The Concept of Reversibility and Irreversibility in Thermostatics

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First a general definition of reversibility is given which is in accordance with the mechanical concept of reversibility. This definition is applied to thermostatics. It is shown that the smooth curves in the space of equilibrium parameters can be approximated arbitrarily by irreversible or by almost reversible real processes. The work done during an almost reversible process is given by a Pfaffian form. The converse is also true. If the differential work is given by a Pfaffian form the processes are practically reversible. Finally the uniqueness of a Pfaffian form is shown, if it is used as differential work.

1. Introduction

In textbooks of thermodynamics or thermostatics one remarks a certain discrepancy in the use of terms like reversible, quasistatic etc. (cp. e.g. [1], p. 4 and [2], p. 3), that is, different notions are given by the same names. To a certain extent definitions are matters of taste, but they are matters of usefulness, too. Therefore, one is free to look for definitions which fulfil certain conditions of usefulness. Concerning the concept of reversibility I consider it useful to look for a definition which can be applied not only in thermostatics but also in other physical theories. Therefore, one has to avoid terms which are inherent in one theory but not in other ones, e.g. such notions as heat, temperature and entropy. Moreover, such a fundamental problem as the relationship between microscopic reversibility and macroscopic irreversibility can only be treated efficiently, if the definitions of reversibility in the macroscopic and in the microscopic theory are identical. Concerning the notion of a quasistatic process I consider it useful to take a definition such that the range of validity of thermostatics is as large as possible.

2. The Definition of Reversibility and Irreversibility

A definition of reversibility which is to be applied to several physical theories must be applicable to mechanics, too, since mechanics is one of the simplest theories of physics and the mechanical concept of reversibility is given in a natural way. Hence we first consider mechanics and transfer the mechanical definition to other theories.

Be given a Hamiltonian mechanical system the state of which is described by the point X of Γ-space, where $X = (p, q)$, $p = (p_1, \dots, p_n)$ and $q = (q_1, \dots, q_n)$. The motion of the system is influenced by some external parameters, which enter the Hamiltonian. The external parameters may be given by a potential ψ and an electromagnetic potential (A, φ), which may vary in space and time. As an abbreviation one uses $\gamma(t) = [A(\cdot, t), \varphi(\cdot, t), \psi(\cdot, t)]$. Furtheron one defines the operation of the reversion of motion $\hat{T}_\mathrm{i}$ by $\hat{T}_\mathrm{i}(p, q) = (-p, q)$. The evolution in time of the considered system be given by a function ξ, so that $\xi(t_0) = X_0$ is the initial state at time t_0. Then the following theorem holds:

Let be $X_1 = \xi(t_1)$, $t_1 > t_0$, and be γ' defined by

$$\gamma'(t) = [-A(\cdot, t_2 + t_1 - t), \varphi(\cdot, t_2 + t_1 - t), \psi(\cdot, t_2 + t_1 - t)] \equiv \hat{T}_\mathrm{a}[\gamma(t_2 + t_1 - t)].$$

Then there exists a function ξ' with the properties $\xi'(t_2) = \hat{T}_\mathrm{i}(X_1)$and $\xi'(t_3) = \hat{T}_\mathrm{i}(X_0)$ where

$$t_3 = t_2 + t_1 - t_0$$

so that ξ' describes the motion of the system under the external conditions γ', if the Hamiltonian is invariant under $\hat{T}_\mathrm{i}$ and $\hat{T}_\mathrm{a}$. In other words: The inverse evolution in time of the external parameters combined with the minus sign of A causes an evolution in time of the system which leads the system back to $\hat{T}_\mathrm{i}(X_0)$ in a time interval of length $t_1 - t_0$, starting from $\hat{T}_\mathrm{i}(X_1)$. Because of this

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[1] K. HUANG, Statistical Mechanics, John Wiley and Sons, Inc., New York, London 1963.

[2] R. HAASE, Thermodynamik der irreversiblen Prozesse. Dr. Dietrich Steinkopff Verlag, Darmstadt 1963.

theorem the proof of which is easy, the mechanical processes are called reversible. Now it is easy to abstract a definition of reversibility from the mechanical example.

