

CHAPTER I

INTRODUCTION TO RHEOLOGICAL CONCEPTS

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During the acceleration of a body as a whole, in translation or rotation, the relative positions of its mass points remain the same, and the forces are defined by the acceleration of the total mass. The deformation, or distortion, of a body refers to relative displacement of mass points by balancing couples, so that neither the center of gravity is moved, nor a concentric rotation of the body as a whole is imparted. Strain, S , is a displacement defined as a relative change of a length and is homogeneous if the displacement varies linearly to reference coordinates. Stress, P , is the acting force per unit area and may be thought of as being composed of normal (tensile and compressive) and tangential (shearing) components. The division is artificial (Chapter II), since every application of force entails inevitably the application of both components. It permits, however, a useful delineation, as the normal components are consistent with volume changes whereas the shearing forces (couples) are sources of, or response to, deformation of a body, which is defined as a coherent entity of matter.

The term deformation is used both for a relative displacement in progress and for the state of displacement reached during this process at any instant of time. Accelerations of body parts occur until a steady velocity of deformation is reached. It is a fundamental property of real matter that apart from the forces of acceleration of the body parts, forces are required to keep a body in a steady state of progressing deformation. Many bodies require also forces to maintain a state of deformation for a finite, or for an indefinite period. Bodies for which the latter property can be neglected, are classified as liquids. No similarly fitting term exists for the non-liquids, although the term solid is usually employed. Thus the deformed state exhibits a spectrum of behavior. Ideally, completely elastic solids require the same stress which was applied during the last moment of deformation to maintain the deformation indefinitely. On the other hand, ideal liquids require no perceptible force to maintain the state at which the process of deformation left off.

Completely elastic bodies also do not show any dependence on the rate of deformation. Their process of deformation may be visualized as a se-

quence of equilibrium states in which the extent of deformation only, and not history, or time effects, determine the required stress. Thus, one has to imagine a system of stresses set up in a body which exactly balances the deforming external set of stresses; or vice versa, imagine the external stresses as necessary to balance the internal resistance to departures from the equilibrium (unstrained) state. This balance remains preserved when stresses subside until the body has returned into its undeformed original state. Ideally elastic bodies follow Hooke's law, according to which the external stress, or stress component, is proportional to the corresponding deformation, or deformation component: $P = GS$, where G is the static modulus of elasticity.

It is also inherent in ideally elastic behavior that deformation, due to its independence of history or path, can be cycled at will as a reversible process. The work A done on, and the work F returned by, the body is equal and corresponds to a reversible input and regain, i.e. to a storage, of free (potential) energy of shape. Such a system is conservative, or frictionless.

In the case of the liquids every new relative position of the mass points represents a new equilibrium state of which these materials possess an infinite number. Since no forces are required to maintain a given shape, the slightest applied force causes deformation so that these materials are completely fluid. In fact, self-diffusion can be shown to change the relative position of mass points spontaneously and continuously. In the absence of unique shape, deformation in the static sense does not exist, progressive deformations suffered are not recovered, and no energy can be stored in the body or be regained. Instead, the process of deformation, i.e. the enforced change through a number of infinitesimally separated equilibrium positions at a given rate, requires force. The work per time spent in this irreversible process is quantitatively dissipated into heat.

One might infer in the elastic case an orderly transition from one ordered (solid) equilibrium state to another of higher energy, and the orderly return to the former. In flow we observe the transition of one disordered equilibrium state to the next, with the temporary order imposed on the system during flow becoming continually dissipated. In the simplest case, that of Newton's law, the stress is proportional to the rate of deformation: $P = \eta \dot{S}$, and the dissipated energy to the square of the rate of deformation, where η is the coefficient of viscosity in macroscopic flow (see Appendix).

These extremes, as stated, of ideally solid and ideally fluid viscous materials are oversimplifications. Real materials exhibit a whole spectrum of behavior from dependence of the forces on the speed of deformation only shown by liquids, to the practical independence on speed of deformation and dependence on the extent of deformation only, of the ideally elastic bodies. Any material may be caused to flow, i.e. become fluid, by varying

temperature and force field. Fluidity, thus, describes a temporary state of matter. Obviously, there is a practically infinite variety of indigenous and imposed responses, and also of composite structures, so that any enumeration or classification must remain arbitrary and inadequate.

