

RHEOLOGY

Theory and Applications

VOLUME 1

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RHEOLOGY

Theory and Applications

Edited by
FREDERICK R. EIRICH
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VOLUME 1



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PREFACE

Rheology as the science of deformation and flow is today well recognized. Dissemination of knowledge of rheology and of its importance in a rapidly increasing number of fields has come about in large part through the years of activity of the American and British Societies of Rheology and of the more recently founded societies and committees in Brazil, France, Germany, Holland, Italy, and Japan. Valuable information in the varied fields of rheology has been made available through the Transactions of meetings of these groups and of the International Rheological Conferences of 1949 and 1953 as well as through recent monographs.

However, searching for information on specific rheological questions only too often turns out to be disappointing. As a rule, it is necessary to consult a large number of books and papers, to piece together evidence, and to adapt a number of assumptions to the case. Often unfamiliarity with rheological concepts and nomenclature presents an additional difficulty.

It is no exaggeration to state that there is no research or production laboratory in which rheological problems of one kind or another are not likely to present themselves at some time, and in many laboratories such problems arise all the time. Searches for information are, therefore, frequent.

In this book noted workers in rheology have pooled their knowledge and made it easily available in condensed form. The contributions although self-contained are interrelated. They are so planned that scientific workers are introduced to well-demarcated areas of rheology through introductory and descriptive material which then leads into integrated surveys of the present knowledge in these areas. The careful selection of topics, the authoritative and well-documented chapters, and the comprehensive index of this book all combine to further an awareness that the general concepts and laws of rheology form an entity. Furthermore, it offers the novice a very general introduction to many topics, and the advanced reader a ready means of comparing the different viewpoints of the contributing authors and of studying new material in fields related to rheology.

Thus it is hoped that this book will be instrumental in bringing about a better understanding of the essential unity of rheology. For although the applicability of many of the basic laws is generally accepted among rheologists, we are far from achieving the full benefits that can come from a more complete interchange of theories and applications among the various fields of rheology.

All of these factors were in the mind of the Editor when he asked his

colleagues to contribute to this volume and the two succeeding volumes that will comprise this work. Thanks are due to the contributors for their careful preparation of articles in this rapidly growing field. It is to be hoped that their efforts will benefit many and will serve to stimulate others to further activities in all branches of research.

In the present volume, the first of three, the reader will find two introductory chapters, one from the physicochemical and the other from the physics and engineering angle, followed by five chapters on various phases of the deformations of solids. The paper on flow under high pressures leads to those on the mechanism of liquid flow, large elastic deformations, viscoelasticity, and melt flow. Four chapters on the basis of the rheology of disperse systems and one on acoustic responses of liquids complete this part.

Volume II will open with an integrated survey which will serve to link the fifteen chapters, woven through the three volumes of the book, that deal with various fields and aspects of linear viscoelasticity. Volume II will continue with relaxation theory and three chapters on experimental techniques; then there follows the series of chapters on special types of materials or behavior such as the relaxation of polymers, the rheology of elastomers, glasses, cellulose derivatives, and fibers; it will include also chapters on concrete and on seismic measurements.

Volume III will contain more specialized chapters, on crystalline and on cross-linked plastics, polyelectrolytes, latexes, inks, pastes, and clay. This part will conclude with a series of technological articles on lubrication, spinning, molding, extrusion, and adhesion and a survey of the general features of industrial rheology.

When this work was planned, it was hoped that a uniform nomenclature might be achieved throughout. It was soon found that, especially in view of the diversity of the work, the time was not ripe for such an undertaking. To help the reader to compare derivations and data, a list of symbols has been appended to each chapter.

The variety, and often variance, of rheological terms employed today presented a major difficulty also in the way of preparing a consistent index commensurate with the purpose of this treatise. It is hoped that for those less acquainted with general rheology the grouping and bracketing of terms as well as the many cross references will help to clarify the synonymity or interrelation of concepts used today by different authors in different fields.

FREDERICK R. EIRICH

Brooklyn, N. Y.
Spring, 1956

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ERRATA

Page 15, last line—instead of “shortening”, read “cancelling”.

Page 47, equation (125)—first parenthesis, replace + by -.

Page 48, equation (127)—should read $M = H - N$.

Page 48, equation (130)—for γ read $\dot{\gamma}$ ($= d\gamma/dt$).

Page 49, equation (131)—for γ_0 read $\dot{\gamma}_0$

Page 400, equation (35)—line 3—second expression right-hand side, read

$$\frac{\bar{\delta}_0}{\bar{\delta}e_0} (\cos \varphi - i \sin \varphi)$$

Page 425, equation (128), lower line, signs within parentheses should be reversed.

