Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fis. Mat. e Nat.
Vol. LXVII (1989) - Conferenza del 20-4-1989

THERMODYNAMICS OF PROCESSES IN DEFORMING MEDIA

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The ideas descibed here are based on the important fact that the rheological processes are irreversible like any other process. The consideration of irreversibility in the mechanical motion of a medium is an old idea and the method described here is only slightly different from its ancestors. In this theory, the second law of thermodynamics is the starting point while in others it is built into a mechanical theory. Simply speaking, *I* presume rheology is a realm governed by the laws of thermodynamics. Another important feature is that *I* insist on the original Onsagerian framework of non-equilibrium thermodynamics and so do not include many restrictive ideas attached to Onsager's theory later. The linearity of the constitutive equations have less importance than in the classical literature of irreversible thermodynamics [3-6].

During the motion of rheological fluids special microscopic structures develop, different from those at rest; this is referred to as «structural viscosity». These structures should have their own right in any thermodynamic theory as well. The dynamic variables, which are sometimes called internal or hidden variables, should be replaced by the above mentioned structures in the theory. The various types of dynamic variables and the great variety of dynamic laws allowed by Onsager's thermodynamics call forth a broad perspective for development in rheology, which cannot be reviewed at this early stage. Even in the simplest case, when a single dynamic variable is used and the dynamic laws are strictly linear in the thermodynamic sense, the model obtained shows a rich variety of mechanical behaviour.

The thermodynamic treatment strats with the balance equation of internal energy, which reads

$$\rho \dot{u} + \mathrm{div}\mathbf{J}_q = \mathbf{t} : \overset{\circ}{\mathbf{d}} \tag{1}$$

for an incompressible fluid. Here ρ is the density, u the specific internal energy, $\mathbf{J}_q$ the heat flux, $\mathbf{t}$ stands for the deviatoric part of Cauchy's stress and $\overset{\circ}{\mathbf{d}}$ is the symmetric part of the velocity gradient. The specific entropy of the medium depends on the internal energy and on some dynamic variables. In the simplest case we regard only one dynamic variable but nothing prevents us from regarding several ones. In equilibrium, the value of the dinamic variables are determined. and according to the Morse lemma, the entropy is given as

$$s = s^e \left(u - \frac{1}{2\rho} \xi^2 \right) \tag{2}$$

if the dynamic variable is suitably chosen. The function $s^e(u)$ is the equilibrium entropy function.

Introducing equations (1) and (2) into the entropy balance

$$\rho \dot{s} + \mathrm{div}\mathbf{J}_s = \sigma_s \tag{3}$$

we obtain

$$T\sigma_s = \mathbf{t} : \overset{\circ}{\mathbf{d}} - \xi : \overset{\circ}{\xi} . \tag{4}$$

The linear equations for the problem at hand read

$$\begin{aligned} \mathbf{t} &= L_{11}\overset{\circ}{\mathbf{d}} - L_{12}\xi \\ \overset{\circ}{\xi} &= -L_{12}\overset{\circ}{\mathbf{d}} - L_{22}\xi. \end{aligned} \tag{5}$$

Here we supposed that the dynamic variable ξ is a second order tensor invariant under time inversion with zero trace. Eliminating the dynamic variable from the equations

$$\tau_t\overset{\circ}{\mathbf{t}} + \mathbf{t} = 2\eta(\overset{\circ}{\mathbf{d}} + \tau_d\overset{\circ\circ}{\mathbf{d}}) \tag{6}$$

is obtained, where the notations

$$\tau_t = \frac{1}{L_{11}};\ \tau_d = \frac{L_{11}}{L_{11}L_{22} + L_{12}^2};\ 2\eta = L_{11} + \frac{L_{12}^2}{L_{22}} \tag{7}$$

are introduced. The small circles above $\mathbf{t}$ and $\overset{\circ}{\mathbf{d}}$ denote Jaumann derivatives. Eq. (6) fulfills the requirement of material objectivity ie. any change of frame leaves its form invariant.

The simplest solutions belong to small amplitude motions, for which the Jaumann derivatives reduce to total time derivatives. In this case the equation reduces to that of the visco-elastic body the alternative mechanical models of which are given in figures 1 and 2.

