

ON THE VALIDITY OF THE CLAUSIUS–DUHEM INEQUALITY

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ABSTRACT

The author discusses the applicability of various theories for describing processes in continuous matter and deals in some detail with the entropy-free thermodynamics of irreversible processes, basing his discourse on the work of J. Meixner in this field.

Today there are essentially three different phenomenological theories available for describing processes in continuous matter:

- (1) The classical Thermodynamics of Irreversible Processes (TIP)¹.
- (2) The Non-linear Field-Theories of Mechanics and their thermodynamic extensions (NFT)².
- (3) The Entropy-free Thermodynamics of Processes (ETIP)^{3, 4}.

These theories have in common the conservation laws of continuous matter and the laws of thermostatics. They differ essentially in the arguments on which the constitutive equations (CE) are based. Classical TIP starts from a generalized Clausius–Duhem Inequality (CDI) for the well-known (specific) thermostatic entropy s_{st}

$$\rho \dot{s}_{st} + \operatorname{div} \mathbf{J}_{st} \geq 0 \quad (1)$$

The quantity s_{st} is well defined by the second law of thermodynamics and is a function $s_{st} = s_{st}(u, \rho)$ for fluids and a function $s_{st} = s_{st}(u, F_{ij})$ for solid systems. Here u means the (specific) internal energy, $\rho \dots$ density, $F_{ij} \dots$ deformation gradient, $\dot{s}_{st} \dots$ substantial time derivative of s_{st} and $\mathbf{J}_{st} \dots$ current of s_{st} . In the case of thermodynamic systems without diffusion one has

$$\mathbf{J}_{st} = \mathbf{q}/T \quad (2)$$

with $\mathbf{q} \dots$ heat flux and $T \dots$ absolute temperature. The inequality 1 has been proved valid in quite a few applications¹. Nevertheless it must be emphasized that in TIP its validity is postulated and cannot be concluded from the second law (ref. 1, p 424; ref. 4, p 33 etc.).

To get CE in NFT one starts with a generalized CDI

$$\rho \dot{s}_N + \operatorname{div} \mathbf{J}_N \geq 0 \quad (3)$$

for a hypothetical (specific) Non-equilibrium Entropy (NEE), s_N . Here \dot{s}_N means the substantial time derivative and J_N the current of s_N . Unfortunately in NFT neither s_N nor J_N is defined uniquely. Therefore today the physical significance of these quantities is not clear. Beside this, in NFT nothing is said about the physical meaning of the inequality 3, the validity of which is merely postulated.

Now within the framework of a phenomenological theory the concept of NEE s_N is at least questionable. The reason is that s_N cannot be defined uniquely. This has been shown by J. Meixner³.

Therefore one may ask whether thermodynamics of processes can be developed without postulating the inequality 1 and without using the concept of NEE or the inequality 3. This is indeed possible. J. Meixner⁴ has developed a theory of processes in continuous matter without using the inequalities 1 or 3 and without using the concept of NEE. This theory will therefore be called ETIP. Instead of the generalized CDI 1 or 3 in ETIP one has the Fundamental Inequality (FI) [ref. 4, p 88, (6)] which is mainly a consequence of the integral form of the second part of the second law

$$S_{st}(B) - S_{st}(A) \geq \int_A^B \frac{\delta Q}{T} \quad (4)$$

Here A and B denote two *equilibrium* states where B is posterior to A and δQ is the heat the system has been supplied with at a temperature T . This inequality has been proved by R. Clausius⁵. In contrast to this, the differential form of the second part of the second law

$$dS_N \geq \delta Q/T \quad (5)$$

is a postulate and cannot be concluded from expression 4 or any other equivalent form of the second law.

Now we shall write down the FI for a fluid or solid system which consists of one component and one phase only and which is not affected by any body forces. Arbitrary time-dependent forces acting on the surface of the system may be prescribed by boundary conditions.

The system can exchange heat and mechanical work through its surface with its surroundings.

In the interior of the system heat conduction, internal friction and a process which will be called 'internal energy exchange' may appear. Following J. Meixner⁴, for each element of such a system and each real process which starts at $t = -\infty$ in an equilibrium state, the FI

$$\int_{-\infty}^{t_0} \left\{ \left(\frac{1}{T_{st}} - \frac{1}{T} \right) \dot{u} + \frac{1}{\rho} \left(\frac{P_{stik}}{T_{st}} - \frac{P_{ik}}{T} \right) \eta_{ik} + \frac{1}{\rho} q_i \partial_i \frac{1}{T} \right\} dt \geq 0 \quad (6)$$

holds. Here T_{st} means the thermostatic temperature, $T \dots$ thermodynamic temperature, $P_{stik} \dots$ thermostatic pressure tensor, $P_{ik} \dots$ thermodynamic pressure tensor, $v_i \dots$ velocity, $\partial_i = \partial/\partial x_i$, $2\eta_{ik} = \partial_i v_k + \partial_k v_i$ ($i, k = 1, 2, 3$), $F_{ij} = (\partial/\partial X_j) x_i(X_k, t) \dots$ deformation gradient, $x_i(X_k, t) \dots$ trajectory of a mass element $\dot{} = (\partial/\partial t) + v_i(\partial/\partial x_i) \dots$ substantial time derivative, $X_k \dots$ initial position of the mass element.