In the following we will discuss nonetheless two classes of materials because of their practical importance. In the viscoelastic solids the elastic element forms the continuous, reversibly deformed, phase but encompasses frictional, viscous, elements; during deformation the movement of the latter permits them to consume energy and to retard the elastic extension; in the same manner energy is dissipated when the elastic phase returns in the process of strain recovery, i.e. strain relaxation, to its undeformed state and gives up its stored energy. Thus, internal friction is responsible for the energy difference, or hysteresis, between work returned and expended.

The elastico-viscous bodies are liquids containing dispersed elastic elements linked by friction. In motion these elements become extended and stay so, while the liquid flows, adding their extension to the fluid deformation. When the external forces cease, there will be partial strain relaxation as the elastic elements return to their original equilibrium state, releasing the stored energy which is partly recoverable and partly dissipated in overcoming the frictional resistance in the way of this return. If the specimen is held at constant deformation, the elastic elements glide past each other in viscous flow so as to return to their original length while conforming to the imposed over-all strain. This process constitutes stress relaxation.

Any stresses or strains which remain unrelaxed due to lack of time are called frozen in, or internal. Subsequent strains may become superimposed on the residual ones and thus give rise to the elastic memory; higher stresses may become necessary to deform prestrained materials, offering a partial explanation for such observations as annealing, case hardening, work hardening, and other mechanical property changes. Real bodies and real stresses, thus, are never quite homogeneous except for mobile liquids. In the glassy state of liquids diffusion and fluctuations are frozen to an extent that no flow can occur and large deformations lead to rupture.

In crystalline solids the primary forms of deformation are gliding, twinning, and kinking; diffusion again is so small as to allow indefinite preservation of cracks, dislocations, vacancies, or foreign elements at which stresses will concentrate. Where either the stress concentration is high enough, or the mass point coherence too weak, deformation will be carried to an extent from which return to the old equilibrium is no longer possible. Thus, a stress activated diffusion or flow on a micro scale has taken place which is often termed anelasticity. The mobilized sections may become readily anchored or may travel and unseat other dislocations, depending on struc-

tural details. Eventually, at the yield stress, a sufficient number of local place changes add up to macroscopic creep, or plastic flow.

In distinction, therefore, to the previous deformation mechanisms which affect the whole body, relatively small sections of mass points may give rise to a major, irreversible, deformation or, conversely, block it if they lie fixed in the path of flow. At stress levels sufficient to create very intense plastic flow, this distinction may become arbitrary as more and more of the body becomes affected. The essential criterion for plastic flow is that it is produced in an otherwise solid body by shearing stresses above a critical level, and that it ceases the moment the stresses fall again below this yield value. Further, as the magnitude and mobility of the flowing areas varies with the applied stress, the energy dissipated depends much more on the yield stress of the material than on the rate of deformation.

A special case is presented by the plastico-viscous (Bingham) bodies whose structure under a critical stress breaks down quickly and completely, so that these bodies change into liquids above a certain stress level and reset to new (deformed) solids on lowering the stress. Stresses will thus liquefy the surface first and the progress of breakdown or stress melting into the interior will depend on the stresses in the fluid areas.

In the plastic case, then, deformations are dictated by the nature and the distribution of the more readily deformed or more resistant regions; in the examples of combined viscous and elastic behavior, on the other hand, we were concerned rather with superposition of nonlocalized responses. The deformational behavior of many materials reflects a threefold combination, comprising the nature of the deformed elements, their distribution through the specimen, and the manner of superposition of the responses, quite apart from stress distributions on account of the geometry of the specimen or of its lack of homogeneity. It is this immense number of possible combinations which is responsible for the statistical behavior of samples even in simple test procedures.

Surveys of theoretical attempts to general, rational, analyses will be found in the chapters of this book. Another very general presentation which affords a simple quantitative formulation of much of the preceding qualitative picture will be briefly discussed in the Appendix.

An important aspect of superimposed elastic and viscous behavior is observed during oscillatory deformations. A simple case of imposed sinusoidal stresses or strains will be used in the Appendix to discuss the essential features. Equivalent descriptions can be given in terms of imposed periodical stress or strain.

Consider a material between two parallel plates which is sheared with sinusoidally decreasing speed from zero deformation to the return point of shear at zero speed. Reversing, the material returns at increasing speed

to zero deformation and then undergoes the symmetrical opposite half-cycle. Thus, the rate of deformation and the viscous processes are at a maximum at zero deformation, and zero at maximum deformation. Timewise, therefore, extent and rate are 90° out of phase, or in quadrature, though the directions of the tensors of shear and shear rate are the same, 45° to the plates, provided the deformations stay small (see Chapter II).