Page 427, first line below equation (137) after “crosslinks” read “in number per milliliter”.

Page 554, equation (31) read

$$l^2 = l_0^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + \overline{\cos \phi}}{1 - \overline{\cos \phi}} \right)$$

Page 701, second paragraph line 14, omit “and G”.

Page 702, 3rd line from bottom, omit “will be compared with the theoretical dependence”.

Page 730, entrance “frictional”, read 115 instead of 114

Page 731, entrance “friction”, read “coefficient, 115” and “model, 44, 115, 116”.

Page 737, after “Lorentz field”, enter “Loss, see Impedance”.

Page 744, after “effect and molecular weight”, enter “effect on stress-strain relation, 303”.

In addition, on p. 645, 18th from the top, third line from bottom; p. 646, second & eighth line from bottom; p. 647, legend for fig. 21 & 22; p. 648, fourth line from bottom: The name Treolar should read Treoar.

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CHAPTER I

INTRODUCTION TO RHEOLOGICAL CONCEPTS

F. R. Eirich

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 elasto-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.

CHAPTER 2

PHENOMENOLOGICAL MACRORHEOLOGY

M. Reiner

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I. Introduction

1. SOME DEFINITIONS

Deformation is a movement of parts or particles of a material body relatively to one another such that the continuity of the body is not destroyed. If under the action of finite forces the deformation of the body increases with time continuously and indefinitely, the material is said to *flow*. *Plastic flow* appears only when the forces exceed a certain limit, indicated by the yield point of the material. *Viscous flow* occurs under the action of any forces, however small, albeit at a reduced rate of deformation, which vanishes with the forces. When the forces are removed, part of the deformation will always be recovered. This part is elastic and is called strain. (The reader must be warned that this definition is not in general use: he will find in many of the best books that strain denotes an irrecoverable deformation.) From this definition it follows that we cannot determine the strain from a loading diagram in which the total deformation is recorded but only upon unloading, when we see how much is recovered. The recovery from deformation is a manifestation of the property of elasticity; accordingly all strain is elastic. Ordinarily all strain vanishes when the load is removed. However, as a result of certain manufacturing processes (e.g., the rolling of mild steel or hardening of cheese¹) a body may become *self-strained* when internal stresses are present in the absence of external forces. In every case there is *no strain without stress*. In contradistinction, while nascent viscous and plastic deformations are accompanied by stresses, these deformations do not disappear with the removal of the load and accordingly there will be *stressless deformations*. The investigation of these different kinds of deformations in relation to the stresses by which they are accompanied is the subject of rheology. It should be noted that there are *stressless volume changes* resulting from variations of temperature or of moisture content of such materials as wood, concrete, and earth which, when not resisted, are not accompanied by stresses, even in the nascent state. While they do not form part of the subject-matter of rheology, they must be taken into account in rheological observations. *Phenomenological rheology*² deals with

¹ M. Reiner, G. W. Scott Blair, and G. Mocquot, *Lait* **29**, 351 (1949).

² Phenomenological rheology is treated in two textbooks by M. Reiner: "Twelve Lectures on Theoretical Rheology." North Holland Publ., Amsterdam, 1949; "Deformation and Flow." H. K. Lewis, London, 1949; cf. also M. Reiner, *Appl. Mechanics Revs.* **4**, 202-204 (1951).

homogeneous or quasi-homogeneous materials on a phenomenological level, i.e., considering them as continuous media. Both the aeolotropic crystal and the ultimate discrete entities, such as molecules and atoms, constituting the medium are outside its range. Gases are not included; as they possess no free boundary surfaces, they do not form bodies.³ Rheology is separated from thermodynamics by the provision that rheological processes take place under isothermal conditions (e.g., placing viscometers in thermostatic baths).

Macrorheology regards all materials as they may appear to the superficial inspection by the naked eye; i.e., homogeneous and devoid of structure. Only pure liquids and perfect single crystals are phenomenologically homogeneous. Most materials are dispersed systems consisting of two or more phases of which one will usually be air contained in pores which may be visible or invisible. For instance such an apparently homogeneous material as gold has its density raised from 19.258 to 19.367 "by compression between dies used in coining."⁴ Dispersed systems are included in phenomenological rheology if the dispersed elements down to molecules can be considered as small bodies differing from large masses only in scale. A material is quasi-homogeneous when the size of the largest dispersed element is smaller than the smallest volume elements, the deformation of which is under consideration; e.g., in the case of a material such as concrete, when the dimensions of the structural elements made of concrete are ordinarily much greater than the dimensions of the largest stones of which it is composed.