All quantities are functions of position x_i and time t . In all quantities

appearing in expression 6 the dependence on position x_i may be thought to be changed into a dependence on time by use of the trajectory $x_i(X_k, t)$ of the element. In other words, expression 6 holds for a fixed material element along its path. The following relations hold

$$ds_{st}(u_1 F_{ij}) = \frac{1}{T_{st}} du + \frac{1}{\rho} \sum_{ikl} (F^{-1})_{ik} (P_{stkl}/T_{st}) dF_{ei} \quad (7)$$

$$2\eta_{ik} = \sum_1 \{ \dot{F}_{il}(F^{-1})_{ik} + \dot{F}_{kl}(F^{-1})_{li} \} \quad (8)$$

$$\rho(t) = \rho(-\infty) (\text{Det} |F_{ij}(t)|)^{-1} \quad (9)$$

The quantities T_{st} , P_{stik} are defined by equation 7. The thermodynamic temperature T and pressure tensor P_{ik} describe the temperature and the stresses which are actually realized in the system at time t and position x_i . In general T will differ from T_{st} in the same way that P_{ik} will differ from P_{stik} .

The FI holds for all times t_0 , arbitrary mass elements and all real processes which start in an equilibrium state at $t = -\infty$, i.e. all systems of continuous functions

$$\{u(t'), F_{ij}(t'), q_i(t'), \rho(-\infty), \quad -\infty < t' \leq t\} \quad (10)$$

The integrand of the FI is, apart from a factor ρ , the 'production σ_{st} of thermostatic entropy', i.e.

$$\rho \dot{s}_{st} + \partial_i(q_i/T) = \sigma_{st} \quad (11)$$

$$\sigma_{st} = \left(\frac{1}{T_{st}} - \frac{1}{T} \right) \rho \dot{u} + \left(\frac{P_{stik}}{T_{st}} - \frac{P_{ik}}{T} \right) \eta_{ik} + q_i \partial_i(1/T) \quad (12)$$

σ_{st} need not be positive only but also may assume negative values! In view of the generalized CDI 1, 3, the FI 6 and the relation 11, the following questions arise:

- (1) Do materials exist for which one may deduce from 4 or 6 respectively the validity of the CDI 1 for s_{st} ? In other words: For what kinds of materials may the thermostatic entropy s_{st} also be interpreted as NEE?
- (2) Assume that question 1 is answered in the negative for the material under consideration. Is it possible to define at least a certain NEE in such a manner that both the FI 6 and the CDI 3 for s_N hold?

Here we shall only consider question 1. In the following we give the answer to this question for the system mentioned above (one component, one phase, no body forces) and for some special classes of materials. Some results concerning question 2 will be the subject of another publication.

Now the answer to question 1 depends mainly on the structure of the CE of the material under consideration. Therefore we must make a few remarks on these equations.

One usually assumes (ref. 2, p 56 etc.; ref. 4, p 91) that the present state of a certain element of mass is uniquely determined by the 'history' of the element. Here we confine ourselves to so-called 'simple materials' which are characterized by the fact that their state at time t is completely specified by the histories of u , q_i and F_{ik} . All other quantities, especially the coefficients

of u , q_i , η_{ik} which appear in the FI 6,

$$\frac{1}{T_{st}} - \frac{1}{T}, \frac{P_{st ik}}{T_{st}} - \frac{P_{ik}}{T}, \partial_i \frac{1}{T} \quad (13)$$

must be functionals of the history 10. These functionals must be single-valued, continuous and invariant against translation of time. Therefore the CE may be written as:

$$\frac{1}{T_{st}} - \frac{1}{T} = \mathcal{F}_0\{\cdot/\cdot\} \quad (a)$$

$$\partial_i \frac{1}{T} = \mathcal{F}_{1,i}\{\cdot/\cdot\} \quad i, k = 1, 2, 3 \quad (b)$$

$$\frac{P_{st ik}}{T_{st}} - \frac{P_{ik}}{T} = \mathcal{F}_{2,ik}\{\cdot/\cdot\} \quad (c)$$

