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RHEOLOGY OF CONTINUOUS MEDIA

Methodical recommendations
for practical training and self-study

Kharkiv – 2023

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The methodological recommendations for the practical studies and individual tasks on the course "Fundamentals of Rheology" are collected. Detailed data on modern rheology, its history, technical equipment for experimental studies of the rheological properties of natural and artificial materials, as well as discrete and continuous models of viscoelastic materials, and the rheology of non-Newtonian fluids are given. The issue is prepared for the students who are interested in mathematical modeling of applied problems in mechanics of materials.

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РЕОЛОГІЯ СУЦІЛЬНИХ СЕРЕДОВИЩ

Методичні рекомендації
до практичних занять та самостійної роботи

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1. INTRODUCTION

Rheology (from Greek *rheos* – flow, *logos* – law) is a field of natural sciences in which flows of gaseous, liquid, and solid deformable media are studied, as well as their rheological properties – elasticity, viscosity, rigidity, strength, including a change in these properties under various physical influences (thermal, electro–magnetic, radiation, etc.) [1].

Rheology is based on the use of experimental and theoretical mechanics and physics. The objects of rheological researches are gases, liquids, solid deformable materials, their mixtures, multicomponent and multiphase media – suspensions, emulsions, aerosols, carbonated liquids, foams, granular media, powders, films, materials with memory and nonlocal properties, including micro– and nano–structured materials, polymer solutions and melts, and many others.

For experimental measurements of elastic and plastic properties, **tensile testing machines, extensometers, universal testing machines** are used to test the tensile strength and compressive strength of materials. **Rheometers** (or **viscometers**) are used for the viscosity measurements. Due to the strong temperature dependence of the viscous and elastic properties of the materials, all measurements are carried out with strict control of the temperature and possible drying due to interaction with air.

Rheology studies the processes associated with the flow of viscous fluids; reversible and irreversible deformations of bodies under external loads; relaxation of stresses and strains after unloading; slow deformations of solids under a fixed load (creep); plastic flows of materials; returning to the initial state of materials with "memory" and similar processes.

Theoretical rheology are built on the basis of experimental data and the corresponding mathematical models that describe the relationships between stresses σ and strains ε , as well as their time derivatives $\dot{\sigma}, \dot{\varepsilon}, \ddot{\sigma}, \ddot{\varepsilon}, \dots$. Such dependencies are called **rheological relations, rheological laws, or constitutive equations** for a given material (medium). Both discrete models of mechanics and continuum models of mechanics of continuous media are used.

For correct determination of valid rheological relations for complex media, one can use the micro–rheological (rheophysical) approach, in accordance with which the features of the interaction of individual molecules, molecular and supramolecular structures, fibers, grains and other components of the medium are considered, and the properties of the material at the meso– and macrolevels are determined by averaging over the individual components and phases of the material.

The macro–rheological or phenomenological approach to modeling of the rheological behavior of a material is based on the analysis of experimental static and dynamical dependencies $\sigma(\sigma), \sigma(\dot{\varepsilon}), f(\dots \dot{\sigma}, \sigma, \dot{\varepsilon}, \dots)$, relaxation $\dot{\varepsilon}(t)$, $\dot{\sigma}(t)$ curves, and other dependencies.

Rheological methods are widely used:

1) in **geophysics** – the study of the rheological properties of oil, gas, groundwater, river and waste waters, sediments, wetland liquids, volcanic masses, magma, etc.;

in the modeling of fluid flows in open channels and pipes, sediment transport, computer simulations of flows of liquids and gases in the development of deposits and other practical tasks;

2) in the **building materials industry** – the study of the rheological properties of concrete, paints, varnishes and other building and decorating materials; the use of knowledge of rheological properties for processing of natural wood and stone materials, metals and glass; the creation of polymer details; heat and waterproofing materials; high-quality artificial materials based on hydration inorganic and coagulation organic binders;

3) in the **food industry** – the rheology of various masses and mixtures – milk, chocolate, sausage, etc., which undergo various stages of heat and chemical processing during the manufacturing process, phase transitions, mix and move from containers through pipes, pass through stages of stamping, spraying, dissolving, drying, etc. Strict viscosity control at each technological stage is necessary to obtain a quality product;

4) in **light industry** – the study of the rheological properties of technological materials – solutions of polymers, fibers, threads, reinforcing components for the control and optimization of technological processes both in the primary processing of raw materials and in the manufacture of products in textile, chemical; the use of materials in furniture, pulp and paper, automotive, aviation, electrical and other industries;

5) in **biology** – the rheological properties of cells and cellular suspensions, populations of microorganisms in water bodies, biological gels and sols; solving the problems of moving and transportation of cells and cellular suspensions; optimizing the work of microbiological reactors, monitoring and optimizing various biotechnological processes and plants (biofuels, etc.);

6) in **medicine** – the study of the rheological properties of biological fluids (blood suspension and blood plasma, cerebrospinal and lacrimal fluid, synovia (lubricating fluid in the joints), bronchial mucus, pulmonary surfactant, bile, milk, etc.), soft (skin, muscles, ligaments, cartilage, brain, walls of vessels, airways, respiratory tract and hollow inner organs, etc.) and solid (bone, tooth, wood) biological tissues, their synthetic analogues and substitutes, implants, prostheses, etc. in connection with the use of their rheological parameters in medical diagnostics, to simulate blood flow in the blood vessels or tubes of medical devices, air flows in the respiratory system, deformation of internal organs and tissues in the natural-governmental loading conditions, as well as bumps, hypo- or hypergravitation, thermal and electromagnetic effects, etc.;

7) in smelting, rolling and stamping of metals, sintering of powders (powder metallurgy), processing, enrichment and transportation of ore, manufacture of glass and paper, processing of polymeric materials, transportation and processing of grain as a granular medium, knowledge of their rheological properties is necessary for organization and optimization of relevant technological processes.

2. HISTORY OF RHEOLOGY

The term “**rheology**” was coined in the 1920–s by Eugene Bingham (1878–1945) and Marcus Reiner (1886–1976), who made a significant contribution to theoretical and experimental rheology [2,3] and founded the first rheological scientific society (The (American) Society of Rheology, founded on December 9, 1929). At the congress dedicated to the organization of the Society, a formal definition of rheology was given as a science that studies the deformations and flows of materials. In 1916, Bingham's work¹ devoted to the study of plastic flows of non-Newtonian fluids was published, and in 1922, his fundamental work² on viscous and plastic flows was issued; the liquids he described in these studies are now called Bingham fluids. He introduced one of the first similarity criteria in rheology – the Deborah number³ $De = t_{rel} / T$, where t_{rel} is the relaxation time of material deformations and T is the observation time.

The study of the deformation properties of materials has a long history, and individual elements of rheology have been known since ancient times. It is no coincidence that the famous phrase of Heraclitus “*panta rhei*” (i.e. “everything flows”) was chosen as the motto of the Society of Rheology. The properties of various natural materials and liquids used in industry, construction, military, shipbuilding, etc., had to be determined, and they were given neither strict formulations nor quantitative characteristics. The elastic properties of solids were first discussed after the discovery of the law of elasticity. In 1660, Robert Hook formulated this law in the form of an anagram CEIINOSSTTUV – the letters of the Latin phrase “*ut tensio, sic vis*” (the strength is like the elongation) in alphabetical order. In 1678 Hook published a decoding in the form of a linear relationship between the applied force and sample elongation. The proportionality coefficient in this dependence was later called the Young's modulus in honor of the famous British scientist Thomas Young, who formulated the law in a modern stress–strain form and first described elasticity as a property of the material. In modern notation, **Hooke's law** is written as $\sigma = E\varepsilon$, where σ is tensile stress, ε is deformation, E is Young's modulus. The term “modulus” came from the Latin word “*modus*”, which translates as “measure”. This coefficient was first described back in 1727 in the works by L. Euler, and the first experiments in which the modulus of elasticity was measured were carried out by the Italian scientist G. Riccati in 1782, who was 25 years ahead of similar works by T. Jung. Then the theory of elasticity was developed in the works of French mathematicians and mechanics Simeon Denis Poisson (1781–1840) and Augustin Louis Cauchy (1789–1857). The first is the relative coefficient of transverse compression of the material under tension (Poisson's ratio), and the second is the stress tensor. In 1875, the fundamental work of the British mechanic William

¹ Bingham E. C. An Investigation of the Laws of Plastic Flow. US Bureau of Standards Bulletin. 1916. Vol. 13. P. 309–353.

² Bingham E. C. Fluidity and Plasticity. New York: McGraw–Hill, 1922. 219p.

³ Reiner M. The Deborah number. Physics Today. 1964. Vol. 17. P. 62–65.

Thomson (Lord Kelvin) on the elasticity of materials was published. The creator of electromagnetic theory, the prominent Scottish scientist James Clerk Maxwell (1831–1879) published an article “On the equilibrium of elastic bodies” in 1849, and in 1868 he published theoretical works on viscoelastic materials with relaxation (Maxwell model⁴ of a viscoelastic fluid), in which he introduced the concept of **stress relaxation**.

The general rheological law for liquids was first formulated in 1687 by Isaac Newton⁵ (1642–1727) on the basis of his experiments on measuring the resistance of a plate moving along the surface of a layer of viscous liquid. Newton’s viscous friction law $\tau = \mu \dot{\gamma}$ is similar to Hooke’s law, but claims a linear relationship between forces (shear stresses τ) and shear strain rates $\dot{\gamma}$. Newton called the ratio μ of the friction force per unit area of the plate to the shear rate the lack of slipperiness. Subsequently, this coefficient was called the **dynamic viscosity coefficient** (from the Latin word “*viscum*”, which means “bird glue” – a very viscous substance that was obtained from mistletoe fruits and has long been used for catching birds by gluing their feet. This interesting liquid does not form drops, it forms a film of the uniform thickness when applied at some surface, does not drip from an inclined surface, does not freeze in the cold, does not dry out in the wind and does not thin out in the sun. The inverse of viscosity (μ^{-1}) is called **fluidity**.

Newton’s law was confirmed in the experiments by Hagen and Poiseuille with pipe flows of liquids. The French doctor Jean Léonard Marie Poiseuille (1797–1869) was interested in blood circulation regularities, in connection with which he conducted experiments on the flows of blood, water and other fluids through thin glass tubes and segments of blood vessels. In the result he obtained a relationship between the volumetric flow rate Q , pressure drop δP at the ends of the tube, its length L and diameter d in the form $Q \sim \delta P d^4 / L$. Poiseuille established this law in 1838, but he published the article in 1846, after verification of this law in hundreds of experiments with various liquids. Similar experiments on the flow of water through metal tubes were carried out by the German engineer Gotthilf Heinrich Ludwig Hagen (1797–1884), but with a slight error in writing the law. Hagen believed that the velocity profile has a triangular shape. The fluid flow law $Q = \delta P \pi d^4 / (128 \mu L)$ is called the **Hagen–Poiseuille law**, the regime of laminar fluid flow through cylindrical tubes under the action of a longitudinal pressure drop is called the **Poiseuille flow**, and the unit of viscosity is called Poise or P ($[\mu] = g / (cm \cdot s) = 1 P$).

