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Irreversible Thermodynamics

What's in a name? that which we call a rose
by any other name would smell as sweet.
William Shakespeare

For all a rhetorician's rules
teach nothing but to name his tools.
Samuel Butler

Neglect of semantics can mislead thought.
The Author

In diesem Aufsatz wird die Rolle der inneren Deformationsvariablen in der Analyse irreversibler Prozesse beschrieben. In allen Systemen können innere Umwandlungen stattfinden. Diese leisten virtuelle Arbeit, wenn die Affinitäten A auf die inneren Deformationen wirken. Wird diese virtuelle Arbeit freigesetzt, wird sie dissipiert.

Der übliche Zustandsraum muß um diese inneren Extensitäten erweitert werden, um alle gehemmten und ungehemmten Zustände des Systems enthalten zu können. Zu jedem Nichtgleichgewichtszustand gehört ein *begleitender Gleichgewichtszustand*, und jedem irreversiblen Prozeß entspricht ein *begleitender umkehrbarer Prozeß*. Die Intensitäten (σ , P usw.) eines Nichtgleichgewichtszustands sowie seine Entropie (s) werden durch die des begleitenden Zustands ausgedrückt, weil man sie im Nichtgleichgewicht weder messen noch definieren kann.

Die vorliegende Theorie zeichnet sich dadurch aus, daß sie nur physikalisch wohldefinierte und deshalb meßbare Größen verwendet.

Der Verfasser hat sich bemüht, nur eine semantisch berechnete Terminologie zu benutzen.

1. Introduction

In a footnote to the phrase *thermodynamics of irreversible processes* I said in my book: "The shorter and more easily pronounced term - *irreversible thermodynamics* is frequently used in this connection. However, this term is a misnomer, because a branch of science can be neither reversible nor irreversible". After a futile show of resistance over the years, I have now succumbed and use the term myself, just as I gave up pointing out that an *English teacher* (in the colloquial sense) need not be English. Hence, reluctantly, the title. But the later emphasis will still be on ensuring that terms

express concepts in a semantically close and consistent way because the subject I am about to discuss is full of semantic traps which, just as is the case in the Geisteswissenschaften, often lead to fuzzy or erroneous reasoning along blind alleys.

To begin with, the dichotomy between reversible and irreversible processes is artificial, because *all* processes in nature are irreversible. The essence of the science of "irreversible thermodynamics" is to discover how to adapt the classical results of equilibrium thermodynamics to the analysis of irreversible processes.

2. Background

The fundamental concept is that of an *equilibrium state* which occurs when the system under consideration does not interact (by the transfer of work, heat or mass) with the surroundings and does not admit interaction between arbitrary subsystems. This concept is seen to be wider than that of equilibrium in mechanics with which it overlaps without being congruent to it. For simplicity we now concentrate on equilibrium states in homogeneous systems, though equilibrium fields, which are sometimes encountered, also belong to the subject.

The state of equilibrium is described by a finite number n of independent state parameters (alias properties). To serve the needs of irreversible thermodynamics, it is purposeful to employ *extensive properties* for this description. In simple fluids, these can be chosen as internal energy u and specific volume v ($n = 2$). In simple solids v is replaced by the strain tensor' e giving $n = 7$. Thus, the entropy s is represented by the *fundamental equation*

$$s = s(u, v) \quad \text{or} \quad s = s(u, e) \quad (1a, b)$$

which for intrinsically stable systems may be inverted to

$$u = u(s, v) \quad \text{or} \quad u = u(s, e) \quad (2 a, b)$$

The set of independent variables a_1, \dots, a_n defines an n -dimensional phase (state) space in which an equilibrium state is represented by a point, such as A in Fig. 1. A *continuous line* R in phase space is called a reversible process. A reversible process, then, is a continuous sequence of equilibrium states; it is a purely mathematical construct, because reversible processes do not occur in nature.

Much that has been written in text-books about reversible processes is irrelevant for the development of our subject. Particularly misleading is the insistence on demanding that reversible processes must occur *infinitely slowly* or the synonymous use of the term *quasistatic* with *reversible*. For example, a metal rod can be deformed very slowly ("quasistatically") in the plastic range, but the resulting sequence of states is not a *continuum* of equi-

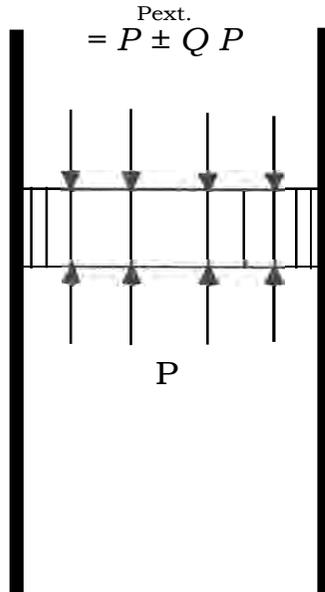


Figure 2. Proverbial piston-cylinder combination

The last point requires some elaboration. A simple illustration is given in Fig. 2 in which a gas contained in a cylinder would be in thermodynamic equilibrium only when the external pressure P_{ext} exactly balances the thermodynamic pressure P which would figure in an equation of state. But under such conditions no process, however slow, would be possible. In order to start a process it is necessary to modify the external pressure so that $P_{ext} = P \pm \Delta P$ i. e. $P, \neq P$. (3 a, b)

