

Composite System Approach to Thermodynamic Stability

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The theory of thermodynamic stability is worked out in terms of composite systems starting from basic principles formulated partially in operational language. In this connection a macroscopic ordering concept is introduced, and entropy is characterized as numerical measure for the degree of disorder. Various aspects of thermodynamic stability are investigated in operational and analytical terms laying special emphasis on appropriate neighbourhood sets. Some implications of metastability and neutral stability for the thermodynamic system concept are pursued.

1. Introduction

The general theory of thermodynamic equilibrium is due to Gibbs [1], who founded his classical investigations on the following principle: “For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.” In spite of the enormous fruitfulness of the theory which Gibbs developed from this axiom the literal formulation of the principle itself is unclear to the point of being paradoxical [2]: If an isolated thermodynamic system is not in equilibrium we cannot assign any definite value of the entropy to it (in the realm of equilibrium thermodynamics), and if the system is in equilibrium then the entropy cannot vary. In the subsequent efforts to clarify the concepts in Gibbs’ principle, many authors made use of the notion of “virtual states” the considered system should take on. Eventually it turned out, however, that normal equilibrium states are perfectly suited if one does not vary over the original state space but over that of a more complex system, which in many cases is to be chosen as a decomposition of the original system into two subsystems (confer e.g. [3], [4], [5], [6]). In [2] and [6] one finds not only a detailed exposition of this composite system approach to thermodynamic stability — as well as historical remarks —, but also the interesting observation that this approach gives fundamental importance to the so-called thermodynamic operations which consist of the composition or decomposition of thermodynamic systems or the imposture or relaxation of a constraint. These operative devices had not been incorporated into the

formalized structure of the theory hitherto, but, of course, were used implicitly. Indeed, if the most fundamental principle of the theory requires for its selfconsistent explication the transition from the considered system to more constrained ones, then this comparison of different systems — made from one and the same material body — must represent for itself most fundamental structural features. We have interpreted this comparison as the essential part of a macroscopic ordering concept, which after some supplements is to be considered as the basic operative structure of the entropy observable.

In a separate work the formal elaboration of this idea is carried through. One starts with the implicit definition of the thermodynamic operations and defines then a (quasi) ordering (representing physical disorder) with these concepts as a mathematical relation in the set of all system-states under consideration. This relation is then shown to have the structure of an extensive empirical observable and is identified with the entropy observable. With such an approach the entropy is characterized by an ordering structure in the sense of fundamental measurement, that means that in principle it may be measured without recourse to other observables introduced previously as, e.g., heat and absolute temperature.

This kind of approach is only *described* in Sect. 2 of the present paper. Nevertheless, it provides the possibility to connect entropy with operational and ordering concepts in the subsequent reasonings and to clarify therewith some points otherwise not being accessible.

Since entropy is by the way of its introduction a numerical measure for the macroscopic disorder, a so-called order homomorphism, Gibbs’ fundamental maximum principle of entropy can be derived — if some additional properties of the compared system-states are valid. This refinement, which also reveals

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new aspects of the notion of thermodynamic stability, is investigated in Section 3. The stability condition is there formulated in the vein of the composite system approach but uses only the formalized symbols for thermodynamic operations. This language also enables us to work out a suitable concept of a thermodynamic system. After having postulated only local thermodynamic stability a system concept emerges with a single-valued entropy fundamental function certainly, but with also the possibility of constitutional changes by means of unstable relaxations.

In Sect. 4 the analytical formulations of thermodynamic stability conditions are derived, and special emphasis is laid on the topology of appropriate domains in the state spaces of extensive as well as of density variables over which a system is stable. These investigations serve to discuss the physical consequences of special types of stability over bounded regions of states.

Some implications of metastability and neutral stability are investigated in Chapter 5, others will be given on another occasion.

Let us add a word on the relationship between a purely phenomenological exposition of stability and the maximum principle of entropy as given here, and a statistical foundation of these structures as treated in [7]. Since the statistical mechanical theory leads to usual thermodynamic laws only after some peculiar idealizations it is indispensable to formulate the theory to be derived as concise as possible. We find it very satisfying that our basic operational notions appear in a natural reformulation also in a statistical theory and we hope that this connection will lead to some clarifications in the old problem of founding thermodynamics on a statistical-microscopic theory.

2. Basic Assumptions

The set of assumptions presented in this Section is meant to describe (implicitly) the most characteristic features of thermodynamic systems with the exception of the third law. It is, however, not a coherent axiomatic scheme, and critical comments will be given at the appropriate places. Anyhow, it is a concise formulation of the properties we shall use to derive further statements on the considered systems. One more assumption will be formulated in Section 3.

The collection of physical systems Σ which concern us here will be denoted by \mathcal{B} . Every $\Sigma \in \mathcal{B}$, called “thermodynamic system”, assumes states Z in a certain set \mathcal{C}_Σ , and we write $\langle \Sigma, Z \rangle$ to indicate that Σ is in the state Z . The use of the system-state pair $\langle \Sigma, Z \rangle$, sometimes shortened by a single symbol like P , enables us to replace Z by a tuple of state variables (see below) without losing the detachedness to a specific system Σ . As basic set for the various relations to be introduced in the sequel, which in general relate system-states of different systems with each other, we consider

$$\mathcal{P} := \bigcup_{\Sigma \in \mathcal{B}} \bigcup_{Z \in \mathcal{C}_\Sigma} \{ \langle \Sigma, Z \rangle \}. \quad (2.1)$$

The starting point of our approach is the characterization of states by means of extensive observables. Here we understand by an extensive observable on \mathcal{P} the following structure.

2.1. Definition. An extensive observable F on \mathcal{P} consists of a family $\{F_a; a \in A\}$ of (empirically determinable) state functions

$$F_a: \mathcal{C}_\Sigma \rightarrow \mathbb{R}, \quad a \in A_\Sigma \subset A,$$

where $A = \bigcup_{\Sigma \in \mathcal{B}} A_\Sigma$. Every non-empty A_Σ contains a special subset E_Σ so that A_Σ is isomorphic to the set of all subsets of E_Σ : $A_\Sigma \ni a \leftrightarrow E_a \subset E_\Sigma$, and it holds

$$F_a = \sum_{a' \in E_a} F_{a'}.$$

For $a \in A_\Sigma$ F_a is called an observable of the kind F of Σ , for $a \in E_\Sigma$ (i.e. $a \leftrightarrow \{a\}$) F_a is an elementary observable of the kind F of Σ . For $a \leftrightarrow E_\Sigma$ F_a is called the total observable of the kind F of Σ .

Let be given $\Sigma_1, \Sigma_2 \in \mathcal{B}$ and $a_1 \in A_{\Sigma_1}$ and $a_2 \in A_{\Sigma_2}$. Then the composed system $\Sigma = (\Sigma_1, \Sigma_2)$ (cf. (III.1) below) has at least the following observables of the kind F : F_{a_1} , F_{a_2} and $F_a = F_{a_1} + F_{a_2}$, where $E_a = E_{a_1} \cup E_{a_2}$. This makes the extensivity property of F explicit. A more detailed exposition of the empirical structure of extensive observables will be given on another occasion.

We are now ready to formulate our basic assumptions which will be grouped together by means of roman numerals*.

(I) State variables

(I.1) There exists a distinguished set $\{F_\varrho; 1 \leq \varrho \leq r\}$ of extensive observables F_ϱ on \mathcal{P} , so

* The content of an assumption (I.i) extends from (I.i) up to the next break.

that $A_\varrho \neq \emptyset$ for all $1 \leq \varrho \leq r$. F_1 is the energy and $A_{1\mathbf{r}} \neq \emptyset$ for all $\Sigma \in \mathcal{B}$. F_2, \dots, F_σ , $2 \leq \sigma < r$, are various kinds of work (or deformation) coordinates.

The energy observables are often denoted by U_a , the work observables by $A_{\varrho a}$, $2 \leq \varrho \leq \sigma$. The observables $F_{\varrho a}$, $a \in A_{\varrho\Sigma}$, are called the inhibited extensive observables of Σ .

(I.2) For every $\Sigma \in \mathcal{B}$ exists a fixed (but not unique) set of elementary extensive observables F^m , $1 \leq m \leq n$, where $F^m \in F_\varrho$ for some ϱ , so that the states $Z \in \mathcal{C}_\Sigma$ are in one-to-one correspondence with the n -tuples $(Z^1, \dots, Z^n) := (F^1(Z), \dots, F^n(Z))$.

The $F^1 \dots F^n$ are called the state variables of Σ . We shall identify Z with the n -tuple (Z^1, \dots, Z^n) .

2.2. *Definition.* $\Sigma \in \mathcal{B}$ is called a work system if all its state variables can be chosen as work observables. The set of all work systems will be denoted by \mathcal{B}_W . $\mathcal{B}_T := \mathcal{B} \setminus \mathcal{B}_W$ is called the set of proper thermodynamic systems.

(I.3) \mathcal{B}_W is a non-trivial subset of \mathcal{B} .

We stipulate throughout the paper that the state variables are to be chosen to include as few energy observables as possible. So will be the state variables of a work system in fact work coordinates.

(I.4) The state variables of a proper thermodynamic system include at least one energy observable.

(I.5) The set of all state tuples of $\Sigma \in \mathcal{B}_T$ constitute a cone in \mathbb{R}^n .

The set of all state tuples of Σ will again be denoted by \mathcal{C}_Σ .

Observe that (I.4) implies the possibility of heat contact for proper thermodynamic systems, the energy being independent of all other (macroscopic) state variables.

We denote by \mathcal{B}_c the set of systems in \mathcal{B} which have at least two state variables of the same kind and write \mathcal{B}_s for $\mathcal{B} \setminus \mathcal{B}_c$. The systems in \mathcal{B}_s are called "simple" (or "totally reduced"), those in \mathcal{B}_c are called "complex". We index here and in other cases the subset of \mathcal{P} in the same manner as the corresponding subsets of \mathcal{B} . So we write

$$\mathcal{P}_c := \bigcup_{\Sigma \in \mathcal{B}_c} \bigcup_{Z \in \mathcal{C}_\Sigma} \{ \langle \Sigma, Z \rangle \} \quad (2.2)$$

and the like for \mathcal{P}_s , \mathcal{P}_T , \mathcal{P}_W etc.; \mathcal{P}_Σ is given by

$$\bigcup_{Z \in \mathcal{C}_\Sigma} \{ \langle \Sigma, Z \rangle \}.$$

(II) Thermodynamic operations

(II.1) Composition of systems. For every $\Sigma_1, \Sigma_2 \in \mathcal{B}$ there exists the "composite system" $(\Sigma_1, \Sigma_2) \in \mathcal{B}$ with

$$\mathcal{C}_{(\Sigma_1, \Sigma_2)} = \mathcal{C}_{\Sigma_1} \times \mathcal{C}_{\Sigma_2}. \quad (2.3)$$

The system composition is associative.

