
Krzysztof Wilmanski

Thermodynamics of Non-Newtonian Fluids

Der Zweck dieser Arbeit ist ein doppelter: erstens wird eine kurze und einfache Beschreibung der nicht-newtonischen Flüssigkeiten gegeben; zweitens wird das thermodynamische Verfahren demonstriert, um ein phänomenologisches Modell des Materials zu konstruieren.

Drei einfachste Modelle der nicht-newtonischen Flüssigkeit werden dargestellt:

- das rein mechanische Modell, das aus der Rheologie folgt,
- das thermodynamische Modell, das auf rheologischen Relationen beruht,
- ein neues thermodynamisches Modell, das aus der sogenannten erweiterten Thermodynamik folgt.

1. Introduction

The non-newtonian fluids, in spite of their provocative name, indicating a rather unusual behaviour, are very common in normal physical circumstances. They also play an essential rôle in various practical applications. For this reason, a theoretical model of such substances is of primary importance.

The purpose of this paper is twofold: to present the notion of non-newtonian fluids in terms understandable to those people, who have no experience in contemporary material science and to demonstrate the typical thermodynamic procedure in constructing a phenomenological model of a material.

We present three simplest models of non-newtonian fluids

- a purely mechanical one, which stems from rheology,
- a thermodynamical one, based on the rheological relations in their original form,
- a new thermodynamical model, based on the relations of a so-called extended thermodynamics.

We show the basic features of those models without technical details. It is being proved that the rheological model - a so-called Rivlin-Ericksen fluid of the second grade - cannot, in general, serve the purpose of describing non-newtonian fluids because it violates the second law of thermodynamics. Simultaneously, the ordinary thermodynamical model is not suitable either because it yields the wrong signs of material coefficients and, conse-

quently, rules out the basic effects, characteristic for non-newtonian fluids. We show also that the model, following from extended thermodynamics, satisfies the basic expectations as far as non-linear behaviour of a non-newtonian fluid is concerned.

We explain the basic notions of continuum mechanics and thermodynamics but, at the same time, we skip the general considerations and microscopical motivation for the governing set of equations.

The mathematical background required to go through the more formal points does not exceed that taught in contemporary high schools.

The modicum of mathematics, left in the paper, reflects the real nature of the modern theories of materials. In principle, one could construct this paper without a single mathematical formula. To write about continuum thermodynamics without at least some mathematics would be, however, like explaining the beauty of a Bach's fugue to somebody, who has never heard a single note of music. I have tried, though, to limit the sweat of a layman as much as possible.

Section 2 of the paper contains a brief presentation of a non-newtonian fluid and those notions of continuum theory, which have to enter a model of such a substance.

In Section 3, the simplest rheological model - Rivlin-Ericksen fluid of the second grade - is described. More details on this subject can be found, for instance, in references [1] and [2].

Section 4 is devoted to a thermodynamic model, based on the same definition of a non-newtonian fluid as in the case of the Rivlin-Ericksen fluid. Again, a more sophisticated, technical presentation can be found in the reference [4].

Section 5 is based on the work of Ingo Müller and myself, which will be presented in our forthcoming paper [5]. On the example of the non-newtonian fluid, it shows the new approach to thermodynamical models, which is called in literature an extended thermodynamics.

In the last Section 6, we compare the above three models.

The references, quoted in the paper, are chosen only as an illustration. Both subjects, rheology and thermodynamics of non-newtonian fluids, have the vast original literature, their own scientific journals, numerous monographs and text-books. However, the extended thermodynamics of non-newtonian fluids is a new subject and this part of the paper is original.

Finally, I would like to express my gratitude to Prof. R. S. Rivlin, who has drawn our attention to the controversies which surround thermodynamical models of non-newtonian fluids during our numerous discussions in the Wissenschaftskolleg zu Berlin.

2. Preliminary remarks

Even the simplest observations of fluids reveal their most common feature - the viscosity. For instance, if we try to pull a plate placed on the film of an oil (Fig. 1), we find that the force required to keep the plate in slow motion

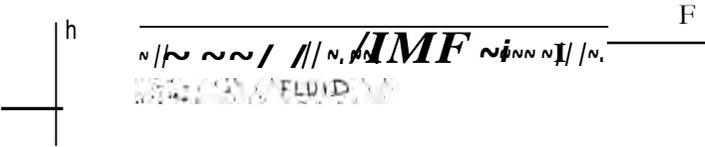


Fig.

along the foundation will be different from zero and its value will depend on the type of oil between the plate and the foundation. In the absence of slip, the uppermost surface of the oil moves with the same velocity as the plate and the lowermost surface of the fluid remains at rest, sticking to the foundation. The force, applied to the plate, will sustain a motion with a constant velocity - say v_o - if its value is chosen to be

$$F = p v_o \frac{A}{h} \tag{2.1}$$

where A is the area of the plate in contact with the fluid and h is the thickness of the film of oil. The coefficient p is called the *shear viscosity* and its value depends on the type of fluid.