Be given a system with the internal states X, and the external parameters Y. Be considered a time interval $[t_0, t_1]$ in which the evolution in time is given by ξ, which itself is caused by the evolution γ of the external parameters. The process ξ with $\xi(t_0) = X_0$ and $\xi(t_1) = X_1$ is called reversible if the following conditions are satisfied:

1) There are two operators $\hat{T}_\mathrm{a}$ and $\hat{T}_\mathrm{i}$ which are defined on certain sets of external or internal states respectively so that $\hat{T}_\mathrm{i}$ intuitively means the reversion of motion and $\hat{T}_\mathrm{a}$ the change of some signs. Then $\hat{T}_\mathrm{i}(X_0)$, $\hat{T}_\mathrm{i}(X_1)$ and $\hat{T}_\mathrm{a}[\gamma(t)]$ for all $t \in [t_0, t_1]$ are defined. Furtheron $\hat{T}_\mathrm{i}^2 = 1$ and $\hat{T}_\mathrm{a}^2 = 1$.

2) There is an evolution in time γ' of the external parameters which is given by

$$\gamma'(t) = \hat{T}_\mathrm{a} \circ \gamma[t_1 - \sigma(t)]$$

where $\sigma(t_2) = 0$ and $\sigma(t_3) = t_1 - t_0$ with $t_3 > t_2$.

3) There is a process ξ' which is caused by γ' so that $\xi'(t_2) = \hat{T}_\mathrm{i}(X_1)$ and $\xi'(t_3) = \hat{T}_\mathrm{i}(X_0)$.

If not all of these conditions are fulfilled, the process ξ is called irreversible. The definition given here can be applied to statistical mechanics by taking for the states X the probability densities F, to quantum mechanics by taking X as statistical operators W, to the Boltzmann kinetic theory of gases by taking X as the Boltzmann densities f and so on. The application of the definition to thermostatics is given in sections 3 and 4.

The three conditions are of different importance. The external parameters may be chosen arbitrarily. Thus, the existence of $\hat{T}_\mathrm{a}(\gamma(t))$ and the second condition are weak requirements. E.g. for $\hat{T}_\mathrm{a} = 1$ the second condition only states that the external process γ' retraces the process γ, possibly with a certain variance in time which is expressed by the function σ. In the first condition it is stated that the reversion of motion can be performed for certain states. This condition is one of the crucial points in the statistical foundation of macroscopic dynamics. Without going into detail it is to be remarked that the irreversibility of macroscopic systems which are described by statistical mechanics is caused by the impossibility of performing the reversion of motion. The third condition intuitively means that a process ξ' leads from the reversed final state back to the reversed initial state. It is to be emphasized that only the endpoints of the processes ξ and ξ' are set into correspondence, but not the intermediate states. Such a correspondence can hold. E.g. in mechanics one has

$$\xi'(t) = \hat{T}_\mathrm{i} \circ \xi(t_2 + t_1 - t). \tag{1}$$

But applying our definition to thermostatics one must bear in mind that for the processes treated there only the endpoints are equilibrium states. Thus using instead of the third condition a stronger condition like (1) the problem of reversibility or irreversibility could not be treated within the frame of thermostatics, but the methods of nonequilibrium thermodynamics would be needed. Therefore we adopt the weak reversibility condition despite of the fact that in mechanics and in quantum mechanics the strong condition (1) holds.

A sufficient condition for irreversibility can easily be given: If there is a function S depending on the states X, Y invariant under $\hat{T}_\mathrm{i}$, $\hat{T}_\mathrm{a}$, and increasing for each process (which is not an equilibrium state) then the processes are irreversible. The proof is trivial.

3. Reversible and Irreversible Approximation of Quasi-Processes

3.1. Definitions

The main object of thermostatics is the set Γ_e of the possible equilibrium states of a system. Now the question arises how processes can be treated within the frame of thermostatics. Since continuous sequences of equilibrium states are not observed in nature, the (piecewise smooth) curves treated in thermostatics are not directly related to real processes. Such piecewise smooth curves provided with a direction here are called quasi-processes after EHRENFEST-AFANASSJEWA[3]. The only natural processes which are in any way related to thermostatics are the sequences of transitions between equilibrium states, which are enforced by the changes of external conditions. Among these are the real "slowly varying" processes, often called quasistatic. This notation will now be generalized: A sequence of transitions between equilibrium

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[3] T. EHRENFEST-AFANASSJEWA, Die Grundlagen der Thermodynamik, E. J. Brill, Leiden 1956.

states is called quasistatic process of the order ω, if the maximal distance between neighbouring states of the sequence is not larger than ω.