For system-states $P \in \mathcal{P}_{(\Sigma_1, \Sigma_2)}$ we write

$$P = \langle (\Sigma_1, \Sigma_2), (Z_1, Z_2) \rangle =: (P_1, P_2) \quad (2.4)$$

where

$$P_i := \langle \Sigma_i, Z_i \rangle, \quad i = 1, 2.$$

The intuitive meaning of (Σ_1, Σ_2) is the combination of Σ_1 and Σ_2 without interaction.

(II.2) Relaxation of a constraint. There exists a relation $* R \subset \mathcal{P} \times \mathcal{P}$ with domain \mathcal{P}_c and range \mathcal{P} . Let be Σ not of the form $\Sigma = (\Sigma_T, \Sigma_W)$, $\Sigma_T \in \mathcal{B}_T$, $\Sigma_W \in \mathcal{B}_W$. Then $\langle \Sigma, Z \rangle R \langle \Sigma', Z' \rangle$ shall imply the following connection between the state tuples: There are components Z^i, Z^j of Z belonging to state variables of the same kind, so that Z' has one component $Z^i + Z^j$ whereas the remaining components of Z' are equal to the Z^m of Z , $m \neq i, j$. If

$$\langle \Sigma, Z \rangle = \langle (\Sigma_T, \Sigma_W), (Z_T, Z_W) \rangle$$

then $\langle \Sigma, Z \rangle R \langle \Sigma', Z' \rangle$ implies either the afore mentioned connection between Z and Z' , where the affected coordinates Z^i and Z^j are not work coordinates of the same kind in Z_T and Z_W respectively, or the following possibility may occur: In the transition from Z to Z' a pair of work coordinates A^i of Z_T and A^m of Z_W is replaced by $A^i + A^m$ and an elementary energy U^i of Z_T is substituted by a not uniquely determined $U^{i'}$, energy conservation for Σ being presupposed; the remaining components of Z reappear unaltered in Z' .

In (II.2) we have introduced a global relaxation relation which may be considered as the union of more specified relaxation relations depending on the coordinates which they affect. One convinces oneself that our definition of R implies conservation of all total observables in the transition from $\langle \Sigma, Z \rangle$

* A relation X is a set of ordered pairs. For $(a, b) \in X$ we write also aXb . The domain $\mathcal{D}(X)$ is the set $\{a; aXb \text{ for some } b\}$, the range $\mathcal{R}(X)$ is $\{b; aXb \text{ for some } a\}$. $aX^{-1}b \Leftrightarrow bXa$; $(a, b) \in X_1 \circ X_2 \Leftrightarrow \exists c \text{ with } (a, c) \in X_1 \text{ and } (c, b) \in X_2$. $X_1 \subset X_2$ and $X_1 \cup X_2$ are defined as in set theory. The diagonal relation $\Delta(A)$ of a set A is $\{(a, a); a \in A\}$.

to $\langle \Sigma', Z' \rangle$. Σ' is in any case different from Σ , because the number of its state variables is one less than that of Σ . And in general there cannot be said more about the relationship between Σ and Σ' .

The intuitive meaning of the R -operation is the removal of an internal constraint of a closed system Σ , which allows for the exchange of a pair of extensive variables which were inhibited in Σ . The physical realization of such an internal constraint — in the form of a wall or the like — as well as the process of its removal is assumed not to be of energetical significance in comparison to the energies of the systems. The realization of certain R -operations may well be complicated to achieve, since the invariance of some state variables in connection with the variability of other ones may be a difficult task. In this connection let us emphasize two points:

(1) A relation like the R -operation only sets up a relationship between the initial and the final system-state and does not imply any restrictions for what happens during the concrete transition. (So closedness of the system may temporarily be given up in the concretization of an R -relation.)

(2) A relation which is elementary in the logical sense must not necessarily be simple in the practical realization.

(II.3) Reversible inhibition. There exists a relation $I \subset \mathcal{P} \times \mathcal{P}$ with $I \subset R^{-1}$ which has the domain \mathcal{P} and the range strictly smaller than \mathcal{P}_c .

By definition $\langle \Sigma', Z' \rangle I \langle \Sigma, Z \rangle$ implies $\langle \Sigma, Z \rangle R \langle \Sigma', Z' \rangle$, and we have the same connections between Z and Z' as specified in (II.2).

The intuitive meaning of I is the imposture of an internal constraint in a specific way, namely so as not to disturb internal equilibrium. This intended meaning of I is not formalized by Assumption (II.3) alone, but would require additional postulates on the compatibility between R and I and the like, which will not be given here (cf. [8]). In the present formulation the meaning of I emerges from the summed up Assumption (III) below. Here it may suffice as motivation to introduce I as basic operational concept that one can give relatively simple practical criteria which decide over the validity of I .

Having accepted the relations R and I as fundamental notions one is able to define a macroscopic ordering structure.

2.3. Definition. (i) For $P, P' \in \mathcal{P}$ we write

$$P \triangleleft P' \quad (2.5)$$

and say “ P' is more disordered than P ”, if there are system-states $P_0 \in \mathcal{P}_T$, $Q, Q' \in \mathcal{P}_{\Sigma_w}$ and a product $\Pi(R, I)$ containing finitely many relations R and I in arbitrary order, so that

$$(P, P_0, Q) \Pi(R, I) (P', P_0, Q') \quad (2.6)$$

is valid; the case that $\Pi(R, I)$ is an empty product shall be included into (2.6) and shall then be interpreted as the diagonal relation $\Delta(\mathcal{P})$ for the composite system-states framing the relation symbol.

(ii) We write

$$P \sim P' \quad (2.7)$$

and say that P and P' are “order equivalent”, if

$$P \triangleleft P' \quad \text{and} \quad P' \triangleleft P \quad (2.8)$$

are valid.

The relation \triangleleft is reflexive and transitive as follows easily from the definition and the fact, that the composition of two work-systems is again a work-system. Such a relation is called “quasi-ordering” (in [9] it is called “transition relation”), and it differs from a (partial) ordering by the lack of the property $\triangleleft \cap \triangleright = \Delta(\mathcal{P})$; that is: order equivalence does not imply equality.

The intuitive meaning of (2.6) is an active formulation of “adiabatic enclosure”, since we do not describe the properties of the *walls* which separate an adiabatically closed system from the surroundings but list up the operations on the system which are still possible for a system-state $P = \langle \Sigma, Z \rangle$ under adiabatic enclosure and which bring it to the system-state $P' = \langle \Sigma', Z' \rangle$. The possibilities incorporated into (2.6) are: finitely many internal relaxations of constraints, reversible inhibitions, and work contacts, where an arbitrary system-state P_0 may be taken under the adiabatic enclosure if it remains unchanged in the sense that its final form is the same as the initial one.

A satisfying feature of this active operational approach is the interpretability of the adiabatic enclosure relation \triangleleft as an intuitive appealing physical disorder concept in purely macroscopic terms. It will first probably be accepted that one and the same material body (observe that the total mass is conserved in (2.6)) is in a more disordered

constitution (described by a system-state), if it has less internal constraints which keep up differences in the intensive variables, and that reversible inhibitions do not change the degree of disorder. As for the work contacts the same intuitive disorder concept may be applied to the internal degrees of freedom of a proper thermodynamic system not showing up in the state coordinates. They must exist, since the energy of such a system can be varied independently from all other macroscopic state variables. These internal degrees of freedom cannot be inhibited by the coarse work coordinates. Thus a work contact can only increase (or maintain) the degree of disorder. Let us stress, that the latter considerations on the internal degrees of freedom serve only for motivational purposes whereas the formalized disorder concept makes solely use of macroscopic observables.

The most interesting point is now, that the quasi-ordering \triangleleft gives rise to an empirical, extensive observable as formulated in [9]. That means that the structural properties of \triangleleft give itself a prescription how to associate a (rational) number for the degree of order and the scale is unique up to positive dilatations and translations (cf. [8]). By extrapolation one gets in this manner a continuous entropy function which measures the macroscopic disorder. We cannot present here this reasoning in its full extent but summarize the resulting properties of the thus obtained entropy observable in form of assumptions.

(III) Entropy

(III.1) There is an order homomorphic mapping

$$S: \mathcal{P} \rightarrow \mathbb{R}_+ \quad (2.9)$$

i.e.

$$P \triangleleft P' \Rightarrow S(P) \leq S(P'). \quad (2.10)$$

The value

$$S(P) = S(\langle \Sigma, Z \rangle) = S_{\Sigma}(Z) \quad (2.11)$$

is called the entropy of $\langle \Sigma, Z \rangle$. For fixed Σ the mapping

$$S_{\Sigma}: \mathcal{C}_{\Sigma} \rightarrow \mathbb{R}_+ \quad (2.12)$$

given by (2.11) is called the entropy fundamental function of Σ . S_{Σ} is assumed to be continuously differentiable and positive homogeneous of degree one.

(III.2) If

$$\langle \Sigma, Z \rangle = \langle (\Sigma_1, \Sigma_2), (Z_1, Z_2) \rangle$$

then

$$S_{\Sigma}(Z) = S_{\Sigma_1}(Z_1) + S_{\Sigma_2}(Z_2). \quad (2.13)$$

(III.3) Let $Z, Z' \in \mathcal{C}_{\Sigma}$ have the same values for all total observables different from energies and work coordinates. Then

$$S_{\Sigma}(Z) \leq S_{\Sigma}(Z') \Rightarrow \langle \Sigma, Z \rangle \triangleleft \langle \Sigma, Z' \rangle. \quad (2.14)$$

In spite of this scheme of assumptions (I)–(III) being not yet completed it is elucidating to inquire already at this stage about the traditional laws of thermodynamics. The first law is incorporated in the assumptions (I) on the state variables: One may deduce from (I) that there exists a total energy observable for every system which depends on the states alone and that this energy may be varied in a form different from work for every proper thermodynamic system. As for the second law, one thinks of (2.10) as its adequate expression, since it tells us that the entropy always increases for an adiabatic transition. However, this is only justified by the inclusion of a lot of other assumptions. So it is above all essential that the \triangleleft -relation is non-trivial in the sense that there are pairs of system-states which are in \triangleleft -relation only in the one direction and not in the other, a fact which follows from the domain assumption for I . Secondly it is of course important that the quantity which increases during an adiabatic state variation, is an extensive observable, depending on the states alone. Since these supplements have also to be added to the usual formulation of the second law, we shall in fact identify it with the order homomorphism (2.10).