It is customary in mechanics to deal with forces per unit area rather than with total force. Such a force, appearing in the above formula, is called a *shear stress*

$$\tau = \frac{F}{A} = p x \tag{2.2}$$

where x is called the *shear rate* and, in this particular case, is defined by the formula

$$x = \frac{v_o}{h} \tag{2.3}$$

Formula (2.2) describes the simplest relation between shear stresses and shear rates in viscous fluids. The viscosity p depends on temperature and, in very many fluids, also on the shear rate itself. In such a case the dependence of shear stresses on x is non-linear. It remains, however, an odd function of x , which reflects the fact that the force F should change direction if we change the direction of the motion of the plate.

The question arises, as to whether we can describe all properties of a vis-

ous fluid by means of the single material coefficient η . It is obvious that in the above experiment, if we measure the force F alone, we cannot answer this question. There is, however, another quantity, which can be easily detected - if present - even in such a simple case. Namely, we can measure the vertical force, which we have to apply to the plate to keep constant the distance between the plate and the foundation. Such substances as water or glycerin do not give rise to such a force. At the same time, it has been known for some 100 years that certain fluids, such as canada balsam, glue in water, almond oil, whale liver oil etc. display a non-zero value of this force.

The fluids of the first type are called *newtonian* and of the second type - *non-newtonian*. The latter have gained in importance particularly due to the utilization of various polymer materials - polymer solutions and melts are in most cases non-newtonian.

To examine analytically the above effect, we have to say a few words about *normal stresses*. If we perform the *Gedankenexperiment*, removing the plate from the fluid then - to obtain again the same motion of the fluid - we have to apply forces, replacing the action of the plate on the fluid (Fig. 2). In

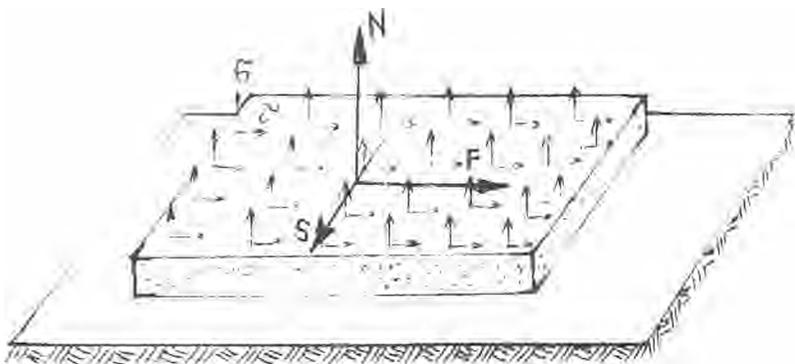


Fig. 2

the case of a newtonian fluid, we have to apply the tangent force F alone, which is distributed uniformly in the form of shear stresses T . Obviously, we can neglect another tangent force S , choosing a proper reference frame.

In the case of non-newtonian fluids, we have to introduce additionally the normal force N . This should depend on the velocity of the plate - similarly to the force F . However, in contrast to the shear force, it should not depend on the direction of the motion. In other words, the force N should have the same value whether the plate moves to the left or to the right. This means that N must be an even function of v_0 . The simplest function, satisfying this condition, has the form

$$N = \beta (\quad - pA, \quad (2.4)$$

where β is a new material coefficient, characterizing the non-newtonian fluid and p is the pressure in the vessel, in which the experiment is performed. If we define the normal stresses in the vertical direction by the formula

$$\sigma_z = \frac{N}{A}, \quad (2.5)$$

then the relation (2.4) can be written in the form

$$\sigma_z = \beta x^2 - p. \quad (2.6)$$

We shall show later that the coefficient β is the combination of two material coefficients a_1 and a_2 , describing a so-called *viscous fluid of the second grade*.

The presence of normal stresses in non-newtonian fluids, called the *Weissenberg effect*, can be easily observed in various experiments. In *Fig. 3*, we show the difference in behaviour of newtonian and non-newtonian fluids in rotary motion. On the left hand side, we see that the form of the upper surface of a newtonian fluid is concave in such a motion. The non-newtonian fluid, shown on the right-hand side, forms the upper surface differently - the middle part is convex. This effect of "climbing" along the axis of rotation can also be observed, for instance, in every kitchen during the production of a paste, which climbs along the roll of the mixer.

The effect of normal stresses can be seen as well in the case of flow through a tube. This is shown in *Fig. 4*. The newtonian fluid on the left-hand side will form a regular stream at the exhaust, whereas the non-newtonian fluid will swell due to the normal stresses in the radial direction.

