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A generalised Gibbs equation for second-order fluids

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Abstract. A generalised Gibbs equation for viscous, incompressible fluids is proposed. It takes into account the dependence of the entropy on the viscous pressure tensor. When the restrictions of the objectivity principle are imposed on the phenomenological equations, the expression for the pressure tensor is seen to be equivalent to that of second-order fluids.

1. Introduction

Some authors (Gyarmati 1977, Jou 1978, Lambermont and Lebon 1973, Lebon 1978, Müller 1966) have proposed for some thermodynamic systems a generalised Gibbs equation which relaxes the hypothesis of local equilibrium by assuming that the entropy may depend on quantities that vanish in equilibrium, such as dissipative fluxes. On the basis of such a generalised Gibbs equation and in the framework of irreversible thermodynamics, they obtain constitutive equations that avoid the paradox of infinite speed wave propagation of perturbations. While Gyarmati (1977), Lambermont and Lebon (1973) and Müller (1966) are restricted to linear phenomenological laws, Lebon (1978) introduces some non-linear terms into the phenomenological equations; Lebon also proposes that the phenomenological laws are objective (Truesdell and Noll 1965, p 44). In this work a more general theory is proposed (Jou 1978) in which the non-linear terms are obtained from general representation theorems of isotropic tensorial functions (Truesdell and Noll 1965, p 27). While the formulations of extended irreversible thermodynamics described above deal with effects that are in general difficult to observe experimentally, such as relaxation in heat conduction, the one proposed here deals with phenomena that are easily observed in flows of liquids, such as polymer solutions, which have attracted much interest in recent years (Astarita and Marrucci 1974).

2. The generalised Gibbs equation and the constitutive relation

We consider a viscous, incompressible fluid in the absence of heat flux. The specific entropy s is assumed to be a function of the specific internal energy u and also of the viscous pressure tensor $\hat{\mathbf{P}}^v$, whose traceless character is indicated by means of the upper index \circ . The state of the system will be characterised by the velocity v and the thermodynamic variables u and $\hat{\mathbf{P}}^v$. Therefore, to obtain a complete description of the system we need the evolution equations for these variables. The evolution equations

for \mathbf{v} and u are the well-known balance equations of momentum and energy, which are respectively

$$\rho \dot{\mathbf{v}} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F} \quad (1)$$

and

$$\rho \dot{u} = -\dot{\mathbf{P}}^{\mathbf{v}} : \dot{\mathbf{V}} + \rho r, \quad (2)$$

to which the constraint of incompressibility has to be added by means of the continuity equation

$$\nabla \cdot \mathbf{v} = 0. \quad (3)$$

In these equations ρ is the constant density, \mathbf{P} is the total pressure tensor, assumed to be symmetric, $\dot{\mathbf{P}}^{\mathbf{v}}$ is the viscous pressure tensor, $\dot{\mathbf{V}}$ is the deviation part of the rate of deformation tensor, \mathbf{F} is the external force acting on the unit of mass and r is the energy radiated by the unit of mass. In the following, we shall assume that both \mathbf{F} and r vanish identically. $\dot{\mathbf{P}}^{\mathbf{v}}$ is related to \mathbf{P} by

$$\dot{\mathbf{P}}^{\mathbf{v}} = \mathbf{P} - p \mathbf{U}, \quad (4)$$

where p is an undetermined scalar giving the hydrostatic pressure, which cannot be identified with thermodynamic pressure as this is not defined in an incompressible fluid. The colon denotes as usual the double contraction of the corresponding tensors.

Of course, this set of five equations is not sufficient because it involves ten unknowns. Therefore, five supplementary equations are needed to determine the evolution of the system. In the usual description of hydrodynamics, the five missing equations are the constitutive relations giving $\dot{\mathbf{P}}^{\mathbf{v}}$ as a function of $\dot{\mathbf{V}}$. In the present work, however, the tensor $\dot{\mathbf{P}}^{\mathbf{v}}$ is an independent variable and the five missing equations are its evolution equations. To establish them, we start from the following generalised Gibbs equation:

$$ds = T^{-1} du - T^{-1} \dot{\mathbf{A}} : d\dot{\mathbf{P}}^{\mathbf{v}} \quad (5)$$

where the temperature T and the coefficient $T^{-1} \dot{\mathbf{A}}$ are given by the corresponding state equations:

$$T^{-1}(u, \dot{\mathbf{P}}^{\mathbf{v}}) \equiv (\partial s / \partial u)_{\dot{\mathbf{P}}^{\mathbf{v}}}, \quad (6)$$

$$T^{-1} \dot{\mathbf{A}}(u, \dot{\mathbf{P}}^{\mathbf{v}}) \equiv (\partial s / \partial \dot{\mathbf{P}}^{\mathbf{v}})_u.$$