Later, the French mechanic **Maurice Couette**, a student of J. Boussinesq, conducted a study of fluid viscosity in a device he had created, based on a laminar circular flow of fluid enclosed between two rotating pine cylinders. The device

⁴ Maxwell J. C. Phil. Trans. Roy. Soc. 1867. Vol. 157. P. 49–88.

⁵ Newton I. Philosophiæ Naturalis Principia Mathematica (Mathematical Principles of Natural Philosophy). London, 1687.

showed high accuracy and the absence of side effects, such as the effect of the Fareus–Lindquist in the tubes, on the measurement results. The regime of the laminar fluid flow between moving parallel surfaces, plane or curved, is called the **Couette flow**. In addition, as a result of a series of detailed experiments, M. Couette confirmed that for viscous fluids the adhesion condition is satisfied as a boundary condition on the surface, i.e. the velocity of the boundary layer of fluid is equal to the velocity of the surface that is treated as **no-slip** effect.

The results of the experiments of Poiseuille and Couette formed the basis for the operation of devices for measuring the viscosity of liquids – viscometers, capillary (Fig. 1a) and rotational (Fig. 1b), respectively. An own viscometer (1752) was used by Russian scientist M. V. Lomonosov (1711–1765) in his study of fluid fluidity. In fact, it was a drip viscometer based on estimating the viscosity of a liquid by counting the number of droplets flowing out of the reservoir for a given period of time. The same principle was used in the Engler viscometer, which consisted of an internal reservoir filled with the test fluid and an external thermostat filled with fluid at a fixed temperature. After the thermostat stage, a valve was opened in the internal reservoir hole and the time of the complete dripping out of the test liquid from the inner reservoir at a given temperature was measured. Engler viscometers are used to determine the viscosity of highly viscous liquids, such as petroleum products. In the oil drilling apparatus, for the rapid estimation of viscosity, standard field viscometers are used. They are equipped by a reservoir with 500 cm³ of the fluid, and the time of the flowing out an amount of 500 cm³ through a conic tip of the tube is estimated as a conventional fluid viscosity.

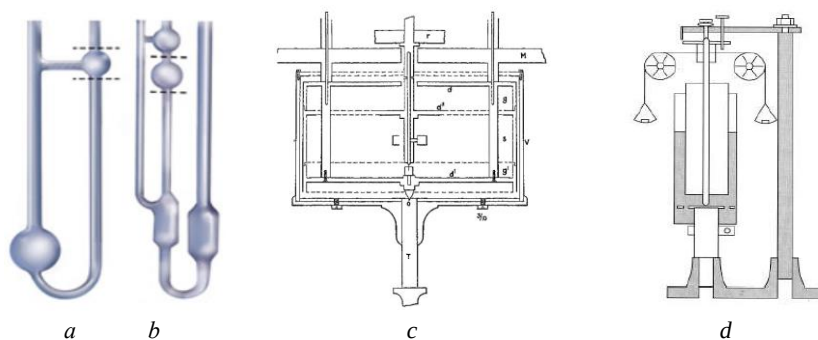


Fig. 1. Capillary viscometers invented by Ostwald (a), Ubbelohde (b), and rotational viscometers by Couette (c) and Searle (d)

German chemist Leo Ubbelohde (1877–1964) proposed a **capillary viscometer** in the form of a U-shaped glass tube in which a known volume of the test fluid flowed from one elbow to another through a straight capillary, and the time of this flow was measured. The Ubbelohde viscometer was improved by the German chemist Wilhelm Ostwald (1853–1932); and in this form it was used until the middle of the 20th century. In this design, both elbows of the tube were equipped with reservoirs,

in one of which the studied liquid was collected, and in the other accumulated after flowing through the capillary (Fig. 1a). The founder of modern rheology, Bingham in 1921 was awarded a diploma from the Franklin Institute (Pennsylvania, USA) for the variable pressure viscometer he developed. To date, capillary and rotational viscometers are the most used both in industry and in scientific laboratories.

In 1880, Russian chemist Dmitri Mendeleev, and in 1883, English hydromechanic Osborne Reynolds showed that the linear dependence of the resistance force on the speed of motion can be measured at low speeds, while at faster flows it is proportional to the square of the speed. Reynolds also dealt with issues of dynamic similarity of fluid flows, and he established a criterion (Reynolds number) for different flow regimes (steady and unsteady, laminar and turbulent). He introduced the term "dilatancy", and in 1886 he derived a differential equation describing the pressure distribution in a viscous fluid filling the gap between the shaft and bearing surfaces, which made a significant contribution to the hydrodynamic theory of lubrication. In 1883, Russian mechanician Nikolai Petrov (1836–1920) published his first work "Friction in Machines and the Effect of Lubricating Oil on It" in the Engineering Journal, and in 1885 he proposed his own design for the viscometer. In 1900 he published his fundamental work "Friction in Machines", in which the **lubrication theory** was presented taking into account the eccentric position of the axis in the bearing. The study of the viscosity and plasticity of lubricants at various temperatures is an important section of modern rheology.

Later development of the viscometry techniques was associated with an increase in the accuracy of flow setting and stress measurements in the devices. For instance, in the Weissenberg rheogoniometer (1960s), the range of shear rates was $\dot{\gamma} = 10^{-4} - 10^4 \text{ s}^{-1}$. In modern viscometers, the measurement of translational and rotational speeds is carried out by electronic optical systems with high accuracy $\sim 10^{-8} \text{ rad/s}$.

In 1932, Fritz Höppler patented a **falling ball viscometer** based on the Stokes formula of the resistance force acting on the sphere moving in a viscous fluid. The English mathematician and mechanic George Stokes (1819–1903) received it in 1851. Later, Auguste Norcross improved this type of viscometer by adding a device that allows the falling part to be automatically raised and cleaned of liquid, which was made in the form of a cylinder converging to a cone or a series of cylinders instead of spheres. The Norcross design allowed the viscosity of thixotropic fluids to be measured with high accuracy. In 1986, high-precision viscometers based on the oscillating motion of the falling part of the device in an external electromagnetic field with the ability to measure the viscosity of microvolumes of liquids were developed on this basis.

The development of viscometry techniques has contributed to the discovery of new rheological properties and models of materials. Russian physicist F. Shvedov (1840–1905) pioneered in the **rheology of dispersed systems**. In 1889, he experimentally investigated the elasticity and viscoelastic behavior of colloidal gelatin solutions using a rotational viscometer. In 1900, he presented his report "La

rigidité des liquides” at the Congress of Physics in Paris. In this presentation he described the rheology of viscoplastic fluids, 16 years ahead of the publication of the famous article by Bingham (see page 6). The class of linearly viscoplastic fluids is called **Shvedov–Bingham fluids** or **Bingham plastic fluids**.

In addition to the series two–element Maxwell model of a viscoelastic fluid (see page 7), the parallel two–element model of a viscoelastic solid is called the **Voigt model** (Kelvin–Voigt) in honor of the German physicist Waldemar Voigt (1850–1919). In 1898, Voigt also introduced the concept of tensor in the modern meaning of the term.

The first experiments that revealed the **viscoelastic behavior of solid materials** were carried out by German physicist Wilhelm Weber (1804–1891) in 1835 on silk threads. During loading, the strands underwent instant deformation, and then continued to elongate slowly, returning to the initial length after unloading. A combination of Maxwell and Voigt rheological models was proposed by H. Jeffreys⁶ in 1929 to describe the deformations of the earth's crust.

The first theoretical work⁷ on the rheology of suspensions was published by great scientist Albert Einstein. In this paper he derived the dependence of the viscosity coefficient μ on the concentration C of particles in a dispersed suspension of spherical solid particles in a Newtonian fluid at low concentrations ($C < 5\%$) in the form $\mu(C) = \mu_0(1 + kC)$, where μ_0 is the viscosity of the basic fluid, and $k = 2.5$ for spherical particles. After this seminal work, a series of theoretical and experimental papers dedicated to confirmation and generalization of the formula for the particles of various shapes, nature and concentrations have been published.

Further development of theoretical rheology was connected, first of all, with the study of rheological equations and their integration. In 1912, B.P. Weinberg integrated the equations of motion of the Bingham fluid between rotating cylinders. By 1924, a series of works by M.T. Huber, R. Mises and G. Hencky on the plastic flows of materials and a criterion for plastic deformations (Huber–Mises–Hencky yield criterion) was proposed. In 1909, Ostwald and his students proposed a **power law** for fluid viscosity $\tau = \mu(\dot{\gamma})\dot{\gamma}$, $\mu = \tilde{\mu}\dot{\gamma}^{n-1}$, where $\tilde{\mu}$ is an indicator of consistency. In 1925–1926 he introduced the concept of "structural viscosity" to describe the differences in the values of the coefficient of viscosity, measured at low and high shear rates. In 1928, P.A. Rebinder discovered the effect of the adsorption decrease in the strength of solids (the **Rebinder effect**), and his works laid the foundation for a new field of knowledge – physical and chemical mechanics, which is associated with rheology, hydrodynamics, physical and colloid chemistry. In 1929, M. Reiner coined the term “non–Newtonian fluids,” and the theory of capillary viscometry was developed in a series of works by B. Rabinovich, M. Muni, G. Barr, A. Metzner, and W. Read.

⁶ Jeffreys H. The Earth. Cambridge Univ. Press, 1929.

⁷ Einstein A. Eine neue Bestimmung der Moleküldimensionen. Annalen der Physik, 1906. Vol. 19. P. 289–306.

Rotational viscometers also underwent changes, associated primarily with errors that were introduced into the measurements by the presence of the bottom of the device, in which the fluid motion was not purely shear (Fig. 1c). M.P. Volarovich suggested a modification of the rotational viscometer using long narrow cylinders with a spherical bottom, and M. Mooney proposed similar ones with a conical bottom. In addition, the cone–plane viscometers were elaborated. M.A. Unger proposed a rotational viscometer in the form of two coaxial rotating hemispheres with a thin gap $\delta \ll R$ between them. I. Friedman, A.F. Dobriansky and A.P. Sivertsev used the viscometers with such narrow gaps between the rotating parts that the tested liquid even did not reach the bottom, which eliminated the measurement inaccuracy produced by the complex flows near the bottom. With the development of industry, ever more complex mixtures, suspensions and melts were created, which needed the improvements of viscometry technology.

Vibration viscometers in which a plate/crystal driven by oscillatory motion is immersed in the microvolumes of the liquid have been developed for biological and medical applications and micro/nano technologies. The rotating ball/cylinder viscometers driven by an external electromagnetic field have also been designed for microscopic volumes of fluids. In parallel with the emergence and expansion of the use of ferromagnetic, electrically conductive, piezoelectric materials and suspensions of the corresponding particles, electro– and magnetorheology, as well as biorheology, the rheology of biological fluids, solid and soft biological tissues, has been developed. Based on knowledge of the rheological properties of materials, novel techniques for the processing and use of liquid and solid materials in modern technologies have been elaborated.