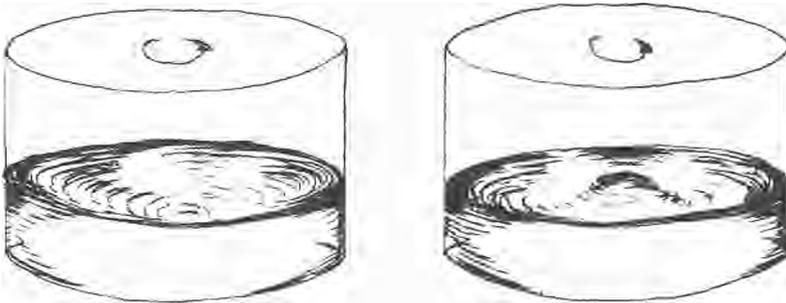


Fig. 3

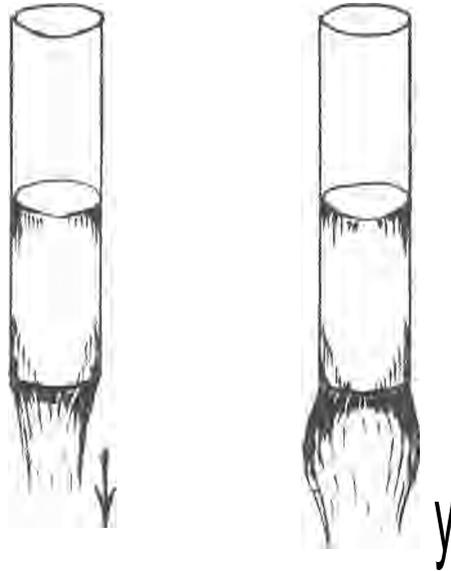


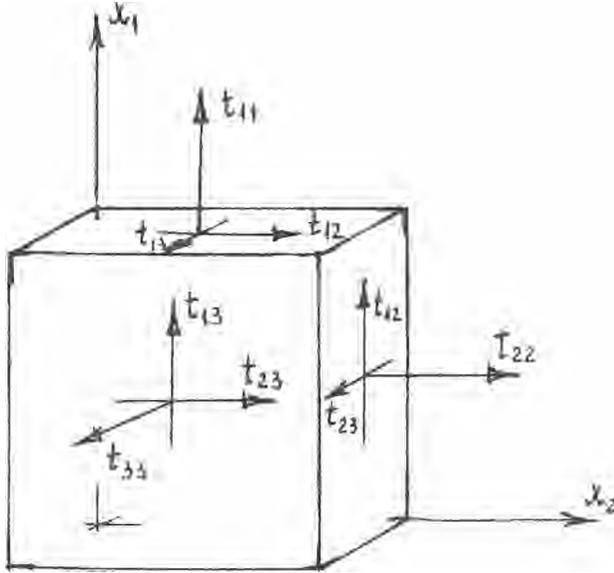
Fig. 4

All those effects have caused the development of a mechanical theory of such fluids since the second half of the XIXth century. The branch of mechanics, dealing with various viscous fluids, including the fluids of the second grade, forms the subject of *rheology*. The modern history of rheology has started in the late forties with numerous works of J.G. Oldroyd, R. S. Rivlin, K. Weissenberg and many others. This has been triggered by the purely intellectual interest in explaining such phenomena as well as by practical problems, arising in technological processes, such as the production of polymers, mixing substances in the production of various fluid mixtures, etc.

Before we go further one point must be particularly stressed. We have already mentioned that the material coefficients, describing the viscous fluids, depend on temperature. How sensitive those coefficients are to the level of temperature one can easily check pouring honey on one's breakfast bread. At the same time, all processes taking place in viscous substances must turn some work into heat - similarly to processes involving friction. This means that, during most non-stationary processes, the values of coefficients will not remain constant and their changes will depend on the way in which the heat is being transferred. Rheology, being a purely mechanical theory, cannot describe such phenomena. This leads us to the conclusion that we should try to find a thermodynamical description of viscous fluids. We will return to the troubles arising in this respect after presenting some ideas of rheology, which form the next Section of the paper.

3. Rivlin-Ericksen fluid of the second grade - the simplest model of a non-newtonian fluid

Let us try to formulate the relations, discussed in the previous Section, in the form capable of describing an arbitrary flow. To this end, we have to introduce other components of stresses. Fig. 5 shows a cube of substance in



x3

Fig. 5

a Cartesian frame of reference (x_1, x_2, x_3) , where all six components of stress are indicated: three normal stresses t_{11}, t_{22}, t_{33} and three shear stresses t_{12}, t_{13}, t_{23} . It is customary to write this collection of components in the compact form t_{kl} where k and l may take the values 1, 2 or 3. It is understood that $t_{12} = t_{21}, t_{13} = t_{31}, t_{23} = t_{32}$.

In the example, presented in Section 2, the components of stress are as follows

$$\begin{aligned}
 t_{11} &= -p + (2a_1 + a_2)x^2, & t_{22} &= -p + a_2x^2, & t_{33} &= -p, \\
 t_{12} &= -\alpha x, & t_{13} &= 0, & t_{23} &= 0.
 \end{aligned}
 \tag{3.1}$$

where the axis x_1 has been chosen to point in the direction of the force N , the

respectively, in the example of the previous Section). It has been proved, however, that in the case of a flow, which changes in time, there is an additional contribution to stresses due to the time evolution of the velocity gradient. The simplest way to account for those changes is to add time

derivative $\frac{d}{dt}$ to the above two quantities. This set of 9 quantities reflects the *memory* of the substance, i. e. the influence of the past history of the substance on its present behaviour. We shall discuss the crucial importance of this problem further in the paper.

