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Continuum thermodynamics and spatial interaction in fluids

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Fisica matematica. — *Continuum thermodynamics and spatial interaction in fluids* (*). Nota di MARIO CARRASSI e ANGELO MORRO, presentata (**) dal Socio C. CATTANEO.

RIASSUNTO. — Viene generalizzato un teorema di Coleman e Mizel prendendo in considerazione materiali visco-elastici definiti da equazioni costitutive che ammettono un tipo molto generale d'interazione spaziale. Il teorema è usato per ricavare le notevoli restrizioni cui devono essere sottoposti il flusso di calore e il tensore degli sforzi in un fluido «Maxwelliano».

§ 1. INTRODUCTION

About ten years ago Coleman and Noll [1] made a basic approach to continuum thermodynamics, and gave the procedure for rigorous derivation of necessary and sufficient conditions on constitutive equations for the validity of the Clausius-Duhem inequality. After this paper, Coleman and Mizel [2] applied the theory to the generalized Fourier's law of heat conduction, and to thermo-elastic materials [3], suppressing some unnecessary hypotheses contained in the first version of the Coleman-Noll theory and applying the rule (1) of equipresence in its full generality. Indeed, one of the most interesting points in this last formulation is the use without restriction of the rule of equipresence according to which " a quantity present as independent variable in one constitutive equation of a material must be so present in all". However, the thermo-elastic material analyzed by Coleman and Mizel is a simple material characterized by constitutive equations which depend only on the following field variables: the temperature θ, the deformation gradient $\mathbf{F}$, the temperature gradient θ, and the velocity gradient $\mathbf{L}$. This " a priori " restriction on the field variables does not allow a consideration of situations for which the " long range effects " of the spatial interactions are relevant, and does not permit a comparison with other independent theories for which such interactions are taken into account, like kinetic theory of moderately rarefied gases.

In this paper, instead, we take as independent variables of the constitutive equations the fields of temperature, deformation gradient, and velocity gradient together with their spatial gradients of all orders, i.e.

$$(\mathrm{grad})^{p}\,\theta \quad , \quad (\mathrm{grad})^{q}\,\mathbf{F} \quad , \quad (\mathrm{grad})^{s}\,\mathbf{L}$$

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(1) As recently suggested by C. C. Wang and C. Truesdell [4], we adopt the word " rule " instead of " principle " generally used in the past.

where p, q, s run from 0 to any finite number. Thus, our starting point is the following set of constitutive equations

$$\begin{aligned}
\varepsilon &= \hat{\varepsilon}(\theta, \mathbf{F}, \mathbf{L}, \cdots, (\mathrm{grad})^p\,\theta, \cdots, (\mathrm{grad})^q\,\mathbf{F}, \cdots, (\mathrm{grad})^s\,\mathbf{L}, \cdots) \\
\eta &= \hat{\eta}(\theta, \mathbf{F}, \mathbf{L}, \cdots, (\mathrm{grad})^p\,\theta, \cdots, (\mathrm{grad})^q\,\mathbf{F}, \cdots, (\mathrm{grad})^s\,\mathbf{L}, \cdots) \\
\mathbf{T} &= \hat{\mathbf{T}}(\theta, \mathbf{F}, \mathbf{L}, \cdots, (\mathrm{grad})^p\,\theta, \cdots, (\mathrm{grad})^q\,\mathbf{F}, \cdots, (\mathrm{grad})^s\,\mathbf{L}, \cdots) \\
\boldsymbol{q} &= \hat{\boldsymbol{q}}(\theta, \mathbf{F}, \mathbf{L}, \cdots, (\mathrm{grad})^p\,\theta, \cdots, (\mathrm{grad})^q\,\mathbf{F}, \cdots, (\mathrm{grad})^s\,\mathbf{L}, \cdots)
\end{aligned} \tag{1.1}$$