Materials are considered to be isotropic or quasi-isotropic when the smallest volume element contains anisotropic dispersed elements of all orientations. Such is the case of a commercial polycrystalline metal when the crystals making it up are orientated at random. A quasi-isotropic material can become anisotropic through deformation as, for instance, a metal sheet through rolling or metal rod through drawing. In the present chapter it is assumed that the materials under consideration are isotropic or quasi-isotropic. Anisotropic materials are treated in Chapters 6 and 15.

Microrheology takes account of quasi-homogeneity and quasi-isotropy, deriving the rheological behavior of the complex materials from the known rheological behavior or its constituents. The first and the most famous microrheological investigation was Einstein's derivation of the viscosity of a suspension,⁵ about which more is said in Chapter 14. Here the solid

³ However, an exploding "body" of gas may be treated by the methods of rheology: it would come under volume flow (compare Section IX).

⁴ Lord Kelvin (Sir W. Thomson), "Elasticity." Encyclopaedia Britannica. 9th ed., 1875; also *Papers (London)* 3 (1890).

⁵ A. Einstein, *Ann. Physik* 19, 289 (1906); 34, 591 (1911).

phase was assumed to consist of rigid spheres and the continuous phase of a simple viscous liquid. The actual composition of dispersed systems makes such a mathematical approach unworkable beyond the simplest cases. In this situation one substitutes for the unknown structure a mechanical model which is supposed to behave analogously to the real structure. Such models consist of different elements such as elastic springs, viscous dash-pots, and friction weights which will in general have no exact counterpart in the real material. More about this method is said in Section VI. Micro-rheology is not treated in the present chapter.

Where phenomenological rheology borders on other branches of physics, chemistry, or psycho-physiology, a belt of subjects is formed which may be comprised under the term *metarheology*. They are dealt in such chapters as 4 and 17. The last mentioned branch which is not represented in the present book is treated in the publications of Scott Blair and his school.⁶

2. MECHANICAL FOUNDATIONS

Mechanics is the physics of movements of material bodies as wholes in relation to the forces causing them. Inasmuch as every particle of a body can be considered as a body subjected in its movements to the laws of mechanics, rheology must be founded on mechanics. The following concepts and equations are used:

Let \mathbf{P} denote *force* and \mathbf{a} *acceleration*, both symbols indicating *vectors*, i.e., quantities which have not only magnitude but also direction. Furthermore let $\sum \mathbf{P}$ be the resultant of all external forces acting upon a body, m be its mass and \mathbf{a}_0 the acceleration of its centre of mass. (In contradistinction to \mathbf{P} and \mathbf{a} , the mass m is a scalar, i.e., a quantity which has magnitude only but no direction). Then for every body

$$\sum \mathbf{P} - m\mathbf{a}_0 = 0 \quad (1)$$

where $m\mathbf{a}_0$ is called the inertia or d'Alembert force.

In the case of equilibrium (when \mathbf{a}_0 vanishes) and written in Cartesian coordinates x, y, z , we have

$$\left. \begin{aligned} \sum P_x &= 0 \\ \sum M_z &= \sum (P_y x - P_x y) = 0 \end{aligned} \right\} (x, y, z) \quad (2)$$

with three pairs of equations, the other two to be derived by cyclical permutation of x, y , and z . This is indicated by (x, y, z) following the equation. M_z is the moment around the z -axis. The second of equations (2) can also

⁶ G. W. Scott Blair, "A Survey of General and Applied Rheology." Pitman, London, 1949.

be written in the form

$$\sum M = \sum (\mathbf{P}r) = 0 \quad (3)$$

where r is the normal distance of each single force \mathbf{P} from any one point in the xy -plane.

Let V be the volume of the body of mass m , dV the volume of a "particle" of the body and dm its mass, then

$$\rho = \frac{dm}{dV} \quad (4)$$

is a quantity characteristic of the material of which the body consists. It is called the *density* of the material and is a "material constant" or rather a coefficient or parameter. It is the only one to appear in mechanics.

II. Traction and Stress

1. CARTESIAN COORDINATES

If we consider a particle within the body, it may be regarded as bounded by imaginary surfaces of any shape. Through these surfaces the rest of the body acts upon the particle. Let us consider a plane element of the boundary surface of area ΔA . Its orientation in space is determined by the direction \mathbf{n} pointing from the particle outwards. Let \mathbf{P}_n be the force which the rest of the body exerts upon the particle through the surface element ΔA , then

$$\mathbf{p}_n = \lim_{\Delta A \rightarrow 0} \frac{\Delta \mathbf{P}_n}{\Delta A} \quad (5)$$

is called the *traction* at the point to which ΔA is reduced when tending to zero. Note that the traction is a vector.