We usually impose an additional requirement on the general form of the relations (3.1). Namely, it should not make any difference whether we observe the flow sitting at rest or, for instance, through a camera, installed on the plate of the set-up, described in Section 2. This requirement, called the *principle of objectivity* or the *principle of frame-indifference*, leads to the conclusion that the stress should depend only on certain combinations of quantities

$$r \quad \text{and} \quad v_{k,l} \quad (3.7)$$

rather than on all of them. It can be shown, for example, that the velocity gradient $v_k /$ contributes only through its symmetric combinations

$$v_{1,1}^2, v_{2,2}^2, v_{3,3}^2, v_{1,2} + v_{2,1}, v_{1,3} + v_{3,1}, v_{2,3} + v_{3,2}, \quad (3.8)$$

which leaves six out of nine components of v_k as proper variables for stresses.

Rivlin and Ericksen have introduced in the years 1955 two objects, reflecting the above requirement. They are called *the first and second Rivlin-Ericksen tensors* and are defined as follows

$$A_k^{(1)} = v_{k,l} + v_{l,k} \quad (3.9)$$

$$A_k^{(2)} = \frac{dA_k^{(1)}}{dt} + \mathbf{I} \sum_{m=1}^1 A_{km}^{(1)} v_m + A_{kh}^{(1)} v_m l + A_{lm}^{(1)} v_m, k l$$

In the simple case, considered in Section 2, they have the following non-zero components

$$A_{12}^{(1)} = A_{21}^{(1)} = x, \quad (3.10)$$

$$A_{11}^{(2)} = 2 x^2.$$

Bearing in mind the above considerations, we can define the simplest non-newtonian fluid - the *Rivlin-Ericksen fluid of the second grade*. For such a substance the stress components are given by the relation

$$\tau_{kl} = -Q \delta_{kl} + p + a_1 A k^2 + a_2 \sum_{m=1}^3 \text{El}_{kin} j_{11}, \tag{3.11}$$

where δ_{kl} is a so-called Kronecker symbol, defined as follows

$$\delta_{11} = \delta_{22} = \delta_{33} = 1, \delta_{12} = \delta_{21} = \delta_{13} = \delta_{31} = \delta_{23} = \delta_{32} = 0 \tag{3.12}$$

We leave it to the reader to check that the relations (3.1) follow from (3.11), when one substitutes the relations (3.10).

As we have already mentioned, the coefficients a, a_1, a_2 , defining this fluid, depend on temperature but not on the velocity gradient and its derivatives. It has been found experimentally that this assumption is not strictly satisfied by most of the real non-newtonian fluids. We quote below a few experimental data obtained for a stationary flow by R. F. Ginn and A.B. Metzner in 1969 for the 10.5 wt.-% solution of polyisobutylene in decahydronaphthalene, which is a non-newtonian fluid, commonly used in laboratories.

It is seen that the values of a, a_1 and a_2 vary rather strongly with the change of the shear rate. It means that theoretical conclusions, drawn on the basis of the relation (3.11), may have rather a qualitative than a quantitative significance.

$\dot{\gamma}$ [1/s]	a [Ns ²]	a_1 [Ns ²]	a_2 [Ns ²]
0.5	107.8	-27.3	44.6
1.0	98.0	-19.0	28.3
2.0	42.0	-11.9	18.1

One of the basic features of the data presented in the above table is the sign of material coefficients. It has been shown that the viscosity A should be *positive* for all fluids, a_1 should be *negative* and a_2 *positive*. Those properties follow from both experimental data and some theoretical considerations within rheology. They also indicate certain stability properties, which, in turn, are of fundamental practical importance.

The question arises as to whether we can extend the above rheological model of a non-newtonian fluid to account for the temperature changes or, in other words, if we can construct a thermodynamical model of such a substance satisfying the following conditions:

i/ in the case of homogeneous temperature the model would be identical with that presented above;

ii/ the material coefficients would have at least the proper sign;

iii/ the model would deliver the equations for the time and space changes of the mass density ρ , velocity v_k and temperature T .

In the next Section, we present the simplest thermodynamical model of the non-newtonian fluids of the second grade.

4. Ordinary thermodynamics of non-newtonian fluids of the second grade

For the sake of simplicity, let us assume right away that we consider the processes in fluids, in which the distribution of temperature is *homogeneous in space*. This means that we neglect all effects connected with heat conduction. Such a class of processes coincides with the class considered in rheology. The aim of such considerations is to check if we get the same answers in thermodynamics and in rheology, as presented in the previous Section.

Continuum thermodynamics is supposed to construct the equations for the *mass density* ρ , *velocity* v_k and *temperature* T . All solutions of those equations should automatically satisfy the *second law of thermodynamics*.