The forces during such cycling may be elastic due to the extent, or frictional due to the rate of deformation. Each of these force components will be in phase with its causative process and, therefore, 90° out of phase with each other in the cycle, while constituting the additive contributions to a resulting force which is parallel to rate and extent of deformation. In an ideally elastic material all stress is due to strain and is in phase with the deformation; in a viscous material the stress is in phase with the rate of deformation. In general, the sinusoidal course of the resultant stress magnitude will be displaced against the cycle of deformation by a phase angle, α , being more nearly in phase with the rate of deformation if the material is more viscous than elastic, and vice versa. As will be seen from the discussion in the Appendix, the reaction of materials to imposed stresses is governed by a characteristic parameter τ (or a set of these) with the dimension of time, the so-called relaxation or retardation time, which itself can be understood as the ratio of a viscosity to an elastic modulus.

The angle α must be a function of the frequency; the elastic component responds instantaneously and does not consume energy, but viscous flow or relaxation require time, dissipating energy proportional to the square of the rate of deformation. At frequencies very small compared with $1/\tau$, the viscous elements will operate but contribute little and the stress will be almost in phase with the deformation. Increasing the frequency, the dissipative effort will rise sharply and the stress will get increasingly out of phase with the deformation, but as the frequency approaches and exceeds the relaxation and retardation times, the viscous mechanisms become more and more incapable of following. As a result, we observe a maximum of dissipation, or a maximum loss. The course of α depends on details of the elastic and viscous properties, and especially on the flow unit which may be part of, or the whole, molecule, or a larger domain.

Related considerations serve to explain certain forms of shear dependence of the viscosity in steady flow. To show this, reference is made to the close relation between the principal shearing stresses on an area element and the principal (shear free) tensile and compressive forces on the same element which can be obtained by its rotation within the plane by 45° . These relations will be discussed in more detail in the next chapter.* In

* See also T. Alfrey, "Mechanical Behaviour of High Polymers", Interscience, N. Y. 1948, pp. 7.

the process of shearing an elastico-viscous element, the axes of the elastic tensile deformation and stress coincide with the direction of rate of deformation and the corresponding stress (45° to the direction of flow) only as long as the elastic deformation is kept very small. As soon as the strain is not immediately relaxed, and finite elastic strains are produced, the axis of tensile deformation rotates towards the direction of flow, while the rate of shear remains at 45° . The resultant of the components of stress therefore will lie at less than 45° to the streamlines, the angle becoming the smaller the larger the elastic contribution to the stress. Since the effective stress is the projection of an applied stress into the direction of the displacement, and since the rate of shear remains at 45° , any rotation of the axis of stress will reduce the amount of dissipation, permit more effective action by the applied stress and accelerate the over-all flow at a given stress level. In mechanistic terms, volume elements of the flowing material are being transported (as a function of the ratio of rate of strain/rotational diffusion, i.e. of relaxation) in a deformed or oriented state at reduced internal friction. This is akin to plastic flow, but different from both plastico-viscous flow and thixotropy in which cases viscous flow is enhanced by a structural breakdown and decreasing viscosity as a reversible function of the shearing stress.

The discussion up to this point followed largely the macroscopic or phenomenological approach. Necessarily, our advancing knowledge of atomic and molecular structures makes it imperative to interpret rheological constants in terms of molecular parameters.

The static as well as the kinematic properties of all materials are determined by the interplay of molecular (attractive-repulsive) potentials and kinetic energy. When at condensation the attractive forces plus pressure become able to reduce the mean free path to below molecular dimensions the rotational and linear vibrations in this liquid state remain large enough to permit in-phase augmentation of nearest neighbor amplitudes to create a hole which permits the slip of a molecule from one constellation to the next. The probability of this self-diffusion depends on an exponential ratio containing the activation energy for place exchange, E_a , over the temperature, and on a frequency factor Z which depends primarily on molecular weight and packing: $D_s \approx Z \exp(-E_a/RT)$.