where ε denotes the specific internal energy, η the specific entropy, $\mathbf{T}$ the stress tensor, and $\boldsymbol{q}$ the heat flux vector. We remark here that we disregard long memory effects of the material, in spite of the very interesting researches developed in these last years, concerned with material having memory. Indeed the main purpose of this work will be to find the restrictions, on constitutive equations (1.1), which follow from the second law of thermodynamics and the principle of material frame indifference when we assume the material to be an isotropic fluid. The results, with the aid of further dimensional invariance arguments, can be easily related to the Truesdell theory of the "Maxwellian" fluid [5], [6]. Thus, as in the spirit of Truesdell's theory, our results can be formally compared with those obtained at the second stage by the Chapman-Enskog process in the kinetic theory of gases: that is, the well known Burnett expression for the stress tensor and the corresponding one for the heat flux [7]. This comparison is always interesting because the question whether there are additional consequences of the Boltzmann equation, beyond the Navier-Stokes level of hydrodynamics, is still open. In this regard it is interesting to mention the effect discovered by Scott *et al.* [8], [9] which was analyzed by Levi and Beenakker [10] on the basis of the Burnett equation; in this analysis, the term depending on $(\mathrm{grad})^2\,\theta$, which is just a term that is not allowed in the continuum thermodynamic theory as we shall show below, plays a fundamental role.

§ 2. OUTLINE OF THE THERMODYNAMIC THEORY

We consider a body $\mathcal{B}$ with material points labelled by their position $\mathbf{X}$ in a fixed reference configuration and denote by $\mathcal{R}$ the region occupied by $\mathcal{B}$ in this reference configuration. A thermodynamic process is described by eight functions of $\mathbf{X}$ and time t: the spatial *position* $\boldsymbol{x} = \chi(\mathbf{X}, t)$; the *stress* tensor $\mathbf{T} = \mathbf{T}(\mathbf{X}, t)$, the *body force* $\boldsymbol{b} = \boldsymbol{b}(\mathbf{X}, t)$, the specific *internal energy* $\varepsilon = \varepsilon(\mathbf{X}, t)$, the *heat flux* vector $\boldsymbol{q} = \boldsymbol{q}(\mathbf{X}, t)$, the *heat supply* $r = r(\mathbf{X}, t)$, the specific *entropy* $\eta = \eta(\mathbf{X}, t)$, the local *temperature* $\theta = \theta(\mathbf{X}, t)$. Such set of eight functions is called a *thermodynamic process* if it is compatible with the laws of conservation.

The main feature of the thermo-mechanic theory, as suggested by Coleman, Mizel and Noll, is that the principles of conservation of mass, linear momentum, moment of momentum, and energy impose no restriction on the constitutive equations. Indeed, these laws can be written in the form:

Conservation of mass

$$\dot{\rho} = \rho \operatorname{div} \dot{\chi} . \tag{2.1}$$

Balance of linear momentum

$$\rho \ddot{\chi} = \operatorname{div} \mathbf{T} + \rho \boldsymbol{b} . \tag{2.2}$$

Balance of moment of momentum

$$\mathbf{T} = \mathbf{T}^{T}. \tag{2.3}$$

Balance of energy

$$\rho \dot{\varepsilon} = tr \{\mathbf{TD}\} - \operatorname{div} \boldsymbol{q} + \rho r \tag{2.4}$$

where ρ is the mass density and $\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^{T})$ is the stretching tensor. Equation (2.1) is equivalent to

$$\rho = \frac{1}{|\det \mathbf{F}|} \rho_0 \tag{2.5}$$

where $\mathbf{F} = \mathbf{F} (\mathbf{X}, t) = \nabla \chi (\mathbf{X}, t)$ and ρ_0 is a positive number equal to the mass density in the reference configuration $\mathfrak{R}$.

If we ask for the totality of all conceivable processes, we see that if any smooth motion and stress field whatever are given, the equation of linear momentum determines a body force $\boldsymbol{b}$ such as to balance their effects; if we prescribe any smooth internal energy and heat flux field, the equation of energy determines a heat absorption r such as to balance them, too.