3. FUNDAMENTALS OF DEFORMATION THEORY

Liquid materials are characterized by density, viscosity, fluidity (inverse to viscosity), and solid materials – by density, elasticity, stiffness (inverse to elasticity), strength, and endurance [2,4]. **Elasticity** is the property of materials to resist any changes in their volume or shape under the influence of external forces and to restore their original state after the load relief. Elastic properties are proper to all solid bodies. **Viscosity** is a property of gases and liquids, characterizing their resistance to the action of external forces that cause the flow of the medium. All real liquids have viscous properties.

To measure the elastic parameters, a sample of the material is deformed by external forces, the strains are measured, and **stress–strain curves** are plotted for further analyses.

Deformation is a change in the relative position of the points of the body under the action of the applied forces. The main types of deformation are **tension–compression, bending, shear, torsion**. As a measure of deformation the following quantitative characteristics are used: $\Delta L = L - L_0$ – **absolute deformation**, $\varepsilon = \Delta L / L_0$ – **relative deformation**, $\lambda = L / L_0$ – **elongation**, $\vec{u} = \vec{r} - \vec{r}_0$ – **displacement vector**.

In modern rheology, single– (Fig. 2a) and biaxial (Fig. 2b) **extensometers**, **tensile testing machines** (Fig. 2c), as well as **indentometers** (micro– and nanoindentometers), in which the penetration depth of the diamond tip (microneedles) is measured at different pressure forces, are used for comprehensive study of the elastic properties of solid rigid, soft and viscoelastic materials.

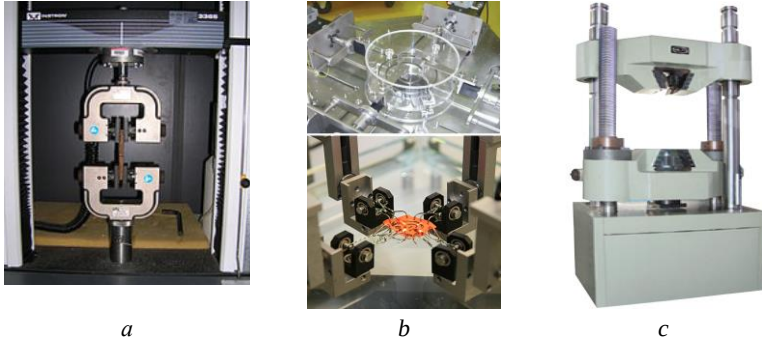


Fig. 2. Single (a) and biaxial (b) extensometers, and tensile testing machine (c)

Types of experiments in rheology of solid materials:

- Stretching by a constant force (creep);
- Uniaxial tension by constant/non–constant force;
- Compression;
- Fixed deformation (stress relaxation study);
- Cyclic tests (periodic loading–unloading);
- Study of the hardening of the material after loading–unloading;
- Rupture of the sample and study of material fatigue;
- Multiaxial tension and compression.

The tensorial strain characteristic is the **strain tensor**

$$\varepsilon_{ik} = \begin{vmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{vmatrix} = \begin{vmatrix} \varepsilon_1 & 0.5\gamma_3 & 0.5\gamma_2 \\ 0.5\gamma_3 & \varepsilon_2 & 0.5\gamma_1 \\ 0.5\gamma_2 & 0.5\gamma_1 & \varepsilon_3 \end{vmatrix}, \quad (1)$$

where γ_j is the angle of rotation of the fibers of the material relative to the axis $0x_j$ or in the plane $0x_i x_k$. The physical meaning of the diagonal components ε_{ii} of the tensor ε_{ik} is tension–compression along the corresponding axis. The off–diagonal components are shear deformations (rotation angles). The components ε_{ik} can be calculated by the **Cauchy formula**, which in the case of small deformations has the form

$$\varepsilon_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \quad (2)$$

In the case of small deformations, the change in each small volume is

$$\begin{aligned}\varepsilon_V &= \frac{V - V_0}{V_0} = \frac{(L_x + \Delta L_x)(L_y + \Delta L_y)(L_z + \Delta L_z) - L_x L_y L_z}{L_x L_y L_z} = \\ &= \varepsilon_x + \varepsilon_y + \varepsilon_z + \varepsilon_x \varepsilon_y + \varepsilon_x \varepsilon_z + \varepsilon_y \varepsilon_z + \varepsilon_x \varepsilon_y \varepsilon_z \approx \varepsilon_x + \varepsilon_y + \varepsilon_z = \text{div}(\vec{u})\end{aligned}$$

Then the **rate of volumetric deformation** $\dot{\varepsilon}_V = \text{div}(\vec{v})$; accordingly, the condition $\text{div}(\vec{v}) = 0$ is a condition of incompressibility of the medium.

The stress state is characterized by a **stress tensor**

$$\sigma_{ik} = \begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{vmatrix},$$

in the i -th line of which are the projections of the stress vector measured at an infinitesimal (physical) point calculated on an arbitrary unit area orthogonal to the axis $0x_i$ (Fig. 3a).

The experimental dependences $\sigma(\varepsilon)$ have the following characteristic points (Fig. 3b):

- σ_p is the **limit of proportionality**; when $\sigma < \sigma_p$ the dependence $\sigma(\varepsilon) = E\varepsilon$ is linear (Hooke's law), where E is the elastic (Young's) modulus;
- σ_e is the **elastic limit**; when $\sigma_p < \sigma < \sigma_e$ the dependence $\sigma(\varepsilon)$ becomes non-linear (for example $\varepsilon = \sigma / E + a\sigma^2$) but upon unloading the sample returns to its original state with $\varepsilon = 0$, and the load and unload curves coincide;
- σ_τ is the **yield strength**; when the sample is unloaded from any point in the region $\sigma_e < \sigma < \sigma_\tau$, it returns to a state characterized by residual deformations $\varepsilon = \varepsilon' \neq 0$, and the discharge curve usually lies below the load curve, although some materials exhibit the opposite behavior (see below); when $\sigma > \sigma_\tau$ the dependence $\sigma(\varepsilon)$ becomes more flat (yield zone), i.e. at low increase in σ , large deformations are observed;
- σ^* is the **tensile strength**; the destruction of the material starts here.

According to their properties, materials could be homogeneous (i.e. density, elastic modulus, and other parameters are the same at all “points” and their gradients are zero), non-homogeneous (properties vary from point to point, $\nabla \neq 0$), isotropic (properties are the same in all directions) or anisotropic (along some directions, the properties differ from others). For anisotropic materials, the Hooke's law takes the form

$$\sigma_{ik} = E_{iklm} \varepsilon_{lm}, \quad (3)$$

where E_{iklm} is the **tensor of elastic modulus** of rank 4; it has $3^4 = 81$ components.

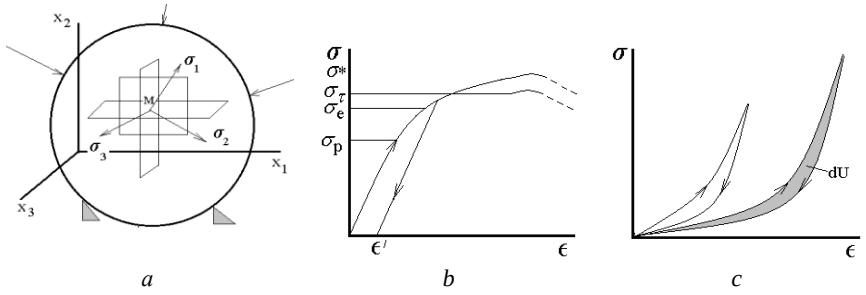


Fig. 3. Calculation of the stress tensor components at the point M (a); curves for hard (b) and soft (c) materials

Due to the symmetry of the tensor ε_{ik} , the tensor E_{iklm} is symmetric in the 2nd pair of indices, so $E_{iklm} = E_{ikml}$. It is known that in the absence of internal moments of rotation in the medium, the stress tensor is also symmetric [5], which means that the tensor E_{iklm} is also symmetrical in the first pair of indices, so $E_{iklm} = E_{kilm}$. Counting the number of independent components of the tensor E_{iklm} , we get that there remain $36 = 6^2$ independent components. This leads to the idea of replacing the 4-th rank tensor E_{iklm} by the 2-nd rank tensor, which is easily represented in the form of a matrix or table with 6 rows and 6 columns. Then instead of stress and strain tensors, the stress and strain vectors can be introduced in the form

$$\vec{\sigma} = \{\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{23}, \sigma_{13}, \sigma_{12}\}, \vec{\varepsilon} = \{\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12}\}$$

Then the Hooke's law (3) can be written as

$$\sigma_i = A_{ik} \varepsilon_k \text{ or } \varepsilon_i = a_{ik} \sigma_k, \quad (4)$$

where A_{ik} is the stiffness matrix, $a_{ik} = A_{ik}^{-1}$ is the compliance matrix

For isotropic materials, the compliance matrix has the form

$$a_{ik} = \begin{pmatrix} 1/E & -\nu/E & -\nu/E & 0 & 0 & 0 \\ -\nu/E & 1/E & -\nu/E & 0 & 0 & 0 \\ -\nu/E & -\nu/E & 1/E & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/G & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/G & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/G \end{pmatrix},$$

where ν is the Poisson's ratio, $G = \frac{E}{2(1+\nu)}$ is the shear modulus or the 2-nd Lamé coefficient [6].

For transversely isotropic materials, the properties of a material in one direction differ from its properties in a plane orthogonal to this direction, i.e. in this plane the material is isotropic. Then the compliance matrix has the form

$$a_{ik} = \begin{pmatrix} 1/E_1 & -\nu_{12}/E_1 & -\nu_{12}/E_1 & 0 & 0 & 0 \\ -\nu_{12}/E_1 & 1/E_2 & -\nu_{13}/E_2 & 0 & 0 & 0 \\ -\nu_{12}/E_1 & -\nu_{13}/E_2 & 1/E_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/G_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/G_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/G_2 \end{pmatrix},$$

where E_1 and E_2 are the Young's module along the selected direction and in the orthogonal plane accordingly, ν_{12} and ν_{13} are the corresponding Poisson's ratios, G_1 and G_2 are the shear module.

For orthotropic materials, the properties are different in three mutually perpendicular directions, for example, along the axes of the Cartesian (glued from layers of plywood), cylindrical (tree trunk) or spherical (anisotropic shell) coordinate systems. For such materials, there are three different moduli of elasticity $E_{1,2,3}$ and shear $G_{1,2,3}$ and

$$a_{ik} = \begin{pmatrix} 1/E_1 & -\nu_{21}/E_2 & -\nu_{31}/E_3 & 0 & 0 & 0 \\ -\nu_{12}/E_1 & 1/E_2 & -\nu_{32}/E_3 & 0 & 0 & 0 \\ -\nu_{13}/E_1 & -\nu_{23}/E_2 & 1/E_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/G_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/G_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/G_3 \end{pmatrix},$$

where the upper quadrant of the matrix is symmetric, so that $\nu_{21}/E_2 = \nu_{12}/E_1$, $\nu_{31}/E_3 = \nu_{13}/E_1$, $\nu_{32}/E_3 = \nu_{23}/E_2$.