In an isotropic system, these state equations have the general form

$$T^{-1} = T^{-1}(u, I_2, I_3), \quad (7)$$

$$T^{-1} \dot{\mathbf{A}} = \nu \alpha_0 T^{-1} \dot{\mathbf{P}}^{\mathbf{v}} + \nu \alpha_1 T^{-1} [\dot{\mathbf{P}}^{\mathbf{v}2} - (1/3) I_2 \mathbf{U}],$$

where \mathbf{U} is the unit tensor, and α_0 and α_1 are in principle scalar functions of u and the scalar invariants of $\dot{\mathbf{P}}^{\mathbf{v}}$, namely $I_2 = \text{tr} \dot{\mathbf{P}}^{\mathbf{v}2}$ and $I_3 = \text{tr} \dot{\mathbf{P}}^{\mathbf{v}3}$. We shall limit ourselves to a second-order theory in the dissipative flux $\dot{\mathbf{P}}^{\mathbf{v}}$. We speak here of order in the following sense: $\dot{\mathbf{P}}^{\mathbf{v}}$ contains quantities of first, second and successive orders; the first space-time derivatives of u are considered to be first-order quantities; the first space-time derivatives of $\dot{\mathbf{P}}^{\mathbf{v}}$ and the second space-time derivatives of u are assumed to be second-order quantities, and so on. Up to the first order, the state equations (7) reduce to

$$T^{-1} = T_{\text{loc.eq.}}^{-1}, \quad T^{-1} \dot{\mathbf{A}} = \nu \alpha(u) T_{\text{loc.eq.}}^{-1} \dot{\mathbf{P}}^{\mathbf{v}}. \quad (8)$$

$T_{loc.eq.}$ is the temperature in the local equilibrium hypothesis corresponding to the value of u . From here on, when we speak of temperature T it will be understood to be the local equilibrium temperature which can be measured using a sufficiently rapid and localised thermometer. Taking (5) and (7) into account we obtain for the time derivative of the entropy

$$\rho \dot{s} = T^{-1} \rho \dot{u} - T^{-1} \alpha (\dot{\mathbf{P}}^v), \tag{9}$$

where the dot denotes the usual material time derivative. Introducing the energy-balance equation (2) with $r = 0$ into (9), we obtain

$$\rho \dot{s} = -T^{-1} \dot{\mathbf{P}}^v : \{ \dot{\mathbf{V}} + \alpha (\dot{\mathbf{P}}^v) \}, \tag{10}$$

and this expression is the entropy production since there is no entropy flux in the absence of a heat flux.

Our aim is to obtain $(\dot{\mathbf{P}}^v)'$ in terms of the variables v , u , $\dot{\mathbf{P}}^v$ and their spatial derivatives. The objectivity principle (Truesdell and Noll 1965, p 44) states that the corresponding equation must be frame-indifferent, i.e. invariant with respect to rigid-body motions. The only non-objective term in (10) is the material time derivative of the tensor $\dot{\mathbf{P}}^v$, so that in order to obtain frame-indifferent constitutive equations this has to be substituted by an objective time derivative. Amongst the various objective time derivatives we select the co-rotational derivative (Astarita and Marrucci 1974, p 94), defined as

$$(\dot{\mathbf{P}}^v)^* = (\dot{\mathbf{P}}^v)' + \mathbf{W} \cdot \dot{\mathbf{P}}^v - \dot{\mathbf{P}}^v \cdot \mathbf{W}, \tag{11}$$

where \mathbf{W} is the antisymmetric part of the velocity gradient with Cartesian components given by

$$W_{ij} = \frac{1}{2}(\partial v_j / \partial x_i - \partial v_i / \partial x_j). \tag{12}$$

We adopt the definition (11) because it keeps the entropy production term (10) invariant and because it has a well-defined physical sense since it is equal to the variation of $\dot{\mathbf{P}}^v$ in a system which translates and rotates with the fluid.