When an external field is added, the accelerations superimpose themselves on the random thermal agitation and create a preponderance of movements in the direction of stress relief. These movements lead to increased numbers of collisions and to an exchange of momentum into directions other than that of the flow, until an equilibrium between the acquisition of velocity and deceleration by momentum dissipation is obtained. Liquid flow thus is governed by the rate of self-diffusion and the rate

of transfer of extra energy from one translational degree of freedom into all other degrees of freedom.

Finally, in the freezing process, the atomic or molecular distances shrink to an extent where the average kinetic energy no longer suffices for self-diffusion. The order imposed by the consequent molecular stacking permits no flow under small superimposed stresses. Rather, the molecules will increase their average distances. Whenever the molecules are pulled beyond the small degree of displacement from which they can return reversibly, stress-activated diffusion will give rise to a slow plastic deformation. Such diffusion will always be locally restricted to the inevitable inhomogeneities and increased stress will act on the more mobile, or already moving, areas. It follows that solids of other than metallic, ionic, or molecular structure in at least one crystal plane, e.g. solids possessing three-dimensional covalent links, cannot flow within the crystallites but only flow at boundaries, or rupture. Another case of "hardness" is presented by glasses for which the high viscosity at and below the freezing point prevents the ordering process of crystallization, even down to the temperatures (glass point) where volume shrinkage causes cessation of diffusion. Tight, three-dimensionally disordered, packing excludes flow so that here, too, the only response beyond elastic deformation is rupture. A third case of hardness is presented by polycrystallinity where intra-crystalline deformation is stopped at the crystal boundaries which themselves are prevented from moving due to structural irregularities. Thus disorder, normally connected with ease of flow, can also become a block to flow.

A special type of deformation is performed by chain molecules. In most low-molecular weight materials the intramolecular forces are so much greater than the intermolecular ones that relative movement of the molecules occurs long before appreciable molecular deformation. Chain molecules, however, as will be discussed in detail in Chapters XI to XV unless crystallized, possess the property of assuming a great number of coiled configurations of very different extension. The work required to uncoil them against internal friction to the more elongated configurations apt to relieve external stresses may be smaller than the work required to move the molecules as a whole relative to each other in flow. The very large deformations resulting from this unique, essentially rotatory, internal flow mechanism may be quite reversible as regards strain, if the chains are prevented from slipping by either cross-linking or by briefness of the extension cycle which does not allow for disentanglement of the rubber molecules.

Rubberiness depends also on the molecular weight and its distribution; a change in time scale, or chemically minor changes such as some slight cross-linking, may alter material characteristics from that of a liquid to that of a solid with respect to strain recovery, but not with respect to internal

friction; one further sees that elastico-viscous liquids should be represented by models of liquids made of springs rather than by models of liquids and springs in series. It is altogether one of the serious limitations of theoretical rheology and of qualitative discussions such as the present one that in order to be readily intelligible models have, as a rule, to be so simple as not to apply correctly, while generally applicable models have to be extremely complex.

Chain molecules of regular structure may be able to crystallize partially so that the solid becomes a composite of interlocked crystalline and amorphous areas. If the latter are above the glass temperature, they will endow the whole material with some extensibility or flexibility, while the crystals tend to increase the modulus and act as cross-linking agents. Elongation will enhance recrystallization of the amorphous areas, and also of soft crystals. A closely related composite structure can be introduced into rubbers by filling them with finely dispersed solids. The opposite effect, a softening to a more rubbery state, is observed in plasticization, i.e. the reduction of macromolecular friction by imbibed liquids, or in polymer blending when rubbery elements become the continuous phase.

It will be seen from this discussion, that simple behavior can only be expected for completely liquid materials as long as biased diffusion can perform the required transport, or for uniform solids provided they are not strained beyond the elastic limit. Even "ideal" liquids begin to behave "non-ideally" at rates so high that liquid diffusion cannot provide enough relaxation, and transport in domains must take over, or at stresses in solids so high that partial diffusion and limited flow are enforced. Materials of more complex structure will show complex behavior under less extreme, or almost all, experimental conditions. Thus, though there is only a limited number of basic deformational patterns, full flow, partial flow, rubberlike extension, and ideal elasticity, they can be invoked to any degree and in any combination either because of a propensity of the material, or because of conditions. It is, therefore, often impossible to judge structures from a limited range of mechanical responses, or vice versa. Only a study over a wide range of stresses, rates, and temperatures can give a sufficiently complete picture from which to predict mechanical behavior or to draw conclusions with respect to molecular structure.