

**APPENDIX TO INTRODUCTION TO RHEOLOGICAL CONCEPTS  
BRIEF SURVEY OF WEISSENBERG'S GENERAL THEORY OF DE-  
FORMATION, AND OF THE BASIC RELATIONS OF  
SINUSOIDAL DEFORMATIONS.**

Weissenberg's theory\* starts by postulating, in analogy to thermodynamics that, in any material, the sum of the changes with time of the transmitted work,  $A$ , the stored free energy,  $F$ , and the heat of dissipation  $H$ , must be zero. The input of work per unit time,  $\dot{A}$ , that is the effort, must be the product  $\dot{A} = P\dot{S}$  for any type of material. The two other time derivatives  $\dot{F}$ ,  $\dot{H}$  will depend on the type of system, i.e. on the nature and number of the stress and deformation derivatives which come into play ( $\dot{P}, \ddot{P} \dots \overset{\text{v}}{P}; \dot{S}, \ddot{S}, \dots \overset{\text{v}}{S}$ ). Further, the changes with time of  $F$ , which by definition is the reversible part of the transmitted energy,  $A$ , must be independent of rate and reflect states of equilibrium. The dissipated part,  $H$ , will depend on the operative stress and strain derivatives, so that the complete balance becomes:  $P\dot{S} - dF(\overset{\text{v}}{P}, \overset{\text{v}}{S})/dt - \dot{H}(\overset{\text{v}}{P}, \overset{\text{v}}{S}) = 0$ .

This general equation covers all the general cases mentioned in the introduction as special ones. Time effects can be described by integration and separating the terms containing  $P$  and  $\dot{S}$ . In the reversible, elastic, case the dissipated energy,  $\dot{H} = 0$ , and only the integration of the first two terms is to be performed. Approximating  $F$  by a power series of either  $P$  or  $S$  in which all terms containing stresses or strains must occur in even powers in order to render them independent of direction (the same is true for series of  $\dot{S}$  and  $\dot{H}$ ), one finds  $F = P^2/2G$ , or  $F = G/2 S^2$ ; substitution then yields Hooke's Law. Similarly, for complete dissipation of the free energy,  $dF = 0$ , and with independence of the applied effort of strain and using the first approximation,  $\dot{H} \approx P^2/\eta \approx \eta\dot{S}^2$ , one obtains Newton's Law.

The laws for the intermediate bodies follow again by considering the resulting processes when the deformation is suddenly stopped, at  $S = S_0$ ,  $\dot{S} = 0$ , or the stress is suddenly released,  $P = 0$ . In both cases  $P\dot{S} = 0$ , and the remaining equation can be solved either for  $S$  or  $P$  by substitution

\* For a short version, and references see K. Weissenberg, in K. H. Meyer, *Natural and Synthetic High Polymers*, 2nd Ed. Interscience, 1954.

into the remaining equations:  $dF(\dot{S})/dt + \dot{H}(\dot{S}) = 0$ , and  $dF(P, \dot{S}_0)/dt + \dot{H}(P, \dot{S}_0) = 0$ .

If one sets  $F = (G/2)S^2$  and  $\dot{H} = \eta\dot{S}^2$ , then one considers essentially a solid with internal friction, as only a solid shows dependence of  $F$  on  $S$  without rate effects. The result of substitution for sudden stress release is  $S = S_0 \exp(-G/\eta_2)t$ , showing a relaxation of strain depending exponentially on the ratio of elastic modulus to the retarding internal viscosity  $\eta_2$ . This characteristic ratio  $G/\eta_2$  has the dimension of a reciprocal time,  $1/\tau$ , where  $\tau$  as the retardation time affords description of the strain relaxation by a single parameter. In the other case, of constant strain, no time phenomena occur and the balancing stress is simply that according to Hooke's Law. At constant force, however, the internal viscosity retards the attainment of (Hookean) equilibrium; the asymptotic approach to the latter is described by the same retardation time in the relation  $S = (P/G) [1 - \exp(-G/\eta_2)t]$ .

Considering now an elastico-viscous liquid, at the moment when at a deformation  $S_0$  the stress application suddenly stops,  $\dot{S} = 0$ , the deformation resulting from liquid flow presents a new equilibrium position and therefore is equal to zero deformation. The elastic elements, however, have been extended during the preceding flow to an extent  $S_e$ . This deformation will be recovered, either instantaneously, if the internal friction is negligible, or according to an exponential decay if the strain recovery is itself retarded. For the decay of stress at constant extension,  $\dot{S} = 0$ , and using the two approximations:  $F = P^2/2G$  and  $\dot{H} = P^2/\eta$ , one obtains  $P = P_0 \exp(-G/\eta)t$ , where  $G/\eta$  is  $1/\tau$ , the reciprocal relaxation time.

The analogy of the equations for stress and for strain relaxation is striking, but the meaning of the two parameters of the two ratios  $G/\eta$  is somewhat different. The shear modulus,  $G$ , of the elastico-viscous liquid is considered independent, i.e. unretarded, in the present approximation and the coefficient  $\eta$  is that of the regular, macroscopic, viscosity pertaining to flow, whereas before  $\eta_2$  was the coefficient of the internal, retarding, viscous friction and  $G$ , often written as  $G_2$ , the modulus of retarded elasticity. The two coefficients of viscosity differ as a rule, above the glass point, by an appreciable factor, the macroscopic viscosity being the larger one.