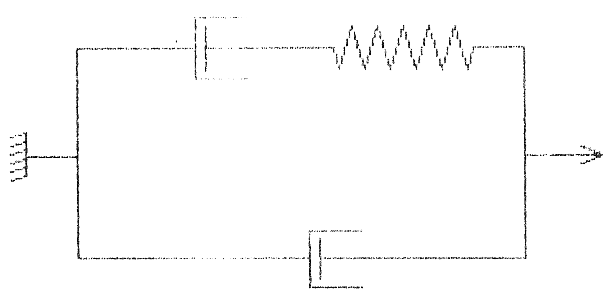

Fig. 1

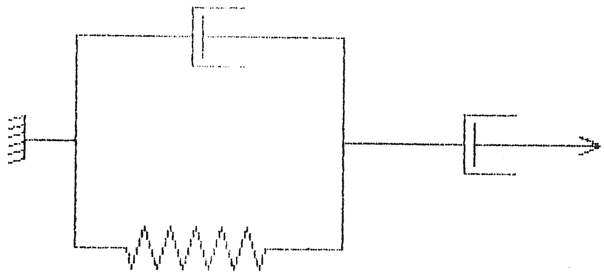

Fig. 2

For simple shear flow, the velocity of which is given as

(8) $$\mathbf{v} = xy\mathbf{i}$$

the viscometric functions can easily easily be determined (figures 3 and 4).

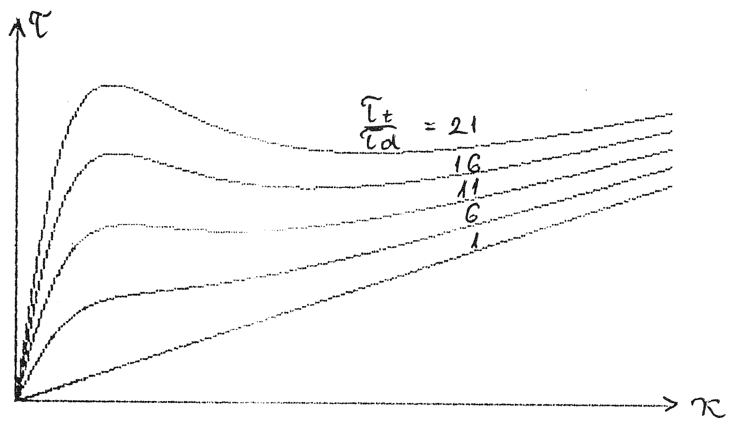

Fig. 3

$$\tau = \eta x \frac{1 + \tau_t \tau_d x^2}{1 + (\tau_t x)^2}; \quad -\sigma_y = \sigma_x = \frac{\eta(\tau_t - \tau_d)x^2}{1 + (\tau_t x)^2} \tag{9}$$

The shear stress function shows the shape of the Ostwald curves while the normal stress functions describe Weissenberg's effects. A computational method based on complex numbers simplifies the calculations. Applying this method to bodies with several dynamic variables, we obtain the Cox-Merz rule and its field of validity turns out to be identical with that of the linear Onsager laws. The complex number form of the differential equation shows that a Hilbert transformation relates the shear stress function to the normal stress functions. The transients can also be computed.

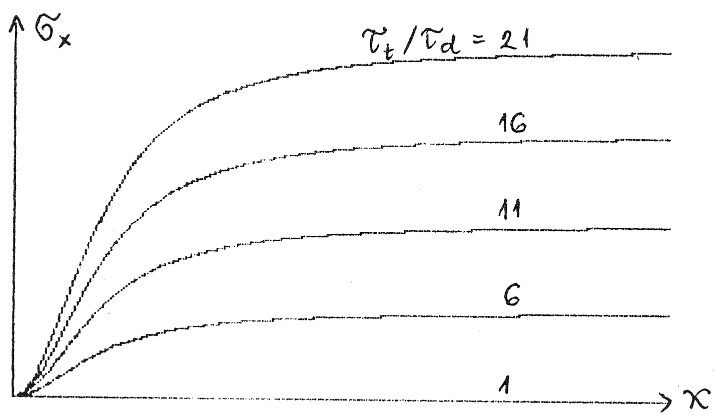

Fig. 4

Analysing the stability of the steady solutions we conclude that the decreasing region of the shear stress function is unstable. (Such a region exists if $\tau_t/\tau_d > 9$). In this case a hysteritic phase change is observed (figure 5), which leads to plasticity if the ratio τ_t/τ_d is sufficiently large.