The zeroth law would follow from the maximum principle of entropy, which would at the same time provide the introduction of the intensive contact observables; but this principle is not yet incorporated into the formalism and requires extra assumptions which will be discussed in the next section. So one has a clear distinction between order homomorphism and the maximum principle of entropy.

3. Operational Formulation of Stability

In this section we shall lay emphasize on those stability statements which are connected with the

thermodynamic operations. So let us consider a relaxation relation of the form

$$\langle \Sigma', Z' \rangle R \langle \Sigma, Z \rangle \quad (3.1)$$

described in Assumption (II.2). According to (II.2) there is only specified a connection between Z' and Z but not between Σ' and Σ . And this cannot, in fact, be done generally, because a relaxation of a constraint may initiate a radical change of the constitution of the physical system. What we have in mind is not the trivial change connected with the decrease of the number of state variables. Beside that there may occur changes in the systemic constitution which cannot be restored by the imposture of a reversible constraint. The relaxation of an inhibition may trigger very powerful physical processes. In the mildest form there may happen phase transitions in the usual sense or material mixing processes. But there may also take place particle reactions of increasing energy transfer, that is chemical, nuclear and elementary particle processes which may lead to new features of the involved systems, which could not be made out in the inhibited constitution. To understand this right one should remember that a frequent form of an inhibition is the spacial separation of the subsystems. One may advocate a less restrictive concept of a thermodynamic system than we use here (here one system has one entropy fundamental function with a fixed set of state variables), it remains nevertheless a special property of a relaxation (3.1), if there exists a simple connection between the initial and the final systems.

3.1. Definition. A relaxation of the form (3.1) is called stable, if there is a $Z_0' \in \mathcal{C}_{\Sigma'}$, with

$$\langle \Sigma, Z \rangle I \langle \Sigma', Z_0' \rangle. \quad (3.2)$$

For a stable relaxation there is thus the possibility of regaining system-states of the initial system by the mere imposture of a reversible inhibition. This should be viewed as a peculiarity of both systems participating in the relaxation. The definition implies that one stable relaxation leads in general to a whole variety of stable relaxations with the same final system-state. So are with (3.1) all relaxations of the form

$$\langle \Sigma', Z^* \rangle R \langle \Sigma, Z \rangle$$

stable, since (3.2) is not affected by those operations which lead to $\langle \Sigma, Z \rangle$.

We have now worked out in an operational manner two concepts, namely order homomorphy and stability of a relaxation, which in combination lead to an explication of Gibbs' maximum principle of entropy with purely thermostatic notions.

3.2. Theorem (Maximum principle of entropy). For given $\langle \Sigma, Z \rangle \in \mathcal{P}$ and $\Sigma' \in \mathcal{B}$ define a subset $\mathcal{D}_{\Sigma'}(Z) \subset \mathcal{C}_{\Sigma'}$ by the relation

$$\mathcal{D}_{\Sigma'}(Z) \ni Z' \Leftrightarrow \langle \Sigma', Z' \rangle R \langle \Sigma, Z \rangle \quad (3.3)$$

and assume all these relaxations to be stable. Then it holds

$$S_{\Sigma}(Z) = \max S_{\Sigma'}(Z'), \quad Z' \in \mathcal{D}_{\Sigma'}(Z). \quad (3.4)$$

Proof. Because of stability of the relaxations (3.3) there is a $Z_0' \in \mathcal{C}_{\Sigma'}$ with

$$\langle \Sigma, Z \rangle I \langle \Sigma', Z_0' \rangle. \quad (3.5)$$

Since $I \subset R^{-1}$ it follows

$$Z_0' \in \mathcal{D}_{\Sigma'}(Z). \quad (3.6)$$

Order homomorphy leads from (3.3) to

$$S_{\Sigma'}(Z') \leq S_{\Sigma}(Z) \quad (3.7)$$

and from (3.5) to

$$S_{\Sigma}(Z) = S_{\Sigma'}(Z_0'). \quad (3.8)$$

Combination of (3.6), (3.7) and (3.8) gives (3.4). \square

Why may we consider Theorem 3.2 as a reformulation of Gibbs' maximum principle of entropy as cited in the introduction? That our reformulation as a theorem has another logical status than a principle does not affect its content but only its connection to other parts of the theoretical formalism. We found it indeed very elucidating to divide the maximum principle into the two mentioned parts. As for the content one sees that in contradistinction to Gibbs' statement the domain of variation in (3.4) is clearly specified and consists of usual equilibrium states. But it is a domain of a thermodynamic system different from the original one, a fact which hardly can be avoided in the realm of equilibrium thermodynamics. If one accepts this method of varying states then one could, of course, proceed to more complex partitioned systems with still more internal variables to vary. The reason to choose the special form (3.4) is simply that all more complicated variation methods can be reduced (locally but not globally) to the given one. This is in principle — but not in all details — a well

known manner of stating the maximum principle of entropy in a definitive language. Our approach has beside that revealed the following points:

(1) The existence of a nontrivial domain of variation in the entropy maximum principle is the consequence of a special connection between some system-states of the two systems involved: they are connected by means of stable relaxations.

(2) The entropy maximum principle does not cover the full content of the second law, since the latter implies, e.g., order homomorphy (\equiv increase of entropy) also in the case of unstable relaxations.

Let us now turn to the notion of thermodynamic stability which is usually formulated by means of a given entropy fundamental function and should also in our operative language refer to one and the same system. For this we replace Σ' by (Σ, Σ) in Def. 3.1 and consider a connection between the system-states in form of a product of relaxations:

$$\langle(\Sigma, \Sigma), (Z_1, Z_2)\rangle R^n \langle\Sigma, Z_1 + Z_2\rangle. \quad (3.9)$$

Relation (3.9) expresses again a special property of all system-states showing up there, and this even more if all relaxations involved are stable. If we shift emphasis to the right hand side we arrive at the following definition:

3.3. Definition. For given $\langle\Sigma, Z\rangle \in \mathcal{P}$ let $\mathcal{D}(Z) \subset \mathcal{C}_\Sigma$ denote a set of state tuples with

$$Z_1 \in \mathcal{D}(Z) \Rightarrow Z - Z_1 \in \mathcal{D}(Z), \quad (3.10a)$$

and

$$\{Z'; Z' = \lambda Z, \lambda \in (0, 1)\} \subset \mathcal{D}(Z). \quad (3.10b)$$

We call $\langle\Sigma, Z\rangle$ stable over $\mathcal{D}(Z)$ if there is a $Z_1^0 \in \mathcal{D}(Z)$ so that

$$\langle(\Sigma, \Sigma), (Z_1, Z - Z_1)\rangle R^n \langle\Sigma, Z\rangle \quad (3.11a)$$

and

$$\langle\Sigma, Z\rangle I^n \langle(\Sigma, \Sigma), (Z_1^0, Z - Z_1^0)\rangle \quad (3.11b)$$

is valid for all $Z_1 \in \mathcal{D}(Z)$.

Observe that we did not assume that the value Z_1^0 of the equilibrium decomposition is unique. Let be in fact $Z_1^* := \lambda Z$, $\lambda \in (0, 1)$. Then $Z_1^* \in \mathcal{D}(Z)$ and

$$\langle(\Sigma, \Sigma), (Z_1^*, Z - Z_1^*)\rangle R^n \langle\Sigma, Z\rangle. \quad (*)$$

On the other hand, homogeneity of S_Σ and (3.11b) imply

$$\begin{aligned} S_\Sigma(Z_1^*) + S_\Sigma(Z - Z_1^*) \\ = S_\Sigma(Z_1^0) + S_\Sigma(Z - Z_1^0). \end{aligned}$$

In virtue of the assumption (III.3) we have then

$$\begin{aligned} \langle(\Sigma, \Sigma); (Z_1^*, Z - Z_1^*)\rangle \\ \sim \langle(\Sigma, \Sigma); (Z_1^0, Z - Z_1^0)\rangle \sim \langle\Sigma, Z\rangle. \quad (**) \end{aligned}$$

By means of a lemma of [8] one concludes from (*) and (**) that

$$\langle\Sigma, Z\rangle I^n \langle(\Sigma, \Sigma), (Z_1^*, Z - Z_1^*)\rangle.$$

Thus all homogeneous partitions of $\langle\Sigma, Z\rangle$ are achieved by means of reversible inhibitions.

Definition 3.3 contains two different aspects of stability, both of which are tested by splitting $\langle\Sigma, Z\rangle$ into a composite system. The one we have stressed here is that of constitutional stability which prevents a radical systemic transformation after relaxations of constraints. The other more usual one concerns this approach to equilibrium which is given by the combination of (3.11a) and (3.11b): A “disturbed state” $\langle(\Sigma, \Sigma), (Z_1, Z - Z_1)\rangle$ tends back to the stable “configuration”

$$\langle(\Sigma, \Sigma), (Z_1^0, Z - Z_1^0)\rangle$$

in a certain region of disturbances $\mathcal{D}(Z)$. The size of $\mathcal{D}(Z)$ is in both regards a measure for the degree of stability.

3.4. Definition. $\langle\Sigma, Z\rangle$ is called globally stable if it is stable over

$$\mathcal{D}_\Sigma(Z) := \mathcal{C}_\Sigma \cap (Z - \mathcal{C}_\Sigma), \quad (3.12)$$

and locally stable if it is stable over the intersection of some n -dimensionally open decomposition region $\mathcal{D}(Z)$ with $\mathcal{D}_\Sigma(Z)$.

Before stipulating the kind of stability which is generally to be expected for thermodynamic systems we discuss some consequences of local (and not global) stability.