The entropy production term (10) is seen to be a bilinear form in $\dot{\mathbf{P}}^v$ and $\dot{\mathbf{V}} + \alpha (\dot{\mathbf{P}}^v)^*$. Since we are interested in the evolution equation for $\dot{\mathbf{P}}^v$ we assume that $\dot{\mathbf{V}} + \alpha (\dot{\mathbf{P}}^v)^*$ is a function of $\dot{\mathbf{P}}^v$. The most general form of this dependence in an isotropic system is:

$$\dot{\mathbf{V}} + \alpha (\dot{\mathbf{P}}^v)^* = \kappa_0 \mathbf{U} + \kappa_1 \dot{\mathbf{P}}^v + \kappa_2 \dot{\mathbf{P}}^{v2}, \tag{13}$$

with the κ_i scalar coefficients depending on u and the scalar invariants of $\dot{\mathbf{P}}^v$. Since we are restricting ourselves to second-order terms in the constitutive equation, κ_0 will be a function of u and I_2 , and κ_1 and κ_2 functions of u only. Introducing (13) into (10) we find

$$\sigma \equiv -T^{-1}(\kappa_1 I_2 + \kappa_2 I_3) \geq 0. \tag{14}$$

Let us now examine the restrictions imposed on (14) by the second principle. The invariant I_2 is an intrinsically positive quantity, while I_3 may have any sign. Therefore, since κ_1 and κ_2 are functions only of u , the inequality (14) implies

$$\kappa_1 \leq 0 \quad \text{and} \quad \kappa_2 = 0 \tag{15}$$

while $\kappa_0 = \text{tr}(\dot{\mathbf{P}}^v)$, and therefore it gives the time evolution of the scalar pressure p . It may be remarked that if $\kappa_2 = 0$ the entropy production term (14) is

$$\sigma \equiv -T^{-1} \kappa_1 \dot{\mathbf{P}}^v : \dot{\mathbf{P}}^v. \tag{16}$$

This is not to be confused with the expression of σ in the classical linear theory of irreversible thermodynamics in which the viscous pressure tensor $\dot{\mathbf{P}}^v$ is substituted by its first-order approximation $\dot{\mathbf{P}}^{v(1)}$. It can be seen from (16) that the reversible situations correspond to the cases $\dot{\mathbf{P}}^v = 0$ and $\kappa_1 = 0$, which in a first-order approximation may be identified respectively with perfect incompressible fluids and with elastic incompressible isotropic solids with the coefficient α related to the Lamé constant G by $\alpha^{-1} = 2G$.

Taking into account (15), (13) reduces to

$$(\dot{\mathbf{P}}^v)^* = \alpha^{-1}(\kappa_1 \dot{\mathbf{P}}^v - \dot{\mathbf{V}} + \kappa_0 \mathbf{U}) \tag{17}$$

which, if interpreted as a constitutive equation giving $\dot{\mathbf{P}}^v$, contains as a first-order approximation the Navier–Stokes linear law

$$\dot{\mathbf{P}}^{v(1)} = -2\mu \dot{\mathbf{V}} \tag{18}$$

in which μ is the shear viscosity. Introducing this first approximation into the left-hand side of (17), and neglecting third-order terms, we obtain for the second-order approximation

$$\dot{\mathbf{P}}^{v(2)} = -2\mu \dot{\mathbf{V}} + 4\mu^2 \alpha (\dot{\mathbf{V}})^* \tag{19}$$

Equations (1), (2) and (17) determine the evolution of the variables v , u and $\dot{\mathbf{P}}^v$, respectively, in terms of v , u , $\dot{\mathbf{P}}^v$ and their spatial derivatives and therefore they give a complete description of the system provided that suitable initial and boundary values are specified.