4. VISCOMETRY

Viscometry (rheometry) is a chapter of experimental rheology devoted to experimental methods for studying rheological parameters (coefficients) of materials. In this case, rheometers are used to measure the deformation (rheometric) coefficients, in particular, viscosity coefficients (by viscometers). The measured viscosities of liquids and gases are in a rather wide range of values (Fig. 4), which imposes limitations on the possible types of devices used for the measurements [7].

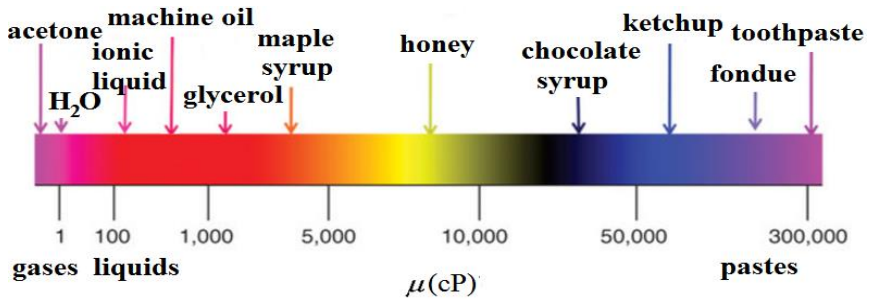


Fig. 4. Viscosities of some liquid substances

Currently, the following types of viscometers are most often used:

1) **Rotational viscometer.** In this case, the test fluid is placed in a narrow gap with a width δ between two coaxial cylinders, one of which rotates at a given angular velocity Ω (Fig. 5a), and the second cylinder with radius R is hanging on the rope and rotates due to the action of the moment M of friction forces from the side involved in fluid rotation and this moment can be measured by the angle of twist of the rope. During the measurements, the dependence $M(\Omega)$ is recorded. In this case, the moment $M = R F_{\text{tp}} = R \cdot 2\pi R \cdot \tau_{\text{tp}}$ of friction forces acting on the lateral surface of the internal cylinder of the device. For friction τ_{tp} , we take the Newtonian fluid model $\tau_{\text{tp}} = \mu \dot{\gamma}$, then for narrow gaps $\delta \ll R$ we have $\tau_{\text{tp}} \approx \mu \Omega R / \delta$. Then we finally obtain the working formula of the viscometer for calculating the viscosity $\mu_{\text{app}} = kM / \Omega$, where $k = \delta / (2\pi R^3 L)$ is the constant of the device. Since the assumption of Newtonian fluid may be incorrect, the calculated values do not correspond to real viscosity. That is why it is called **apparent viscosity**.

If in the experimental measurements with different Ω , the same values for μ_{app} are obtained, the test fluid is Newtonian. In other cases, there is an effect on the viscosity of the rotation speed value Ω (non-linearly viscous properties), duration of the experiment or the pause between successive experiments, the effect of unsteady twisting $\Omega(t)$ (temporal properties). In such cases the computed viscosities are different that means the liquid under consideration is non-Newtonian. Modern rotational viscometers make it possible to study the viscosities of various liquids in the $\mu = 10^{-3} - 10^6 \text{ Pa}\cdot\text{s}$ range.

2) In the **capillary viscometer**, the test fluid moves along a thin long cylindrical tube under the influence of a pressure drop between its inlet and outlet. Assuming that the Poiseuille flow is realized in the tube, and the liquid under investigation is Newtonian, it is easy to obtain the working formula of the viscometer from the Poiseuille formula $\mu_{\text{app}} = k\delta P / Q$, where $k = \pi R^4 / (8L)$ is the constant of the capillary viscometer used. The movement of fluid in a capillary viscometer can be

caused by gravity (Ostwald, Ubellode viscometers; Fig. 1a) or by creation of a vacuum at one end (Hess capillary viscometer, Fig. 5b). Hess viscometers are used to study the relative viscosity of a liquid μ_f compared to the viscosity of water at the same temperature. In this case, using the switching valve 1, water and the test liquid are drawn into the two tubes, respectively. After that, the valve is installed in an intermediate position and due to the pressure drop identical for both capillaries, both liquids move along the tubes by the same pressure drop. The inlet pressure equals to the atmospheric pressure for both tubes. We create a pressure drop and move the liquid until the water column reaches mark 1; at the same time, the column of the studied liquid reaches the mark corresponding to the value μ_f . In this case

$$\frac{Q_f}{Q_{H_2O}} = \frac{V_f \cdot t}{V_{H_2O} \cdot t} = \frac{\mu_f}{\mu_{H_2O}}.$$

The range of operation of capillary viscometers is $\mu = 10^{-4} - 10^5 \text{ Pa}\cdot\text{s}$. Again, if experiments with different δP values give the same values for μ_{app} , then the liquid under study is Newtonian.

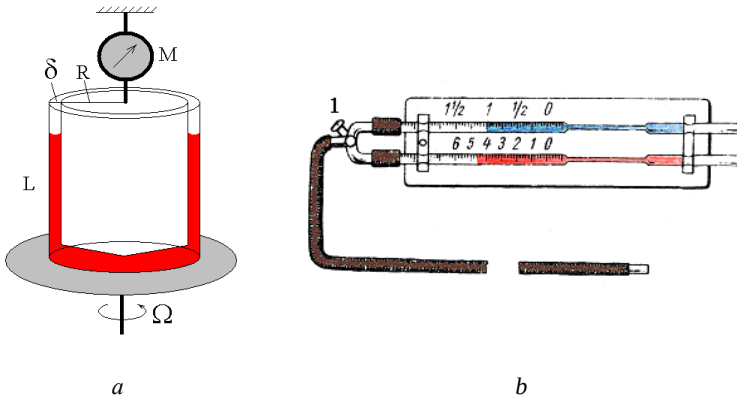


Fig. 5. Scheme for calculating the working formula of rotation (a) and Hess viscometer (b)

3) **The falling ball method.** A vertical tube of a given length L is filled with a known liquid of the density ρ_f . Then a small boll of radius R made of a material of known density ρ_s is thrown from the upper end of the tube. We fix the time T of the ball falling to the bottom of the tube. Using the formula for the velocity ($v = L/T$) that is supposed to be constant and the radius of the ball is much smaller than the radius of the tube, the simple formula $v = \frac{2(\rho_s - \rho_f)}{9\mu_f} gR^2$ can be computed from the balance equation of the gravity, buoyancy and Stokes forces acting on the

ball. The formula for the fluid viscosity can be obtained then as $\mu_{\text{app}} = k(\rho_s - \rho_f)T$, where $k = 2gR^2 / (9L)$. The range of the viscometer is $\mu = 10^{-4} - 1 \text{ Pa}\cdot\text{s}$.

In spite the apparent simplicity of the measurement procedure, viscometers should also be equipped with:

- thermostat – to control and maintain a constant temperature of the sample (from -10 to $+130$ °C);
- adapter for samples with low viscosity ($<10^{-3} \text{ Pa}\cdot\text{s}$);
- adapter for samples of small volume (up to $2-16 \text{ ml}$);
- resistant spiral motion – allows you to measure the viscosity of low-flowing materials (resins, gelatins, pastes, putties, creams);
- a device for the destruction of the film formed on the surface of the liquid volume in contact with air, evaporation.

In that way, the viscometers of different types are precise and quite sophisticated devices that can be connected to PC for automatic recording, treatment and analyses of the measured data.

5. RHEOLOGY OF VISCOELASTIC MEDIA

Natural and artificial materials reveal quite complex rheologic properties. Such materials can be composed from the fluid, solid particles and gases, so they are multicomponent and multiphase ones. There are the most important among them:

- **Composites** – are heterogeneous multicomponent materials with exact boundaries between the components;
- **Emulsions** – are suspensions of liquid particles in the immiscible fluid (like a hydrophobic fluid with a hydrophilic one);
- **Suspensions** – are mixtures of solid rigid or soft particles in a fluid;
- **Gels** – are elastic deformed materials contained fluid phase inside in the form of drops or hydrogenated structures;
- **Aerogels** – are gels, in which the fluid phase was replaced by gas; the percentage of gas is high, $\sim 90-99\%$;
- **Sols** – are elastodeformed fluids contained solid phase in the form of separate moving inclusions; sols can be obtained by mixing or heating of gels;
- **Aerosols** – are mixtures of liquid particles (droplets) in the air (gas);
- **Gaseous fluids** – are fluids with gas bubbles;
- **Foams** – are whipped fluids or foamed and dried solid structures, similar to aerogels.

5.1 Viscoelasticity

Viscoelasticity is the property of materials to exhibit both elastic and viscous properties. Mathematically the elasticity is described as the dependence of stress on the deformation $\sigma = \sigma(\varepsilon)$, for example in the form of (4). The simplest

physical model of elastic body is a spring (Fig. 6a). At the loading the spring is stretching instantly, and after the unloading, it instantly returns to the unstrained state (Fig. 6b). Both the linear (Hooke's law) and the nonlinear elasticity law (nonlinear springs) can be accepted for the spring.

The viscosity is described as the dependence of the shear stress on the strain rate ($\sigma(\dot{\gamma})$) in the linear Newton's law of viscous friction or the generalized non-linear non-Newtonian laws. If the dependence is liner $\sigma = \eta \dot{\epsilon}$ then the fluid is Newtonian; if it is not linear like in the case $\sigma = \eta \dot{\epsilon} + \tilde{\eta} \ddot{\epsilon}$ or others, the fluid is non-Newtonian. At fast (impulse or shock) loads ($\dot{\epsilon} \rightarrow 0$) the fluids exhibit elastic properties. The physical model for viscous behavior in the piston moving into a tube filled with a viscous liquid (Fig. 6c). It means, when the applied stress is constant the form of the specimen is changed (Fig. 6d) and after the unloading ($\sigma = 0$) the elongation of the sample remains constant ($\epsilon = \text{const}$, see Fig. 6d) that corresponds to the **residual strain**.

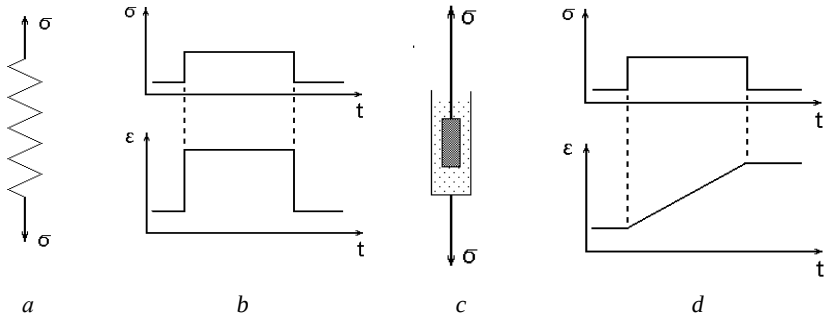


Fig. 6. The models of elastic (a) and viscous (c) elements and their behavior at the step-function loads by force, (b) and (d) respectively

In viscoelastic materials the stress depends on the strain and the strain rate ($\sigma = \sigma(\epsilon, \dot{\epsilon})$), and possibly on their higher derivatives on time: $\sigma = \sigma(\epsilon, \dot{\epsilon}, \ddot{\epsilon}, \dots)$ or in the implicit form

$$f(\sigma, \epsilon, \dot{\sigma}, \dot{\epsilon}, \ddot{\sigma}, \ddot{\epsilon}, \dots) = 0. \quad (5)$$

The properties of viscoelastic media are usually modeled as parallel and series connections of elastic (spring) and viscous (damper) elements which sketched out in the discrete rheological models as analogous of electric circuits composed by resistors, capacitors, inductance, current sources, etc. The rheological models give opportunities to get the form of the dependence (5) and study the behavior of material at given external load in the form of applied forces or deformations. The lumped parameter models are constructed for one dimensional (1D) problems and do not take into account possible non-uniform distribution of fibers (and mechanic properties) inside the material. As the models of complex spatial deformation of the specimen it is necessary to use corresponding tensorial characteristics (4).