The traction \mathbf{p}_n is generally inclined against the surface element upon which it acts and can be resolved into a *normal component* p_{nn} or σ and a *tangential component* p_{nt} or τ . If the arrow of p_{nn} points outward, a positive sign is applied and it is known as *tension*. In the opposite case the traction is named *pressure*. The traction \mathbf{p}_n can also be resolved into three components in accordance with the matrix

$$\mathbf{p}_n = \parallel p_{nx} \ p_{ny} \ p_{nz} \parallel \quad (6)$$

These components will have different values for different orientations \mathbf{n} .

The aggregate of all tractions corresponding to all orientations \mathbf{n} passing through a point is called the stress at that point. If the surface element is oriented normal to the x -axis, the components of the traction \mathbf{p}_x are p_{xx} ,

p_{xy} , and p_{xz} , of which the first is normal = σ_x and the other two tangential = τ_{xy} and τ_{xz} .

Let the particle have the shape of an elementary prism of edges dx , dy , and dz . The following tractions act upon its sides:

$$\begin{aligned} \mathbf{p}_x &= \left\| p_{xx} \quad p_{xy} \quad p_{xz} \right\| \\ \mathbf{p}_y &= \left\| p_{yx} \quad p_{yy} \quad p_{yz} \right\| \\ \mathbf{p}_z &= \left\| p_{zx} \quad p_{zy} \quad p_{zz} \right\| \end{aligned} \quad (7)$$

with p_{xx} differing on two parallel sides dx apart by $\frac{\partial p_{xx}}{\partial x} dx$. etc. The stress is defined by the three tractions \mathbf{p}_x , \mathbf{p}_y , and \mathbf{p}_z which are its components. Indicating the stress by $\left\| p \right\|$ we write

$$\left\| p \right\| = \left\| \begin{array}{c} \mathbf{p}_x \\ \mathbf{p}_y \\ \mathbf{p}_z \end{array} \right\| = \left\| \begin{array}{ccc} p_{xx} & p_{xy} & p_{xz} \\ p_{yx} & p_{yy} & p_{yz} \\ p_{zx} & p_{zy} & p_{zz} \end{array} \right\| = \left\| \begin{array}{ccc} \sigma_x & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_y & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_z \end{array} \right\|_{x, y, z} \quad (8)$$

for which we can also write p_{rs} with r and s being given in turn the meaning x , y , and z .⁷ Such a quantity having vectors as components and therefore being of higher rank than a vector is called a *tensor*. Applying the first of equations (2), the forces acting upon the particle through the boundary surface are the tractions multiplied by the areas. These are called *surface forces*. In addition there is gravity acting directly upon the mass. This is a *body force*. Van der Waals forces are internal body forces. The d'Alembert forces can also be regarded as body forces.

The tractions are continuous functions of the coordinates. Application of equation (1) accordingly gives for every particle of the body of unit volume

$$\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{yx}}{\partial y} + \frac{\partial p_{zx}}{\partial z} + \rho(B_x - a_x) = 0 \quad (x, y, z) \quad (9)$$

where B is the body force per unit mass. These are called the *stress equations*. Applying the second of equations (2) we find that the surface tractions give a torque

$$M_x = (p_{xy} dy dz) dx - (p_{yz} dz dx) dy \quad (x, y, z) \quad (10)$$

neglecting higher terms, while the body forces which pass through the center of the prism do not give rise to a moment. Assuming that the ma-

⁷ The p_{rs} notation is used in the classical mechanics of continua, the σ and τ notation in engineering literature.

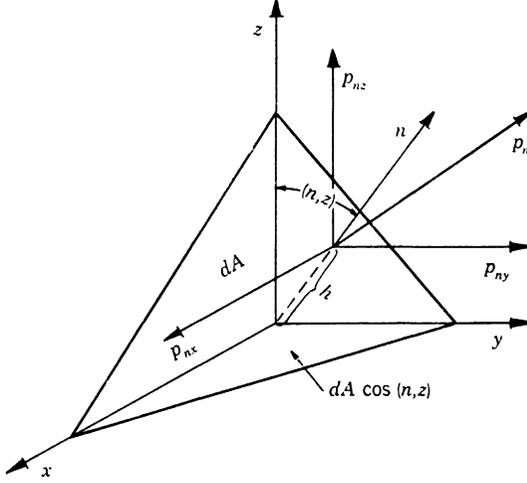


FIG. 1. Traction on an arbitrarily directed surface element. \mathbf{n} , direction of the outer normal to the surface element dA .