As is seen below, the quasistatic processes of "low" order are of special interest. It is intuitively clear that a quasistatic process the order of which is of the order of magnitude of the measuring inaccuracy must have to do something with a quasiprocess, so that the necessity of a distinction is not seen at the first glance. But studying questions of reversibility and irreversibility in thermostatics it is useful to distinguish between quasi-processes and quasi-static processes. For, under some suppositions for closed systems the equilibrium states of which are given by a temperature T and the volume V the following theorem holds:

Each quasi-process can be approximated arbitrarily by an irreversible or by an almost reversible quasistatic process.

The notion "almost reversible" means that given any neighbourhood of the initial state, the process can be chosen so that the invers process leads back to the (reversed) neighbourhood of the initial state. Here the initial states are equilibrium states, so that the operator of the reversion of motion is the identity.

The theorem will be proved in the following subsections 3.2.—3.5.

3.2. *External Parameters*

V itself is an external parameter the values of which can be given arbitrarily, but larger than a positive number. Those variations in time of V which lead to quasistatic processes must be so that after a variation the volume is held fixed so that the system relaxes.

Other external parameters are given by the thermal contact of the system. If the system at temperature T is in thermal contact with a body of temperature T', a variation of the state is caused, if $T \neq T'$. For $T = T'$ a variation only can occur if the volume is changed at the same time. As external parameters describing the heat contact one can use e.g. the coordinates of the bodies which can be brought into contact with the system. But in the further considerations only the coupling between the system and a body of the same temperature is treated so that only one temperature and the heat capacity enter the formalism. Adiabatic isolation can formally be treated as thermal contact with a body of mass zero. In the following it is supposed, that for each temperature there is a body the heat capacity C (at constant external parameters) of which is constant in a small temperature interval. Here the (finite!) bodies are called heat reservoirs.

3.3. *Special Quasistatic Processes*

The system being in a state (T, V) is brought into thermal contact with a heat reservoir of the temperature T and the heat capacity C, then the system is expanded to the volume V' under the external pressure p_{a}^{-} (which is smaller than the internal pressure p) and finally the thermal contact is interrupted after the system having relaxed in a state (T', V'). According to the first law one has

$$U(T', V') - U(T, V) = -\int_{V}^{V'} p_{\mathrm{a}}^{-}(\tilde{V})\,\mathrm{d}\tilde{V} - C(T' - T)\,. \tag{2}$$

The reversed external process is as follows: The system is coupled with a heat reservoir of temperature T' and heat capacity C, then it is compressed to V (under the external pressure $p_{\mathrm{a}}^{+} > p$) and finally when the system has relaxed, the thermal contact is interrupted. The operators $\hat{T}_{\mathrm{i}}$ and $\hat{T}_{\mathrm{a}}$ here are the identities, because no magnetic fields or velocities enter the state. The first law yields:

$$U(\tilde{T}, V) - U(T', V') = -\int_{V'}^{V} p_{\mathrm{a}}^{+}(\tilde{V})\,\mathrm{d}\tilde{V} - C(T - T')\,. \tag{3}$$

For the combination of the two processes one has

$$U(\tilde{T}, V) + C\tilde{T} = U(T, V) + CT + \int_{V}^{V'} (p_{\mathrm{a}}^{+}(\tilde{V}) - p_{\mathrm{a}}^{-}(\tilde{V}))\,\mathrm{d}\tilde{V}\,. \tag{4}$$

Because of $p_{\mathrm{a}}^{+}(\tilde{V}) > p_{\mathrm{a}}^{-}(\tilde{V})$ the work integral in (4) is positive. The inner energy is increasing in T. Therefore one has at once $\tilde{T} > T$. Thus the expansion process is irreversible.

It is easily seen that the formulae (2), (3) and (4) also hold for a combination of such single steps as considered above. The result is that every quasistatic process is also irreversible in a strict sense.

But formula (4) also gives hints how to get almost reversible processes:

1) If one chooses p_{a}^{+} and p_{a}^{-} approximately equal to the inner pressure p, the work integral in (4) becomes small and one has $\tilde{T} \approx T$.

2) One divides (4) by C and considers heat reservoirs the capacity of which goes to infinity. Then $\tilde{T} \to T$.