Depending on the sign of $\pm \Delta P$ this would impart a definite direction to the process. The magnitude of ΔP would determine the rate of the process. Under such conditions a perceptive observer would notice the development of a velocity field and it becomes clear that the resulting nonequilibrium state cannot be characterized by a single pressure, and certainly not by P . The readers are undoubtedly familiar with the standard reasoning which leads to the statement that a reversible process results when $\pm \Delta P$ is made "infinitely small" and the rate of motion of the piston is rendered "infinitely slow". A thoughtful student would find such a stratagem logically lacking in rigor and in this he would find himself in a situation similar to that which existed at the inception of calculus. I shall return to this point later and give a couple of illustrative historic quotations in the Appendix. An experienced

reader will notice that engineers have never felt constrained by the injunction that reversible alias quasistatic processes must be infinitely slow and successfully used such formulae as that for work

$$dW = Pdv \quad (4)$$

etc. for the analysis and design of processes in fast-running engines or in supersonic flows. The question is: How could they get away with it?

The conclusion, therefore, is twofold. First, that the same quandary occurs with respect to all intensive properties (stress σ , temperature T etc.) and, secondly, that the quantities like P_{exf} (Muschik's Kontaktgrößen) are unsuitable to characterize nonequilibrium states. However, extensive properties can be both defined and measured in nonequilibrium and are, therefore, suitable.

4. Phase space

The diagram in Figure 3 represents schematically the phase space of equilibrium extensive properties e_1, \dots, e_n , to which we must add an infinity e_m of further extensive properties to secure an image of a nonequilibrium

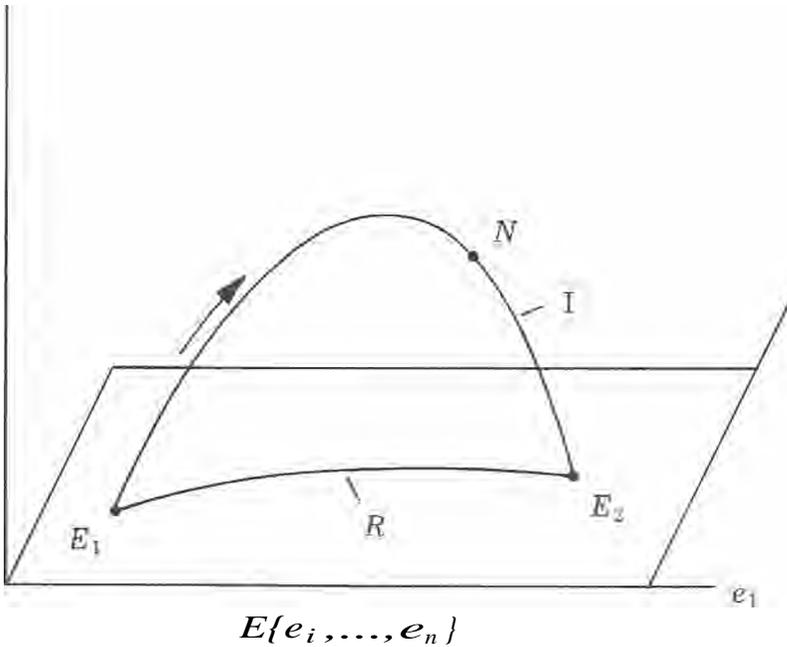


Figure 3. Nonequilibrium states reach out of phase space

state, such as N . The locus of all states which represent a reversible process must be imbedded in the space $E \{e_1, \dots, e_n\}$, whereas that for an irreversible process, starting and ending in the equilibrium states E_1 and E_2 , respectively, must reach outside the phase space E . Furthermore, we recall that natural, i. e. irreversible, processes proceed in a definite *direction*. By contrast, no direction can be assigned to the purely conceptual reversible process.

If we consistently choose extensive properties, we can regard a reversible process R as the projection of an irreversible process I into E , noting that a given irreversible process has a single reversible projection along e_n , but that a given reversible process may be the projection of an infinity of irreversible processes.

5. Fundamental problem: Description of nonequilibrium states

The preceding considerations lead us to the conclusion that in order to construct a logically tenable theory of irreversible processes (strictly speaking of thermodynamics an sich) which agrees with observation, we must solve a *fundamental problem*:

Formulate a physical principle which will allow us to obtain rational definitions of the intensive thermodynamic variables such as P , T , Q etc. for nonequilibrium states.

A purist may demand that this must also be done for internal energy u , and all will recognize that entropy s is also in need of such a definition, presumably in conjunction with that for T , because we must retain the principle that entropy can be calculated (defined) only by integration along a reversible path (curve R in E).

6. Concept of a continuum

Since all irreversible processes occur in continua, it is useful to pause and review how such a concept arises.