The field equations are customarily constructed on the basis of balance equations, which are as follows:

1) mass balance

$$\frac{a}{at} + \sum_{k=1}^3 (Q v_k), k = 0 \tag{4.1}$$

2) momentum balance

$$\frac{a(Qv_k)}{at} + \sum_{k=1}^3 (Q V_k v_i - t_k), I = 0 \tag{4.2}$$

3) energy balance

$$\frac{a}{at} \left(\sum_{k=1}^3 (Q E + \sum_{l=1}^3 Q V_k V_l) + I \right) + \sum_{l=1}^3 \frac{r_l}{L} \sim \sum_{k=1}^3 2 Q v_k v_k + \sum_{j=1}^3 \frac{1}{j} \dots - \sum_{k=1}^3 \frac{t_k v_k}{\rho} = 0. \tag{4.3}$$

The equation (4.1) reflects the fact that the *mass* of a substance cannot be created or destroyed in any process.

The equation (4.2) says that the *momentum* of the substance cannot be

created or destroyed in any process without an interaction with the external world.

The equation (4.3), called also the *first law of thermodynamics*, describes the conservation of total energy

$$Q_E + \sum_{k=1}^2 \int v_k v_k, \quad (4.3)$$

where the first term denotes the *internal energy* and the second one - the *kinetic energy* of the fluid.

The five equations (4.1-3) become *field equations* for five fields Q, v_k, T, ρ . If we add the relations for $\rho_{k,l}$ and e . In the case of the Rivlin-Ericksen fluid of the second grade, they have the form

$$\begin{aligned} \rho_{k,l} &= -P \delta_{kl} + p_{A_{k,l}} + a_1 A^{(k2)} + a_2 \sum_{m=1}^3 A_{klm} A_{mll} \\ E &= E_0 + E_1 \sum_{k,l=1}^3 A_{kl} A_{k1} \end{aligned} \quad (4.4)$$

where in the case of an incompressible fluid ($Q = const$), p, a_{1i}, a_2, c_0 and c_i are functions of T alone. If we knew these coefficients, the substitution of (4.4) in (4.2-3) would give us the required field equations. This is, however, not the case. The coefficients p, a_1, a_2 are measured in mechanical experiments, as mentioned before. We expect from thermodynamics to predict the properties of the remaining two coefficients c_0 and e . To this end, we have to exploit the second law of thermodynamics.

In the case of a homogeneous distribution of temperature, i. e. without processes involving heat conduction, the second law assumes a particularly simple form. If we denote by η the *entropy density* per unit mass of the fluid, then the *second law* has the form

$$\frac{d\eta}{dt} + \sum_{k=1}^3 r_{l,k} v_k > 0 \quad (4.5)$$

where, for the Rivlin-Ericksen fluid of the second grade,

$$\sum_{k,l=1}^3 r_{lo} + r_{ll} \sim \sum_{k,l=1}^3 A_{kl}^{(1)} A_{k1}^{(1)} \quad (4.6)$$

being coefficients which depend on temperature T alone.

Various methods have been developed to exploit the inequality (4.5). We omit, however, those technical details and present the final result. First of all, the coefficients c_0 and η_0 must represent so-called equilibrium values of the internal energy and entropy, respectively. It means that c_0 and η_0 are measured in ordinary calorimetric experiments. On the other hand, the coefficients r_{11}, a_1 and a_2 are related by the following formula

$$\tilde{\rho} = \frac{E}{T} - \frac{a_1}{4}$$

while the coefficient $\tilde{\rho}$ should satisfy the inequality

$$\tilde{\rho} > 0. \tag{4.8}$$

The relations (4.7), (4.8) exhaust the consequences of the second law in the particular case under consideration. The only inequality for the material coefficients $\tilde{\rho}$, a_1 , a_2 is expressed by (4.8) and this is in agreement with experiments (Section 3).

There is, however, another argument concerning the signs of coefficients and connected with thermodynamics. Namely, it is a commonly accepted property of all physical systems that they should develop in the direction of thermodynamical equilibrium, reaching it finally after a sufficiently long lapse of time, when left alone without being influenced by the external world. This means, however, that if we disturb the equilibrium of the system it will return to the same state, when the disturbance is removed. This property is called the *thermodynamic stability condition* for equilibrium. The situation resembles that of the ball lying in the valley (Fig. 6). In this simple

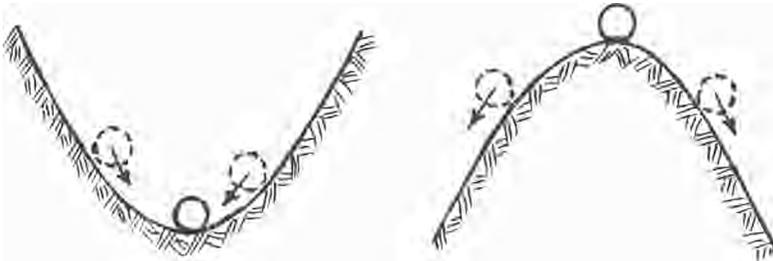


Fig. 6

mechanical case, the ball will try to minimize its potential energy, going back to the bottom of the valley when disturbed. This is in contrast to the behaviour of the ball on the top of a hill, shown on the right-hand side, where an arbitrary disturbance will drive the ball away from the *unstable* equilibrium at the highest position.