5.2. Two–element rheological models

Viscoelastic properties are proper to complex materials that are made from deformed fibers (particles, grains, microstructures) with the space between them filled with viscous fluid(s) (Fig. 7a). The first viscoelasticity concept appeared at the end of the XIX–th century after the experiments of Maxwell, Boltzman, Kelvin and after the researching of the creeping and the relaxation of materials, rubber, glass and some other materials. The simplest models of such continuous media are two–element models that consist of the fibers of one type (a spring) and a fluid (damper) that are connected in a parallel (Fig. 7b) or series (Fig. 7c) connection.

5.2.1. Voigt model of viscoelastic solids

The **Voigt model** (or the Kelvin–Voigt model) consists of the spring and damper that are connected in parallel (Fig. 7b). For the material stretched in Fig. 7a, the Voigt’s model corresponds to the loading along the fibers by the forces F_1 . The relative deformation ε of the material is defined as the change of distance between the points of A and B (Fig. 7b), that relates to the relative deformation of the both spring and damper which are in parallel connection. The elongating stresses σ are applied at the points A and B; they are proportionally distributed between the elastic and viscous elements depending on their relative resistances to the deformation. There is a direct analogy with the parallel connection of resistors and capacitors in an electric circuit scheme. In this mechanic electric analogy the electric current I corresponds to the mechanical stress σ , and the electric potential U corresponds to the relative deformation ε . In the parallel connection both electric resistivity and mechanical stresses are additive. In the series connection the electric potentials and the mechanical deformations are additive. The system of equations for the rheological Voigt model consists of the Hook’s law for elastic elements and the Newton viscous law for viscous elements. The distributions of stresses and deformations in the nodes of the mechanical scheme are analogical for the Kirchhoff’s rules and the Ohm’s law for the electric circuit. For the rheological scheme given in Fig. 7b, those laws are:

$$\begin{aligned}\sigma &= \sigma_1 + \sigma_2, \\ \sigma_1 &= \eta \dot{\varepsilon}, \\ \sigma_2 &= E\varepsilon.\end{aligned}\tag{6}$$

Let us exclude the unknown stresses σ_1, σ_2 by substitution of the two last equations (6) into the first one, one gets the rheological equation for the Voigt model in the form

$$\eta \dot{\varepsilon} + E\varepsilon = \sigma\tag{7}$$

One can solve the differential equation (7) only when one of the two unknown functions $\sigma(t)$ and $\varepsilon(t)$ is given. In the experiments the material can be loaded by

a determined stress $\sigma(t)$ and the corresponding deformations could be measured, and vice versa. When the material is loaded by a constant stress ($\sigma^* = \text{const}$, Fig. 7d), the experiment is called isotonic. When the material is stretched and fixed (or compressed and fixed, $\varepsilon^* = \text{const}$, Fig. 7e), the experiment is called isometric. One can conduct both isometric and isotonic experiments with rheological equation in the form of (7) or other forms by substitution of $\sigma^* = \text{const}$ or $\varepsilon^* = \text{const}$ into the equation and studying its solutions.

The **isotonic experiment** with the Voigt model (7) gives the linear non-homogeneous ordinary differential equation (ODE) of first order with constant coefficients for the deformation $\varepsilon(t)$:

$$\eta \frac{d\varepsilon}{dt} + E\varepsilon = \sigma^*. \quad (8)$$

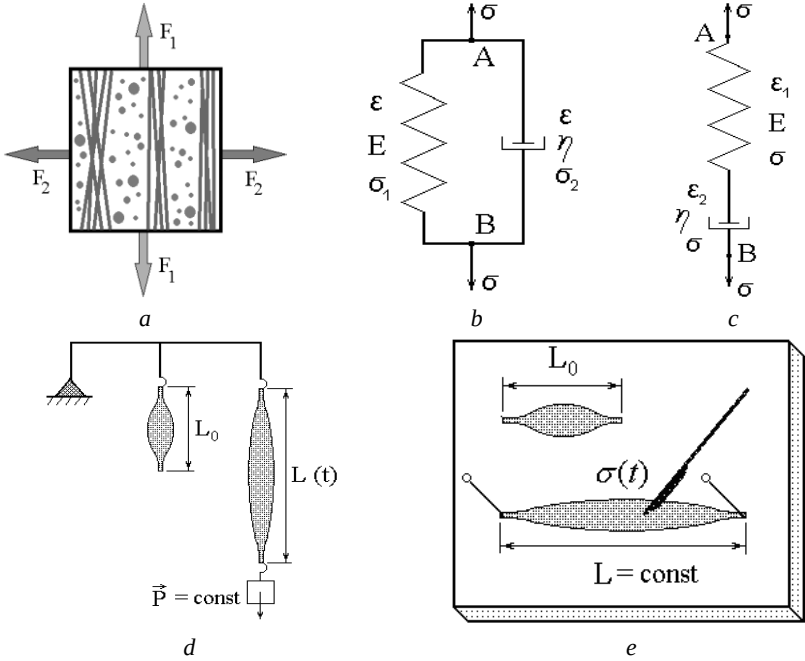


Fig. 7. The scheme of the internal structure of the viscoelastic material (a); Voigt model (b); Maxwell model (c), isotonic (d) and isometric (e) experiments

Let us assume that loading begins at $t=0$ from a non-deformed state, i.e. $\varepsilon(0)=0$. Then the solution of (8) has the form $\varepsilon(t) = (1 - e^{-Et/\eta})\sigma^*/E$. The function $\varepsilon(t)$ is increasing and convex (Fig. 8a) because $\dot{\varepsilon}(t) = e^{-Et/\eta}\sigma^*/\eta > 0$, $\ddot{\varepsilon}(t) = -e^{-Et/\eta}E\sigma^*/\eta^2 < 0$. Thus, at constant load, the deformation of the sample

will slowly increase with time (creep). After unloading at a time t_1 , the behavior of the material will be described by equation (8) with $\sigma^*=0$ and with the initial condition $\varepsilon(t_1)=\varepsilon_1$, where ε_1 is the deformation of the material at the instant time of unloading. In accordance with the solution of equation (8), $\varepsilon_1=(1-\exp(-Et_1/\eta))\sigma^*/E$. The solution of equation (8) for $\sigma^*=0$ with the selected boundary condition has the form $\tilde{\varepsilon}(t)=\varepsilon_1 \exp(-E(t-t_1)/\eta)$. Computing the derivatives of $\tilde{\varepsilon}(t)$, we find that this function is decreasing concave (Fig. 8a). At $t \rightarrow \infty$ one has $\tilde{\varepsilon} \rightarrow 0$.

In physics the process of changing the parameters of a material toward an equilibrium state is called relaxation. To characterize the relaxation, a parameter t_{rel} (the relaxation time) that is the time during which the parameter(s) of the material decrease in e times is introduced. As follows from solution (8), for the Voigt material $t_{\text{rel}}=\eta/E$, i.e. the material with bigger elasticity of its fibers and lower viscosity of the fluid goes to equilibrium faster. When the Voigt body is loaded in the domain $\sigma < \sigma_e$, the spring returns to its original state and drives the piston, which also returns to its original state after the unload. Thus, a parallel-connected elastic element plays the role of a returning force, and the Voigt body is a model of a viscoelastic solid that goes back in the initial state after discharge.

One can carry out identification of the model parameters E and η if there are experimental curves $\varepsilon(t)$ and $\tilde{\varepsilon}(t)$ measured on a viscoelastic material. Then one can choose several values of time $t_2, t_3, t_4, \dots$ and definite the correspondent values of deformation $\varepsilon_2=\varepsilon(t_2)$, $\varepsilon_3=\varepsilon(t_3)$, $\varepsilon_3=\varepsilon(t_3), \dots$ on the experimental curves. Then the values E and η can be calculated from the relations $\varepsilon_j=(1-\exp(-Et_j/\eta))\sigma^*/E$ and $\tilde{\varepsilon}_j=\varepsilon_1 \exp(-E(t_j-t_1)/\eta)$ as transcendent equations. If for all the points $t_2, t_3, t_4, \dots$ one gets the same values of E and η then the material under consideration can be modeled as Voigt body, otherwise more complex rheological models must be used (see § 5.3).

Let us carry out an **isometric experiment** with Voigt body. In this case, a sample of material must be deformed (to say, stretched) and fixed (Fig. 7e). Then the stress relaxation $\sigma(t)$ over the sample can be measured by stress gauges. The behavior of the material will be determined by equation (7) at $\varepsilon=\varepsilon^*=\text{const}$, i.e. $\sigma=E\varepsilon^*$ and relaxation is absent (Fig. 8b). Thus, if the material under study demonstrates relaxation under isotonic loading and an instantaneous reaction under isometric stress, then Voigt's body can serve as a model of such a material. Most of natural and synthetic viscoelastic materials exhibit relaxation under both isotonic and isometric loads that correspond to more complicated rheological models.