terial is not magnetic, this moment must vanish and therefore

$$p_{yz} = p_{zy} \quad (x, y, z) \quad (11)$$

Using running notation p_{rs} , we can write for (9)

$$\sum_r \frac{\partial p_{rs}}{\partial x_r} + \rho(B_s - a_s) = 0 \quad (12)$$

where x_r is, in turn, x , y , and z ; and for (11)

$$p_{rs} = p_{sr} \quad (13)$$

A tensor for which the indices may be exchanged in this way is called *symmetrical* and the stress is therefore a symmetrical tensor. Applying the first of equations (2) upon a particle in the shape of a pyramid with basis dA and sides $dA \cos(nx)$, $dA \cos(ny)$, and $dA \cos(nz)$ (as shown in Fig. 1) we find

$$\begin{aligned} p_{nx} dA &= p_{xx} dA \cos(nx) + p_{yz} dA \cos(ny) + p_{zz} dA \cos(nz) \\ &\quad + \frac{\rho h dA}{3} a_x \quad (x, y, z) \end{aligned} \quad (14)$$

Shortening by dA and making $h \rightarrow 0$ we find, using running index notation,

$$p_{ns} = \sum_r p_{rs} \cos(nx_r) \quad (15)$$

2. MOHR'S STRESS CIRCLE

There are three directions in space, i, j , and k , normal to each other, for which the τ 's vanish and the σ 's have extreme or principal values σ_i, σ_j , and σ_k , so that

$$p_{rs} = \begin{vmatrix} \sigma_i & 0 & 0 \\ 0 & \sigma_j & 0 \\ 0 & 0 & \sigma_k \end{vmatrix}_{i,j,k} \quad (16)$$

Consider the two-dimensional case referred to axes i and j . In this case from (15)

$$\left. \begin{aligned} \sigma_n &= \sigma_i \cos^2(ni) + \sigma_j \cos^2(nj) \\ \tau_n &= \sigma_i \cos(ni) \cos(ti) + \sigma_j \cos(nj) \cos(tj) \end{aligned} \right\} \quad (17)$$

or after some rearrangement,

$$\left. \begin{aligned} \sigma_n &= \frac{(\sigma_i + \sigma_j)}{2} + \frac{(\sigma_i - \sigma_j)}{2} \cos 2(ni) \\ \tau_n &= -\frac{(\sigma_i - \sigma_j)}{2} \sin 2(ni) \end{aligned} \right\} \quad (18)$$

From (18) we see that if we plot τ_n versus σ_n , the locus of the points is a circle with a radius $(\sigma_i - \sigma_j)/2$ which has its centre on the abscissa axis at the distance $(\sigma_i + \sigma_j)/2$. This is called *Mohr's circle* (Fig. 2). The figure shows how the components p_{xx} and p_{yy} are found for some direction x , if the σ_i, σ_j , and the angle (ix) are given. The component p_{yy} follows from the invariant

$$p_{xx} + p_{yy} = p_i + p_j \quad (19)$$

By applying Mohr's circle one finds for the case of *simple shearing stress*

$$p_{rs} = \begin{vmatrix} 0 & \tau & 0 \\ \tau & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix}_{x,y,z} = \begin{vmatrix} \tau & 0 & 0 \\ 0 & -\tau & 0 \\ 0 & 0 & 0 \end{vmatrix}_{i,j,z} \quad (20)$$

with $(xi) = 45$ deg.

Simple tension can be resolved as follows:

$$p_{rs} = \begin{vmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} = \frac{\sigma}{3} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} + \frac{2\sigma}{3} \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{vmatrix} \quad (21)$$

The Mohr circle for the first component on the right side is reduced to a

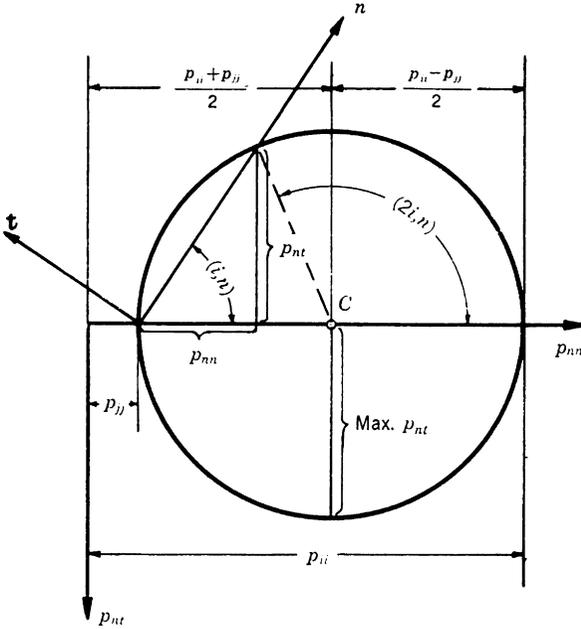


FIG. 2. Plane Mohr circle for stresses. p_{ii} , p_{jj} , principal stresses; p_{nn} , p_{nt} , normal and tangential components of traction \mathbf{p}_n acting upon a surface element the "outer" normal of which is \mathbf{n} .