The key of the new thermodynamics, as stressed by Truesdell [11], is the following remark: *the principle of growth of entropy*, called Clausius-Duhem inequality, *determines no new quantity uniquely*. The entropy, unlike the other fields of thermo-mechanics, cannot be given arbitrarily even by the most artificial adjustment of forces and supplies of heat. Indeed, the principle of growth of entropy yields

$$\rho \dot{\eta} \geq - \operatorname{div} \left(\frac{\boldsymbol{q}}{\theta} \right) + \frac{1}{\theta} \rho r. \tag{2.6}$$

Using the equation of energy to eliminate the heat supply r (2.6) can be written in the form

$$\rho (\theta \dot{\eta} - \dot{\varepsilon}) + tr \{\mathbf{TD}\} - \frac{1}{\theta} \boldsymbol{q} \cdot \operatorname{grad} \theta \geq 0 . \tag{2.7}$$

If we substitute for ε, η, $\mathbf{T}$ and $\boldsymbol{q}$, the response functions given in (1.1) we obtain an inequality which must be satisfied identically for arbitrary configurations $\boldsymbol{x} = \chi (\mathbf{X}, t)$ and arbitrary temperature fields $\theta = \theta (\mathbf{X}, t)$. In this context, the principle of growth of entropy together with the principle of material frame indifference must be considered as restrictions upon the constitutive equations.

§ 3. CONSEQUENCES OF THE CLAUSIUS-DUHEM INEQUALITY

On the basis of the Clausius-Duhem inequality, we have demonstrated [12] the following theorem which is a generalization of the one stated by Coleman and Mizel [3].

THEOREM. *Consider a body* $\mathfrak{B}$ *and assume only that constitutive equations of the general form* (1.1) *hold at each* **X** *in* $\mathfrak{B}$. *Under this assumption, a necessary and sufficient condition that the inequality* (2.7) *hold for all admissible processes in* $\mathfrak{B}$ *is that the following statements be true at each* **X** *in* $\mathfrak{B}$.

I) ε and η are functions of θ and $\mathbf{F}$ alone; i.e.

$$\varepsilon = \hat{\varepsilon}(\theta, \mathbf{F}) \quad , \quad \eta = \hat{\eta}(\theta, \mathbf{F}). \tag{3.1}$$

II) The entropy is given by the relation

$$\hat{\eta}(\theta, \mathbf{F}) = -\frac{\partial\hat{\psi}(\theta, \mathbf{F})}{\partial\theta} \tag{3.2}$$

where $\psi = \varepsilon - \theta\eta$.

III) The stress $\mathbf{T}$ can always be written as $\mathbf{T} = \mathbf{T}^0 + \mathbf{T}^e$ where $\mathbf{T}^0$ is given by the " equilibrium stress relation "

$$\hat{\mathbf{T}}^0(\theta, \mathbf{F}) = \rho\mathbf{F}\left[\frac{\partial\hat{\psi}(\varepsilon, \mathbf{F})}{\partial\mathbf{F}}\right]^{\mathrm{T}}. \tag{3.4}$$

IV) The extra stress $\mathbf{T}^e$ and the heat flux $\boldsymbol{q}$ obey the dissipation inequality

$$tr\{\mathbf{T}^e\mathbf{D}\} - \frac{1}{\theta}\,\boldsymbol{q}\cdot\operatorname{grad}\theta \geq 0 \tag{3.5}$$

for all the values of θ, $\mathbf{F}$, $\mathbf{L}$, and all the values of the spatial gradients of these quantities.