To describe the state of a continuum, Fig. 4, we divide it into k cells of volume θ ($A V$), calculate the instantaneous value of any extensive property as the sum

$$(t) = \sum \dot{Y} \beta_i^d V_i \quad (5a)$$

and use the Euler-Maclaurin approximation of a sum by an integral

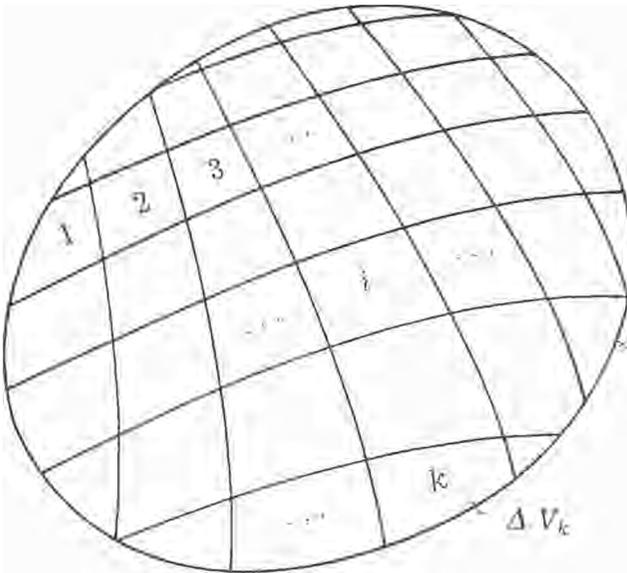


Figure 4. Concept of a continuum

$$\int_V (t) = \int_V Q(x, t) \rho(x, t) dV + R. \quad (5 b)$$

We now make the following observations:

- The system need not be continuous or homogeneous in the strict physical sense; the property of continuity is ascribed to the field functions $Q(x, t)$ and $\rho(x, t)$.
- The description is improved by rendering the remainder R (which we neglect) smaller and smaller; this we do by choosing an appropriate volumetric scale dV . The order of dV determines the *spatial level of description*.
- On changing the spatial level of description, we would notice a change in the field functions $Q(x, t)$ and $\rho(x, t)$.
- The application of the procedure of eqns. (5 a, b) to an intensive property would not result in a physically meaningful sum; the values of intensive properties change with a change in the scale of dV .
- Extensive properties remain additive on a change of scale dV .

7. Internal deformation variables

Observation convinces us that the set of external deformation variables, e , augmented by internal energy, u , is inadequate for the description of equilibrium states of most systems. All systems are regarded as seats of dissipative processes which occur internally as the system is operated on externally. To describe the internally constrained equilibrium states we need a set of m internal deformation variables. The compulsion to introduce such variables was recognized by Bridgman, Sommerfeld, Leontovich, Eckart, Meixner and probably others. The clearest specification was given by Bridgman, which we quote:³

"I believe that in general the analysis of such systems, i. e., systems undergoing irreversible processes, will be furthered by the recognition of a new type of large-scale thermodynamic parameter of state, namely the parameter of state which can be measured but not controlled. Examples are the order-disorder rearrangements in mixed crystals, measurable by X-rays, and the dislocations in a solid, measurable by the attenuation of supersonic vibrations. These parameters are measurable, but they are not controllable, which means that they are coupled to no external force variable which might provide the means of control. And not being coupled to a force variable, they cannot take part in mechanical work. Such a parameter of state, which enters into no term in the mechanical work, can be shown by simple analysis to be one which can take part only in irreversible changes. In working out the thermodynamics of actual systems in which such uncontrollable parameters play a part, the first step will be the determination of the equation of state in terms of the new parameters"

Even though the dissipative mechanisms do not participate in the exchange of work with the surroundings, it is possible to *imagine* that they might, by introducing fictitious, balancing forces. Thus an elementary dissipative system can be made to perform a reversible process in thought, even though its realization in practice may not be possible.

To make full use of the concept of internal variables, it is necessary to add the following:

- The internal variables are (extensive) deformation variables (denoted here by f).
- It is possible to imagine fictitious links with the surroundings which balance the internal deformation variables; these links exert fictitious forces (affinities, denoted here by A). Leontovich introduces at this point fictitious fields which can be externally switched on and off at will.
- The terms $A_m d$ (sum) represent virtual reversible work. It then follows that in the absence of such links this work $A_m d b_m$ is dissipated

(like in an unresisted expansion). Therefore, $A_n d \dots, IT$ contribute terms of entropy production.

- Each dissipative process is characterized by an intrinsic rate \dot{z}_{bm} and can be characterized by a relaxation time

$$z = S/\lambda,$$

(denominator in Reiner-Rivlin's Deborah number).

- The fundamental equation of state that Bridgman speaks about in the last sentence is then

$$u = u(s, e), \quad (6)$$

and the corresponding Gibbs equation follows. (The fundamental equation (6) specifies $1 + n + m$ independent extensive variables.)