To construct Mohr's stress circle if the principal stresses $\sigma_i > \sigma_j$ are given, draw the p_{nn} -axis parallel to the i -direction and the p_{nt} -axis in the direction opposite to j . Plot σ_i and σ_j on the p_{nn} -axis and find point C , the centre of the circle from $(\sigma_i + \sigma_j)/2$. Draw circle with radius $(\sigma_i - \sigma_j)/2$. To find the tractions p_{nn} and p_{nt} on any surface element the normal of which is in the direction of \mathbf{n} , draw parallel to \mathbf{n} through leftmost point of circle; the intersection of this line with the circle has the coordinates p_{nn} and p_{nt} . If \mathbf{n} is parallel to x , the coordinates are σ_x and τ_{xy} . For infinitesimal deformations or strains use the same method with d_i (or e_j) for σ_i and d_{xy} (or e_{xy}) = $\gamma_{xy}/2$ for τ_{xy} .

point and the normal component of the stress tensor is therefore the same in all directions, while all tangential components vanish. Such a tensor is called *isotropic*. Hydrostatic pressure is an example. The second component, where the mean of the diagonal components

$$p_m = \frac{p_{xx} + p_{yy} + p_{zz}}{3} \tag{22}$$

vanishes is that by which the tensor "deviates" from isotropy. It is accordingly called the *deviator* of the tensor. We shall indicate the deviator of a tensor by the index (o) , e.g., $p_{rs(o)}$ is the deviator of p_{rs} .

3. CYLINDRICAL COORDINATES

In rheology, problems which can best be solved in cylindrical coordinates are prominent.

The cylindrical coordinates of a point are

$$x_r = \|r \theta z\| \quad (23)$$

In most cases there will be axial symmetry or vanishing $\partial/\partial\theta$. Then assuming that z points vertically upward, the three stress equations (12) become

$$\begin{aligned} \frac{\partial p_{rr}}{\partial r} + \frac{\partial p_{zr}}{\partial z} + \frac{p_{rr} - p_{\theta\theta}}{r} - \rho a_r &= 0 \\ \frac{\partial p_{r\theta}}{\partial r} + \frac{\partial p_{z\theta}}{\partial z} + \frac{2p_{r\theta}}{r} - \rho a_\theta &= 0 \\ \frac{\partial p_{rz}}{\partial r} + \frac{\partial p_{zz}}{\partial z} + \frac{p_{rz}}{r} - \rho(a_z - g) &= 0 \end{aligned} \quad (24)$$

where g is the acceleration of gravity.

III. Deformation

1. INFINITESIMAL DEFORMATION

The kinematic state of a body is determined by the position x_r (where x_r stands for x, y, z), and the *velocity* v_r

$$v_r = \frac{dx_r}{dt} = \dot{x}_r \quad (25)$$

of all its particles at all times. The continuity mentioned in Section I-1 requires that the velocities are continuous functions of the coordinates. They can be expressed through the *displacements* u_r by means of

$$v_r = \lim_{\Delta t \rightarrow 0} \frac{u_r}{\Delta t} \quad (26)$$

The displacements must also be continuous functions of the coordinates and therefore, proceeding in the spatial direction \mathbf{s} ,

$$\frac{du_x}{ds} = \frac{\partial u_x}{\partial x} \cos(ds x) + \frac{\partial u_x}{\partial y} \cos(ds y) + \frac{\partial u_x}{\partial z} \cos(ds z) \quad (x, y, z) \quad (27)$$

Accordingly du_x/ds can be considered as a vector.

$$\left(\frac{d\mathbf{u}_x}{ds} \right) = \left\| \frac{\partial u_x}{\partial x} \quad \frac{\partial u_x}{\partial y} \quad \frac{\partial u_x}{\partial z} \right\| \quad (x, y, z) \quad (28)$$

We thereby arrive at the tensor of the *displacement gradient*.