We remark here that the theorem quoted above has a general validity for visco-elastic materials with any sort of spatial interaction (without memory). One of us [13], indeed, has shown that an analogous theorem must hold also if one assumes the constitutive equations in the form

$$\zeta(\mathbf{X}, t) = \zeta^x[\theta(\cdot, t), \chi(\cdot, t), \dot{\chi}(\cdot, t)] \tag{3.6}$$

where ζ stands for the four quantities ε, η, $\mathbf{T}$, and $\boldsymbol{q}$. According to (3.6) it is assumed that ε, η, $\mathbf{T}$, and $\boldsymbol{q}$, at a point $\mathbf{X}$ and time t, are *functionals* of the temperature field $\theta(\cdot, t)$, of the configuration $\chi(\cdot, t)$, and of its time derivative $\dot{\chi}(\cdot, t)$ over the entire body, at the same time t.

§ 4. FLUIDS. FURTHER RESTRICTIONS ON T AND *q*

We say that a material is a *fluid* if the tensor **F** occurs in (1.1) only through the absolute value $|\det \mathbf{F}|$ of its determinant $\det \mathbf{F}$ or, equivalently, if the constitutive equations (1.1) depend on **F** only through the specific volume $v = 1/\rho$. Taking into account the assertion III) of the theorem, the equilibrium stress $\mathbf{T}^0$ can now be written in the form

$$\hat{\mathbf{T}}^0(\theta, v) = -\hat{p}(\theta, v)\,\mathbf{I} \tag{4.1}$$

where $p = \hat{p}(\theta, v)$ is a scalar function of θ and v defined by $\hat{p}(\theta, v) = -\dfrac{\partial\hat{\psi}(\theta, v)}{\partial v}$. Of course, we can choose, as independent variable, p instead of v if $\dfrac{\partial\hat{\psi}}{\partial v}$ is a smoothly invertible function in the variable v. Furthermore, we must take into account the restrictions upon the response functions **T** and $\boldsymbol{q}$ due to the principle of material frame indifference. Without any further discussion we take the results reported by Truesdell and Noll [6] according to which the response functions **T** and $\boldsymbol{q}$ depend on the velocity gradients only through **D** and $(\mathrm{grad})^s\,\mathbf{L}$. Using this result, the dissipation inequality (assertion IV of our theorem) must now be written

$$\Gamma = \theta\, tr\{\mathbf{T}^e\mathbf{D}\} - \boldsymbol{q}\cdot\mathrm{grad}\,\theta \geq 0 \tag{4.2}$$

where $\mathbf{T}^e$ and $\boldsymbol{q}$ are given by

$$\begin{aligned} \mathbf{T}^e &= \mathbf{T}^e(\theta, p, \mathbf{D}, \mathrm{grad}\,\theta, \mathrm{grad}\,p, \mathrm{grad}\,\mathbf{L}, \cdots) \\ \boldsymbol{q} &= \boldsymbol{q}(\theta, p, \mathbf{D}, \mathrm{grad}\,\theta, \mathrm{grad}\,p, \mathrm{grad}\,\mathbf{L}, \cdots)\,. \end{aligned} \tag{4.3}$$

The dissipation inequality (4.2) tells us that Γ has a minimum at $\mathbf{D} = \mathrm{O}$ and $\mathrm{grad}\,\theta = \mathrm{O}$. Thus, it is a consequence of the Clausius–Duhem inequality that, when $\mathbf{D} = \mathrm{O}$ and $\mathrm{grad}\,\theta = \mathrm{O}$, both $\mathbf{T}^e$ and $\boldsymbol{q}$ must vanish, regardless of the values of all the other variables which appear in (4.3). This means that if we consider approximation formulas for $\mathbf{T}^e$ and $\boldsymbol{q}$ for small values of the variables, it does not matter here if we have no " a priori " criteria about the " smallness " of the variables, all terms of the expansion must include $(\mathbf{D})^m$ and/or $(\mathrm{grad}\,\theta)^n$ as a factor, where m and n run from 1 to any finite number. This result is the main point of our analysis which derives from the theorem stated above; in the next section we will show explicitly its meaning when we specify the definition of first and second order terms in the expansion of $\mathbf{T}^e$ and $\boldsymbol{q}$. There is another restriction that will be very useful in the following. This is a consequence of the principle of material frame indifference or, in a more simple way, it is a consequence of the invariance of the physical laws under spatial inversion. Indeed, under a change of frame defined by the transformation

$$\boldsymbol{x}^* = \mathbf{Q}\boldsymbol{x}$$

where $\mathbf{Q}$ is an orthogonal tensor, the thermo-mechanic effects are indifferent, i.e.