The more complete description occurs in a enlarged phase space whose every point is a state of constrained or unconstrained equilibrium. It follows (certain proposals in the literature notwithstanding) that this space *must not* include the heat flux q or $\text{grad } T$ as coordinates, because

$$q \neq 0 \text{ and } \text{grad } T \neq 0$$

cannot exist in equilibrium, whether constrained or not.

8. Gibbs's equation

The Gibbs equation in the extended phase space assumes the form

$$du = T^* ds^* + [(v^*/Q) de - A^* S], \quad (7)$$

where

$$\text{def. } T^* = \frac{\partial u(s^*, e, \dots)}{\partial s^*}, \quad (8a)$$

$$\text{def. } a^* = \frac{\partial u(s^*, e, \dots)}{\partial e}, \quad (8b)$$

$$\text{def. } A^* = \frac{\partial u(s^*, e, \dots)}{\partial S}. \quad (8c)$$

Needless to say, it is stipulated that the hypersurface of eqn. (6) satisfies the conditions of intrinsic stability and that, therefore, Legendre transformations can be performed.

9. First and Second Laws of Thermodynamics

We write the First Law in the form

$$du = dQ + (a/Q) de \quad (9)$$

which is valid for reversible as well as irreversible processes. As indicated earlier, we anticipate that the concept of internal energy can be extended to apply to nonequilibrium states.

The combined First and Second Law, applicable only to reversible processes, can be written

$$du = T^* ds^* + [(a^*/Q) de - A^* de]. \quad (10)$$

In contrast with eqn. (7), the symbols T^* , a^* , A^* have a clear physical meaning which turns the definitions (8 a, b, c) into statements of physical fact. We further recognize that the work and heat in reversible processes are

$$dQ^* = T^* ds^*, dW^* = -(a^*/Q) de + A^* d. \quad (\text{lia, b})$$

It is emphasized that

$$dQ^* dQ^*, dW^* dW^*, a^* a^* \quad (12a, b, c)$$

for the same du, de .

10. Dissipative mechanisms

When left unresisted ($A = 0; A^* \neq 0$), the internal dissipation variable changes at a rate \dot{a} and performs no work. At $u = \text{const}$ and $e = \text{const}$, the internal process comes to an unconstrained equilibrium, and the internal variables attain values eventually. In other words, the variables behave like extents of chemical reactions.

In constrained equilibrium $\dot{a} = 0, A^* \neq 0, \dot{a}^* = 0$

In unconstrained equilibrium $\dot{a} = A^* = 0, \dot{a}^* = g;$

In a nonequilibrium state, i. e.

during an irreversible process $\dot{a} \neq 0, A^* \neq 0;$

The rates \dot{a} are governed by *rate equations* whose structure is determined by the second part of the Second Law and whose particular forms for each system must be obtained empirically; it is not implied in the fundamental equation (6). Together, the fundamental equation and the set of rate equations can be described as the *constitutive law of the system*.

The rates \dot{a} can be characterized by a set of internal relaxation times τ = $V\lambda$ as already stated earlier. The rate of external working and heating can also be characterized by the relaxation times

$$\tau_{,,} = e/\dot{e} \quad \text{and} \quad \tau_0 = \text{div } q / \text{div } r_j. \quad (13 a, b)$$

We can form a set of dimensionless Deborah numbers

$$De = z/z, r_q/z \text{ etc.} \quad (13c)$$

to characterize the interplay between external actions with the internal processes. For example, if the external working dominates over external heating ($z_q \gg r_H$), we can consider that

$T \ll r_{,,}$, corresponds to unconstrained equilibrium

$T \approx z_{,,}$ leads to an irreversible process

$z \gg r_H$ corresponds to constrained equilibrium.

11. Accompanying (equilibrium) state (Meixner)

11.1. One internal variable

With an arbitrary nonequilibrium state n we associate a frozen (constrained) equilibrium state e which is reached *adiabatically* from it at $e = \text{const}$, $\dot{e} = \text{const}$ preserving the forward velocity V if the system (or element) is in motion. A schematic of this process is shown in Fig. 5.

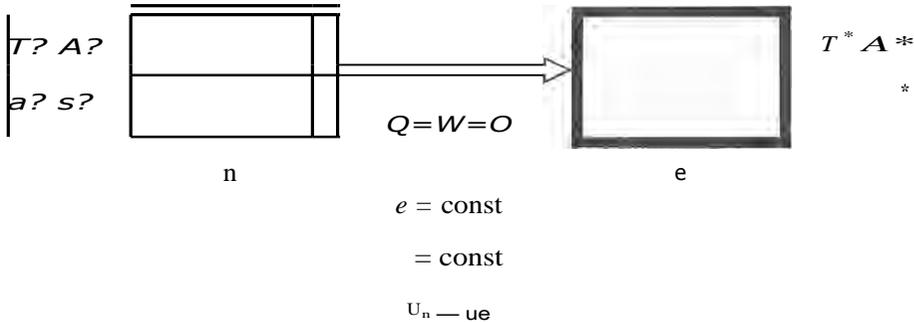


Figure 5. Creating an accompanying equilibrium state (Gedankenexperiment)

By an extension of the First Law to process $n \rightarrow e$, we conclude that

$$u_n = u_e \quad (14)$$

which gives us a clear operational definition of the internal energy of a nonequilibrium state, as anticipated earlier in this essay.