3.5. Proposition. Let $\langle\Sigma, Z\rangle$ be locally stable over $\mathcal{D}(Z)$, and define

$$\mathcal{D}'(Z) := \mathcal{D}_\Sigma(Z) \setminus \mathcal{D}(Z) \neq \emptyset. \quad (3.13)$$

Then there exists for every $Z_1^\alpha \in \mathcal{D}'(Z)$ a thermodynamic system Σ_α such that

$$(i) \quad \langle(\Sigma, \Sigma), (Z_1^\alpha, Z - Z_1^\alpha)\rangle R^n \langle\Sigma_\alpha, Z\rangle \quad (3.14)$$

and

$$(ii) \quad S_\Sigma(Z) < S_{\Sigma_\alpha}(Z). \quad (3.15)$$

Proof. (i) The existence of a system Σ_α can, of course, be deduced only from existence assumptions put into the formalism previously, which here is

done via the domain assumptions for $R, Z_1^\alpha \in \mathcal{D}'(Z)$ makes (3.11) invalid. (3.11 b) being independent of the value of Z_1 one has to modify (3.11 a). By assumption is $Z_1^\alpha \in \mathcal{C}_\Sigma$ and can thus be assumed of Σ . Since $(Z_1^\alpha, Z - Z_1^\alpha)$ has at least n pairs of components of the same kind one sees that

$$\langle (\Sigma, \Sigma), (Z_1^\alpha, Z - Z_1^\alpha) \rangle$$

is in the domain of R^n and must have a partner $\langle \Sigma_\alpha, Z \rangle$. The only way to break (3.11 a) is then $\Sigma_\alpha \neq \Sigma$.

(ii) Assume now

$$S_\Sigma(Z_1^\alpha) + S_\Sigma(Z - Z_1^\alpha) \leq S_\Sigma(Z), \quad (3.16)$$

for $Z_1^\alpha \in \mathcal{D}'(Z)$. Because of local stability there is a $Z_1^0 \in \mathcal{D}(Z)$ with

$$\begin{aligned} S_\Sigma(Z_1^\alpha) + S_\Sigma(Z - Z_1^\alpha) \\ \leq S_\Sigma(Z_1^0) + S_\Sigma(Z - Z_1^0). \end{aligned} \quad (3.17)$$

By Assumption (III.3) we have then

$$\begin{aligned} \langle (\Sigma, \Sigma), (Z_1^\alpha, Z - Z_1^\alpha) \rangle \\ \triangleleft \langle (\Sigma, \Sigma), (Z_1^0, Z - Z_1^0) \rangle \end{aligned} \quad (3.18)$$

and by (3.11 b)

$$\langle (\Sigma, \Sigma), (Z_1^0, Z - Z_1^0) \rangle \sim \langle \Sigma, Z \rangle \quad (3.19)$$

which together gives

$$\begin{aligned} P^\alpha &:= \langle (\Sigma, \Sigma), (Z_1^\alpha, Z - Z_1^\alpha) \rangle \\ &\triangleleft \langle \Sigma, Z \rangle =: P. \end{aligned} \quad (3.20)$$

The explicit meaning of (3.20) is

$$(P^\alpha, P_0, Q') \Pi(R, I)(P, P_0, Q) \quad (3.21)$$

for some $P_0 \in \mathcal{P}$, a pair $Q', Q \in \mathcal{P}_{\Sigma_W}$, and some product $\Pi(R, I)$. Since evidently all total observables are conserved in (3.20), no work can be exchanged between (Σ, Σ) and Σ_W and we have $Q' = Q$. A careful analysis of the combinatorial rules for R and I — outside the scope of this presentation — shows, that

$$P^\alpha R^n P$$

can be derived from (3.21). This would, however, contradict our assumption $Z_1^\alpha \in \mathcal{D}'(Z)$. Thus (3.16) must be replaced by its negation

$$S_\Sigma(Z) < S_\Sigma(Z_1^\alpha) + S_\Sigma(Z - Z_1^\alpha). \quad (3.22)$$

Combination of (3.22) with (3.14) and order homomorphism lead to (3.15). \square

In general there cannot be said anything about the relationship between the Σ_α and Σ and between

the Σ_α amongst each other. This generality is obviously too wide for a definite theory. On the other hand the restriction of the thermodynamic formalism to globally stable states only would exclude, e.g., the fruitful treatment of metastability by equilibrium thermodynamics. We, therefore, choose the middle road by making the following assumption.

(IV) Local stability

Every $\langle \Sigma, Z \rangle \in \mathcal{P}$ is locally stable in the sense of Definition 3.4.

Let us indicate some immediate consequences of (IV). First, Σ_α of (3.14) has to be locally independent of Z_1^α , which leads to an agreeable structure for the formation of new thermodynamic systems. Second, we may deduce that every $\langle \Sigma, Z \rangle$ is the outcome of a family of stable relaxations. Remembering the definition of a product of relations, (3.11 a) and (3.11 b) are equivalent with

$$\begin{aligned} \langle (\Sigma, \Sigma), (Z_1, Z - Z_1) \rangle \\ \cdot R^{n-1} \langle \Sigma', Z' \rangle R \langle \Sigma, Z \rangle \end{aligned} \quad (3.23)$$

and

$$\begin{aligned} \langle \Sigma, Z \rangle I \langle \Sigma', Z_0' \rangle \\ \cdot I^{n-1} \langle (\Sigma, \Sigma), (Z_1^0, Z - Z_1^0) \rangle \end{aligned} \quad (3.24)$$

respectively. So, for all $\langle \Sigma', Z' \rangle$ which may appear in (3.23) if Z_1 varies in the n -dimensionally open region $\mathcal{D}(Z)$, the last step in (3.23) constitutes a stable relaxation. Applying the maximum principle of entropy to this set of relaxations, one obtains from the necessary conditions a characterization of the internal equilibrium by the equality of a pair of intensive parameters. This being mentioned to underline the importance of local stability.

Let us conclude our operative discussion of stability by the symbolic description of what happens in a spontaneous transition from the locally stable system-state $\langle \Sigma, Z \rangle$ to the more disordered configuration $\langle \Sigma_\alpha, Z \rangle$ predicted in Proposition 3.5. Since the state variables have the same values in both system-states, the increase in disorder cannot be due to a work contact or to direct internal relaxations of constraints. The chain of configurations the closed system has to go through may be written as

$$\begin{aligned} \langle \Sigma, Z \rangle (R^{-1})^n \langle (\Sigma, \Sigma), (Z_1', Z - Z_1') \rangle \\ \cdot R^n \langle \Sigma_\alpha, Z \rangle \end{aligned} \quad (3.25)$$

where $Z_1' \in \mathcal{D}'(Z)$, the domain with greater density differences between the subsystems (cf. (3.13)). The crucial step is the first relation in (3.25), considered as a spontaneous decomposition of $\langle \Sigma, Z \rangle$ into subsystems with unequal densities. (Usually the R^{-1} -relation is interpreted as the effect of external manipulations.) In a quasi-static realization of this decomposition, the state tuple of the first subsystem had to vary from the equilibrium value Z_1^0 through neighbouring values Z_1 to the more distant Z_1' . The transition $Z_1^0 \rightarrow Z_1$ is connected with a decrease of entropy, whereas $Z_1 \rightarrow Z_1'$ is accompanied by an increase of entropy. The first step is prevented by the second law and the second step by a gap in the state space, as is shown in Section 5. Thus the first part of (3.25) can only be accomplished, if at all, in one single non-equilibrium transition, and this in general not for the whole system but in subsequent processes for small parts of the system. That is, we have to rescale (3.25) to a lower size. A more refined discussion of such phenomena requires of course analytical methods.

4. Analytical Formulation of Stability

We investigate now the consequences of local stability for the entropy fundamental function and stress the topological properties of a suitable decomposition region $\mathcal{D}(Z)$ which will always be assumed to contain all $Z_1 = \lambda Z$, $\lambda \in (0, 1)$, and to satisfy

$$Z_1 \in \mathcal{D}(Z) \Rightarrow Z - Z_1 \in \mathcal{D}(Z). \quad (4.1)$$

4.1. Definition. An entropy fundamental function S_Z is said to satisfy stability at Z over $\mathcal{D}(Z) \subset \mathcal{C}_Z$, if

$$S_Z(Z) = \max_{Z_1 \in \mathcal{D}(Z)} [S_Z(Z_1) + S_Z(Z - Z_1)]. \quad (4.2)$$

In virtue of Assumption (IV) for every $\langle \Sigma, Z \rangle \in \mathcal{P}$ there must exist an appropriate n -dimensional $\mathcal{D}(Z) \subset \mathcal{C}_Z$, so that (4.2) is valid. This is an easy consequence of order homomorphy. On the other hand does (4.2) not imply (3.11) without Assumption (IV). For, if $Z_1^0 \in \mathcal{D}(Z)$ is the maximizing decomposition coordinate tuple, then

$$S_Z(Z) = S_Z(Z_1^0) + S_Z(Z - Z_1^0) \quad (4.3)$$

does strictly speaking not imply the operational relation

$$\langle \Sigma, Z \rangle I^n \langle (\Sigma, \Sigma), (Z_1^0, Z - Z_1^0) \rangle \quad (4.4)$$

by means of (I)–(III) alone. It is, however, interesting that

$$\begin{aligned} & S_Z(Z_1) + S_Z(Z - Z_1) \\ & \leq S_Z(Z_1^0) + S_Z(Z - Z_1^0), \quad \forall Z_1 \in \mathcal{D}(Z) \end{aligned} \quad (4.5)$$

gives because of (III.3)

$$\begin{aligned} & \langle (\Sigma, \Sigma), (Z_1, Z - Z_1) \rangle \\ & \triangleleft \langle (\Sigma, \Sigma), (Z_1^0, Z - Z_1^0) \rangle. \end{aligned} \quad (4.6)$$

And this would lead to

$$\langle (\Sigma, \Sigma), (Z_1, Z - Z_1) \rangle R^n \langle \Sigma, Z \rangle \quad (4.7)$$

if (4.4) would be available. So, only with Assumption (IV), which provides (4.4), Eq. (4.2) is equivalent with (3.11).

We consider here (4.2), however, as a purely analytical property of the function S_Z and admit also decomposition regions $\mathcal{D}(Z)$ of smaller dimensionality m than the dimension n of \mathcal{C}_Z . Because of homogeneity stability of S_Z at Z over $\mathcal{D}(Z)$ induces stability at λZ over $\lambda \mathcal{D}(Z)$ for all $\lambda > 0$. This redundancy and a certain clumsiness of (4.2) may be avoided by using density variables. In order to pass freely from extensive state variables to density coordinates and vice versa, some geometrical properties must be shown of $\mathcal{D}(Z)$. We elaborate this point carefully, because some analytical statements in the density picture lead only to physical statements if they can be retranslated into the language of extensive variables.