$$\gamma_{rs} = \left\| \begin{array}{ccc} \frac{\partial u_x}{\partial x} & \frac{\partial u_x}{\partial y} & \frac{\partial u_x}{\partial z} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} & \frac{\partial u_y}{\partial z} \\ \frac{\partial u_z}{\partial x} & \frac{\partial u_z}{\partial y} & \frac{\partial u_z}{\partial z} \end{array} \right\|_{x,y,z} \quad (29)$$

This tensor is in general *not* symmetrical. For instance, in simple shear

$$u_x = \gamma \quad (30)$$

shown in Fig. 3, we have

$$\gamma_{rs} = \left\| \begin{array}{ccc} 0 & \gamma & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{array} \right\| \quad (31)$$

If $\partial u_x/\partial y$ is infinitesimal, γ is the reduction of the angle between x and y , initially a right angle.

The tensor γ_{rs} can be resolved into a symmetrical and an antisymmetrical tensor as follows:

$$\begin{aligned} \gamma_{rs} = & \left\| \begin{array}{ccc} \frac{\partial u_x}{\partial x} & \frac{1}{2} \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial u_y}{\partial x} + \frac{\partial u_x}{\partial y} \right) & \frac{\partial u_y}{\partial y} & \frac{1}{2} \left(\frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z} \right) & \frac{1}{2} \left(\frac{\partial u_z}{\partial y} + \frac{\partial u_y}{\partial z} \right) & \frac{\partial u_z}{\partial z} \end{array} \right\| \\ & + \left\| \begin{array}{ccc} 0 & \frac{1}{2} \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial u_x}{\partial z} - \frac{\partial u_z}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial u_y}{\partial x} - \frac{\partial u_x}{\partial y} \right) & 0 & \frac{1}{2} \left(\frac{\partial u_y}{\partial z} - \frac{\partial u_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z} \right) & \frac{1}{2} \left(\frac{\partial u_z}{\partial y} - \frac{\partial u_y}{\partial z} \right) & 0 \end{array} \right\| \end{aligned} \quad (32)$$

As can be seen from Fig. 4 the expression $(\partial u_x/\partial y - \partial u_y/\partial x)/2 = (\gamma_{xy} - \gamma_{yx})/2$ describes a rotation of an element *without deformation*, provided the γ 's are infinitesimal. Such a "rigid" rotation of a particle belongs to mechanics proper and is of no interest in rheology. Therefore, always

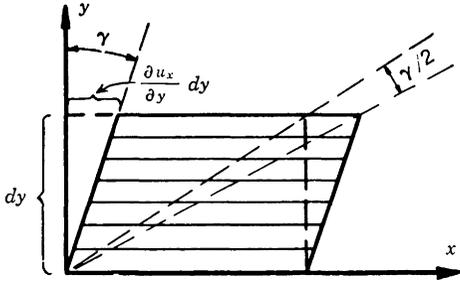


FIG. 3. Simple shear. u_x , displacement in direction x ; γ , displacement gradient; $\gamma/2$, angle of rotation.

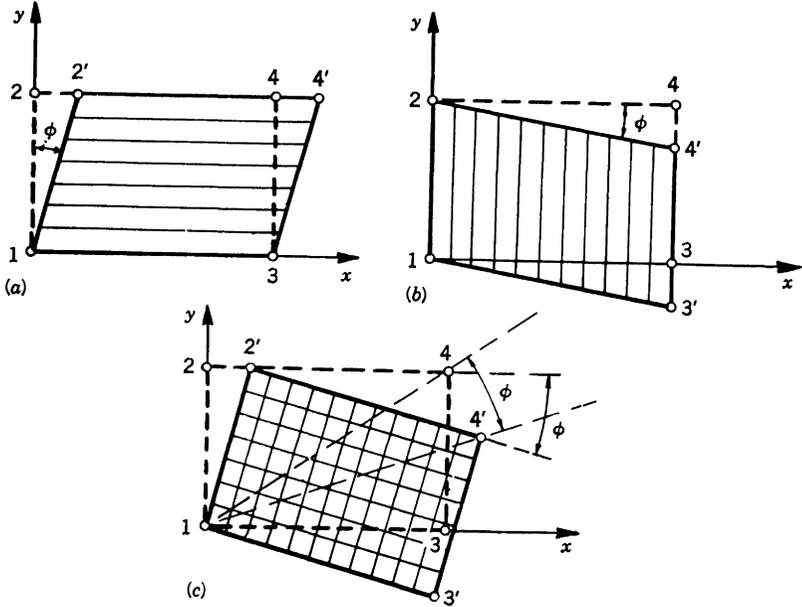


FIG. 4. Superposition of two simple shears resulting in a rotation. ϕ , angle of rotation. Note that γ_{yx} is positive = $+\phi$ and γ_{xy} negative = $-\phi$.