Here the bracket $\{\cdot/\cdot\}$ is given by 10. The equations 14b and 14c are generalized laws of heat conduction and internal friction respectively. Equation 14a describes the so-called 'internal energy exchange'. Example: Relaxation of temperature in a homogeneous mixture of ortho- and para-hydrogen. The functionals \mathcal{F}_α ($\alpha = 0, 1, 2$) must vanish in thermostatic equilibrium. Therefore, it is presumed that for all $t \geq t_0$

$$\dot{u}(t) = 0, \quad q_i(t) = 0, \quad \dot{F}_{ij}(t) = 0$$

the relation

$$\lim_{t \rightarrow \infty} \mathcal{F}_\alpha\{u(t') \dots \rho(-\infty); -\infty < t' \leq t\} = 0, \quad \alpha = 0, 1, 2 \quad (15)$$

holds. Moreover, the functions \mathcal{F}_α must obey the FI 6 and the principle of material frame indifference (ref. 2, p 44). For literature, see ref. 4, pp 93, 43 respectively.

Two important classes of materials are those of differential type and of integral type (ref. 2, p 93, 98; ref. 4, p 95). The following statements hold*:

(1) For simple thermodynamic materials of the differential type with arbitrary complexity $r \geq 1$, one can conclude under certain conditions from the FI 6 that the CDI 1 holds for s_{st} . To be more precise we formulate a theorem:

C_1 : The material is simple, of the differential type and has arbitrary complexity $r \geq 1$. That is, the functionals are restrained to single-valued and continuous (generally non-linear) functions.

$$\mathcal{F}_\alpha\{\cdot/\cdot\} = \Phi_\alpha^{(r)}(-), \quad \alpha = 0, 1, 2 \quad (16)$$

with $(-) = (\dots \dot{u}^{(k)}(t) \dots, \dots \dot{q}_i^{(l)}(t) \dots, \dots \dot{F}_{ij}^{(k)}(t) \dots,$
 $\rho(-\infty), k = 0 \dots r, l = 0 \dots r - 1) \quad (17)$

C_2 : The equilibrium condition 15. In view of 16 and 17 this condition reads

$$\Phi_\alpha^{(r)}(u, 0, 0 \dots, 0 \dots 0, F_{ij}, 0 \dots, \rho(-\infty)) = 0$$

* C... condition, pre-requisite, T... theorem, P... proof.

C₃: The differences between T_{st} and T , P_{stik} and P_{ik} and the temperature gradient $\partial_i T$, which will occur in the material during the process, exist for all finite and infinite values of the higher time derivatives of u , q_i , F_{ij} namely $\dot{u}_i^{(k)}$, $\dot{q}_i^{(k-1)}$, $\dot{F}_{ij}^{(k)}$, $k = 2 \dots r$. In other words: Let $\dot{u}_i^{(k)} = a_k$, $\dot{q}_i^{(k-1)} = b_{ik}$, $\dot{F}_{ij}^{(k)} = c_{ijk}$ be arbitrary constants, then

$$\lim_{\tau \rightarrow \infty} \Phi_\alpha^{(r)}(u, \dot{u} \dots \tau a_k \dots, q_i \dots \tau b_{ik} \dots, F_{ij}, \dot{F}_{ij} \dots \tau c_{ijk} \dots)$$

= $\Phi_\alpha^{(r)}(u, \dot{u}, q_i, F_{ij}, \dot{F}_{ij}) \dots$ exists and is a single-valued and continuous function of its arguments.

C4: The Fundamental Inequality 6 with 14 and 16, i.e.

$$\int_{-\infty}^{t_0} \{ \dot{u} \Phi_0^{(r)} + \frac{1}{\rho} \eta_{ik} \Phi_{2,ik}^{(r)} + \frac{1}{\rho} q_i \Phi_{1,i}^{(r)} \} dt \geq 0$$

for all histories 10 the functions of which are differentiable r times and vanish or converge to a constant value for $t' \rightarrow -\infty$ faster than t'^n with $n = 1, 2, \dots$ arbitrary.

$$T: \sigma_{st} = \rho \dot{u} \Phi_0^{(r)} + \eta_{ik} \Phi_{2,ik}^{(r)} + q_i \Phi_{1,i}^{(r)} \geq 0$$

When $r = 1$ the condition C₃ is obeyed trivially because the functions $\Phi_\alpha^{(1)}$ ($\alpha = 0, 1, 2$) do not depend on the higher time derivatives $\ddot{u} \dots$ etc. In this case the CE 14 with 16 are, disregarding the distinction between T_{st} and T , the CE of TIP (ref. 1, p 425). Therefore one can say that, as a consequence of the above theorem, in TIP the CDI 1 for s_{st} does indeed hold. Moreover, one can say that in fact the CDI 1 for s_{st} holds for a much larger class of materials than those used in TIP, namely for materials which are of the differential type with arbitrary complexity $r \geq 1$ and which obey C₃.