$$\varepsilon^* = \varepsilon \quad , \quad \eta^* = \eta \quad , \quad \mathbf{T}^* = \mathbf{Q}\mathbf{T}\mathbf{Q}^{\mathrm{T}} \quad , \quad \boldsymbol{q}^* = \mathbf{Q}\boldsymbol{q}$$

and all constitutive equations are indifferent, too. If we put $\mathbf{Q} = -\mathbf{I}$, we obtain two identities which must be fulfilled by the stress tensor $\mathbf{T}$ and the heat flux $\boldsymbol{q}$, i.e.

$$\begin{aligned}(4.4)\qquad & \mathbf{T}(\theta, p, \mathbf{D}, -\operatorname{grad}\theta, -\operatorname{grad}p, -\operatorname{grad}\mathbf{L}, \cdots) = \\ & = \mathbf{T}(\theta, p, \mathbf{D}, \operatorname{grad}\theta, \operatorname{grad}p, \operatorname{grad}\mathbf{L}, \cdots)\end{aligned}$$

and

$$\begin{aligned}(4.5)\qquad & \boldsymbol{q}(\theta, p, \mathbf{D}, -\operatorname{grad}\theta, -\operatorname{grad}p, -\operatorname{grad}\mathbf{L}, \cdots) = \\ & -\boldsymbol{q}(\theta, p, \mathbf{D}, \operatorname{grad}\theta, \operatorname{grad}p, \operatorname{grad}\mathbf{L}, \cdots) .\end{aligned}$$

Equations (4.4) and (4.5) imply that if we use some series expansion – whatever the physical meaning of the parameter selected to justify the series expansion – the response function $\mathbf{T}$ can depend only on those terms which *do not change sign under inversion* whereas the response function $\boldsymbol{q}$ can depend only on the terms that *change sign under inversion.*

§ 5. THE " MAXWELLIAN " FLUID. CONCLUSIONS

The Truesdell theory of the " Maxwellian " fluid was an attempt to construct a model reflecting some of the properties of rarefied gases. Truesdell proposed constitutive equations for the stress tensor $\mathbf{T}$ and the heat flux vector $\boldsymbol{q}$ taking as independent variables the fields of velocity, pressure, and temperature, and their spatial gradients of all orders. Using the principle of equipresence for the first time, both $\mathbf{T}$ and $\boldsymbol{q}$ were assumed to be analytic functions of the same variables and of two fundamental physical dimensional constants, namely a natural viscosity μ_0 and a natural thermal conductivity χ_0. Thus, from this starting point, Truesdell was able to show, by means of dimensional analysis, that μ_0 emerges as a possible *ordering parameter* and in this way it was possible to compare the results with those of the kinetic theory; particularly with first and the second approximations for the stress and the heat flux obtained by the Chapman-Enskog process for the solution of the Boltzmann equation.

Coming back to our thermodynamic theory of a fluid, we must now make an assumption which allows us to give a physical definition of " first " and " second " approximations in the expansion of $\mathbf{T}$ and $\boldsymbol{q}$. We suppose, as Truesdell does, that the constitutive equation for the stress tensor $\mathbf{T}$ and the heat flux vector $\boldsymbol{q}$ depend upon the viscosity coefficient μ_0 and the heat conduction coefficient χ_0. Then we can develop the stress $\mathbf{T}$ and the heat flux $\boldsymbol{q}$ in a power series in the variables which appear in (4.3). Hence, with the aid of the previous assumption, we can order, using the same dimensional analysis employed by Truesdell, the terms of the power series according to the power of the viscosity coefficient. In this way we shall find just the restrictions which the second law of thermodynamics imposes on the " Maxwellian " fluid. Instead of μ_0 and χ_0, we use μ_0 and the ratio $R_n = \chi_0/\mu_0$ which is related to the dimensionless ratio $f = \chi_0/\mu_0 c_v$ whose value is nearly a constant with the same value 5/2 for all monoatomic gases (in this case, hence, R_n is proportional to the ideal gas constant R). The whole expansion of **T** and $\boldsymbol{q}$ can be written

