To the Mathematical Concept of Thermostatics

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We discuss the integrated form of the laws of thermostatics by using Stokes theorem on manifolds. We give a new insight to the basic properties of thermostatics, in particular we show that only the second law is a necessary condition to identify the integrating factor with the temperature. Moreover we consider the thermodynamical field equations for discontinuous media and discuss the properties of thermostatics.

1. Introduction

By using the exterior differential calculus for differential forms the well-known results of classical thermostatics are given in a new formulation. Therefore, we use the notation and terminology of the exterior differential calculus for forms on manifolds throughout this paper.

We study the principles of thermostatics, especially the underlying structural features, in order to find a formulation of thermodynamics, namely a thermodynamical field theory. The foundations of thermodynamics today are field theoretical concepts. In the field theory, we can start with a Lagrange-functional from which Anthony [1] has deduced all balance equations and constitutive equations by using Noether's theorem. In contrast to this theory we start with the balance equations combined with the constitutive equations which yield field equations for the thermodynamical fields. The constitutive equations must be established by assumptions on the material which we want to consider. The first way is very fundamental and the interested reader is refered to [1] in which the author explains the theory, furthermore, the author gives us an application to liquid crystals. In the second way there exist two problems, namely the systematic approach of the constitutive equations and the solutions of the field equations. The functional form of the constitutive equations can be restricted by the transformation properties of the functional form and a local entropy inequality, namely the Clausius-Duhem inequality, or an entropy inequality given by Müller [2], or an entropy inequality in the formulation of Lagrange multipliers given by Liu [3]. A thermodynamical field theory for discontinuous media is described by Grauel [4]. In [4] we have introduced surface Lagrange multipliers to formulate a surface entropy inequality to restrict the constitutive equations.

In this paper we call thermostatics the thermodynamics in which the time does not occur explicitly. In thermodynamics the equilibrium is understood as a thermodynamical process where all constituents are at rest in a frame of reference and the temperature is time independent and uniform. The consequences of this definition are explained in [4], and furthermore in case of mixtures of chemically reacting fluids at an interface in [5]. In a static process all the time derivatives in the field equations are equal to zero. In general we understand as a thermodynamic process a solution of the field equations obeying certain initial and boundary data. The relevant fields of a mixture are the fields of the mass densities, the velocities of the particles[1] and the temperature, and we do not distinguish between extensive and intensive variables of the system which is under consideration.

In the present paper we presuppose the knowledge of the basic assumptions of the thermodynamics of Caratheodory [7] and Ehrenfest-Afanassjewa [8–10]. We give a confrontation of two formulations of thermostatics, namely of the thermostatics in the exterior calculus on manifolds and the thermostatics of field theoretical considerations.

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[1] We shall not attempt here to give a correct definition of particles. The particles are understood as small volume elements [6].

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2. Thermostatics in Exterior Calculus

We assume that the possible equilibrium states are represented by the points of a finite-dimensional differentiable manifold M. This manifold is endowed with a C^∞-structure.

The definition of temperature is based on the existence of an equivalence relation between different thermal systems in different states. By physical experience we say that two thermal systems, $\mathfrak{B}_1$ and $\mathfrak{B}_2$, in thermal equilibrium have the same temperature provided that when they are brought in thermal contact with each other, they remain in thermal equilibrium. This can be mathematical expressed by the 0th principle.

a) Every thermal system in a definite state has only one temperature. In this state the system is in equilibrium with itself

$$\mathfrak{B}_1 \sim \mathfrak{B}_2 .$$

b) Reciprocity means

$$\mathfrak{B}_1 \sim \mathfrak{B}_2 \leftrightarrow \mathfrak{B}_2 \sim \mathfrak{B}_1 .$$

c) In thermal contact we have:

If $\mathfrak{B}_1 \sim \mathfrak{B}_2$ and $\mathfrak{B}_2 \sim \mathfrak{B}_3$, then $\mathfrak{B}_1 \sim \mathfrak{B}_3$.