We solve the fundamental problem announced in Sec. 5 by accepting the following *principle of local state*:

The undefined intensive properties and entropy of state n are identified as those of the accompanying state.

Thus

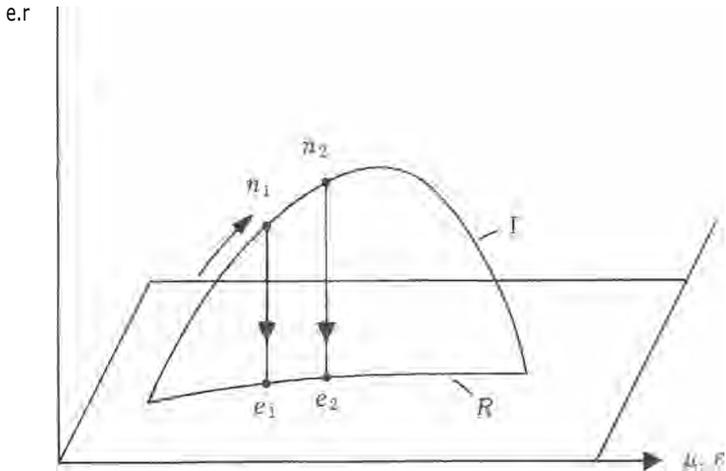
$$T_{,,} = T_e = T^*, Q_{,,} = Q_e = a^*, A_{,,} = A_e = A^* \tag{15}$$

and

$$s_{,,} = s_e = s^* , \tag{16}$$

where T^*, a^*, A^*, s^* follow from the fundamental equation (6) with (7) and (8 a-c).

The accompanying states e_1, e_2 result from n_1, n_2 by projection into the phase space, as shown in Fig. 6, and with every irreversible process /we can



$$\sim \mathbf{H} \, du, \, ds$$

Figure 6. Accompanying reversible process

associate an *accompanying reversible process R*. For this accompanying reversible process we preserve the direction of the irreversible process and associate with it the same increments du, de , as well as the rates \hat{u}, \sim . The rates

are obtained from other information--a fact we mentioned earlier. It follows that we can re-write the Gibbs equation (7) in the rate form

$$= T^*s^* + (a^*/Q) s - A^* , \tag{17}$$

valid for reversible processes. Those of us who believe that reversible processes *must* be infinitely slow would either forbid this form or maintain that it is trivial, presumably thinking that *rigorously* $s^* = = = 0$. An analogous false paradox in calculus is discussed in the Appendix.

The cognoscendi among us realize that the preceding concepts amount to what some refer to as the *assumption of local equilibrium* and the author needs waste no further words to justify his objection to this term on account of its misleading semantics.

11.2. Several internal variables

In systems inside which m different dissipative mechanisms can become active, we can arrange the corresponding relaxation times according to magnitude:

$$\tau_1 > \tau_2 > \tau_3 > \dots > \tau_m.$$

Depending on how we manipulate the internal constraints, we shall be able to associate with a state n a set of states e , all of equal values of u and e , as shown in Fig. 7. Here we have assumed that relaxation times τ_3, \dots, τ_m are so short that they need not be taken into account. In state e_2 we have constrained mechanisms 1 and 2. In state e_1 we have allowed b_2 to reach its

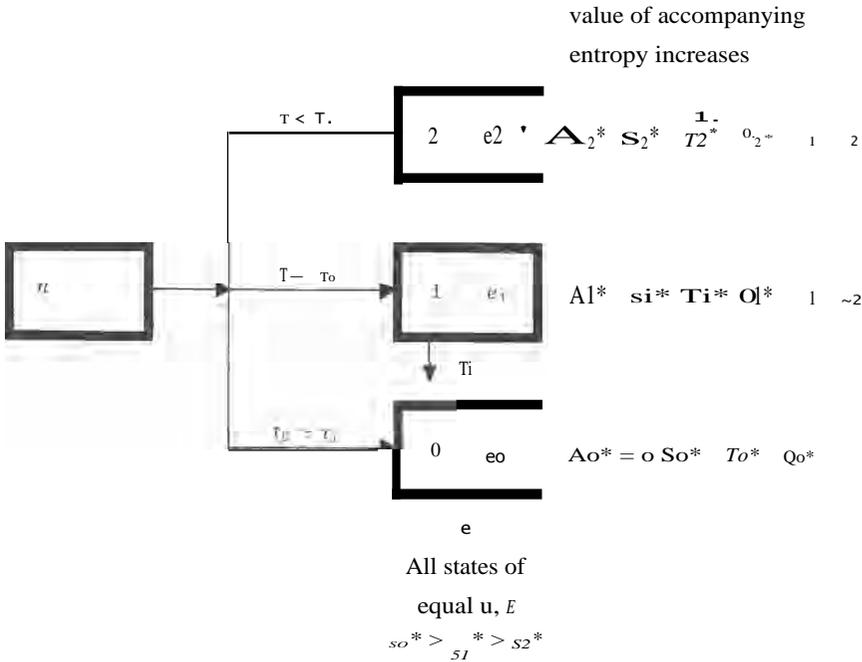


Figure 7. Set of accompanying equilibrium states

unconstrained value s_2 , but left y constrained. In state e_0 all internal variables are unconstrained. Thus for our system, we may write several Gibbs equations