3) If $V' - V$ is small enough, one also has $\tilde{T} \approx T$. But this case is trivial, because practically no process happens at all.

3.4. *Special Quasi-Processes*

Now the combination of formal differential processes of the kind considered in 3.3. is treated, i.e. their integration. It is supposed that the external pressures are equal to λp, where p is the internal pressure and λ a constant with $0 \leqq \lambda \neq 1$. For a differential process of this kind one has

$$\left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T = - C\,\mathrm{d}T - \lambda p\,\mathrm{d}V\,.$$

Thus one finds the differential equation

$$\frac{dT}{\mathrm{d}V} = - \frac{\left(\frac{\partial U}{\partial V}\right)_T + \lambda p}{C + m\,c_v} \tag{5}$$

where m is the mass and c_v is the specific heat at constant volume. If c_v is given as a function of T for a certain $\tilde{V}$, then the right hand side of (5) is completely determined by the equation of state for p.

In the following it is assumed that $(\partial U/\partial V)_T \geqq 0$ and that (5) has a unique solution through each possible state (T_0, V_0). This solution, depending on certain parameters, may be written in the form

$$T = f(V, T_0, V_0, \lambda, C)\,. \tag{6}$$

Because the right hand side of (5) is not positive by assumption, f is non-increasing. f is a constant, if $C = \infty$ or if the numerator is zero. The numerator is zero if and only if the equation of state reads

$$p = T^{1-\lambda} \cdot h(V)\,. \tag{7}$$

Thus λ always can be chosen so that the numerator is unequal zero. For real reservoirs, i.e. $C < \infty$ one has f strictly decreasing except perhaps for some λ.

The curves described by f are quasi-processes, and the question arises how they can be related to quasistatic processes. This question is answered by the following lemma: For each λ and C there is a quasistatic process the equilibrium states of which are on the curve $T = f(V, T_0, V_0, \lambda, C)$ for each (T_0, V_0). Furtheron the work in each step of the quasistatic process is done with a constant pressure $p_a = \lambda' p$, where $\lambda' \to \lambda$ with decreasing order of the quasistatic process.

The proof reads as follows: Let be (T, V) and (T', V') points of $T = f(V, T_0, V_0, \lambda, C)$. With the abbreviation $T' = T + \Delta T$ and $V' = V + \Delta V$ one has for the inner energy

$$\begin{aligned} U(T + \Delta T, V + \Delta V) - U(T, V) \\ = - C\,\Delta T - \lambda' p(T, V)\,\Delta V \end{aligned} \tag{8}$$

where by definition

$$\Delta T = - T + f(V + \Delta V, T_0, V_0, \lambda, C)\,. \tag{9}$$

Combining these two equations one finds that λ' is continuous in ΔV and $\lambda' = \lambda + O(\Delta V)$.

The result is that these quasistatic processes have the same properties concerning the almost reversibility or irreversibility as the corresponding quasi-processes, if the order of the quasistatic processes is sufficiently low.

3.5. *Approximation of Quasi-Processes*

As a last step in the proof of the theorem of 3.1. it will be shown, that each quasi-process can be arbitrarily approximated by curves given by $f(V, T_0, V_0, \lambda, C)$ with either $\lambda \ll 1$ and $\lambda \gg 1$ or $\lambda \approx 1$.

Each quasi-process consists of parts which correspond to an expansion, a compression or to constant volume. Therefore it is sufficient to consider such parts. First the expansion is considered. Let be $T = r(V)$ a finite nondecreasing part of a quasi-process with $V \in [V', V'']$ and

$$\Omega_\varepsilon(r) = \{(T, V)\,|\,T = r(V) \pm \eta, 0 \leqq \eta \leqq \varepsilon\}$$

a strip around the curve r.