Now let us assume that the class of thermally equivalent systems can be characterized by the value of a function ϑ (called empirical temperature). We assume that the states which have the same temperature are collected by a submanifold with $\vartheta = \text{constant}$; this submanifold is called an isothermal manifold.

Let us now formulate the first principle of thermostatics by integration on manifolds. We give an integrated form of the principles of thermostatics. To do so let us confine our attention to a thermodynamical system, namely a one-constituent medium (gas or fluid) and assume its possible equilibrium states by the points of a finite-dimensional differentiable manifold M (called phase space).

Assumptions:

(i) The thermodynamical system shall be thermally isolated.

(ii) From the set of all equilibrium states M we consider only those which can be reached by a quasistatic path from the given states. This subset is considered as submanifold $N \subset M$ which we call an adiabatic submanifold.

(iii) The $X_0 = E, X_1, \ldots, X_n$ are the variables which describe the equilibrium states of the considered system, where E denotes the total energy of the system and the other variables X_1 to X_n describe the thermal system.

The traditional description of the first law of thermostatics is

$$\delta Q = \mathrm{d}E + \delta A , \tag{1}$$

where δQ is the abmount of heat, δA the external work and E the total energy. The first law, mathematically expressed [11, 12], can be written in the form

$$\beta = \mathrm{d}E + \alpha , \tag{2}$$

where we assumed that the external work transmitted by the system under a differential variation of its variables to the outside can be expressed by

$$\alpha = \sum_{p=1}^{q} a^p \, \mathrm{d}X_p . \tag{3}$$

The a^p are homogeneous functions of the $\{X_k\}_{k=0}^{q}$ and $X_0 = E$. Expression (2) is a relation among one-forms.

Remark: If we write $\beta = \mathrm{d}E + P\mathrm{d}V$, we shall interpret this expression as a relation among one-forms on a two-dimensional manifold. Now we discuss the integrated forms of the first and second principles of thermostatics by using the theorem of de Rham.

Proposition: The first principle can be written in the form

$$\oint_{\mathfrak{C}} \alpha = 0 \tag{4}$$

for non-dissipative systems.

Proof: Let us consider the submanifold N (adiabatic submanifold) as described by assumption (ii). On N we assume an adiabatically closed path $\mathfrak{C}: I \to N$, where I is an interval of the real t axis and $\mathfrak{C}$ is a differentiable map of I onto the manifold N with tangent vectors $\dot{\mathfrak{C}}$. If $\mathfrak{C}$ is an adiabatic path, then we conclude from (2) and (3) that

$$\beta|_{\mathfrak{C}} = 0 \quad \text{and} \quad A = \oint_{\mathfrak{C}} \alpha . \tag{5}$$

Therefore we can write the first principle in the form of (4). This equation says that there exists a circular reversible process which can not produce external work. From de Rhams theorem [13] we conclude that α is an exact form. This means that $\alpha = d\lambda$ and consequently $d\alpha = 0$. Moreover

$$d\alpha = 0 = d\beta \tag{6}$$

holds.

Let us now show that only the second law is a necessary condition to identify the integrating factor with the temperature. To do that we assume

$$\beta = 0 \tag{7}$$

on N (adiabatic manifold); consequently it follows that

$$dE + \alpha = 0 \tag{8}$$

by using the first law of thermostatics (2) given in the formulation of differential forms. From (8) we conclude

$$d\alpha = 0 \tag{9}$$

and therefore (6) holds. Moreover we conclude (8) from the Frobenius condition

$$\beta \wedge d\beta = 0\,. \tag{10}$$

From the Frobenius theory [13] we know that the condition $\beta \wedge d\beta = 0$ is an integrability condition for the Pfaffian equation $\beta = 0$. The relation $\beta = \tau\, d\eta$ is interpreted as corresponding to the statement that the Pfaffian equations $\beta = 0$ and $d\eta = 0$ are the same [13]. Therefore (10) is a necessary condition for the existence of a function τ. We have

$$\beta = \tau\, d\eta \quad \text{or} \quad d\beta = d\tau \wedge d\eta\,, \tag{11}$$

where $\tau, \eta \colon N \to \mathbb{R}$ and $\tau \neq 0$. The quantity η is called the empirical entropy.