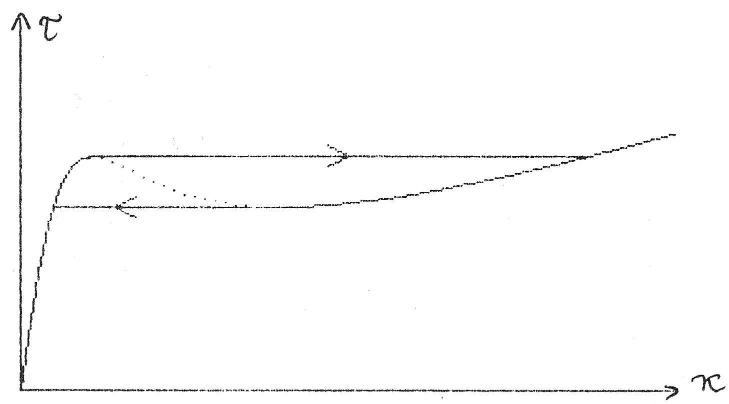

Fig. 5

In case of uniaxial load (traction or compression), the plastic flow is explained as follows. To a steady stress $\mathbf{t}$, we always can find a solution of eq. (6) with zero angular velocity

$$\overset{\circ}{\mathbf{d}} = \frac{1}{2\eta}\mathbf{t} \tag{10}$$

The motion is slow, the body creeps. This solution is stable if the load is below a critical value

$$\sigma_{cr} = \frac{2\eta}{\tau_t - \tau_d} \tag{11}$$

Above the critical load, another solution is found, corresponding to a faster motion. The angular velocity is perpendicular to the traction. There is also a second critical load, which is three times greater than the first. Above that, the angular velocity rotates around the traction and the motion once again speeds up. (figure 6).

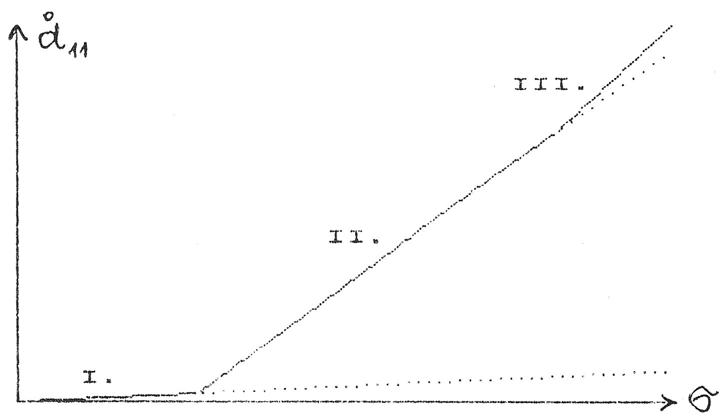

Fig. 6

If several dynamic variables are to be used region II of the diagram becomes curved but the plastic behaviour often remains the same.

In case of small but rapid loads creeps is negligible and eq. (6) reduces to

$$\overset{\circ}{\mathbf{t}} = \frac{2\eta}{\tau_t - \tau_d}(\overset{\circ}{\mathbf{d}} + \tau_d \overset{\circ\circ}{\mathbf{d}}), \tag{12}$$

which can easily be integrated in a corotating frame:

$$\mathbf{t} = \frac{2\eta}{\tau_t - \tau_d}(\mathbf{d} + \tau_d \overset{\circ}{\mathbf{d}} - \mathbf{d}_0) \tag{13}$$

This is the constitutive equation of a Kelvin-body describing the elastic states before or after a plastic flow.

The value of the thermodynamic method has been elucidatad, and a few solutions of the simplest model considered. Even eq. (6) has more solutions, moreover we can use several dynamic variables, quasi-linear or non-linear thermodynamic equations, which result in a very rich set of solutions. Comparison of our predictions from the Onsager theory with experiments and other theories has shown very good agreement.

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