sides of the adiabat through X that are in thermal equilibrium with each other. The points Y_0 and Y_1 (corresponding to some other point Y) need not be in thermal equilibrium with X_0 and X_1.

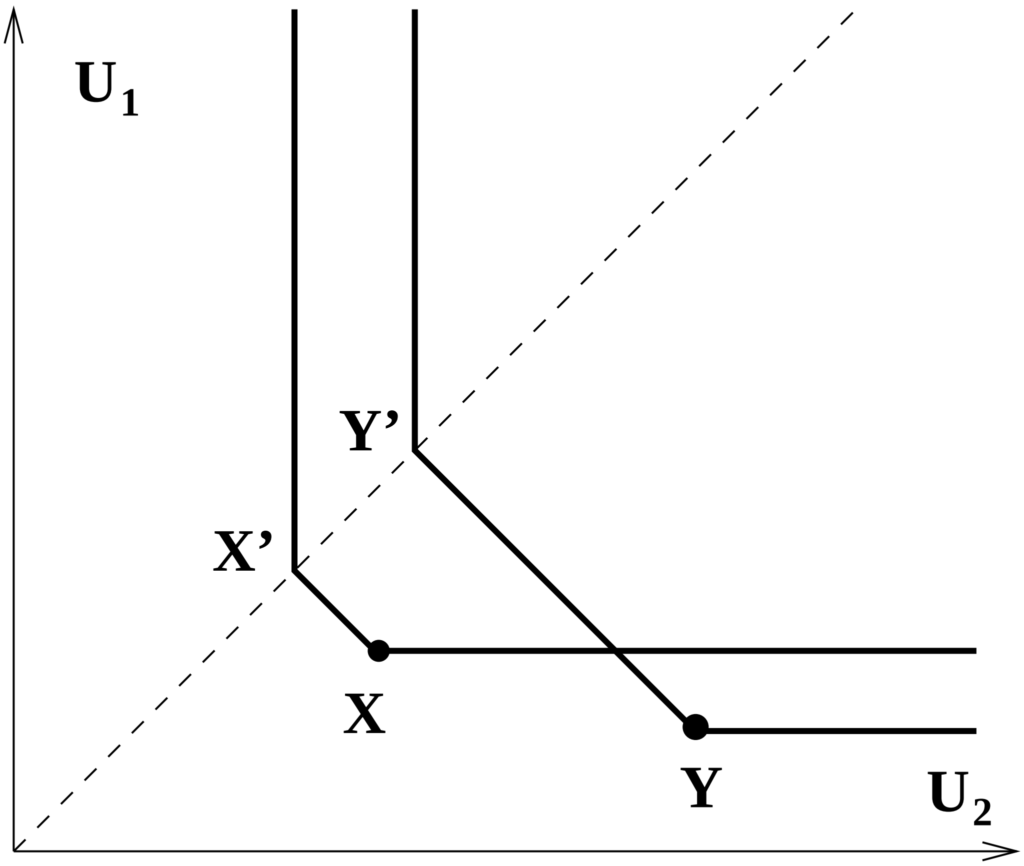

Figure 7. This shows the state space of two 'thermometers', which means that there are only energy coordinates. The forward sectors of X and Y are shown under the assumption that the only allowed adiabatic operations are thermal equilibration (which moves X to X' and Y to Y') and rubbing (which increases, but never decreases the energy). We see clearly that these sectors are not nested (i.e., one does not lie inside the other), as they are for compounds of simple systems, satisfying the transversality axiom T4.

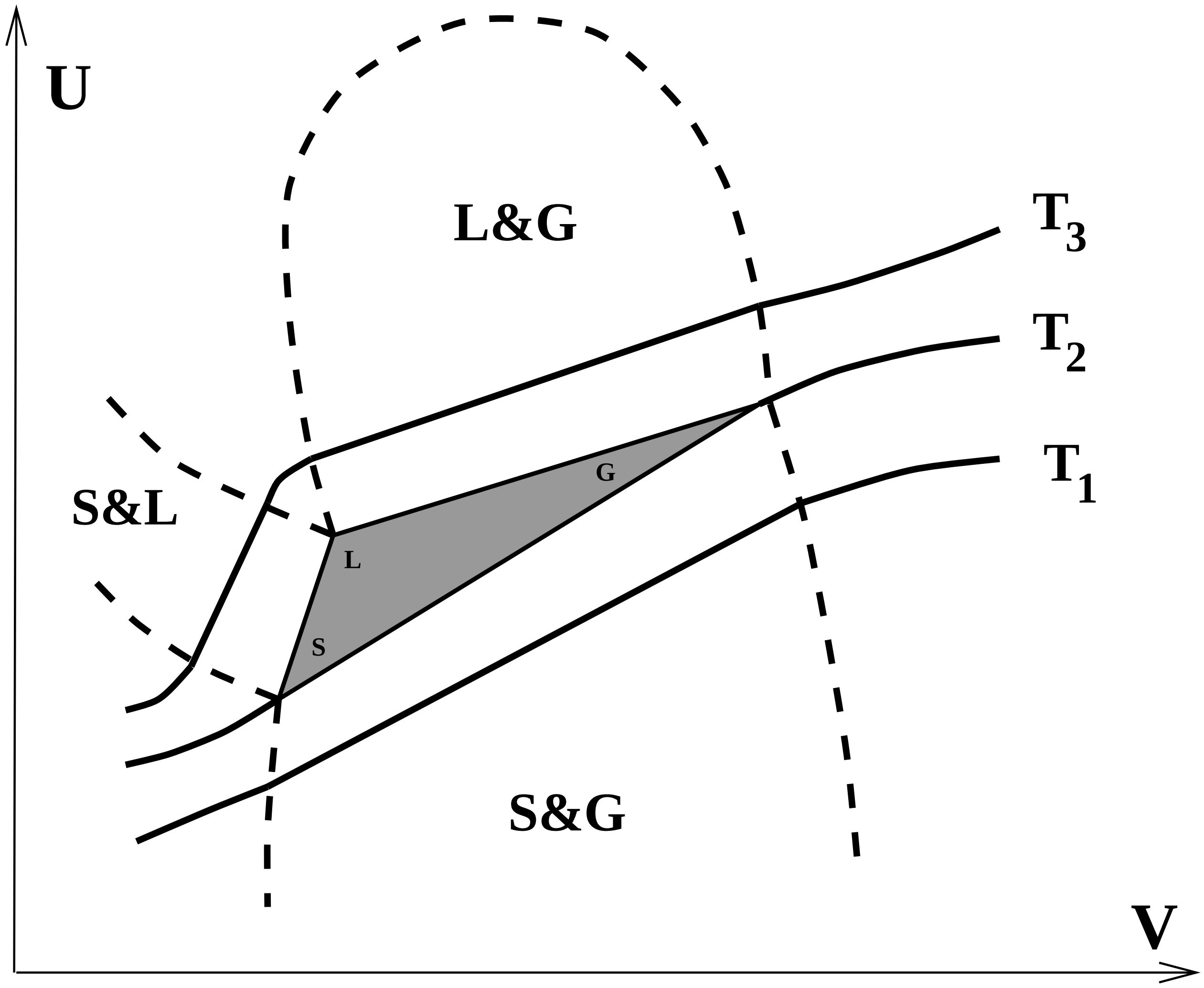

Figure 8. This shows isotherms in the (U, V) plane near the triple point of a simple system. If one substituted pressure or temperature for U or V as a coordinate then the full two-dimensional region would be compressed into a one-dimensional region. In the triple point region the temperature is constant, which shows that isotherms need not be one-dimensional curves.