Homogeneity is the reason that every positive state variable can be used as “size variable” which characterizes the largeness of the system. (One may thus, e.g., use the energy of a subsystem as size observable for the composite system.) We assume w.r.i.g. that Z^n is the size variable and define for $Z \in \mathcal{C}_Z$ the $(n-1)$ -tuple of density coordinates by

$$z := (Z^1/Z^n, \dots, Z^{n-1}/Z^n). \quad (4.8)$$

We write also

$$Z = Z^n(z, 1). \quad (4.9)$$

Introducing for all $\lambda \in \mathbb{R}$ the hyperplanes

$$\mathcal{H}_\lambda^n := \{Z; z \in \mathbb{R}^{n-1}, Z^n = \lambda\}, \quad (4.10)$$

we define the crossections of $\mathcal{D}(Z)$ as

$$\begin{aligned} \mathcal{D}_\lambda(Z) &:= \mathcal{D}(Z) \cap \mathcal{H}_\lambda^n \\ &=: \lambda(\mathcal{D}_\lambda, 1), \quad \lambda \in \mathbb{R}, \end{aligned} \quad (4.11)$$

where by definition

$$\mathcal{D}_\lambda := \{z; z \in \mathbb{R}^{n-1}, \lambda(z, 1) \in \mathcal{D}_\lambda(Z)\}. \quad (4.12)$$

We assume throughout the paper that $\mathcal{D}(Z)$ is not contained in \mathcal{H}_0^n . If then $\mathcal{D}(Z)$ is an m -dimen-

sionally open set, then \mathcal{Q}_λ is $(m-1)$ -dimensionally open, the empty set being so by definition. Relation (4.1) is valid, iff

$$\begin{aligned} z_1 \in \mathcal{Q}_\lambda &\Leftrightarrow z + \frac{\lambda}{Z^n - \lambda} (z - z_1) \\ &=: z_2 \in \mathcal{Q}_{(Z^n - \lambda)} \end{aligned} \quad (4.13)$$

for all $\lambda \in (0, Z^n)$. Whenever convenient we replace λ by

$$\kappa := \lambda/Z^n. \quad (4.14)$$

The specific entropy is given by

$$s_Z(z) := S_Z(Z)/Z^n = S_Z(z, 1). \quad (4.15)$$

4.2. Proposition. S_Z is stable at Z over $\mathcal{D}(Z)$, iff

$$s_Z(z) = \max_{z_1 \in \mathcal{Q}_\kappa} [\kappa s_Z(z_1) + (1 - \kappa) s_Z(z_2)] \quad (4.16)$$

for all $\kappa \in (0, \frac{1}{2}]$, where $\mathcal{Q}_\kappa \equiv \mathcal{Q}_{(\kappa Z^n)}$ is given by (4.12), and where

$$z_2 = z + \frac{\kappa}{1 - \kappa} (z - z_1) =: z_2(\kappa, z_1). \quad (4.17)$$

Proof. Since

$$\mathcal{D}(Z) = \bigcup_{\lambda \in (0, Z^n)} \mathcal{D}_\lambda(Z). \quad (4.18)$$

Equation (4.2) is equivalent to

$$\begin{aligned} S_Z(Z) &= \max [S_Z(Z_1) + S_Z(Z - Z_1)] \\ Z_1 &\in \mathcal{D}_\lambda(Z), \quad \forall \lambda \in (0, Z^n/2]. \end{aligned} \quad (4.19)$$

Dividing (4.19) by Z^n gives (4.16). \square

Since (4.16) is not changed if we replace Z and $\mathcal{D}(Z)$ by βZ and $\beta \mathcal{D}(Z)$, $\beta > 0$, the dilation degeneracy is removed. On the other hand a whole family of regions is now involved instead of a single one. A simplification is only possible for special decomposition regions.

4.3. Definition. A decomposition region $\mathcal{D}(Z)$ will be called simple, if it has the form

$$\mathcal{D}(Z) = \mathcal{C} \cap (Z - \mathcal{C}), \quad (4.20)$$

where \mathcal{C} is an m -dimensionally open cone with a bounded cross section circled around z , i.e.

$$\mathcal{C} = \{Z; Z = \lambda(z', 1), \lambda > 0, z' \in \mathcal{Q}(z)\} \quad (4.21)$$

and the $(m-1)$ -dimensionally open region $\mathcal{Q}(z)$ satisfies

$$z' \in \mathcal{Q}(z) \Rightarrow z' + \varepsilon(z - z') \in \mathcal{Q}(z) \quad (4.22)$$

for all $\varepsilon \in [0, 1]$.

In this case the regions \mathcal{Q}_κ in (4.16) can be obtained from $\mathcal{Q}(z)$.

4.4. Lemma. Let be $\mathcal{D}(Z)$ a simple decomposition region with $\mathcal{Q}(z)$ as in (4.21) and \mathcal{Q}_κ , $\kappa \in (0, \frac{1}{2}]$, its cross sections according to (4.12). Then the following relations are valid.

(i) For $\kappa \in (0, \frac{1}{2}]$ holds

$$\mathcal{Q}_\kappa = \{z_1; z_1 \in \mathcal{Q}(z) \text{ and } z_2(\kappa, z_1) \in \mathcal{Q}(z)\} \quad (4.23)$$

(cf. (4.17)).

(ii) For $\kappa < \kappa'$ holds

$$\mathcal{Q}_{\kappa'} \subset \mathcal{Q}_\kappa. \quad (4.24)$$

(iii) $\exists \kappa_0 \in (0, \frac{1}{2}]$ with $0 < \kappa \leq \kappa_0$ implies

$$\mathcal{Q}_\kappa = \mathcal{Q}(z) \quad (4.25)$$

and $\kappa_0 < \kappa \leq \frac{1}{2}$ implies

$$\mathcal{Q}_\kappa \neq \mathcal{Q}(z).$$

(iv) $\kappa_0 = \frac{1}{2}$, iff

$$z_1 \in \mathcal{Q}(z) \Rightarrow z_2 = 2z - z_1 \in \mathcal{Q}(z). \quad (4.26)$$

(v) $\mathcal{D}(Z) \cap \mathcal{H}_\lambda^n = \lambda(\mathcal{Q}(z), 1)$

$$(4.27)$$

for all $0 < \lambda \leq \kappa_0 Z^n$.

Proof. (i) $Z_1 \in \mathcal{D}_\lambda(Z)$ for $\lambda \in (0, Z^n/2]$, iff

$$Z_1^n = \lambda \text{ and } Z_1 \in \mathcal{C} \text{ and } Z - Z_1 \in \mathcal{C}. \quad (4.28)$$

The first two properties in (4.28) lead to $Z_1 = \lambda(z_1, 1)$, $z_1 \in \mathcal{Q}(z)$, the last one gives

$$Z_2 = Z - Z_1 = (Z^n - \lambda)(z_2, 1)$$

where

$$\begin{aligned} z_2 &= z_2(\kappa, z_1) \\ &= z + \frac{\kappa}{1 - \kappa} (z - z_1) \in \mathcal{Q}(z). \end{aligned} \quad (4.29)$$

Since the argumentation can easily be reversed, $z_1, z_2(\kappa, z_1) \in \mathcal{Q}(z)$ is necessary and sufficient for $z_1 \in \mathcal{Q}_\kappa$ (where again $\lambda = \kappa Z^n$).

(ii) Because $\mathcal{Q}(z)$ is circled around z Eq. (4.29) implies

$$z_2(\kappa', z_1) \in \mathcal{Q}(z) \quad \text{for all } 0 < \kappa' \leq \kappa. \quad (4.30)$$

This proves (4.24).

(iii) Define for all z_1 in the closure $\bar{\mathcal{Q}}(z)$ of $\mathcal{Q}(z)$

$$\kappa_0(z_1) := \sup \{\kappa; \kappa \in (0, \frac{1}{2}], z_2(\kappa, z_1) \in \mathcal{Q}(z)\}. \quad (4.31)$$

$\kappa_0(z_1) > 0$ for all $z_1 \in \bar{\mathcal{Q}}(z)$ since $\mathcal{Q}(z)$ is $(m-1)$ -dimensionally open, and decrease of κ diminishes the Euclidean distance $\|z - z_2\|$, so that z_2 enters finally $\mathcal{Q}(z)$ for $\kappa > 0$.

Define furthermore

$$\kappa_0 := \inf \kappa_0(z_1), \quad z_1 \in \bar{\mathcal{Q}}(z) \quad (4.32)$$

which is greater zero, $\bar{\mathcal{Q}}(z)$ being compact. We observe that the infimum in (4.32) is not assumed in $\mathcal{Q}(z)$ since for a given $z_1 \in \mathcal{Q}(z)$ there is always an z_1' on the line determined by z and z_1 for which

$$\kappa_0(z_1') < \kappa_0(z_1)$$

is valid. Therefore $\kappa \leq \kappa_0$ implies

$$\kappa < \kappa_0(z_1) \quad \text{for all } z_1 \in \mathcal{Q}(z)$$

which gives

$$z_2(\kappa, z_1) \in \mathcal{Q}(z), \quad \forall z_1 \in \mathcal{Q}(z),$$

what in turn is equivalent to $\mathcal{Q}_\kappa = \mathcal{Q}(z)$.

If on the other hand $\kappa > \kappa_0$, then there is a $z_1 \in \mathcal{Q}(z)$ with $\kappa(z_1) < \kappa$ and $z_2(\kappa, z_1) \notin \mathcal{Q}(z)$. Thus $\mathcal{Q}(z) \setminus \mathcal{Q}_\kappa \neq \emptyset$.

(iv) $\kappa_0 = \frac{1}{2} \Leftrightarrow \mathcal{Q}_{1/2}(z) = \mathcal{Q}(z) \Leftrightarrow$ for all $z_1 \in \mathcal{Q}(z)$ is $z_2(\frac{1}{2}, z_1) = 2z - z_1 \in \mathcal{Q}(z)$.

(v) In virtue of (4.11), (4.14), and (4.24) the validity of (4.27) is immediate. \square

We see from the Lemma that for simple decomposition regions the domains of variation in the density picture, the sets \mathcal{Q}_κ , $\kappa \in (0, \frac{1}{2}]$, are obtainable from the single set $\mathcal{Q}(z)$ by (4.23). If $\mathcal{Q}(z)$ is invariant under reflections at z , then all \mathcal{Q}_κ coincide with it. But reflection symmetry is too narrow an assumption to be suitable for all applications. So, instead of setting up further requirements on the variation domains we shall look for alternative forms of the stability condition itself.