A similar rôle to the potential energy of the ball is played by the so-called *Helmholtz free energy* for thermodynamical systems

$$\rho r = e - T r l. \tag{4.9}$$

For our fluid this function has the form

$$\tilde{\rho} = (\rho_0 - T r l_0) + \frac{a_1}{40} P, P: = \sum_{k, l=1}^3 A_{kll} A_{llk} \tag{4.10}$$

where the relation (4.7) has been used. This function has a minimum in equilibrium (where $\dot{w} = \dot{g}_0 := E_p - T \dot{l}_0$), if

$$a, > 0 \quad (4.11)$$

The above inequality has disastrous consequences. It obviously contradicts the experimental data and theoretical arguments of rheology. Hence, we have to face the alternative; either

i/ Rivlin-Ericksen fluid of the second grade contradicts the second law of thermodynamics and cannot be accepted as a model of any real substance, for which $a, < 0$,

or

ii/ Thermodynamics of continua contains a flaw, ruling out a sound physical model.

We come back to this problem in Section 6, after the presentation of an alternative thermodynamic model of a fluid, described by three material coefficients i, a_1, a_2 .

The above presented thermodynamic description of a non-newtonian fluid has been published in a more general context by Dunn and Fosdick in 1974 and then developed for various models in numerous publications. All of them have, however, the common feature, reflected by the inequality (4.11) that they contradict the experimental data for non-newtonian fluids.

5. Extended thermodynamics of non-newtonian fluids of the second grade

To resolve the problem of a thermodynamic description of non-newtonian fluids without contradicting experimental data Ingo Müller and myself have constructed a different thermodynamical model of such substances. I will present here the basic ideas of this work, referring the reader, interested in technical details, to our forthcoming publication.

The main aim of extended thermodynamics is to establish field equations for a larger number of fields than in ordinary thermodynamics, replacing by those fields the gradients appearing in constitutive relations of ordinary thermodynamics. For instance, in our case of a non-newtonian fluid, the model within ordinary thermodynamics was based on the assumption that the fields of mass density ρ (or, equivalently, the field of pressure p), velocity v_k and temperature T were supposed to describe the fluid. The deviation from thermodynamic equilibrium - in the case of a homogeneous temperature field - was described by the velocity gradient $v_{k,j}$ and its time derivative. For an incompressible fluid, only 5 components of the velocity gradient were required to describe the non-equilibrium state.

The additional fields of extended thermodynamics, chosen to describe the processes in non-newtonian fluids, replace those 5 components of the velocity gradient. The simplest natural choice is obvious - *components of stresses*. We have then the following fields:

- velocity field v_k (3 fields)
- temperature T (1 field)
- stress t_{ki} (6 fields).

There are then 10 fields instead of 5, appearing in ordinary thermodynamics. This means, however, that five balance equations, described in the previous Section, do not suffice for the purpose of constructing field equations. We must have 5 additional equations!

The whole idea of extended thermodynamics has arisen from the kinetic theory of fluids and, in particular, from the *Grad method*. This microscopical theory serves as a motivation of ordinary thermodynamics and is also behind the notions and equations of extended thermodynamics. It should be stressed that, if we were able to construct a kinetic theory of non-newtonian fluids, there would be no need for any phenomenological extended thermodynamics of such substances. We could then calculate all macroscopic properties of such substances from a very few microscopic quantities. This, however, is not the case. Such a kinetic theory does not exist yet and, even if it did, it would most likely be too complicated for exact calculations. In other words, it would require additional simplifying assumptions, spoiling its advantages over a phenomenological theory.

The above remarks justify our attempt to construct extended thermodynamics - a phenomenological (macroscopical) theory, which possesses, however, some features of the microscopic theory, not reflected in ordinary thermodynamics.

We will omit the details concerning the derivation of additional 5 equations, mentioned above, referring the reader again to our paper. The final approximate form of those equations is as follows

$$a_l \frac{\partial}{\partial x_l} + \frac{a_2^2}{2} \frac{\partial^2}{\partial x_l \partial x_l} (s'_{kr}; s_{ir} - a_{kr} \sim S_{j\sim} S_{j\sim} l - s_{ki} + !/ 41/) = 0 \quad (5.1)$$

where

$$S_{ki} = t_{ki} - \frac{1}{3} \delta_{ki} \frac{\partial v_l}{\partial x_l} \quad (5.2)$$

is called the *deviator of stresses*. It is symmetric, i. e.

$$S_{12} = S_{21}, S_{13} = S_{31}, S_{23} = S_{32} \quad (5.3)$$

and it has only 5 independent components due to the condition

$$S_{t1} + S_{22} + S_{33} = 0, \quad (5.4)$$

which follows from the definition (5.2).