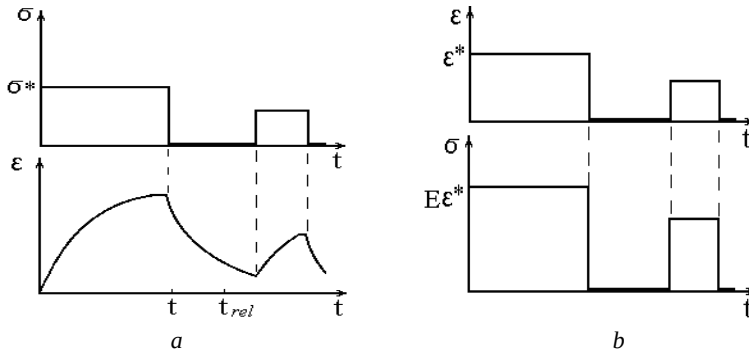


Fig. 8. The behavior of the Voigt body at isotonic (a) and isometric (b) stresses

One can also carry out dynamical experiments with materials and their rheological models. In such experiments oscillating stresses $\sigma^*(t)$ or deformations $\varepsilon^*(t)$ are applied to the material. Let us apply **harmonic oscillations of deformations** (the length of the sample) $\varepsilon(t) = \varepsilon_0 e^{i\omega t}$ with the frequency ω to the equation (7). Then one can obtain that the stresses in the material $\sigma(t) = \varepsilon_0 (E + i\omega\eta) e^{i\omega t}$ (or in standard form $\sigma(t) = \varepsilon_0 \sqrt{E^2 + \omega^2 \eta^2} e^{i(\omega t + \vartheta)}$) will oscillate with the same frequency ω , amplitude $\sigma_{\text{amp}} = \varepsilon_0 \sqrt{E^2 + \omega^2 \eta^2}$ and with the phase shift $\vartheta = \arctg(\omega\eta/E)$. This result can also be used for identification of the rheological parameters E and η based on the measured amplitude σ_{amp} and phase shift ϑ . As an analogy to the static Young modulus, the dynamic modulus of elasticity can be introduced as a ratio of the amplitudes of the stresses and strains $E_{\text{dyn}} \equiv \sigma_0 / \varepsilon_0 = \sigma \cdot e^{-i\omega t} / \varepsilon_0$. In this case one gets $E_{\text{dyn}} = (E + i\omega\eta)$; it means the real part of the dynamical modulus equals to the static (Young's) modulus $\text{Re}(E_{\text{dyn}}) = E$, and the ratio of the imaginary and real parts $\text{Im}(E_{\text{dyn}}) / \text{Re}(E_{\text{dyn}})$ corresponds to the phase shift. In purely viscous materials the phase shift is 90° , and in pure elastic materials it is 0° , while in the viscoelastic materials $\vartheta \in [0; 90^\circ]$.

5.2.2. Maxwell model of viscoelastic liquids

In the **Maxwell rheological model**, the elastic and viscous elements are in series connection (Fig. 7c). This model corresponds to the loading of the material sample (Fig. 7a) by the forces F_2 orthogonal to the direction of springs (i.e. elastic fibers of the material). The stress σ is applied at the points A and B and it is the same in both elastic and viscous elements. The total deformation ε measured

between the points A and B is the sum of the deformations ε_1 and ε_2 of the elastic and viscous elements accordingly. The stress and deformation of the spring obey the Hook's law, and the stress and strain rate of the damper obey the Newton's law of viscosity. Thus we have the closed systems of equations

$$\begin{aligned}\varepsilon &= \varepsilon_1 + \varepsilon_2, \\ \sigma &= E\varepsilon_1, \\ \sigma &= \eta\dot{\varepsilon}_2.\end{aligned}\tag{9}$$

In order to exclude ε_1 and ε_2 and obtain the rheological law $\sigma(\varepsilon)$, one must apply the differentiation operator d/dt to each component of the two equations (9). The obtained equations

$$\begin{aligned}\dot{\varepsilon} &= \dot{\varepsilon}_1 + \dot{\varepsilon}_2, \\ \dot{\sigma} &= E\dot{\varepsilon}_1,\end{aligned}$$

together with the last equation (9) allows excluding $\dot{\varepsilon}_1$ and $\dot{\varepsilon}_2$. Finally, the rheological equation for the Maxwell model can be obtained as

$$\dot{\varepsilon} = \frac{\sigma}{\eta} + \frac{\dot{\sigma}}{E} \quad \text{or} \quad \eta E \dot{\varepsilon} = E\sigma + \eta\dot{\sigma}.\tag{10}$$

Let us proceed with **isotonic experiments** with this model of viscoelastic materials by substitution $\sigma^* = \text{const}$ into (10). Then the equation $\dot{\varepsilon} = \frac{\sigma^*}{\mu}$ can be integrated over time with initial condition for the non-deformed sample

$\varepsilon(0) = 0$ is a liner function of time $\varepsilon(t) = \frac{\sigma^*}{\eta} t$. For the reloading of the material

one must substitute $\sigma^* = 0$ into (10) and obtain its solution $\varepsilon = \text{const}$. It means the piston will keep the same position after the discharge because there is no any returning force for the spring (Fig. 9a). The repetition of the stress loads leads to accumulation of strains (Fig. 9a). Such behavior is proper to pure liquids because it means the absence of elastic properties.

The **isometric experiments** with the Maxwell body can be modeled by substitution of $\varepsilon = \varepsilon^* = \text{const}$ into (10) that gives linear homogeneous ODE of the first order with constant coefficients.

$$\frac{d\sigma}{dt} + \frac{E}{\eta}\sigma = 0.\tag{11}$$

The initial stress is non-zero $\sigma(0) = \sigma_0$ because the material was deformed that produced internal stresses. Then the solution of (11) has the form $\sigma(t) = \sigma_0 e^{-Et/\eta}$. The relaxation of stresses goes faster at lower values of viscosity and greater values of the Yung's modulus (Fig. 9b).

The **dynamic experiments** on Maxwell model at the applied **harmonic oscillations of stress** $\sigma(t) = \sigma_0 e^{i\omega t}$, correspondingly to (10), produce harmonic oscillations of the deformation in the form $\varepsilon(t) = \sigma_0(\omega\eta + iE)e^{i\omega t} / (\omega\eta E)$ (or $\varepsilon(t) \equiv \varepsilon_0 e^{i\omega t} = \sigma_0 \sqrt{\omega^2 \eta^2 - E^2} e^{i(\omega t - \vartheta)} / (\omega\eta E)$) with the phase shift $\vartheta = \arctg(E / \omega\eta)$, amplitude $\sigma_0 \sqrt{\omega^2 \eta^2 - E^2}$, and the dynamic modulus of elasticity $E_{\text{dyn}} = \omega\eta E / (\omega\eta + iE)$.

The **dynamic experiments** at **harmonic variations of deformation** $\varepsilon(t) = \varepsilon_0 e^{i\omega t}$ (the length) of the specimen lead to the internal stress oscillations $\sigma(t) = i\omega\eta E \varepsilon_0 e^{i\omega t} / (E + i\omega\eta)$ with the same phase shift $\vartheta = \arctg(E / \omega\eta)$, amplitude $\sigma_{\text{amp}} = \omega\eta E \varepsilon_0 \sqrt{\omega^2 \eta^2 + E^2} / (E^2 + \omega^2 \eta^2)$ and the dynamic modulus of elasticity $E_{\text{dyn}} = (E\omega^2 \eta^2 + iE^2 \omega\eta) / (E^2 + \omega^2 \eta^2)$.

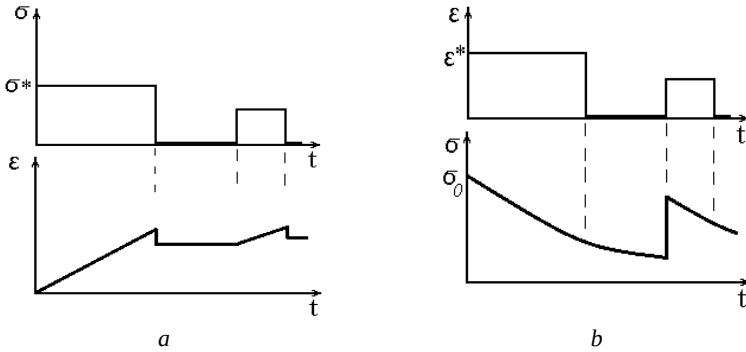


Fig. 9. The behavior of Maxwell body at isotonic (a) and isometric (b) loading and unloading (relaxation)

Therefore, after discharge the material does not return to initial zero-strain state and the Maxwell model corresponds to a viscoelastic liquid⁸.

5.3. Three-element rheological models

Rheological properties of real viscoelastic materials do not describe accurately by two-element models like Voigt and Maxwell bodies. The accurate enough and still simple models are composed by at least two elastic and viscous elements; the so-called **three-element rheological models**.

⁸ In the course of theoretical physics by L.D. Landau and E.M. Lifshits (Theoretical Physics. Vol. 7. Theory of Elasticity) the Maxwell's model is described in §35 untitled «Very viscous liquids».

5.3.1. Three–element models of viscoelastic solids

When the material consists of two types of fibers with different elasticity and the one liquid (Fig. 10a), its load by the forces F_2 can be described by the discrete model presented in Fig. 10b, and the load by the forces F_1 – by the discrete model presented in Fig. 10b).

The first model is known as general Kelvin–Voigt model (the model of standard linear body) and the second one is the Zener model. The correspondent distributions of inner stresses σ_1, σ_2 and deformations $\varepsilon_1, \varepsilon_2$ of the elements are presented in Fig. 10b,c accordingly. Note that here again the parallel elements have the same deformations and their stresses are additive, while the elements in series have the same mechanical stresses and their deformations are additive (like potentials and currents in the electric circuits).

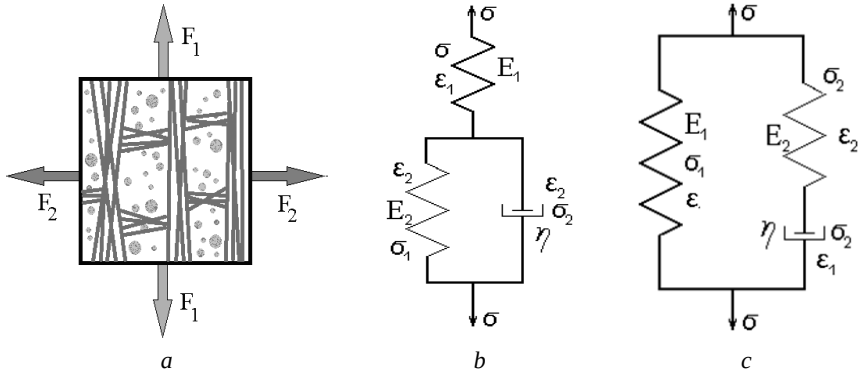


Fig. 10. The scheme of the material with two types of elastic fibers and one type of liquid (a), three–element Kelvin–Voigt model (b) and Zener model (c) for viscoelastic solid bodies

Let us consider first the **model by Zener**. The additive conditions (analogues to the Kirchhoff's rules for electric circuits) for stresses in parallel connections of elements and for deformations in series connection of elements, the Hook's laws for the springs and the Newton's law of viscosity for the damper give the following system of equations

$$\begin{aligned}\sigma &= \sigma_1 + \sigma_2, & \varepsilon &= \varepsilon_1 + \varepsilon_2, \\ \sigma_1 &= E_1 \varepsilon, & \sigma_2 &= \eta \dot{\varepsilon}_1, & \sigma_2 &= E_2 \varepsilon_2.\end{aligned}$$

One can exclude the unknowns σ_1, σ_2 and $\varepsilon_1, \varepsilon_2$ from this system and get the rheological relation for the Zener model in the form

$$\eta \dot{\sigma} + E_2 \sigma = E_1 E_2 \varepsilon + \eta (E_1 + E_2) \dot{\varepsilon}.$$

The **isotonic experiment** with **Zener model** can be carried out by substitution $\sigma^* = \text{const}$ in the rheological law. Then one has the linear non-homogeneous ODE of the first order with constant coefficients

$$\eta(E_1 + E_2) \frac{d\varepsilon}{dt} + E_1 E_2 \varepsilon = E_2 \sigma^*. \quad (12)$$

The solution of (12) with initial condition $\varepsilon(0) = 0$ has the form $\varepsilon(t) = \frac{\sigma^*}{E} (1 - \exp(-E_1 t / \eta))$, $E = E_1 E_2 / (E_1 + E_2)$. Since $\dot{\varepsilon}(t) > 0$, $\ddot{\varepsilon}(t) < 0$, the dependence $\varepsilon(t)$ is increasing and convex (Fig. 11 a). After the reloading started at $t = t_1$ the solution of (12) at $\sigma^* = 0$ and new initial condition $\varepsilon(t_1) = \varepsilon_1$ gives $\tilde{\varepsilon}(t) = \varepsilon_1 \exp(-E(t - t_1) / \eta)$, where $\varepsilon_1 = \sigma^* (1 - \exp(-E_1 t_1 / \mu)) / E$ (Fig. 11a). The time of relaxation of deformations $t_{\text{rel}} = \eta / E_1$ does not depend on E_2 , since the relaxation is connected with redistribution of deformations from elastic elements to viscous ones and the role of the returning force for the damper performs the element with E_1 . The identification procedure is sketched in Fig. 11b.