provided that the displacement gradient is infinitesimal, the deformation, which itself is infinitesimal, is defined by the first tensor on the right-hand side of (32) or the symmetrical tensor

$$d_{rs} = \frac{\partial u_r / \partial x_s + \partial u_s / \partial x_r}{2} \tag{33}$$

If we consider in a similar manner the velocity vector v_r , we arrive at the flow tensor

$$f_{rs} = \frac{\partial v_r / \partial x_s + \partial v_s / \partial x_r}{2} \tag{34}$$

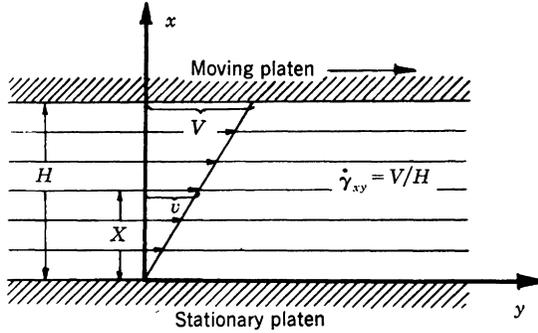


FIG. 5. Velocity gradient between two parallel platen. V , velocity of moving platen.

In simple laminar shear the tangential components of these two tensors are one-half of the displacement gradient $\gamma_{yx} = U/H$ in the first case and one-half of the velocity gradient $\dot{\gamma}_{yx} = V/H$ in the second case (compare Fig. 5). If there are displacements in both the x and y directions, the tangential component is the mean gradient. For instance,

$$d_{xy} = \frac{\gamma_{xy} + \gamma_{yx}}{2} \tag{35}$$

The meaning of the *normal components* can be visualized by considering a prism of length l_0 moving axially in extension. Let u_i be the displacement of one end and u_o the displacement of the other end and $u_i > u_o$, then $(u_i - u_o)/l_0$ is the longitudinal displacement gradient; and if we choose the element dx as the length l_0 , we see from (33) that the *extension*

$$d_{xx} = \frac{\Delta(dx)}{dx} = \frac{\partial u}{\partial x} \tag{36}$$

This measure of deformation was formulated by Cauchy; it is the *elongation per unit original length* in the appropriate direction.

On the other hand, if $u_o = 0$ i.e. the prism is fixed at one end, while the other end travels with the velocity v , the normal component of f_{xs} or the longitudinal flow f_l is from (34)

$$f_l = \frac{v}{l} \tag{37}$$

But

$$v = \frac{dl}{dt} = l \tag{38}$$

and therefore

$$f_l = \frac{\dot{l}}{l} \quad (39)$$

2. FINITE DEFORMATION

When the flow extends through some time $\Delta t = t - t_0$, this results in a longitudinal deformation D_l^H

$$D_l^H = \int_{t_0}^t f_l dt = \int_{l_0}^l \frac{dl}{l} = \ln \frac{l}{l_0} \quad (40)$$

This is called the "natural" or logarithmic measure of deformation or the Hencky measure. There exist other measures of finite deformation about which more will be said in Section V.

We can define the tensor of deformation D_{rs} by its principal values D_i , D_j , and D_k :

$$D_{rs} = \left\| \begin{array}{ccc} D_i & 0 & 0 \\ 0 & D_j & 0 \\ 0 & 0 & D_k \end{array} \right\|_{i,j,k} \quad (41)$$

From (40) and (36) we see that

$$d(D_l^H) = \frac{dl}{l} = d_l \quad (42)$$

It should be noted that this relation cannot be generalized to make d_r^s equal to the differential of D_{rs}^H because relation (42) is only valid in respect of the principal components. On the other hand, the rate of infinitesimal deformation is equal to the flow, or

$$\dot{d}_{rs} = f_{rs} \quad (43)$$

3. POISSON'S RATIO

While the prism of Section 2 is elongated, its width generally decreases. The transversal contraction is a fraction of the longitudinal extension, the ratio being called *Poisson's ratio* ν . One has to distinguish different Poisson ratios, one (the usual) referring to elastic strain, the others to (plastic) deformation and (viscous) flow, etc. The reciprocal of Poisson's ratio is called Poisson number.

4. CUBICAL DILATATION AND DISTORTION

The deformation of a prismatic volume element will in general change the length of its edges and the right angles between its sides. If the deformation is infinitesimal the increase of volume per unit volume, or the