At the same time

$$\begin{aligned} \dot{S}_{kl} = & \frac{a_1 S_{kl}}{a_1} + \frac{3}{2} S_{kl,m} v_m \\ & + \sum_{i=1}^3 (\epsilon^{kiv} + S_{l^i} v_{l,k} - 3 a_{kl}) \quad j=1 \end{aligned} \quad (5.5)$$

is the time derivative of the deviator of stresses, chosen in such a way that the principle of objectivity is satisfied.

The coefficients p , a_1 , a_2 may still depend on p and T .

Equations (5.1) replace the constitutive relations (4.4) of ordinary thermodynamics. They have the form of *evolution equations* for the deviator of stresses S_{kl} . Such equations appear in ordinary thermodynamics in the case of models with internal variables (e. g. in the case of chemical reactions). There are, however, two important differences. First, in contrast to internal parameters, the stress deviator is not an additional variable - it also appears in ordinary thermodynamics of non-newtonian fluids. It has only changed its status - from a constitutive quantity it has been changed into one of the basic fields. Secondly, the evolution equations (5.1) have a strong microscopical motivation, they follow from some general considerations and correspond rather to the *balance equations* than to arbitrarily constructed evolution equations of internal parameters.

Before we proceed further with the exploitation of thermodynamics, let us check the consequences of the equation (5.1) in the simple case of shear flow, considered in Section 2. In this case

$$\dot{S}_{kl} = \sum_{i=1, j=1}^3 S_{ki} v_{i,l} + S_{l^i} v_{l,k} - \sum_{j=1}^2 a_{kl} S_{ij} v_{l,j} \quad (5.6)$$

This gives rise to the following set of relations

$$\mathbf{T} = x$$

$$S_{11} = 3(4a_1 + a_2) x^2,$$

$$S_{22} = -3(2a_1 - a_2) x^2 \quad (5.7)$$

$$S_{33} = -3(a_1 + a_2) x^2.$$

At the same time, according to equations (3.1), we have

$$\sum_{i=1}^3 = -3p + 2(a_1 + a_2) x^2. \quad (5.8)$$

If we combine (5.8) with the definition (5.2), we easily arrive at the relations (5.7). This means that our model gives the *same* constitutive equations as the rheological model in the case of *stationary* (time-independent) shear flow.

It can be easily shown that the above statement holds true for *all stationary flows*. This means also that the material coefficients, u , a_1 , a_2 have in our model the same meaning as in the rheological model of the non-newtonian fluid of the second grade.

The question arises as to what relations follow from (5.1) in arbitrary non-stationary flows. We will show on the example of shear flow again that they are entirely different than those of rheology, as presented in Section 2.

Neglecting again the terms of the order of magnitude x^3 and higher we get from (5.1) the following equation for shear stresses ($k = 1, 1 = 2$)

$$\frac{d\tau}{dt} + \frac{a_1}{a_2} \tau = \eta \dot{\gamma}, \quad \tau = \tau_{12}. \quad (5.9)$$

This differential equation can be easily solved. Let us assume that we know the value of shear stresses to be zero at the instant of time $t = 0$. Then its value at an arbitrary instant of time t (the solution of the equation (5.9)!) is given by the formula

$$\tau(t) = \frac{\eta}{a_1} \int_0^t \dot{\gamma}(s) \exp\left(-\frac{a_1}{a_2}(t-s)\right) ds. \quad (5.10)$$

Let us first check this formula for the case of a stationary flow, i. e. for the constant shear rate, say $\dot{\gamma}(t) = \dot{\gamma}_0$ for all instances t . We have then

$$\tau(t) = \eta \dot{\gamma}_0 \left[1 - \exp\left(-\frac{a_1}{a_2}t\right) \right]. \quad (5.11)$$

If we assume that $\dot{\gamma}_0 > 0$ and $a_1 < 0$ then, for a sufficiently long time interval, we have

$$\tau(t) \rightarrow \eta \dot{\gamma}_0, \quad (5.12)$$

which is equation (5.7).

If, however, the shear rate is not constant in time, then the shear stress is described by equation (5.10) - much more involved than (5.7).

One of the most striking features of the relation (5.10) is that the present value of stresses $\tau(t)$ depends not only on the present value of the shear rate $\dot{\gamma}(t)$ but also on all its past values $\dot{\gamma}(t-s)$, $s \in [0, t]$. In the theory of materials, this effect is called the *memory* of the material.

If we integrate twice by parts on the right-hand side of equation (5.10) then we arrive at the formula

$$\begin{aligned}
 -r(t) &= \dot{\gamma} x(t) + a_1 \int_0^t e^{-a_1(t-s)} (\dot{\gamma} x(0) + a_1 \int_0^s \dot{\gamma} ds) \exp\left(-\frac{d^2}{a_1} s\right) ds. \quad (5.13)
 \end{aligned}$$

Again, for $a_1 > 0$ and $a_1 < 0$ and a sufficiently long lapse of time we can neglect the term in the box. If there existed any grounds to claim that the integral on the right-hand side is small when compared with the remaining two terms, then we would get

$$T(t) = \eta \dot{\gamma} x(t) + a_1 \int_0^t \dot{\gamma} ds. \quad (5.14)$$

This would mean that the dependence of stresses not only on the present value of the shear rate $\dot{\gamma}$ but also on the present value of its time derivative $\ddot{\gamma}$ reflects, approximately, the memory of a non-newtonian fluid. This would correspond to the rheological model of a non-newtonian fluid of the second grade, relying on two Rivlin-Ericksen tensors A_{k1} and $A^{(0)}$

We will omit the calculation of the remaining components of stresses. It is only worth mentioning that the relations for normal stresses would have a similar structure to that for shear stress (5.10).