Let us introduce the vector $p(z)$ with components

$$p_i(z) := \partial s_\Sigma(z) / \partial z^i, \quad 1 \leq i \leq n-1, \quad (4.33)$$

and the subtracted entropy density

$$s_\Sigma^*(z; z_0) := s_\Sigma(z) - p(z_0) \cdot z. \quad (4.34)$$

4.5. Theorem. S_Σ is stable at Z_0 over the simple decomposition region $\mathcal{Q}(Z_0)$ (with cross section $\mathcal{Q}(z_0)$), iff

$$s_\Sigma^*(z_0; z_0) = \max_{z \in \mathcal{Q}(z_0)} s_\Sigma^*(z; z_0). \quad (4.35)$$

Proof. (x) We assume stability and use (4.16). For arbitrary $z_1 \in \mathcal{Q}(z)$ there is a $\kappa \in (0, \frac{1}{2}]$ with

$z_1 \in \mathcal{Q}_{\kappa'}$ for all $0 < \kappa' \leq \kappa$. This results from (4.25) and (4.24). Then, dropping for a while the index Σ , we get from (4.16)

$$s(z_0) \geq \kappa' s(z_1) + (1 - \kappa') s(z_2) \quad (4.36)$$

where

$$z_2 = z_0 + \frac{\kappa'}{1 - \kappa'} (z_0 - z_1) = z_2(\kappa', z_1).$$

Thus

$$s(z_0) - s(z_1) \geq \frac{1 - \kappa'}{\kappa'} [s(z_2) - s(z_0)] \quad (4.37)$$

for all $\kappa' \in (0, \kappa]$. Performing $\kappa' \rightarrow 0$ we obtain

$$s(z_0) - s(z_1) \geq (z_0 - z_1) \cdot p(z_0) \quad (4.38)$$

which is equivalent with (4.35).

We start from (4.35). For every $\kappa \in (0, \frac{1}{2}]$ holds for all $z_1 \in \mathcal{Q}_\kappa(z_0)$ that $z_2(\kappa, z_1) \in \mathcal{Q}(z_0)$. Thus for all $z_1 \in \mathcal{Q}_\kappa(z_0)$ (4.35) leads to

$$s(z_0) - s(z_1) \geq (z_0 - z_1) \cdot p(z_0) \quad (4.39)$$

and to

$$(z_2 - z_0) \cdot p(z_0) \geq s(z_2) - s(z_0). \quad (4.40)$$

Since

$$z_2 - z_0 = \frac{\kappa}{1 - \kappa} (z_0 - z_1)$$

(4.39) and (4.40) give

$$s(z_0) - s(z_1) \geq \frac{1 - \kappa}{\kappa} (s(z_2) - s(z_0))$$

which easily leads to (4.16). \square

The geometrical meaning of (4.35) is best understood in the form

$$s_\Sigma(z) \leq s_\Sigma(z_0) + (z - z_0) \cdot p(z_0), \quad \forall z \in \mathcal{Q}(z_0). \quad (4.41)$$

The r.h.s. is the tangent hyperplane on the entropy surface through $(z_0, s_\Sigma(z_0))$ and all entropy values for $z \in \mathcal{Q}(z_0)$ have to lie below this hyperplane.

Multiplication by Z_0^n transforms (4.35) back into the space of extensive variables.

4.6. Proposition. S_Σ is stable at Z_0 over the simple domain $\mathcal{Q}(Z_0)$ with crosssection $\mathcal{Q}(z_0)$, iff

$$\begin{aligned} S_\Sigma(Z_0) - \sum_{i=1}^{n-1} p_i(Z_0) Z_0^i \\ = \max_{Z \in \mathcal{V}(Z_0)} \left[S_\Sigma(Z) - \sum_{i=1}^{n-1} p_i(Z_0) Z^i \right] \end{aligned} \quad (4.42)$$

where

$$\mathcal{V}(Z_0) := Z_0^n(\mathcal{Q}(z_0), 1). \quad (4.43)$$

One should observe that beside the specification of domain properties our reasoning gives the exact equivalence of (4.42) with (4.2). This could not have been achieved treating (4.2) by means of the Lagrange multiplier method.

Also in (4.42) are the domain properties somewhat peculiar. $\mathcal{V}(Z_0)$ is an $(m-1)$ -dimensional region if $\mathcal{Q}(Z_0)$ has the dimension m . If $m = n$, one extensive variable is to be kept constant. But this must not necessarily be the total energy. Neither are there specific order-relations among the states in $\mathcal{V}(Z_0)$. Both facts indicate that (4.42) cannot be the physically meaningful explication of the fundamental Gibbs principle in spite of being mathematically equivalent to it in some cases.

5. Metastability and Phase Coexistence

By further development of the analytical methods we refine our discussion about what may happen to a system in a special kind of locally stable state. We proceed first in the density picture. In virtue of Theorem 4.5 it is reasonable to define the various notions of stability directly for the specific entropy s_Σ . The physical domain of s_Σ is the crosssection \mathcal{Q}_Σ of \mathcal{C}_Σ , i.e.

$$\mathcal{C}_\Sigma = \bigcup_{\lambda > 0} \lambda(\mathcal{Q}_\Sigma, 1).$$

\mathcal{Q}_Σ is an $(n-1)$ -dimensional set. Often the mathematical domain of s_Σ is larger than \mathcal{Q}_Σ .

5.1. Definition. (i) s_Σ is stable at z_0 over the region $\mathcal{U}(z_0)$, $\mathbb{R}^{n-1} \supset \mathcal{U}(z_0) \ni z_0$, if

$$s_\Sigma^*(z_0; z_0) = \max_{z \in \mathcal{U}(z_0)} s_\Sigma^*(z; z_0). \quad (5.1)$$

(ii) s_Σ is locally stable at z_0 , if there is an $(n-1)$ -dimensional, circled region $\mathcal{Q}(z_0) \ni z_0$, so that (5.1) is valid with $\mathcal{Q}(z_0)$ replacing $\mathcal{U}(z_0)$.

(iii) s_Σ is stable in a region \mathcal{U} , if it is locally stable at all $z \in \mathcal{U}$.

According to Assumption (IV) s_Σ has to be stable in the physical domain \mathcal{Q}_Σ .

5.2. Definition. (i) For $z_1, z_2 \in \mathbb{R}^{n-1}$ define the line segment

$$l[z_1, z_2] := \{z; z = z_1 + \varepsilon(z_2 - z_1), \varepsilon \in [0, 1]\}. \quad (5.2)$$

(ii) $\mathcal{U} \subset \mathbb{R}^{n-1}$ is called convex, if $z_1, z_2 \in \mathcal{U}$ implies $l[z_1, z_2] \subset \mathcal{U}$.

We see that a region \mathcal{U} is convex, iff it is circled around all its elements.

5.3. Proposition. (i) Let be s_Σ locally stable at z_0 and assume there is a z_1 with

$$s_\Sigma^*(z_1; z_0) > s_\Sigma^*(z_0; z_0). \quad (5.3)$$

Then $l[z_1, z_0]$ contains points in which s_Σ is not locally stable or not defined.

(ii) s_Σ is stable in the convex region \mathcal{U} , iff for all $z_0 \in \mathcal{U}$ s_Σ is stable at z_0 over \mathcal{U} (cf. (5.1)).

(iii) s_Σ is stable in the convex region \mathcal{U} , iff for all $z_0, z \in \mathcal{U}$

$$(z_0 - z) \cdot p(z_0) \leq (z_0 - z) \cdot p(z). \quad (5.4)$$

Proof. (i) Assume s_Σ to be defined in $l[z_1, z_0]$ and select therein that point z' , in which $s_\Sigma^*(z; z_0)$ is locally minimal, and which has the greatest distance to z_0 . Such a z' must exist since $s_\Sigma^*(z; z_0)$ is locally maximal at z_0 and nevertheless increases to a value larger than this maximum (cf. (5.3)). Define

$$z(\varepsilon) := z_0 + \varepsilon(z_1 - z_0)$$

and set $z' = z(\varepsilon')$. Then (dropping the index Σ)

$$\begin{aligned} \left. \frac{ds^*(z(\varepsilon); z_0)}{d\varepsilon} \right|_{\varepsilon=\varepsilon'} &= 0 \\ &= (z_1 - z_0) \cdot p(z') - (z_1 - z_0) \cdot p(z_0). \end{aligned} \quad (5.5)$$

For every $\varepsilon \in (\varepsilon', 1)$ we have

$$s^*(z(\varepsilon); z_0) > s^*(z'; z_0) \quad (5.6)$$

or equivalently

$$s(z(\varepsilon)) - s(z') > (z(\varepsilon) - z') \cdot p(z_0). \quad (5.7)$$

Because of

$$z(\varepsilon) - z' = (\varepsilon - \varepsilon')(z_1 - z_0)$$

(5.5) leads to

$$(z(\varepsilon) - z') \cdot p(z_0) = (z(\varepsilon) - z') \cdot p(z') \quad (5.8)$$

which modifies (5.7) so that

$$s^*(z(\varepsilon); z') > s^*(z'; z') \quad (5.9)$$

emerges, for all $\varepsilon \in (\varepsilon', 1)$. But (5.9) contradicts local stability of z' .

(ii) Assume there is a $z_0 \in \mathcal{U}$, so that s_Σ is not stable at z_0 over \mathcal{U} . Then there exists a $z_1 \in \mathcal{U}$, so that (5.3) holds true. Since s_Σ is locally stable at z_0

we can apply (i). Then on the one hand $l[z_1, z_0]$ contains points in which s_{Σ} is not locally stable, on the other hand, because of convexity $l[z_1, z_0] \subset \mathcal{U}$. This contradiction is only avoided if s_{Σ} is stable at z_0 over \mathcal{U} for every $z_0 \in \mathcal{U}$.

(iii) Let be $z_0, z \in \mathcal{U}$, then (ii) gives

$$s(z_0) - z_0 \cdot p(z_0) \geq s(z) - z \cdot p(z_0)$$

and

$$s(z) - z \cdot p(z) \geq s(z_0) - z_0 \cdot p(z).$$

Thus

$$\begin{aligned} (z_0 - z) \cdot p(z_0) &\leq s(z_0) - s(z) \\ &\leq (z_0 - z) \cdot p(z) \end{aligned}$$

leading to (5.4).

Let reversely (5.4) be valid for all $z_0, z \in \mathcal{U}$. According to the mean value theorem one has

$$s(z_0) - s(z) = (z_0 - z) \cdot p(z')$$

for a

$$z' = z_0 + \varepsilon'(z - z_0), \quad \varepsilon' \in (0, 1).$$

Now (5.4) holds also for the pair $z_0, z' \in \mathcal{U}$, i.e.

$$(z_0 - z') \cdot p(z_0) \leq (z_0 - z') \cdot p(z')$$

which after multiplication by $1/\varepsilon'$ leads to

$$\begin{aligned} (z_0 - z) \cdot p(z_0) &\leq (z_0 - z) \cdot p(z') \\ &= s(z_0) - s(z). \end{aligned}$$

This gives local stability for all $z_0 \in \mathcal{U}$. \square

We immediately draw an important conclusion.