Starting at the point $(T_0, V_0) = (T' + \varepsilon, V')$ one follows the decreasing curve $T = f(V, T_0, V_0, \lambda_1, C)$ with $\lambda_1 < 1$ and $C > 0$ to a boundary point $(\hat{T}_1, \hat{V}_1)$ of $\Omega_\varepsilon(r)$. Because r is nondecreasing, this point is on the line $V = V''$ or on the curve $T = r(V) - \varepsilon$. In the first case the approximation is shown. In the latter case it is impossible to proceed further by an expansion step. Thus one follows the curve $T = f(V, \hat{T}_1, \hat{V}_1, \hat{\lambda}_1, 0)$ with $\hat{\lambda}_1 > 1$, i.e. performes a compression, to a point (T_1, V_1) which is on the curve $T = r(V) + \varepsilon$. Because of the fact that the curves for $C = 0$ are steeper than for $C \neq 0$, one has $V_1 > V_0 = V'$. In the same way one proceeds from (T_1, V_1). This procedure cannot converge. For, assuming the convergence there must be points in which the curves $T = f(V, \tilde{T}, \tilde{V}, \lambda, C)$ have the same tangent for $\lambda > 1$, $C = 0$ and for $\lambda < 1$, $C > 0$. But the differential equation for f shows that this doesn't happen. Thus after a finite number of steps the line $V = V''$ must be reached. It may be remarked that the same procedure can be established starting from $T_0 = T' \pm \eta$, $\eta < \varepsilon$. In an analogue way the expansion via a decreasing r, and the compression can be treated.

Finally for the isochoric parts of a quasi-process a similar procedure can be applied starting with a set

$$\Lambda_\varepsilon = \{(T, V) \mid T \in [T', T''],\ V \in [V' - \varepsilon, V' + \varepsilon]\}$$

instead of $\Omega_\varepsilon(r)$.

Because the approximation doesn't depend on the magnitude of λ, i.e. whether $\lambda \gg 1$, $\lambda \gg 1$ or whether $\lambda \approx 1$, the irreversible and the almost reversible approximation is shown. With this remark the proof is complete.

3.6. Remarks

It must be emphasized that the irreversible approximation is by no means unique. E.g. the isochoric quasi-process can be followed exactly by heat transfer without doing work at all. But it was seen that the almost reversible approximation requires always $p_a^{\pm} \approx p$ and heat transfer at identical temperatures. In this sense the reversible approximation is unique.

As the result of the foregoing subsections it can be stated that as far as only quasi-processes are concerned, the concept of reversibility or irreversibility is not inherent in the formalism of thermostatics. This problem requires the concept of work.

4. Reversible and Irreversible Work

4.1. The Work of an Approximating Process

First the work of the quasistatic processes which follow the curves $T = f(V, T_0, V_0, \lambda, C)$ is calculated. Summing up steps of the form (8) in 3.4. one has for the work W:

$$W = -\sum_j \lambda_j' \, p_j \, \Delta V_j \,. \tag{10}$$

Because of $\lambda_j' = \lambda + O(\Delta V_j)$ one has with $\delta = \max\{\Delta V_1, \Delta V_2, \ldots\}$

$$W = -\lambda \int p(f(V, T_0, V_0, \lambda, C), V) \, \mathrm{d}V + O(\delta). \tag{11}$$

Thus the "work" done by the quasi-process $T = f(V, \ldots)$ is practically equal to the work of the corresponding real quasistatic process if the order of the latter is sufficiently small.

Generally the quasistatic processes show quite an other feature. In order to investigate this the expansion part r of a quasi-process is considered which was already treated in 3.5. The work done by an approximating quasistatic process using (11) is given by

$$\begin{aligned} W = &-\sum_j \lambda_j \int\limits_{V_{j-1}}^{\hat{V}_j} p(f(V, T_{j-1}, V_{j-1}, \lambda_j, C), V) \, \mathrm{d}V \\ &-\sum_j \hat{\lambda}_j \int\limits_{\hat{V}_j}^{V_j} p(f(V, \hat{T}_j, \hat{V}_j, \hat{\lambda}_j, 0), V) \, \mathrm{d}V + O(\delta). \end{aligned} \tag{12}$$

This can be written in the form

$$\begin{aligned} W = &-\sum_j \lambda_j \int\limits_{V_{j-1}}^{V_j} p(f(V, T_{j-1}, V_{j-1}, \lambda_j, C), V) \, \mathrm{d}V \\ &-\sum_j \int\limits_{V_j}^{\hat{V}_j} [\lambda_j \, p(f(V, T_{j-1}, V_{j-1}, \lambda_j, C), V) - \\ &-\hat{\lambda}_j \, p(f(V, \hat{T}_j, \hat{V}_j, \hat{\lambda}_j, 0), V)] \, \mathrm{d}V + O(\delta). \end{aligned} \tag{13}$$