$$u = u(s_2, e, b, l, 2) \text{ for } e_1 \quad (18a)$$

$$u = u(4, e, s_1, Z_2) \text{ for } e_2 \quad (18b)$$

$$u = u(s\hat{o}, e, S1, S2) \text{ for } e_a \quad (18c)$$

The unconstrained value z_2 is a solution of

$$A2[u, e, S1, S2(u, E, S1)] = a \geq u(e, s_1, s_2) = 0 \quad (19)$$

etc. for the others. It is easy to see that the entropy must increase as constraints are sequentially relaxed, and that at each level the intensive variables assume different values.

11.3. "Distance" from equilibrium

In the literature of thermodynamics we often encounter the phrases "state close to equilibrium" or "state far from equilibrium". A moment's thought should convince the reader that in such phrases the tertium comparationis is missing; in other words, the equilibrium state with which the comparison is made is left unspecified. The concept of an accompanying equilibrium state makes it possible to render these phrases precise. It is, namely, compelling to use the states e_0, e_{1i}, e_2 etc. for this purpose and to measure "distance" by the relaxation time ratio (inverse Deborah number) required to attain a state e from the given state n . In effect, we invert the above phrases and say that state e_2 is closer to n than e_{1i} , that e_j is closer to n than e_2 , and that the distance of state n is furthest from equilibrium, meaning from equilibrium state e_0 in which all internal constraints have been relaxed.

11.4. Physical principle

We can accept the following physical principle ("postulate"):

It is always possible to determine a finite set r of internal deformation variables (scalar, vectorial or tensorial)

$$\{1, \mathbf{v}, \dots, \mathbf{bri}\} \quad (20)$$

in such a way that their number is adequate to render the nonequilibrium state under consideration sufficiently close to a constrained state of other-thermodynamic equilibrium to allow us to use the temperature T^* , stress al ,

and the entropy s^* of this state as descriptive of the nonequilibrium state.

This amounts to establishing a rational *temporal level of description* which supplements the spatial level of description of Section 5.

In thermostatics and in most engineering text-books it is tacitly implied that the equilibrium properties of state e_0 are used as a basis for the analysis of processes in engines. It is thus that engineers "get away with it" (see Section 3 supra).

12. Second Law (Clausius-Duhem inequality)

We expect that the following inequality holds

$$e \frac{ds^*}{dt} + \operatorname{div} \left(\frac{q^*}{T_r} \right) > 0 \quad (= \mathfrak{g} > 0). \quad (21)$$

Here B denotes the volumetric *entropy production rate*^s and $\operatorname{div} (q/T_r)$ is accepted as a physically justified expression for the entropy flux in the absence of diffusion.

We can convince ourselves that in our present formalism, the *Clausius-Duhem inequality* of eqn. (21) is only approximate, the degree of approximation achieved depending on the established levels of spatial and temporal description. This we do in conjunction with Fig. 8. In it, the system is pic-

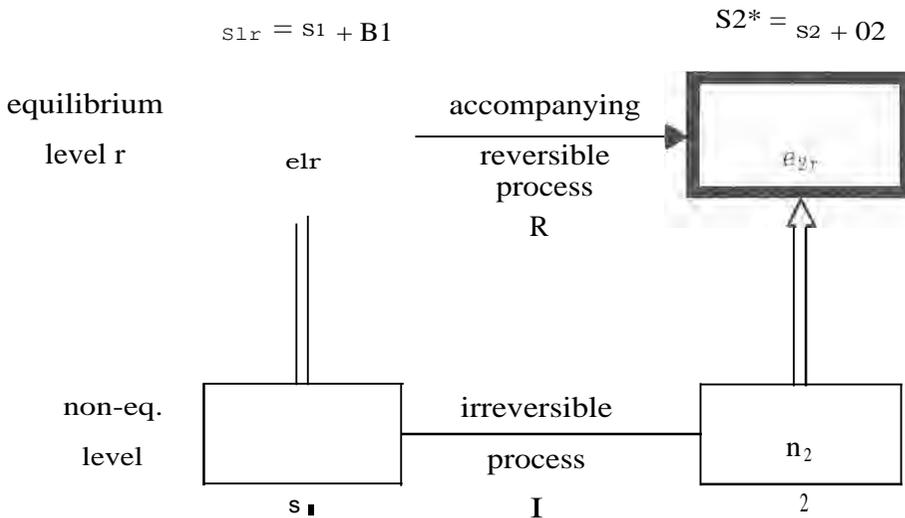


Figure 8. Validity of the Clausius-Duhem inequality

tured as performing the irreversible process I between states n_1 and n_2 associated with the accompanying states e_{1n} , e_{2n} , and reversible process R. If we could associate values of entropy s_1 and s_2 with states n_1 and n_2 , we would expect that the accompanying equilibrium states, which result from (fictitious) adiabatic irreversible processes $n_1 \rightarrow e_{1r}$ and $n_2 \rightarrow e_{2r}$, would possess entropies which are higher by the (positive) quantities O_1 and O_2 .