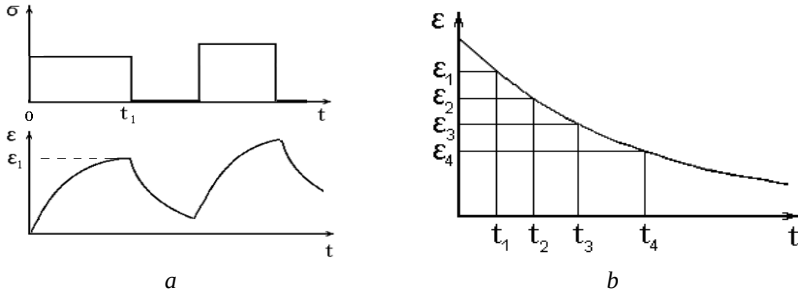


Fig. 11. The behavior of Zener's body at isotonic loading (a), and identification of the parameters of the model (b)

For isometric experiments with Zener model one can get the linear ODE of the first order with constant coefficients and initial condition

$$\eta \frac{d\sigma}{dt} + (E_1 + E_2) \sigma = E_1 E_2 \varepsilon^*, \quad (13)$$

$$\sigma(0) = \sigma_0.$$

The solution of (13) has the form

$$\sigma(t) = \frac{E_1 E_2 \varepsilon^*}{E_1 + E_2} + \left[\sigma_0 - \frac{E_1 E_2 \varepsilon^*}{E_1 + E_2} \right] \exp(-(E_1 + E_2)t / \eta). \quad (14)$$

Note that the initial stress σ_0 corresponds to the instantaneous elastic deformations of springs. For the parallel connection $\sigma_0 = (E_1 + E_2)\varepsilon^*$; therefore, the component in the square brackets in (14) is positive and $\dot{\varepsilon}(t) < 0$, $\ddot{\varepsilon}(t) > 0$. After the reloading started at $t = t_1$ the behavior of the body is described as solution of the equation (13) with $\varepsilon^* = 0$ and the initial condition $\sigma(t_1) = \sigma_1$. The solution is $\tilde{\sigma}(t) = \sigma_1 \exp(-(E_1 + E_2)(t - t_1)/\eta)$, where $\sigma_1 = \frac{E_1 E_2 \varepsilon^*}{E_1 + E_2} + \left[\sigma_0 - \frac{E_1 E_2 \varepsilon^*}{E_1 + E_2} \right] \exp(-(E_1 + E_2)(t - t_1)/\eta)$. This dependence is similar to the one presented in Fig. 9b. For the identification of the rheological coefficients E_1, E_2, η one has to find several points with coordinates $\{(\varepsilon_j, t_j)\}_{j=1}^n$, $n > 3$ and calculate the relative values ε_j at the chosen t_j from the dependences $\sigma(t)$ (for the increasing ones) or $\tilde{\sigma}(t)$ (for the decreasing ones). These relations can be solved as a system of transcendental equations. If the calculated coefficients E_1, E_2, η are the same for different points, the model by Zener describes very well the material properties. If different values for E_1, E_2, η are computed on different triplets of points on the stress–strain curves, the model by Zener is not satisfactory and more complex models must be tried.

As it is clear from Fig. 10c, the spring with E_1 generates the returning force for the damper. Similar conclusion that Zener's model describes the viscoelastic solid body can be derived from the rheological equation (12) that contains the term with ε . In the rheological equations for viscoelastic liquids deformations are always absent, only their time derivatives are present.

The dynamic experiments with Zener's model can be started with harmonic oscillations of stresses $\sigma(t) = \sigma_0 e^{i\omega t}$, that lead to the oscillations of deformations with different amplitudes and unknown yet phase shift in the general form $\varepsilon(t) = \varepsilon_0(\sigma_0, \omega, \dots) e^{i(\omega t + \vartheta)}$. Similar experiments can be conducted with the oscillations of deformation $\varepsilon(t) = \varepsilon_0 e^{i\omega t}$ imposed. The correspondent solution can be found as $\sigma(t) = \sigma_0(\varepsilon_0, \omega, \dots) e^{i(\omega t + \vartheta)}$.

Individual task: substitute the general forms into the rheological equation and obtain solutions for the dynamical experiments and the correspondent dynamic elastic modules of the Zener's model.

Individual task: Derive the rheological relation for the three–element Kelvin–Voigt model and study its properties in the isotonic, isometric and dynamic experiments. Describe the method for identification of the rheological coefficients when the corresponding stress–strain curves are known from experiments.

5.3.2. Three–element models of viscoelastic fluids

Let us consider the three–element models of viscoelastic fluids composed by two different fluids and one type of elastic fibers (Fig. 12a). There are two types of the corresponding models called Jeffrey rheological model (Fig. 12b,c) which are similar in structure to the models sketched in Fig. 10b,c. An example of such fluids is a suspension of elastic capsules or biological cells with their internal liquid contents with the viscosity η_1 in the base fluid with viscosity η_2 . Then the elastic modulus E characterizes the elasticity of the shell (capsule or the cellular membrane).

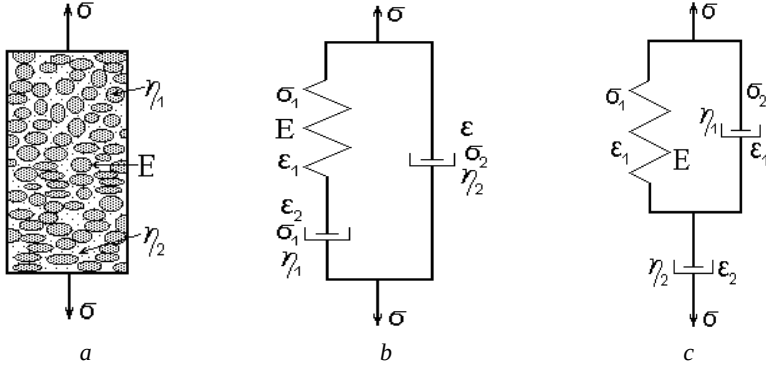


Fig. 12. Liquid material formed by liquid drops in elastic capsules suspended in another viscous liquid (a) and two different Jeffrey's models (b,c) of a viscoelastic liquid

Let us start with the model presented in Fig. 12b. The system of equations has the form

$$\begin{aligned}\sigma &= \sigma_1 + \sigma_2, & \varepsilon &= \varepsilon_1 + \varepsilon_2, \\ \sigma_1 &= \eta_1 \dot{\varepsilon}_1, & \sigma_2 &= \eta_2 \dot{\varepsilon}, & \sigma_1 &= E \varepsilon_2.\end{aligned}$$

By elimination of σ_1, σ_2 and $\varepsilon_1, \varepsilon_2$ one can derive the rheological relation in the form

$$\eta_1 \dot{\sigma} + E \sigma = E(\eta_1 + \eta_2) \dot{\varepsilon} + \eta_1 \eta_2 \ddot{\varepsilon}. \quad (15)$$

At **isotonic loading** $\sigma^* = \text{const}$ the linear non–homogeneous ODE of the second order with constant coefficients

$$\eta_1 \eta_2 \frac{d^2}{dt^2} \varepsilon + E(\eta_1 + \eta_2) \frac{d}{dt} \varepsilon = E \sigma^* \quad (16)$$

can be obtained from (15)

The general solution of the homogeneous equation (16) has the form $\varepsilon(t) = C_1 \exp(\lambda_1 t) + C_2 \exp(\lambda_2 t)$, where λ_1, λ_2 – the roots of the characteristic

equation for (16). The partial solution of the non-homogeneous equation is the linear function $\sigma^* t / (\eta_1 + \eta_2)$. To find the constants C_1, C_2 one must have two initial conditions for deformations. If the loading starts from the non-deformed state and with zero load velocities, the boundary conditions for (16) are $\varepsilon(0) = 0$ and $\dot{\varepsilon}(0) = 0$. Since $\lambda_1 = 0$, finally the solution of (16) is

$$\varepsilon(t) = \frac{\sigma^* t}{\eta_1 + \eta_2} - \frac{\sigma^* \eta_1 \eta_2}{E(\eta_1 + \eta_2)^2} \left(1 - \exp\left(-\frac{E(\eta_1 + \eta_2)}{\eta_1 \eta_2} t\right) \right). \quad (17)$$

Individual task: obtain the relaxation curve $\tilde{\varepsilon}(t)$ after the reloading of the material and calculate the relaxation time. Check the first and second order time derivatives of $\varepsilon(t)$ and $\tilde{\varepsilon}(t)$, and plot the curves $\varepsilon(t)$ and $\tilde{\varepsilon}(t)$ similar to Fig. 11a.

Individual task: Carry out the dynamical experiments with this rheological model and determine the dynamical elastic modules for the loads by oscillating stresses and strains. Compare the properties of this viscoelastic fluid model with the Maxwell's body.

Individual task: Repeat all the experiments and conclusions for the second Jeffrey's model (Fig. 12c) and compare it to the Maxwell's body.

5.4. Multi-element rheological models

Multi-elements models consists of $n \geq 4$ elements. The first example is the **double Maxwell model** (Fig. 13a) useful for the description of deformation of polymers. The **double Voigt model** (Fig. 13b) is used as the simplest model of the vertebral bone (viscoelastic body of the bone and the intervertebral disc). The **Burgers model** is a series connection of the Voigt and Maxwell models (Fig. 13c).