When in a series of retarded elastic bodies the internal viscosities go to zero, the relaxation equations show that the retardation time also becomes zero and the behavior approaches that of a frictionless elastic body; on the other hand, if in a series of viscoelastic liquids the elasticity vanishes and  $G = 0$ , the stress reduces to the flow stress, independent of deformation, and we obtain Newton's Law. Real bodies behave, as a rule, like a compounded series of elements with distributions of  $G$ ,  $\eta_2$  and  $\eta$ .

Describing period deformations, the strain is assumed to vary as the sine,  $S = S_0 \sin \omega t$ , and the rate of deformation correspondingly as the cosine,  $\dot{S} = S_0 \omega \cos \omega t$ , where  $\omega = 2\pi\nu$ ,  $\nu$  is the frequency in c.p.s., and  $S_0$  is the maximum amplitude of deformation. The corresponding stress components are  $GS$ , and  $P_{vis} = \eta\dot{S}$ . In elastico-viscous liquids, the elastic and viscous deformations are additive while the force, acting instantaneously through the elastic on the viscous parts, is the same:  $P_e = P_{vis}$ . In viscoelastic solids, the deformation is that of the retarded spring, with the stress composed of the elastic and the viscous components:  $P = P_e + P_{vis} = S_0 (G \sin \omega t + \omega\eta_2 \cos \omega t)$ .\* This sum can be conveniently converted by the relation:  $\cos x \cos \alpha + \sin x \sin \alpha = \cos (x - \alpha)$ , where  $\cos \alpha$  and  $\sin \alpha$  can be replaced by suitable coefficients, e.g.:  $A_1 \cos \omega t - A_2 \sin \omega t = \sqrt{A_1^2 + A_2^2} \cos (\omega t - \alpha)$ ; here  $\alpha$  is defined by:  $\cos \alpha = A_1/\sqrt{A_1^2 + A_2^2}$  and  $\sin \alpha = -A_2/\sqrt{A_1^2 + A_2^2}$ . Since  $A_1 = G$  and  $A_2 = \eta\omega$ , the resultant stress becomes:  $P/S_0 = \sqrt{G^2 + \eta^2\omega^2} \cos (\omega t - \alpha)$ . In this, the root factor represents a modulus and  $\alpha$  the phase angle; further,  $\tan \alpha = \eta\omega/G = \omega\tau$ , where  $\tau$  is the retardation time.  $P$  reaches its maximum value when  $\alpha = \omega t$ . The modulus thus defined by maximum stress and amplitude, often called absolute modulus, is  $P_{max}/S_0 = [G] = (G^2 + \omega^2\eta^2)^{\frac{1}{2}}$ .

Alternatively, the second order linear differential equations which describe the above mechanical (and electrical) periodic processes can be solved by exponentials, leading to the sum of a real and an imaginary term as general solution.\*\* This complex number can be rendered real by adding its conjugate; or, by virtue of being a quantity in the plane formed by the two coordinates of real and imaginary numbers, the complex number can be used to represent in- and out-of-phase quantities such as combined elastic and rate responses. Considering, e.g., the elastic response in phase with

\* In the following  $\eta = \eta_2$  for brevity.

\*\* See e.g. Slater and Frank, Introduction into Theoretical Physics, McGraw-Hill, N.Y. 1933, pp. 20.

$S_0 \sin(\omega t)$ , the complex value  $A^* \exp(i\omega t)$  rotates in the above plane with the velocity  $\omega$ , whereby its projections onto the real and imaginary axes amount to the elastic and viscous contributions respectively. It has thus become customary to speak of the real, or dynamic, modulus  $G'$  and of the imaginary modulus  $\omega\eta = G''$ , and the complex modulus  $G^* = G' + iG''$  and the absolute modulus  $|G| = (G'^2 + G''^2)^{\frac{1}{2}}$ . If one chooses to count the viscous contribution on the real axis and the elastic one on the imaginary, one obtains the real and imaginary parts of the complex viscosity, i.e., an impedance:  $\eta^* = \eta' - i\eta''$ , where  $\omega\eta'' = G'$ . The more detailed discussion of periodic behavior, and the use of electrical analogies, will be found in Chapter XI of Volume I and Chapters I and III of Volume II.

The derivation from the basic differential equation, being a general one, has to be applied to each particular type of mechanical response, i.e. to each model, in order to establish the relation between  $G'$  and  $G''$  and the constants of the mechanical model. This can be done exactly as in the treatment of A.C. currents.\* For the viscoelastic solid, i.e. the Voigt body with spring and viscous element in parallel, one finds simply that  $G' = G$ , and  $\eta' = \eta$ ; also  $|G| = G(1 + \omega^2\tau^2)^{\frac{1}{2}}$  which in view of  $\eta\omega/G = \omega\tau$  is identical with the result of the above derivation. Thus, in this simplest case, only  $|G|$  is frequency dependent.

For the elastico-viscous liquid, the Maxwell model with spring and viscous element in series, one finds  $G' = G\omega^2\tau^2/(1 + \omega^2\tau^2)$ ,  $\eta' = \eta/(1 + \omega^2\tau^2)$ , and  $|G| = G\omega\tau/(1 + \omega^2\tau^2)^{\frac{1}{2}}$ ; i.e. all three values are frequency dependent in terms of the model constants. In general, then the experimentally found frequency variation of  $G'$ ,  $\eta'$  and  $|G|$  will be compared with the theoretical variation of  $G'$ ,  $\eta'$  and  $|G|$  will be compared with the theoretical dependence of various models in order to permit conclusions with respect to the type of behavior of the material.

\* See for example, T. Alfrey, "Mechanical Behaviour of High Polymers", Interscience, N. Y. 1948; and J. D. Ferry, W. M. Sawyer, and J. N. Ashworth, *J. Polymer Sci.*, **2**, 593 (1947).