5.4. Proposition. Let be s_{Σ} locally stable at every $z \in \mathcal{U} \subset \mathbb{R}^{n-1}$ but not at all $z \in \mathcal{U}$ be stable over \mathcal{U} . Then \mathcal{U} is not convex.

Proof. If \mathcal{U} would be convex, then local stability would in virtue of Prop. 5.3(ii) lead to stability over \mathcal{U} at all $z \in \mathcal{U}$. \square

Thus, if a thermodynamic system has locally but not globally stable states then \mathcal{Q}_{Σ} as well as \mathcal{C}_{Σ} cannot be convex. Let us mention in this connection that the topology of the physical state space of Σ is made still more complicated by the third law: hypersurfaces with absolute temperature 0 (and ∞) are to be excluded from \mathcal{Q}_{Σ} and corresponding cones from \mathcal{C}_{Σ} (cf. [10]).

We resume here the discussion of the changes a system may undergo in the neighbourhood of a locally stable system-state $\langle \Sigma, Z \rangle$ and remember that in general the more disordered constitution of

that material system, here denoted by $\langle \Sigma', Z \rangle$, stands in no simple relationship to the original one. There are, however, important cases where Σ' may again be expressed by configurations of Σ .

5.5. Definition. A system-state $\langle \Sigma, Z \rangle$ which is only locally stable (over the decomposition region $\mathcal{D}(Z)$), is called metastable, if there exists an n -dimensionally open decomposition region $\hat{\mathcal{D}}(Z)$ with

$$\mathcal{D}(Z) \subsetneq \hat{\mathcal{D}}(Z) \subset \mathcal{D}_{\Sigma}(Z) \quad (5.10)$$

and a Z_1^* ,

$$Z_1^* \in \mathcal{D}'(Z) := \hat{\mathcal{D}}(Z) \setminus \mathcal{D}(Z) \quad (5.11)$$

such that

$$\begin{aligned} \langle (\Sigma, \Sigma), (Z_1', Z - Z_1') \rangle &\gg R^n \langle \Sigma', Z \rangle \\ \circ I^n \langle (\Sigma, \Sigma), (Z_1^*, Z - Z_1^*) \rangle, \quad \forall Z_1' \in \mathcal{D}'(Z) \end{aligned} \quad (5.12)$$

is valid.

In our definition of metastability we have included properties of the surrounding region of state space which are usually assumed implicitly but not stated explicitly. They say that also in the more distant part $\mathcal{D}'(Z)$ of the decomposition region the relaxed composite system approaches a system state $\langle \Sigma', Z \rangle$ which is order equivalent with a composite system-state of the previous type. The implications of this relatively simple property shall support the adequacy of our definition.

For simplicity let us assume, that there are cones

$$\begin{aligned} \mathcal{C} &:= \bigcup_{\lambda > 0} \lambda(\mathcal{Q}(z), 1) \\ \hat{\mathcal{C}} &:= \bigcup_{\lambda > 0} \lambda(\hat{\mathcal{Q}}(z), 1) \end{aligned} \quad (5.13)$$

with $\mathcal{Q}(z)$ and $\hat{\mathcal{Q}}(z)$ ($n-1$)-dimensionally open, so that

$$\begin{aligned} \mathcal{D}(Z) &= \mathcal{C} \cap (Z - \mathcal{C}) \quad \text{and} \\ \hat{\mathcal{D}}(Z) &= \hat{\mathcal{C}} \cap (Z - \hat{\mathcal{C}}). \end{aligned} \quad (5.14)$$

Observe that the cross sections are, however, not assumed to be circled around z . The restricted crosssections $\mathcal{Q}_{\Sigma} \subset \mathcal{Q}(z)$ etc. are defined as in (4.23).

5.6. Proposition. Let be $\langle \Sigma, Z_0 \rangle$ metastable according to Definition 5.5. Then the following relations, formulated with the denotations of Def. 5.5, are valid.

$$\begin{aligned} \text{(i)} \quad S_{\Sigma}(Z_0) &< S_{\Sigma'}(Z_0) \\ &= \max_{Z_1' \in \hat{\mathcal{D}}(Z_0)} S_{(\Sigma, \Sigma)}(Z_1', Z_0 - Z_1') \end{aligned} \quad (5.15)$$

$$\begin{aligned}
\text{(ii)} \quad s_{\Sigma}(z_0) &< \kappa^* s_{\Sigma}(z_1^*) + (1 - \kappa^*) s_{\Sigma}(z_2^*) \\
&\geq \kappa' s_{\Sigma}(z_1') + (1 - \kappa') s_{\Sigma}(z_2') \quad (5.16) \\
\forall \kappa' \in (0, \tfrac{1}{2}] \quad \text{and} \quad \forall z_1' \in \mathcal{Q}_{\kappa'}(z_0)
\end{aligned}$$

where $\kappa^* := Z_1^{*n}/Z_0^n \in (0, \tfrac{1}{2}]$ (choose the indices of the subsystems accordingly) and where

$$z_2' = z_2'(\kappa', z_1') = z_0 + \frac{\kappa'}{1 - \kappa'}(z_0 - z_1').$$

$$\text{(iii)} \quad p(z_1^*) = p(z_2^*), \quad (5.17)$$

whereas z_1^*, z_0, z_2^* are pairwise distinct.

$$\text{(iv)} \quad s_{\Sigma}^*(z_1^*; z_1^*) = s_{\Sigma}^*(z_2^*; z_2^*). \quad (5.18)$$

(v) For (at least) one $z_i^*, i=1, 2$, one has

$$s_{\Sigma}^*(z_i^*; z_0) > s_{\Sigma}^*(z_0; z_0). \quad (5.19)$$

(vi) \mathcal{Q}_{κ^*} is not circled around z_0 (and thus not convex).

Proof. (i) (5.15) follows from (3.15) and by order homomorphism from (5.12) combined with local stability of $\langle \Sigma, Z_0 \rangle$.

(ii) Divide (5.15) by Z_0^n and set $\kappa' = Z_1'^n/Z_0^n$.

(iii) Apply (5.16) with $\kappa' = \kappa^*$ fixed and z_1' varying in an $(n-1)$ -dimensional neighbourhood of z_0 contained in \mathcal{Q}_{κ^*} . The necessary condition for the maximum at z_1^* leads to

$$\kappa^* p(z_1^*) + (1 - \kappa^*) p(z_2^*) \left(-\frac{\kappa^*}{1 - \kappa^*} \right) = 0,$$

which gives (5.17).

Since $Z_1^* \in \hat{\mathcal{D}}(Z_0) \setminus \mathcal{D}(Z_0)$, it cannot be of the form $Z_1^* = \lambda Z_0$, for a $\lambda \in \mathbb{R}$. Thus $z_1^* \neq z_0$. Since $\kappa^* > 0$ one obtains pairwise inequality of z_1^*, z_0, z_2^* .

(iv) Set in (5.16) $z_1' = z_1^*$ and vary κ' near κ^* . Because $\hat{\mathcal{D}}(Z)$ being open $z_1^* \in \mathcal{Q}_{\kappa'}$ for $|\kappa^* - \kappa'|$ small enough. The necessary extremal condition at $\kappa' = \kappa^*$ is

$$\frac{d}{d\kappa'} [\kappa' s(z_1^*) + (1 - \kappa') s(z_2(\kappa', z_1^*))]_{\kappa'=\kappa^*} = 0,$$

which gives

$$0 = s(z_1^*) - s(z_2^*) + p(z_2^*) \frac{z_0 - z_1^*}{1 - \kappa^*},$$

and via (5.17) and the definition of z_2^* leads to (5.18).

(v) Assume

$$s^*(z_0; z_0) \geq s^*(z_i^*; z_0)$$

be valid for $i = 1, 2$. Then follows

$$\begin{aligned}
&\kappa^* s^*(z_1^*; z_0) + (1 - \kappa^*) s^*(z_2^*; z_0) \\
&\leq s^*(z_0; z_0)
\end{aligned}$$

which is equivalent with

$$\kappa^* s(z_1^*) + (1 - \kappa^*) s(z_2^*) \leq s(z_0)$$

and contradicts the first part of (5.16).

(vi) From (5.18) and Prop. 5.3(i) follows that $l[z_i^*, z_0]$ contains not locally stable points and is, therefore, not contained in $\mathcal{Q}_{\kappa^*} \ni z_i^*, z_0$. \square

Because of Prop. 5.6(vi) there are in $l(z_i^*, z_0]$ points which cannot be taken on as states from Σ . Consider, however, the composite system

$$\langle (\Sigma, \Sigma), (\alpha_1 Z_1^*, \alpha_2 Z_2^*) \rangle$$

with $\alpha_i > 0, i = 1, 2$. Since

$$\begin{aligned}
p(\alpha_1 Z_1^*) &= p(Z_1^*) = p(Z_2^*) \\
&= p(\alpha_2 Z_2^*) \quad (5.20)
\end{aligned}$$

and since the R and I relations should be invariant against positive dilatations we may deduce from (5.12) that

$$\begin{aligned}
&\langle (\Sigma, \Sigma), (\alpha_1 Z_1^*, \alpha_2 Z_2^*) \rangle R^n \\
&\circ I^n \langle (\Sigma, \Sigma), (\alpha_1 Z_1^*, \alpha_2 Z_2^*) \rangle \quad (5.21)
\end{aligned}$$

is valid for $\alpha_i > 0, i = 1, 2$. Let us denote

$$\mathcal{C}^* := \{Z'; Z' = \alpha_1 Z_1^* + \alpha_2 Z_2^*, \alpha_1, \alpha_2 > 0\}. \quad (5.22)$$

5.7. Definition. For $Z' \in \mathcal{C}^*$ we define $\langle \Sigma', Z' \rangle$ by the relation

$$\langle (\Sigma, \Sigma), (\alpha_1 Z_1^*, \alpha_2 Z_2^*) \rangle (I^{-1})^n \langle \Sigma', Z' \rangle \quad (5.23)$$

the existence of the right hand side partner following from (5.21). (The uniqueness of the partner should be an intrinsic property of a well formalized R -relation.)