Remarks: i) Any Pfaffian differential equation on $\mathbb{R}^2 \setminus \{0\}$ admits on integrating factor. To find an integrating factor the condition (10) is necessary and sufficient for Pfaffian forms with three independent variables. To find an integrating factor in the case of an arbitrary number of independent variables we refer to [14].

ii) The 1-form β admits an integrating factor.

iii) We have not used the second principle of thermostatics.

iv) In order to establish an integrating factor with the special properties of temperature we need a further condition. To formulate this further condition we consider an isothermal reversible process.

Let us now characterize an isothermal process as a process where $\vartheta =$ constant and

$$d\vartheta\,|_{\zeta} = 0, \tag{12}$$

where ζ is an isothermal path on an isothermal surface Σ. On Σ, where $d\vartheta = 0$, we have

$$\int_{\partial\Sigma} \alpha = 0\,. \tag{13}$$

This equation expresses the second principle. Now we apply Stokes theorem on manifolds [13] to (13) and obtain

$$\int_{\Sigma} d\alpha = \int_{\partial\Sigma} \alpha = 0\,. \tag{14}$$

From (13) we conclude that

$$d\alpha = 0 = d\beta\,. \tag{15}$$

We assume

$$\tau(\vartheta, \eta, X_2, \ldots, X_p, \ldots)\,. \tag{16}$$

This assumption together with (11) and condition (15) allow us to conclude

$$\partial\tau/\partial X_p = 0\,, \tag{17}$$

where the function τ depends only on the empirical temperature ϑ and the empirical entropy η. We have

$$\tau(\vartheta, \eta)\,. \tag{18}$$

Moreover for two bodies in isothermal contact we conclude that the integrating factor τ has the representation

$$\tau(\vartheta, \eta) = T(\vartheta)\,\varphi(\eta)\,. \tag{19}$$

We call $T(\vartheta)$ the absolute temperature function depending on the empirical temperature ϑ. If we assume $dS = \varphi(\eta)\, d\eta$, then it follows that

$$\beta = T(\vartheta)\, dS\,, \tag{20}$$

where dS is the differential of the entropy. Furthermore, by rewriting (20) we obtain

$$dS = \beta T^{-1}\,, \tag{21}$$

which is the so-called second principle of thermostatics. The temperature $T(\vartheta)$ can be justified on a temperature scale. We give a definition of this temperature scale at the end of Section 3.

3. Thermostatics in the Field Theoretical Description

In the following we consider the thermodynamical field equations for discontinuous media to explain the thermostatics. To that let us consider a mixture of fluids at an interface without chemical reactions [4]. In this case we have the balance of mass, momentum and energy in the following form

$$\begin{aligned}
&\dot{\gamma} + \frac{\dot{g}}{2g}\gamma + \gamma \underset{\tau}{w}{}^{A}_{;A} + [\varrho(v^j - w^j_\lambda) e_j] = 0 ,\\
&\gamma \dot{w}^k - T^{kA}_{;A} + [\varrho(v^k - w^k)(v^j - w^j_\lambda)\\
&\qquad \cdot e_j - t^{kj} e_j] = \gamma F^k , \qquad (22)\\
&\gamma \dot{E}_S + \underset{\tau}{Q}{}^{A}_{;A} - T^{kA} w_{k;A}\\
&\qquad + [\varrho(\varepsilon - E_S + \tfrac{1}{2}(v^k - w^k)^2)(v^j - w^j_\lambda) e_j\\
&\qquad + q^j e_j - t^{kj}(v_k - w_k) e_j] = \gamma r_S ,
\end{aligned}$$

The quantities γ the mass density, w^k the components of the velocity field, E_S the internal energy, $g = \det(g_{AB})$ the determinant of the metric tensor, T^{kA} the stress tensor, $\underset{\tau}{Q}{}^A$ the components of the heat flux vector, F^k the components of the force density, r_S the supply of internal energy, are defined at the interface with respect to the interfacial coordinates u^1, u^2 and time t, and the quantities ϱ the mass density, v^j the components of the velocity field, ε the internal energy, t^{kj} the stress tensor, q^j the components of the heat flux vector, are functions of the space coordinates x^i and time t. For the partial and covariant derivatives with respect to the surface coordinates u^1 and u^2 we use comma and semicolon, respectively.