We calculate the total entropy flow of the process as

$$H_{12} = - \int_{1 \downarrow}^{2 \uparrow} \text{div} \dots dt, \tag{22 a}$$

$$O_{12} = O dt, \tag{22 b}$$

and note that

$$s_{1r}^* - s_1 = O_1 > 0 \tag{23 a}$$

$$s_{2r}^* - s_2 = O_2 > 0. \tag{23 b}$$

We further note that

$$s_2 - s_1 = O_{12} + H_{12} \tag{24}$$

- or

$$s_2^* - s_1^* - H_{12} = O_{12} + (O_2 - O_1). \tag{25}$$

Since the difference $O_2 - O_1$ may be of any sign, we must choose the level r of description to render

$$|O_2 - O_1| \ll O_{12} \tag{26 a}$$

and accept the notion that choosing variables at a level of description which is closer and closer to state n results in

$$|O_2 - O_1| \rightarrow 0. \tag{26 b}$$

13. Dissipation

Eliminating du or $it = duf dt$ from equations (9) and (10) or (17), we obtain an explicit expression for the rate of entropy production in the form of the following *dissipation theorem*

$$e \frac{d s^*}{d t^*} + \text{div} \left(\frac{g^I}{r^*} \right) = \frac{a - a_r}{Z_r} t^* + g \cdot \text{grad} I \frac{1}{T^*} \tag{27 a}$$

This can also be written

$$= Q \frac{1}{W^* T_r W} + q \cdot \text{grad} \left(\frac{1}{T_r} \right) \tag{27 b}$$

The existence of an explicit form for the rate of entropy production paves the way for the determination of the form of forces and fluxes, for the application of the Onsager-Casimir relations in the linear case etc. etc.

The forms (27 a, b) lead us to recognize that the fundamental equation must be supplemented with the following set of (homogeneous) rate equations to obtain a *complete constitutive* statement:

$$\begin{aligned} -\dot{o}^* &= E [e, ATr^{-1}; u, e, I, \dots, s_j] \\ \dot{A} &= Q [\text{-----}] \text{-----} \quad (28) \\ \dot{A}_1 &= [\quad \quad \quad] \\ br - ter &= [\text{-----}, \text{-----}]. \end{aligned}$$

14. Projection into the sub-space u

We conclude this essay by observing that in cases where the differential equations for t, \dots , can be solved and the variables $t_1 \dots, t_r$ themselves eliminated, we would derive a set of functionals

$$\begin{aligned} s^* &= S [e(t-t'), T^*(t-t'), \forall T_r^*(t-t')] \\ &\quad t \geq 0 \\ \dot{Q}^* &= \underset{rza}{\sim} [\text{-----}] \quad (29) \end{aligned}$$

$$q = Q$$

This is certainly possible in the linear case.

It has become customary to refer to these as "memory" functions and to claim that the systems they describe represent a special class of "materials with memory." In the linear case, Meixner used the preferable term *aftereffects* (Nachwirkungen). Readers who recall the motto of this essay will not be surprised to be told that the author objects to this terminology. In his frame of reference, the explicit inclusion of time in a description deserves the name *process* which describes the evolution of a set of states with time.

I conclude with the formulation of several questions:

1. Is the memory representation equivalent to the internal-variables representation and vice versa?
2. If we place eqns. (29) at the foundation of a theory, how are we going to measure and catalog all those "histories" and what do we do about the nonequilibrium intensive variables?
3. Finally, is it not true that any process described by an integral, or just an integral for that matter, has a claim to be designated as a "history"?

Appendix

Similarity between two resolved paradoxes.

The following is a description of the inhibitions which accompanied the early development of calculus; it is based on Richard Morris's "Time's Arrows" (Simon and Schuster 1984).

The author illustrates the concept of a derivative on the example of calculating the instantaneous velocity of motion explaining first the idea of forming average velocities over smaller and smaller time intervals, and then continues: "But suppose we now go a step further and assume that the object travels an infinitesimal distance in an infinitesimal period of time. Even though such small quantities could presumably not be measured, it seems that we could make use of them for the purposes of creating a definition: Instantaneous velocity is an infinitesimal distance divided by an infinitesimal time?"

"At first glance, it isn't obvious that we have really gotten anywhere. It isn't clear that it is legitimate to deal with such infinitesimal quantities. In fact, it isn't even obvious whether such quantities really exist. On one hand, they have to be larger than zero. After all, the mathematical expression $0/0$ is meaningless; it can be set equal to anything. On the other hand, infinitesimals would have to be smaller than any number one could think of. If they were not, we would not have succeeded in defining instantaneous velocity; we would have an average velocity over some small period of time. It seems that in attempting to define instantaneous velocity, we have had to make use of an idea that is rather suspect.