Now, let us go back to thermodynamics. We have to exploit again the entropy inequality (4.5).

The internal energy e and the entropy η are given by

$$\begin{aligned}
 e &= e_0 + \int_0^3 S_{ij} s_{ij}, \\
 \eta &= \eta_0 + \int_0^3 \tilde{L}_{ij} S_{ij}
 \end{aligned} \quad (5.15)$$

where the coefficients $c_{\alpha, \ell, r, \theta}$ and t_{j1} are the functions of pressure and temperature.

As the consequence of the entropy inequality we get once more the inequality for the viscosity

$$\tau > 0 \quad (5.16)$$

and, instead of the relation (4.7), the following expression for the entropy coefficient η

$$\gamma_1 = \frac{1}{T} (81 + 4 \frac{a_1}{i_2}) \quad (5.17)$$

in the case of the incompressible fluid.

Bearing in mind (5.17), we obtain the following formula for the Helmholtz free energy

$$\psi = E - T n = t V_0 - \frac{3}{4^{1/2}} \sim s_{ri} s_{ij} \quad (5.18)$$

where γ_{r0} , an equilibrium value of γ , depends only on the temperature T

The stability argument, presented in Section 4, now gives the following condition

$$a_1 < 0, \quad (5.19)$$

which is in agreement with experimental data and opposite to the result (4.11) of ordinary thermodynamics of non-newtonian fluids of the second grade!

In the next Section, we present an analysis of those results. Let us only mention, in addition, that the result (5.19) is also supported by our previous analysis of equation (5.10). In other words, the inequality (5.19) assures the convergence of the integrals, appearing in the relations for stresses and yields the transition from the non-stationary to stationary processes.

6. Conclusions

Let us summarize the results of the previous Sections. We have seen that the description of the same material - non-newtonian fluid of the second grade - is different in rheology, ordinary and extended thermodynamics. Namely, the relation of stresses τ_{kl} to the velocity gradient $v_{k,h}$ described by three material coefficients μ, a_1, a_2 has the form

$$\tau_{kl} = -p \delta_{kl} + a_1 \dot{\gamma}^2 + a_2 \sum_{m=1}^3 \sim A^m \dot{\gamma}^m \quad (6.1)$$

$$\mu > 0, a_1 < 0, a_2 > 0$$

in rheology,

$$\tau_{kl} = -p \delta_{kl} + p A k \dot{\gamma}^2 + a_1 A l 2 > + a_2 \sum_{m=1}^3 A k^m \dot{\gamma}^m \quad (6.2)$$

$$p > 0, a_1 > 0, a_1 + a_2 = 0$$

in ordinary thermodynamics,

$$tkl = -V akl + Ski,$$

$$S = Aicl + \frac{a1}{ra} Skl + \frac{a2}{In=1} km S_{mi} \quad \begin{matrix} l \\ 3 \end{matrix} \quad \begin{matrix} akl \\ i= \end{matrix} S_{mi} S \quad (6.3)$$

$$u > 0, a < 0, a_2 \text{ —arbitrary}$$

in extended thermodynamics.

We also know that the above relations become identical in the case of rheological and extended-thermodynamics models of stationary flows and those, in turn, agree qualitatively with experiments.

From the above remarks, it follows immediately that both rheological and ordinary thermodynamics models must be ruled out as candidates for the description of non-newtonian fluids, in which the normal stress (Weissenberg) effect appears.

The rheological model, with the negative coefficient a_1 , contradicts the second law of thermodynamics, as we have shown in Section 3. It has been used successfully for many years only due to an accidental agreement of the stress relation (6.1) with equations (6.3) in the case of all stationary flows, which, in turn, are of principal practical interest.

On the other hand, the thermodynamical model (6.2) gives the wrong sign of the coefficient a_1 , eliminates the Weissenberg effect from the theory and gives rise to various non-physical instabilities.

The new model, based on the extended thermodynamics approach, gives the proper description of stationary flows - in agreement with earlier rheological considerations, it yields the proper sign of the coefficient a_1 , and, in spite of quantitative discrepancies, may serve as the first approximation in the description of non-stationary flows. The type of memory effects, which follow from (6.3), agrees also quite well with the predictions of Boltzmann, following from his model for viscous materials. This seems further to indicate that the theoretical model of the normal stress effects in non-newtonian fluids requires much stronger memory effects than those reflected by the time derivatives of the velocity gradient (rate-type materials).

The model, based on extended thermodynamics, opens also the possibility to describe the effects, connected with heat conduction in non-newtonian fluids. As we have already mentioned, they are of primary importance for such substances.

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