$$
\begin{aligned}
\mathbf{T} &= {}^{(0)}\mathbf{T} + {}^{(1)}\mathbf{T} + {}^{(2)}\mathbf{T} + \cdots \\
\boldsymbol{q} &= {}^{(0)}\boldsymbol{q} + {}^{(1)}\boldsymbol{q} + {}^{(2)}\boldsymbol{q} + \cdots
\end{aligned}
\tag{5.1}
$$

where the upper index on the left means now the power of μ_0 which appears in the expansion. Thus, if we simply limit ourselves to writing out all the terms of order 0, 1 and 2 in the viscosity coefficient we obtain, for the stress tensor

$$
\left\{
\begin{aligned}
{}^{(0)}T_{ij} &= -p\delta_{ij} \\
{}^{(1)}T_{ij} &= \mu_0 \, {}^{1}\tau_{ijkl} \, D_{kl} \\
{}^{(2)}T_{ij} &= \frac{\mu_0^2}{p} \, {}^{21}\tau_{ijrshk} \, D_{rs} \, D_{hk} + \frac{\mu_0^2 R_n}{p\theta} \, {}^{22}\tau_{ijrs} \, \theta_{,r} \, \theta_{,s} + \frac{\mu_0^2 R_n}{p^2} \, {}^{23}\tau_{ijrs} \, \theta_{,r} \, p_{,s}
\end{aligned}
\right.
\tag{5.2}
$$

and for the heat flux

$$
\left\{
\begin{aligned}
{}^{(0)}q_i &= 0 \\
{}^{(1)}q_i &= \mu_0 R_n \, {}^{1}K_{ij} \, \theta_{,j} \\
{}^{(2)}q_i &= \frac{\mu_0^2}{p} R_n \, {}^{21}K_{irsh} \, D_{rs} \, \theta_{,h} + \frac{\mu_0^2 R_n \theta}{p^2} \, {}^{22}K_{irsh} \, D_{rs} \, p_{,h}
\end{aligned}
\right.
\tag{5.3}
$$

where $^{\cdot\cdot}\tau....$ and $^{\cdot\cdot}K....$ are functions only of dimensionless variables. For a full comparison with the theory of the " Maxwellian " fluid and with the results obtained at the second stage by the Chapman-Enskog process in the kinetic theory of gases, we must impose the isotropy of the fluid. These detailed calculations are carried out in ref. [12]. Here we want to stress that equations (5.2) and (5.3) manifest all the consequences of the thermodynamic theory. Indeed, we have applied all the restrictions which can be derived from the Clausius-Duhem inequality, the principle of material frame indifference including the invariance under the inversion operator. Thus the main results of this analysis can be summarized as follows:

a) The ${}^{(2)}\mathbf{T}$ expression for the stress tensor **T** cannot contain terms of the type $(\text{grad})^2\,\theta$, $(\text{grad})^2\,p$, and $\text{grad}\,p \otimes \text{grad}\,p$ owing to the Clausius-Duhem inequality or second law of thermodynamics.

b) Likewise, in the ${}^{(1)}\boldsymbol{q}$ expression for the heat flux $\boldsymbol{q}$, a term depending on grad p, called by Truesdell the " Brillouin effect ", is not allowed, and, in the ${}^{(2)}\boldsymbol{q}$ expression, terms depending on grad **L** cannot appear because of the Clausius-Duhem inequality.

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