(2) For simple thermodynamic materials of the integral type of order 1 and complexity 1 which obey a certain principle of fading memory the CDI 1 cannot hold. This is a consequence of the following theorem:

C₁: The material is simple, of the integral type*, of order 1 and complexity 1. That is, the functionals are restricted to

$$\mathcal{F}_\alpha \{ \% \} = A_\alpha^{(1)}(\text{---}) + \int_{-\infty}^t dt' \kappa_\alpha^{(1)}(\text{()}) \quad \alpha = 0, 1, 2 \quad (18)$$

with

$$\begin{aligned} (\text{---}) &= [u(t), \dot{u}(t), q_i(t), F_{ij}(t), \dot{F}_{ij}(t), \rho(-\infty)] \\ (\text{()}) &= [u(t'), \dot{u}(t'), q_i(t'), F_{ij}(t'), \dot{F}_{ij}(t'), t - t', \rho(-\infty)] \end{aligned} \quad (19)$$

and $\{ \% \}$ given by 10.

Further, $A_\alpha^{(1)}$ and $\kappa_\alpha^{(1)}$ are single-valued, finite and continuous functions of their arguments. Moreover, $\kappa_\alpha^{(1)}$ is integrable in $-\infty < t' \leq t$ for all histories 10 the functions of which vanish or converge to a constant value for $t' \rightarrow -\infty$ more rapidly than t'^n with $n = 1, 2 \dots$ arbitrary. The integral

* Our definition of materials of the integral type of order 1 is somewhat more general than the definition given by Truesdell and Noll in ref. 2 (We don't presume the integral kernels $\kappa_\alpha^{(1)}$ to be resolvable in factors which depend on different arguments.)

in equation 18 must converge for $t' \rightarrow -\infty$ uniformly with respect to t for all $t \geq t_0$.

C_2 : The equilibrium condition 15. We confine attention here to materials 18 for which the following conditions hold:

$$A_\alpha^{(1)}(u, 0, 0, F_{ij}, 0, \rho(-\infty)) = 0 \quad (a)$$

$$\kappa_\alpha^{(1)}(u, 0, 0, F_{ij}, 0, t - t', \rho(-\infty)) = 0 \quad (b) \quad (20)$$

$$\lim_{t \rightarrow \infty} (t - t') \kappa_\alpha^{(1)}(u, \dot{u}, q, F_{ij}, \dot{F}_{ij}, t - t', \rho(-\infty)) = 0 \quad (c)$$

This limit may be approached uniformly with respect to t' for all $t' \leq t_0$.

The assumption 20c means that the 'memory' of the material decreases for $t' \rightarrow -\infty$ faster than t'^{-1} . It can easily be seen that 20 is sufficient, though not necessary, for 15 to hold.

C_3 : The CDI 1 with 11, 12, 14 and 18, i.e.

$$\begin{aligned} \dot{u}(t) \left\{ A_0^{(1)} + \int_{-\infty}^t dt' \kappa_0^{(1)} \right\} + \frac{1}{\rho} \eta_{ik} \left\{ A_{2ik}^{(1)} + \int_{-\infty}^t dt' \kappa_{2,ik}^{(1)} \right\} \\ + \frac{1}{\rho} q_i \left\{ A_{1,i}^{(1)} + \int_{-\infty}^t dt' \kappa_{1,i}^{(1)} \right\} \geq 0 \end{aligned}$$

holds for all t and all histories 10, the functions of which are at least differentiable.

T: $\kappa_\alpha^{(1)}(1) = 0$.

P: See ref. 7.

Therefore when the memory functions $\kappa_\alpha^{(1)}$ in 18 are not identically zero, one can conclude that the CDI 1 for s_{st} cannot be valid for all times t .

(3) For simple thermodynamic materials of the integral type of order 1 and complexity $r = 2$, i.e. the functions $A_\alpha^{(2)}$ $\kappa_\alpha^{(2)}$ may depend on $(u, \dot{u}, \ddot{u}, q, \dot{q}, F_{ij}, \dot{F}_{ij}, \ddot{F}_{ij})$, the CDI 1 may or may not hold⁷.

The question whether CDI 1 holds for simple materials of integral type of higher order and higher complexity is postponed to future investigations.

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