Let us now consider a single fluid at the interface without material and heat exchange with the bulk fluids. The balance equations reduce to

$$\begin{aligned}
&\dot{\gamma} + \frac{\dot{g}}{2g}\gamma + \gamma \underset{\tau}{w}{}^{A}_{;A} = 0 ,\\
&\gamma \dot{w}^k - \tau^{kA}_{;A} = 0 , \qquad (23)\\
&\gamma \dot{\varepsilon}_S + \underset{\tau}{q}{}^{A}_{;A} = \tau^{kA} w^k_{;A} + \gamma r_S ,
\end{aligned}$$

where we have assumed that the components of the force density of an external field F^k are identical zero. The quantities ε_S, τ^{kA} and $\underset{\tau}{q}{}^A$ denote the material dependent parts of

$$E_S , \; T^{kA} \quad \text{and} \quad \underset{\tau}{Q}{}^A .$$

The balance equations (23) together with the constitutive equations

$$\begin{aligned}
&\tau^{BA} = -\sigma(\gamma, \vartheta_S) g^{AB} ,\\
&\varepsilon_S = \tilde{\varepsilon}_S(\gamma, \vartheta_S) ,\\
&\underset{\tau}{q}{}^A = -K^{AB} \vartheta_{S,B} , \qquad (24)
\end{aligned}$$

for an inviscid fluid yield a set of field equations for the interfacial fields $\gamma(u^A, t)$, $w^k(u^A, t)$, $\vartheta_S(u^A, t)$. Here we do not give a systematic discussion about the constitutive equations (24). The interested reader is refered to [4] or [5] in the case of constitutive equations on surfaces and interfaces, and in the case of spatial constitutive equations we refer to [2].

We define a thermostatic process as a process without acceleration terms in the field equations, without spatial dependence of the fields of density and temperature and, moreover, where exist time dependent functions $\gamma(t)$ and $\vartheta_S(t)$. The field equation of the internal energy can be written as

$$\gamma \dot{\varepsilon}_S = -\sigma\left(\underset{\tau}{w}{}^{A}_{;A} + \dot{g}/2g\right) + \gamma r_S . \qquad (25)$$

By using the mass balance we obtain the first law of thermostatics on interfaces in the form

$$r_S = \dot{\varepsilon}_S + \sigma(1/\gamma)^{\cdot} \qquad (26)$$

or

$$r_S = \frac{\partial \varepsilon_S}{\partial \vartheta_S}\dot{\vartheta}_S + \left(\frac{\partial \varepsilon_S}{\partial(1/\gamma)} + \sigma\right)(1/\gamma)^{\cdot} . \qquad (27)$$

This equation has an integrating factor, namely

$$\dot{\eta} = \Lambda_S(\vartheta_S)\left\{\frac{\partial \varepsilon_S}{\partial \vartheta_S}\dot{\vartheta}_S + \left(\frac{\partial \varepsilon_S}{\partial(1/\gamma)} + \sigma\right)(1/\gamma)^{\cdot}\right\} , \qquad (28)$$

where η is the entropy. This form has the integrability condition

$$\frac{\mathrm{dln}\, \Lambda_S}{\mathrm{d}\vartheta_S} = \frac{\partial\sigma/\partial\vartheta_S}{\gamma^2 \dfrac{\partial \varepsilon_S}{\partial \gamma} - \sigma} . \qquad (29)$$

In a previous paper we have identified the quantity $\Lambda_S(\vartheta_S)$ with the reciprocal of the absolute temperature, which depends on the empirical temperature. By integrating of (29) we obtain

$$T_S(\vartheta_S) = \underset{(0)}{T_S} \exp\left\{-\int\limits_{\underset{(0)}{\vartheta_S}}^{\vartheta_S} \frac{\partial\sigma/\partial\vartheta_S}{\gamma^2 \dfrac{\partial \varepsilon_S}{\partial \gamma} - \sigma}\, \mathrm{d}\vartheta_S\right\} . \qquad (30)$$

If we know the quantity σ (called "surface tension") and the interfacial internal energy for any material then we can calculate the right hand side of (30).