3. The constitutive equation of second-order fluids

With the assumption that the viscous pressure tensor depends on the rate of deformation tensor, Reiner and Rivlin (Truesdell and Noll 1965, p 477) have obtained for the corresponding constitutive relation in isotropic systems the general equation

$$\dot{\mathbf{P}}^v = \gamma_0 \mathbf{U} + \gamma_1 \dot{\mathbf{V}} + \gamma_2 \dot{\mathbf{V}}^2 \tag{20}$$

in which the coefficients γ_i are functions of u and the scalar invariants of $\dot{\mathbf{V}}$. While this equation predicts normal-stress effects which are excluded from the classical Navier–Stokes formulation, it leads to an equal value for the two normal-stress viscometric functions, in contradiction to experiments with some fluids, for example polyisobutylene solutions (Coleman *et al* 1966). In order to avoid this limitation, Rivlin and Ericksen (Truesdell and Noll 1965, p 481) proposed a more general constitutive equation of the kind

$$\dot{\mathbf{P}}^v = \dot{\mathbf{P}}^v(\mathbf{A}_1, \mathbf{A}_2, \dots, \mathbf{A}_n), \tag{21}$$

defining the fluid of the n -differential type, where \mathbf{A}_m is the objective Rivlin–Ericksen tensor of order m . In isotropic systems, and up to second order, equation (21) reduces to

$$\dot{\mathbf{P}}^v = \beta_0 \mathbf{U} - \mu \mathbf{A}_1 + \beta_1 \mathbf{A}_1^2 + \beta_2 \mathbf{A}_2 \tag{22}$$

with \mathbf{A}_1 and \mathbf{A}_2 given by

$$\mathbf{A}_1 = 2\mathbf{V} \quad \text{and} \quad \mathbf{A}_2 = \overset{\Delta}{\mathbf{A}}_1 = (\mathbf{A}_1)' - (\nabla v)^T \cdot \mathbf{A}_1 - \mathbf{A}_1 \cdot (\nabla v), \tag{23}$$

where $\overset{\Delta}{\mathbf{A}}_1$ is the objective convected derivative of \mathbf{A}_1 . The constitutive equation (22)

predicts different values for the normal-stress viscometric functions, and therefore it is suitable for the description of fluids such as polymer solutions, as long as memory effects can be neglected.

Dunn and Fosdick (1974) have studied the thermodynamic restrictions imposed by the second law on the constitutive equation (22) when the coefficients β_i are independent of the invariants of $\dot{\mathbf{V}}$, and they have found, amongst various other results, that the viscosity is non-negative, i.e. $\mu > 0$, and that the normal stress coefficients β_1 and β_2 are related by $\beta_1 = -\beta_2$. With these restrictions, equation (22) reduces to

$$\dot{\mathbf{P}}^v = -\mu \mathbf{A}_1 + \beta_2 (\dot{\mathbf{A}}_1 + \mathbf{W} \cdot \mathbf{A}_1 - \mathbf{A}_1 \cdot \mathbf{W}). \quad (24)$$

The equivalence between (24) and (19) is easily established with the identification $2\beta_2 = 4\mu^2\alpha$.

Therefore the simple formulation that we have proposed here leads in a straightforward way to a phenomenological equation that predicts a difference in the normal-stress viscometric functions as long as one is interested in second-order effects in the pressure tensor, whereas the developments in rational thermodynamics do not necessarily lead to this conclusion in the same approximation.

4. Conclusions

Starting from a generalised Gibbs equation which takes into account a dependence of the entropy on the viscous pressure tensor, we have developed a formulation of extended irreversible thermodynamics for viscous and incompressible fluids. The principal features of our development are:

(1) The generalisation of previous formulations of 'extended irreversible thermodynamics', whose constitutive equations are essentially linear, to a non-linear theory.

(2) The application of generalised irreversible thermodynamics to easily measured phenomena (e.g. viscous effects in polymers), while previous theories stressed their interest in more academic phenomena such as the finite velocity of propagation of heat signals.

(3) The dynamical interpretation of the second-order constitutive equation, which is seen as an evolution equation for the viscous pressure tensor, rather than an expression of it in terms of $\dot{\mathbf{V}}$ and its derivatives. This feature is due to the fact that in our formulation the viscous pressure tensor is an independent variable of the entropy.

(4) The obtainment of constitutive equations equivalent to those of second-order Rivlin–Ericksen fluids from a Gibbs equation in the framework of generalised irreversible thermodynamics when the objectivity principle is taken into account.

It seems, in consequence, that extended irreversible thermodynamics is able to deal with such systems as second-order fluids which in recent years have been of great practical and theoretical interest.

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