The first sum is abbreviated by W_1 the second one by W_2. Furtheron some auxiliary functions are introduced. Let be

$$\left.\begin{aligned} \varrho(V) &= \lambda_j \\ \tau(V) &= T_{j-1} \\ \chi(V) &= V_{j-1} \end{aligned}\right. \qquad \text{for} \qquad V \in [V_{j-1}, V_j]$$

and

$$g(V) = f(V, \tau(V), \chi(V), \varrho(V), C)$$

then

$$W_1 = -\int\limits_{V'}^{V''} \mathrm{d}V \, \varrho(V) \, p(g(V), V) \,.$$

Thus far approximations of $T = r(V)$ in a fixed strip of thickness ε around r were considered. For several ε one gets different expressions, which are denoted by ϱ_ε, g_ε and $W_{1\varepsilon}$.

By definition g_ε converges to r pointwise, if $\varepsilon \to 0$. For all ε the ϱ_ε are bounded by 1. Furtheron, if $\varepsilon < \varepsilon_0$, ε_0 finite, the pressure p is bounded in $\Omega_\varepsilon(r)$, because it is continuous in T, V. If ϱ_ε converges to a function ϱ_0, what is supposed here, the limit $\lim\limits_{\varepsilon \to 0} W_{1\varepsilon}$ exists and can be calculated by interchanging the limit and the integral. Therefore one has

$$W = -\int\limits_{V'}^{V''} \varrho_0(V) \, p(r(V), V) \, \mathrm{d}V + W_2 + O'(\varepsilon) + O(\delta) \,. \tag{14}$$

Here $O'(\varepsilon)$ means only that $O'(\varepsilon) \to 0$, if $\varepsilon \to 0$. The function ϱ_0 can be a constant λ and $\lambda < 1$. Thus the work W contains two parts. The first (the integral in (14)) can be interpreted as the ,,irreversible work" done by the quasiprocess. The second part W_2 contains work done during a compression and is always nonnegativ. W_2 cannot be calculated easily in every case, but in the reversible limit W_2 vanishes. More exact: If one expands the system with $\lambda = 1 - \varkappa$, $\varkappa > 0$ and compresses it with $\lambda' = 1 + \varkappa$, then $W_2 = O'(\varepsilon) + O(\varkappa)$ if $\varkappa \to 0$. The proof is as follows:

By definition one has

$$W_2 = -\sum_j \int_{V_j}^{\hat{V}_j} [p(f(V, T_{j-1}, V_{j-1}, 1, C), V) - p(f(V, T_j, V_j, 1, 0), V)] \, \mathrm{d}V + O(\varkappa) .$$

Now some auxiliary functions depending on ε are introduced

$$h_\varepsilon(V) = \begin{cases} f(V, T_{j-1}, V_{j-1}, 1, C), & V \in [V_j, \hat{V}_j] \\ r(V), & V \notin \bigcup_j [V_j, \hat{V}_j] \end{cases}$$

$$\hat{h}_\varepsilon(V) = \begin{cases} f(\hat{V}, \hat{T}_j, V_j, 1, 0), & V \in [V_j, \hat{V}_j] \\ r(V), & V \notin \bigcup_j [V_j, \hat{V}_j] . \end{cases}$$

Both h_ε and $\hat{h}_\varepsilon$ converge to r pointwise for $\varepsilon \to 0$. Since W_2 depends on ε one writes $W_{2\varepsilon}$. Then one has

$$W_{2\varepsilon} = -\int_{V'}^{V''} p(h_\varepsilon(V), V) \, \mathrm{d}V + \int_{V'}^{V''} p(\hat{h}_\varepsilon(V), V) \, \mathrm{d}V + O(\varkappa) .$$

Because of the continuity of p the limit and the integral can be changed and one has

$$W_{2\varepsilon} = O'(\varepsilon) + O(\varkappa) .$$

For the almost reversible quasistatic processes the wellknown result holds:

$$W = -\int_{V'}^{V''} p \, \mathrm{d}V + O(\varkappa) + O'(\varepsilon) + O(\delta) .$$

Thus far we have treated only one part of a quasiprocess, but the other branches can be investigated similarly with the same results.