By definition Σ' is a phase coexistence system. Its domain of states covers regions where Σ also exists and others where Σ cannot assume states. So Σ' exists, e.g., for all points in $\ell[Z_1^*, Z_2^*] \subset \mathcal{C}^*$. From (5.23) follows immediately that

$$\begin{aligned}
S_{\Sigma'}(Z') &= \alpha_1 S_{\Sigma}(Z_1^*) + \alpha_2 S_{\Sigma}(Z_2^*), \\
\forall Z' \in \mathcal{C}^*. \quad (5.24)
\end{aligned}$$

5.8. Proposition. (i) Let be $\langle \Sigma', Z' \rangle$ defined in \mathcal{C}^* according to Def. 5.7, and let be again $Z_0 = Z_1^* + Z_2^*$. Then $\langle \Sigma', Z_0 \rangle$ is neutrally stable over the region

$$\mathcal{D}^*(Z_0) := \mathcal{C}^* \cap (Z_0 - \mathcal{C}^*) \quad (5.25)$$

i.e.,

$$s_{\Sigma'}(Z_0) = s_{\Sigma'}(Z_1') + s_{\Sigma'}(Z_0 - Z_1') \quad (5.26)$$

for all $Z_1' \in \mathcal{D}^*(Z_0)$.

(ii) For all z' of the form

$$z' = \kappa' z_1^* + (1 - \kappa') z_2^*, \quad \kappa' \in [0, 1] \quad (5.27)$$

holds

$$s_{\Sigma'}(z') = \kappa' s_{\Sigma'}(z_1^*) + (1 - \kappa') s_{\Sigma'}(z_2^*). \quad (5.28)$$

$$(iii) \quad s_{\Sigma'}^*(z'; z_0) = s_{\Sigma'}^*(z_0; z_0) \quad (5.29)$$

for all $z' \in \ell[z_1^*, z_2^*]$.

Proof. (i) $Z_1' \in \mathcal{D}^*(Z_0) \Leftrightarrow Z_1' = \alpha_1 Z_1^* + \alpha_2 Z_2^*$ with $\alpha_i \in [0, 1]$, $i = 1, 2$. Then

$$Z_0 - Z_1' = (1 - \alpha_1) Z_1^* + (1 - \alpha_2) Z_2^*,$$

and we find in virtue of (5.24)

$$\begin{aligned} s_{\Sigma'}(Z_1') + s_{\Sigma'}(Z_0 - Z_1') &= s_{\Sigma}(Z_1^*) + s_{\Sigma}(Z_2^*) \\ &= s_{\Sigma'}(Z_0) \end{aligned} \quad (5.30)$$

for all $Z_1' \in \mathcal{D}^*(Z_0)$.

(ii) Multiply (5.27) by $Z'^n > 0$. Then

$$Z' := Z'^n(z', 1) = \alpha_1 Z_1^* + \alpha_2 Z_2^* \in \mathcal{C}^*$$

and the entropy of $\langle \Sigma', Z' \rangle$ is given by (5.24). Dividing the latter expression by Z'^n leads immediately to (5.28).

(iii) Differentiation of (5.28) with respect to κ' gives

$$(z_1^* - z_2^*) \cdot p(z') = s_{\Sigma}(z_1^*) - s_{\Sigma}(z_2^*). \quad (5.31)$$

Using (5.17) and (5.18) we obtain

$$\begin{aligned} (z_1^* - z_2^*) \cdot p(z_1^*) &= s_{\Sigma}(z_1^*) - s_{\Sigma}(z_2^*) \\ &= (z_1^* - z_2^*) \cdot p(z'). \end{aligned} \quad (5.32)$$

Leaving z' fixed we introduce

$$z''(\kappa) := z' + \frac{\kappa}{1 - \kappa} (z' - z_1^*) \quad (5.33)$$

for variable $\kappa \in (0, \kappa']$. $s_{\Sigma'}(z''(\kappa))$ satisfies then an analogous equation as (5.28) (with κ' being replaced by $(\kappa' - \kappa)/(1 - \kappa)$). With this we find

$$s_{\Sigma'}(z') = \kappa s_{\Sigma}(z_1^*) + (1 - \kappa) s_{\Sigma'}(z''(\kappa)). \quad (5.34)$$

Differentiating to κ at $\kappa = 0$ changes (5.34) into

$$0 = s_{\Sigma}(z_1^*) - s_{\Sigma'}(z') + (z' - z_1^*) \cdot p(z') \quad (5.35)$$

where z' is an arbitrary point of $\ell[z_1^*, z_2^*]$. Since $z_0 \in \ell[z_1^*, z_2^*]$, Equation (5.32) and (5.35) are valid for $z' = z_0$, too. Subtracting the two Eqs. (5.35) for

z' and z_0 and using (5.32) we arrive at

$$s_{\Sigma'}(z_0) - s_{\Sigma'}(z') + (z' - z_0) \cdot p(z_0) = 0,$$

which proves (5.29). \square

We see from the foregoing results, that for a metastable system-state $\langle \Sigma, Z_0 \rangle$ there exists the possibility of a phase-coexistence constitution of the same material body in which the state regions not accessible in the Σ -constitution may now be assumed. In this phase-coexistence constitution Σ' the entropy fundamental function $s_{\Sigma'}$ is neutrally stable at Z_0 over the two dimensional double cone $\mathcal{D}^*(Z_0)$ and the specific entropy $s_{\Sigma'}$ is neutrally stable at z_0 over $\ell[z_1^*, z_2^*]$, all assertions being consequences of metastability. The specification of how many phases coexist in $\langle \Sigma', Z_0 \rangle$ requires the study of further topological properties in the state space by the continuous variation of Z_0 itself. This and related questions will be treated in a separate investigation.

6. Conclusions

Let us summarize what kind of system concept did emerge from our assumptions and derived results in the foregoing considerations. We have incorporated into the formalized theory that every thermodynamic system Σ has a fixed set of state variables describing all states which may be taken on and a single valued entropy fundamental function S_{Σ} ; this being the restrictive part of our approach. On the other hand we have incorporated the possibility to form new systems from given ones by composition of subsystems and by the imposture and relaxation of constraints; and we have only assumed stability to be valid over a local neighbourhood. These two features express the flexible part of the approach.

Consider now a system state $\langle \Sigma, Z \rangle$ which in fact is only locally stable in a decomposition region $\mathcal{D}(Z) \subseteq \mathcal{D}_{\Sigma}(Z)$ where $\mathcal{D}_{\Sigma}(Z)$ denotes as before the maximal set of states a subsystem may assume. We were then able to show, that there must exist a new constitution $\langle \Sigma_{\alpha}, Z \rangle$ with $S_{\Sigma_{\alpha}}(Z) > S_{\Sigma}(Z)$ of the same material system, since the interior constraints of the composite system

$$\langle (\Sigma, \Sigma); (Z_1', Z - Z_1') \rangle,$$

$$Z_1' \in \mathcal{D}'(Z) := \mathcal{D}_{\Sigma}(Z) \setminus \mathcal{D}(Z)$$

can be relaxed and the outcome is again a thermodynamic system in a locally stable state. Here α

indexes subregions $\mathcal{D}_\alpha'(Z) \subset \mathcal{D}'(Z)$. Then there are two possibilities: In all of $\mathcal{D}'(Z)$ is no further equilibrium state of the composite system which would be characterized by a local maximum of $S_{(\Sigma, \Sigma)}$. Then there is no connection between the $\langle \Sigma_\alpha, Z \rangle$ configurations and the Σ configuration which could be expressed in terms of equilibrium thermodynamics. A complete microscopic theory should be capable to describe all macroscopic configurations Σ, Σ_α in micro-dynamical terms. The actual possibilities at the present stage of the microscopic statistical formalism do not scope, however, with such an ambitious program. Therefore it is important, that the second possibility, namely the existence of a further local maximum of $S_{(\Sigma, \Sigma)}$ — say at $Z_1' = Z_1^* \in \mathcal{D}_1'(Z)$ — leads to a fruitful application of purely thermostatic concepts. In this and only this case we have called $\langle \Sigma, Z \rangle$ metastable. $\langle \Sigma_1, Z \rangle$ is then interpretable as a phase-coexistence state, where the participating phases are system-states of Σ . The region $\mathcal{D}_1'(Z)$ is operatively characterized by

$$\langle (\Sigma, \Sigma), (Z_1', Z - Z_1') \rangle R^n \langle \Sigma_1, Z \rangle \\ \cdot I^n \langle (\Sigma, \Sigma), (Z_1^*, Z - Z_1^*) \rangle$$

for all $Z_1' \in \mathcal{D}_1'(Z)$. The states of Σ_1 are described by the same set of state variables as for Σ . Nevertheless, Σ_1 has new observables which are not present in the Σ configuration. These are the density differences $z_2^* - z_1^*$ where

$$z_1^* = (Z_1^{*1} \dots Z_1^{*(n-1)}) / Z_1^{*n} \quad \text{and} \\ z_2^* = [(Z^1 \dots Z^{n-1}) - (Z_1^{*1} \dots Z_1^{*(n-1)})] / (Z^n - Z_1^{*n}).$$

One should be aware of the fact that this set up comprises a large variety of phenomena, since the extensive coordinates Z include also those quantities

which are only detectable by means of external fields, like magnetic or electric moments etc. The density differences are sometimes identified with order parameters, so e.g. the mass density difference for the fluid phase transition or the density difference of magnetic moments at zero magnetic field for the ferromagnetic phase transition. These density differences are fixed in the equilibrium state and may be varied only formally. By construction follows that $\langle \Sigma_1, Z \rangle$ for variable Z bridges regions where $\langle \Sigma, Z \rangle$ cannot exist.

Having explored matters in $\mathcal{D}_1'(Z)$ the next alternative is: $\mathcal{D}_1'(Z)$ equals $\mathcal{D}'(Z) = \mathcal{D}_\Sigma(Z) \setminus \mathcal{D}(Z)$ or not. In the first case $\langle \Sigma_1, Z \rangle$ is absolutely stable and there exists no other constitution of the material body with total observables Z and higher entropy. In the second case one knows that there is a $\langle \Sigma_2, Z \rangle$ with $S_{\Sigma_2}(Z) > S_{\Sigma_1}(Z)$. It again has to be investigated if $\langle \Sigma_2, Z \rangle$ is only locally stable or metastable, and so forth. Thus, there may be a whole hierarchy of system-states $\langle \Sigma, Z \rangle, \langle \Sigma_1, Z \rangle, \langle \Sigma_2, Z \rangle \dots$ for one and the same state tuple Z with increasing entropy. The spontaneous transition $\langle \Sigma_i, Z \rangle \rightarrow \langle \Sigma_{i+1}, Z \rangle$, described at the end of Sect. 3, is in reality often a matter of time, so that to the hierarchy of configurations corresponds a hierarchy of relaxation times in the non-equilibrium treatment of these phenomena. In fact do exist many variants of metastability for real material systems which require an adequate formulation of the thermodynamic principles.

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