The results presented here are similar to those of the thermodynamics for spatial fields [2]. We obtain the above results if we replace the spatial quantities by interfacial quantities, namely the internal energy ε by the internal energy ε_S, on the interface, the supply of internal energy r by supply of internal energy r_S on the interface, the pressure p by σ on the interface and the mass density ϱ by the mass density γ on the interface and vice versa. The analogous equation to (30) for spatial fields is given by

$$T(\vartheta) = T_0 \exp\left\{-\int\limits_{\vartheta_0}^{\vartheta} \frac{\partial p/\partial\vartheta}{\varrho^2 \dfrac{\partial\varepsilon}{\partial\varrho} - p}\, \mathrm{d}\vartheta\right\}, \quad (31)$$

and the integration constant can be justified on the temperature scale. The temperature scale is given by $T(\vartheta_1)$ and $T(\vartheta_2)$, where ϑ_1 is the temperature of freezing water, ϑ_2 is the temperature of boiling water and the temperature difference $T(\vartheta_2) - T(\vartheta_1)$ is equal to 100 degrees. This defines the absolute temperature scale (see [14]).

4. Conclusions

The above investigations are true for a one-constituent medium (gas or fluid). For this medium we have seen that the absolute temperature function depends on the empirical temperature and we have to justify the notion of absolute temperature. Moreover, by measuring $\sigma(\gamma, \vartheta_S)$ and $\varepsilon_S(\gamma, \vartheta_S)$ in any fluid, the right hand side of (30) is determined and it is a positive-valued and monotonically decreasing function if $\gamma^2(\partial\varepsilon_S/\partial\gamma) - \sigma > 0$. For a multiconstituent fluid we do not assume that for each constituent there exists an integrating factor, rather we require that for the mixture of the whole composite system there exists an integrating factor. This is not automatically true for a general interacting system. The above requirement possibly restricts the mathematical nature of the considered composite system. If we know at least one integrating factor, then we know all integrating factors of the system under consideration.

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[1] K.-H. Anthony, in: Continuum Models of Discrete Systems, ed. E. Kröner und K.-H. Anthony, University of Waterloo Press, Waterloo Canada 1980, p. 761.
[2] I. Müller, Thermodynamik, Bertelsmann Universitätsverlag, Düsseldorf 1972.
[3] I-Shih Liu, Arch. Rational Mech. Anal. **46**, 131 (1972).
[4] A. Grauel, Physica **103 A**, 468 (1980).
[5] A. Grauel, International Journal of Mathematical Modelling (1982).
[6] C. Truesdell and R. A. Toupin, in Handbuch der Physik III, 1 (Prinzipien der Klassischen Mechanik und Feldtheorie, ed. S. Flügge) Springer-Verlag, Heidelberg 1960.
[7] C. Caratheodory, Math. Ann. **67**, 355 (1909).
[8] T. Ehrenfest-Afanassjewa, Z. Physik **33**, 933 (1925).
[9] T. Ehrenfest-Afanassjewa, Z. Physik **34**, 638 (1925).
[10] T. Ehrenfest-Afanassjewa, Die Grundlagen der Thermodynamik, E. J. Brill, Leiden 1956.
[11] J. M. Jauch, Found. Physics **2**, 328 (1972).
[12] J. M. Jauch, Reprint (Lectures on Differentiable Manifolds in Modern Physics), University of Minnesota, School of Mathematics, Minneapolis, Minnesota 1973.
[13] C. von Westenholz, Differential Forms in Mathematical Physics, North-Holland, Amsterdam 1978.
[14] I. P. Basarow, Thermodynamik, VEB Deutscher Verlag der Wissenschaften, Berlin 1972.