4.2. Pfaffian Forms as Differential Work

In the last subsection it was shown that the work of the almost reversible quasistatic processes can be calculated up to negligible quantities by an integral with the differential form $-p \, \mathrm{d}V$ over a quasi-process. The same is true for the almost reversible quasistatic processes which approximate the inverse quasiprocess. But for the irreversible quasistatic processes a Pfaffian form for the differential work doesn't exist. For, the integrals in (13) depend on the factors λ which are different for different directions of the process. This fact is understood by the following theorem:

Be considered a system with equilibrium states given by a temperature T and the external parameters $Y = (y_1, \ldots, y_m)$. The system may undergo quasistatic processes, the single steps of which can be calculated (in sufficient approximation) as differentials. Furtheron the summation of these steps can be replaced by an integration. The heat transfer is to be done as described above and the differential work δW be given (in sufficient approximation) by a Pfaffian form independently of the process. Finally the external processes be piecewise differentiable. Then the considered quasistatic processes are (practically) reversible.

The proof runs as follows: 1) Let be

$$\delta W = \sum_{\nu=1}^{m} K_\nu(T, Y) \, \mathrm{d}y_\nu .$$

Furtheron the heat capacity C of the reservoirs is supposed to be constant in small temperature intervals. As an abbreviation one uses

$$K = (K_1, \ldots, K_m) .$$

Then the first law reads for one step

$$\left(\frac{\partial U}{\partial T}\right)_Y \mathrm{d}T + \left(\frac{\partial U}{\partial Y}\right)_T \cdot \mathrm{d}Y = K \cdot \mathrm{d}Y - C \, \mathrm{d}T .$$

The variation in time of the external parameters in the interval $[t_0, t_1]$ be given by $\gamma(t)$. Then one has the differential equation:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \left[\frac{\partial U}{\partial T}(T, \gamma(t)) + C\right]^{-1} \cdot \left[K(T, \gamma(t)) - \frac{\partial U}{\partial Y}(T, \gamma(t))\right] \cdot \frac{\mathrm{d}\gamma}{\mathrm{d}t} \equiv F(T, t) . \tag{15}$$

A solution of this equation be $T = \Phi(t)$ with the initial condition $\Phi(t_0) = T_0$. Furtheron let be

$$\Phi(t_1) = T_1 .$$

2) The inverse external process γ' be defined by $\gamma'(t) = \gamma(t_1 + t_2 - t)$, hence $\hat{T}_{\mathrm{a}} = 1$.

The first law applied to the single steps of the inverse process yields a differential equation, like (15), of the form

$$\mathrm{d}T/\mathrm{d}t = F'(T, t) \qquad (16)$$

where

$$F'(T, t) = -F(T, t_2 + t_1 - t).$$

Now it is easily seen that Φ' defined by $\Phi'(t) = \Phi(t_2 + t_1 - t)$ is a solution of (16). Furtheron one has $\Phi'(t_2) = \Phi(t_1)$ and $\Phi'(t_3) = \Phi(t_0)$ with $t_3 = t_2 + t_1 - t_0$. Thus Φ' and γ' form the total inverse process of (Φ, γ).

3) By assumption the processes considered here are composed of parts as descriped in 1). Thus the statement is valid.

The result is, that Pfaffian forms and quasi-processes together are the idealized equivalent of the almost reversible quasistatic processes, whereas the same for the quasi-processes alone is not true.

4.3. Uniqueness of Pfaffian Forms

There is only one Pfaffian form as the differential work for a given system under the same suppositions as in 4.2.

The proof is as follows: Supposed there are two such forms $\delta W^j = K^j \,\mathrm{d}Y$. Then the following cyclic process is considered: The system being in the state (T, Y) is brought into thermal contact with a very large heat reservoir of temperature T so that the process is isothermal; the parameter y_μ is changed into $y_\mu + \mathrm{d}y_\mu$, $\mathrm{d}y_\mu > 0$, whereas y_ν, $\nu \neq \mu$ is held fixed, then $y_\mu + \mathrm{d}y_\mu$ is changed by $-\mathrm{d}y_\mu$, so that the system goes back to the initial state. If e.g. $K^1_\mu(T, Y) \leqq K^2_\mu(T, Y)$, in the first step K^1_μ and in the second one K^2_μ is used. The first law yields:

$$(K^1_\mu(T, Y) - K^2_\mu(T, Y))\,\mathrm{d}y_\mu + \delta Q = 0\,.$$

Thus $\delta Q \geqq 0$. After the second law one has $\delta Q = 0$. Hence $K^1_\mu = K^2_\mu$ and also $\delta W^1 = \delta W^2$.