Newton and Leibniz felt uneasy about the concept of infinitesimals themselves. In fact, more than a century was to pass before mathematicians found a way to dispense with them, and to put calculus on a firm logical foundation. However, it was immediately obvious that the idea, if somewhat suspect, could be extremely useful?"

"Strangely, Newton made little use of calculus in the *Principia*. As he admitted later, he used calculus to work out the mathematical proofs that he needed, and then replaced these with arguments based on complicated geometrical diagrams. Newton apparently found calculus invaluable, but nevertheless distrusted a method that was based on so questionable a concept as the infinitesimal.

Newton's own writings on calculus illustrate his uneasiness about the logical foundations of the method. In his first paper on the subject, published in 1669, he commented that his method would be 'shortly explained rather than accurately demonstrated?' In his second paper on the subject (1671), he explained calculus in a slightly different way than he had in the first. In his third paper, he criticized his previous work, and gave yet another explanation, which, however, was really no more satisfactory than the previous two.

Newton could not decide whether infinitesimals were to be regarded as fixed quantities or as quantities that varied continuously. He spoke of them as increments that were 'as small as possible; and yet he couldn't say precisely how small they were. Nor could he settle on a name for them. He referred to them variously as 'indivisibles', as 'nascent increments', and as 'evanescent indivisible quantities:

Similar difficulties were experienced by Newton's rival Leibniz. Leibniz defined infinitesimals as quantities that were 'vanishingly small' or 'infinitely small: He seems to have realized almost at once that his idea led to difficulties. An infinitely small number had to be greater than zero, and smaller than any fraction that one could name. In an article that was published in 1689, Leibniz spoke of infinitesimals not as real numbers but as fictitious ones. If anything, this attempt at explanation made matters even worse. After all, how could one use fictitious numbers to calculate real quantities? Apparently even Leibniz didn't know. In an article published six years later, he attacked 'overprecise' critics, and made the rather lame observation that excessive scrupulousness should not cause one to reject a method that had proved so useful?

"One might think that the physicists and mathematicians of the seventeenth century would have been reluctant to make use of calculus until such time as it could be put on a firm logical foundation. Perhaps they were reluctant. However, they did not stop using it?"

"In 1734, seven years after Newton's death, the British philosopher Bishop George Berkeley published a book entitled *The Analyst Or a Discourse Addressed to an Infidel Mathematician. Wherein It Is Examined Whether the Object, Principles, and Inferences of the Modern Analysis Are More Distinctly Conceived, or More Evidently Deduced, Than Religious Mysteries and Points of Faith. 'First Cast the Beam Out of Thine Own Eye; and Then Shalt Thou See Clearly to Cast Out the Mote of Thy Brother's Eye.'* Berkeley charged that the mathematicians who made use of calculus were proceeding in an illogical manner. Calculus, he said, was incomprehensible. Furthermore, mathematicians were guilty of using reasoning that would not be allowed in theology. Pointing out that infinitesimals were 'neither finite quantities, nor quantities infinitely small, nor yet nothing; Berkeley concluded that they must be 'the ghosts of departed quantities'. Anyone who used such methods, he observed sardonically, 'need not ... be squeamish about any point in Divinity.'"

Much of the above has a familiar ring in the ears of professional thermodynamicists. The pseudo-paradox in calculus was resolved with the aid of the concept of limit. The pseudo-paradox of an "infinitely slow reversible process" is solved with the aid of the concept of the accompanying equilibrium state, accompanying reversible process and relaxation time.

Footnotes

- 1 We shall not use different faces to distinguish between scalars, vectors and tensors because the nature of these quantities should be clear from the context.
- 2 In the following we stop making a distinction between fluids and solids remembering that $v = \sigma^{-1} e_{,i}$ is included in the tensor a as a special case.
- 3 P.W. Bridgman "The Nature of Thermodynamics", Harper 1961, and "Reflections on Thermodynamics", Proc. Am. Acad. Arts and Sci. 82 (1953) 301-309.

- 4 Where needed, we add an asterisk to the symbol of a quantity which, at least so far, has been defined for equilibrium states only.
- 5 The author makes a clear distinction between "entropy" - a state function and "entropy production" - an unavoidable intruder in irreversible processes; he thus never describes the Second Law as the principle of entropy increase preferring to call it the principle of positive entropy production.
- 6 We note that the work in a reversible process

$$W_{12} = \int_1^2 w^* dt = \int_1^2 [-(o, */q) \dot{e} + A^*] dt$$

reduces to a time-independent line integral along the curve representing the projection of the process into the preferred phase space $E \text{ } I r \}$

$$w^*_{;2} = \int_1^2 [-(oI/Q) de + A^* d \dots]$$

along curve R , (see Fig. 6). The same is true about heat

$$Q_{12} = \int_1^2 \dot{Q}^* dt = \int_1^2 [du + (-o*/Q) dt + Ad \dots]$$

along curve R . Some authors might be inclined to say that curves I and R represent the "history" of the system and that the above are integrals over the "system's history".