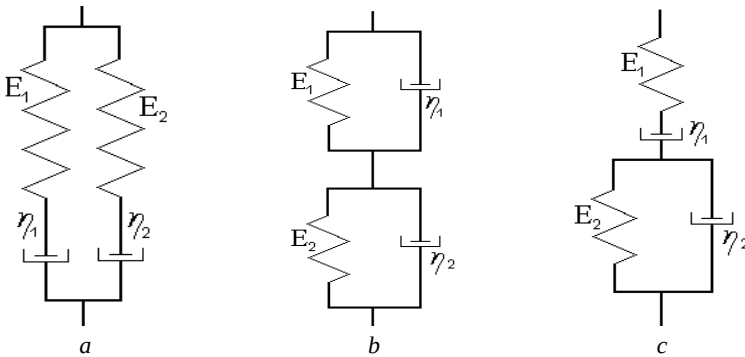


Fig. 13. Four-element rheological models: double Maxwell model (a), double Voigt model (b) and Burgers model (c)

Let us start with the **double Maxwell model** (Fig. 13a). To obtain its rheological relation, one can use the Maxwell's body equation (10). Let's in the left Maxwell element the general stress is σ_1 , in the right element the stress is σ_2 . Then the rheological equations (10) for the elements will be $E_1\eta_1\dot{\varepsilon} = E_1\sigma_1 + \eta_1\dot{\sigma}_1$ and $E_2\eta_2\dot{\varepsilon} = E_2\sigma_2 + \eta_2\dot{\sigma}_2$. Since the general stress σ in the parallel connection of both Maxwell's elements is $\sigma = \sigma_1 + \sigma_2$. One can express σ_1 and σ_2 by the method of inverse operator. The rheological equations for σ_1, σ_2 in the form of differential operators are

$$E_1\eta_1 \frac{d\varepsilon}{dt} = \left[E_1I + \eta_1 \frac{d}{dt} \right] \sigma_1, \quad E_2\eta_2 \frac{d\varepsilon}{dt} = \left[E_2I + \eta_2 \frac{d}{dt} \right] \sigma_2,$$

where I – is the unitary operator.

Then the expressions for σ_1, σ_2 as functions of $\varepsilon_1, \varepsilon_2$ can be obtained as

$$\sigma_1 = \left[E_1I + \eta_1 \frac{d}{dt} \right]^{-1} \left(E_1\eta_1 \frac{d\varepsilon}{dt} \right), \quad \sigma_2 = \left[E_2I + \eta_2 \frac{d}{dt} \right]^{-1} \left(E_2\eta_2 \frac{d\varepsilon}{dt} \right)$$

Designated the operators in the square brackets on the left-hand sides as $[G_1]$ and $[G_2]$ accordingly, one can obtain for the general stress $\sigma = \sigma_1 + \sigma_2$ $\sigma = E_1\eta_1[G_1]^{-1}\dot{\varepsilon} + E_2\eta_2[G_2]^{-1}\dot{\varepsilon}$. After application of the double operator $[G_1] \cdot [G_2]$ to each term in the rheological equation, one can get $[G_1][G_2]\sigma = (E_1\eta_1[G_2] + E_2\eta_2[G_1])\dot{\varepsilon}$. Substitution of the expressions for $[G_1]$ and $[G_2]$ one can get the final form of the rheological relation for the double Maxwell body for a viscoelastic liquid in the form

$$\eta_1\eta_2\ddot{\sigma} + (E_1\eta_2 + E_2\eta_1)\dot{\sigma} + E_1E_2\sigma = E_1E_2(\eta_1 + \eta_2)\dot{\varepsilon} + (E_1 + E_2)\eta_1\eta_2\ddot{\varepsilon}.$$

In the same way the rheological equation for the double Voigt model for a viscoelastic solid (Fig. 13b) can be obtained based on two equations (7) with different elastic and viscous material parameters. Since the two models are in a series connection, their deformations must be added $\varepsilon = \varepsilon_1 + \varepsilon_2$. Then, using the method of inverse operators one can obtain the final rheological relation in the form

$$(\eta_1 + \eta_2)\dot{\sigma} + (E_1 + E_2)\sigma = E_1E_2\varepsilon + (E_1\eta_2 + E_2\eta_1)\dot{\varepsilon} + \eta_1\eta_2\ddot{\varepsilon}.$$

The Burgers model of a viscoelastic liquid (Fig. 13c) can be treated in the same way. For the series connection of one Voigt model and one Maxwell model one can use (7) and (10) with different rheological coefficients $E_1\eta_1\dot{\varepsilon}_1 = E_1\sigma + \eta_1\dot{\sigma}$ and $\eta_2\dot{\varepsilon}_2 + E_2\varepsilon_2 = \sigma$. Then the total deformation can be calculated as

$$\dot{\varepsilon} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 = \frac{1}{E_1\eta_1} (E_1\sigma + \eta_1\dot{\sigma}) + [G]^{-1}\sigma, \quad [G] = EI + \eta \frac{d}{dt}.$$

Application of the operator $[G]$ to each term of the rheological equation gives its final form

$$\eta_1 \eta_2 \ddot{\sigma} + [(E_1 + E_2) \eta_1 + E_1 \eta_2] \dot{\sigma} + E_1 E_2 \sigma = E_1 E_2 \eta_1 \dot{\varepsilon} + E_1 \eta_1 \eta_2 \ddot{\varepsilon}.$$

Individual task: Conduct the isotonic, isometric and dynamic experiments on the double Maxwell model.

Individual task: Conduct the isotonic, isometric and dynamic experiments on the double Voigt model.

Individual task: Conduct the isotonic, isometric and dynamic experiments on the Burgers model.

Note, in all the cases any non-harmonic dynamic loads by the stresses $\sigma^*(t)$ or strains $\varepsilon^*(t)$ can also be carried out. Then the solutions of the corresponding non homogeneous ODEs will differ by only the partial solutions in the form of integrations of the given functions $\sigma^*(t)$ or $\varepsilon^*(t)$ according to the general theory of OEDs.

In the same way the rheological relations for the multi-element Maxwell model (known as Maxwell-Wiherst model, Fig. 14a), n -element Voigt model (Fig. 14b) with n different elastic and n different viscous parameters can be obtained. *It is proposed to do calculations yourself.*

An example of more complex 5-element model that corresponds to passive muscle tissue that is composed mostly by three types of fibers and two types of liquids presented in Fig. 15. The distributions of the internal stresses and deformations of each element is given in Fig. 15. The additive conditions for the stresses and strains, and the corresponding Hook's and Newton's laws are

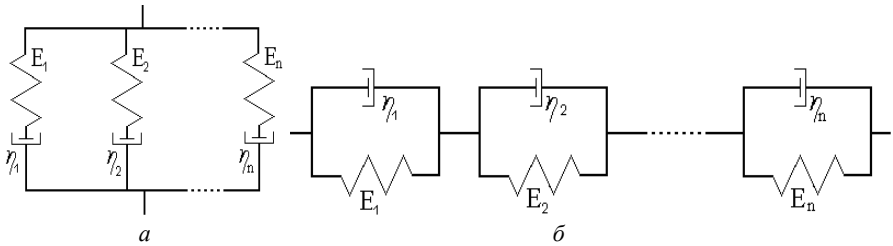


Fig. 14. General n -element Maxwell (a) and Voigt (b) models

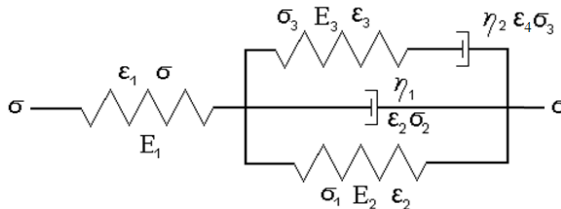


Fig. 15. Five-element rheological model

$$\varepsilon = \varepsilon_1 + \varepsilon_2, \quad \varepsilon_2 = \varepsilon_3 + \varepsilon_4, \quad \sigma = \sigma_1 + \sigma_2 + \sigma_3,$$

$$\sigma = E_1 \varepsilon_1, \quad \sigma_1 = E_2 \varepsilon_2, \quad \sigma_2 = \eta_1 \dot{\varepsilon}_2, \quad \sigma_3 = E_3 \varepsilon_3, \quad \sigma_3 = \eta_2 \dot{\varepsilon}_4.$$

Excluding the unknown values $\varepsilon_{1,2,3,4}$, $\sigma_{1,2,3}$ with the method of inverse operators give the rheological relationship

$$\begin{aligned} \eta_1 \eta_2 \ddot{\sigma} + [(E_1 + E_2) \eta_2 + (\eta_1 + \eta_2) E_3] \dot{\sigma} + (E_1 + E_2) E_3 \sigma = \\ = E_1 E_2 E_3 \varepsilon + ((\eta_1 + \eta_2) E_1 E_3 + E_1 E_2 \eta_2 \dot{\varepsilon} + E_1 \eta_1 \eta_2 \ddot{\varepsilon}). \end{aligned}$$

Individual task: Conduct the isotonic, isometric and dynamic experiments on the n–element Maxwell model.

Individual task: Conduct the isotonic, isometric and dynamic experiments on the n–element Voigt model.

Individual task: Conduct the isotonic, isometric and dynamic experiments on the five–element rheological model presented in Fig. 15.

Individual tasks: Several more sophisticated n–element rheological models are proposed for the detailed studies based on the schemes presented in this issue (Fig. 16a–f).

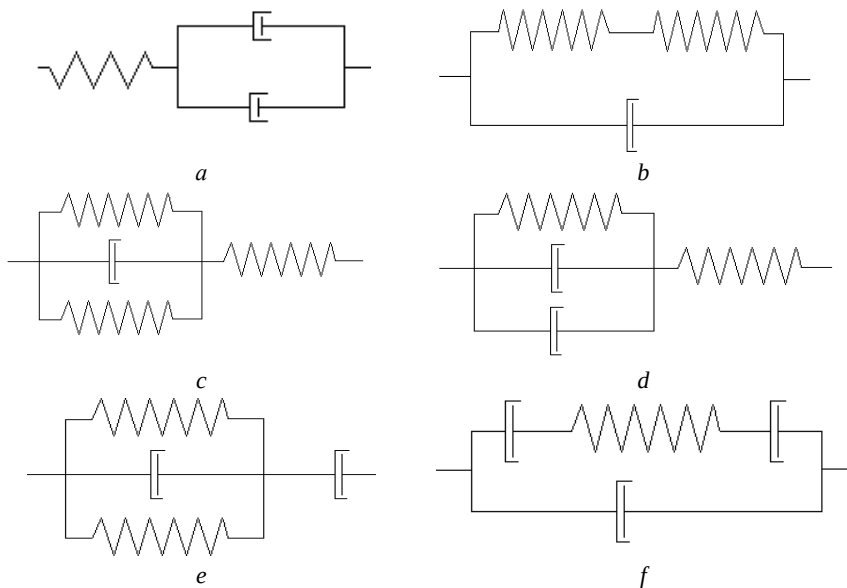


Fig. 16. The discrete rheological models for individual tasks

In the most general form the rheological equations for the viscoelastic solid and liquid bodies are

$$\dots + \varsigma_2 \frac{d^2 \sigma}{dt^2} + \varsigma_1 \frac{d \sigma}{dt} + \sigma = E \varepsilon + \eta \frac{d \varepsilon}{dt} + \kappa_1 \frac{d^2 \varepsilon}{dt^2} + \dots, \quad (18)$$

$$\dots + \varsigma_2 \frac{d^2 \tau}{dt^2} + \varsigma_1 \frac{d\tau}{dt} + \tau = \eta \frac{d\varepsilon}{dt} + \kappa_1 \frac{d^2 \varepsilon}{dt^2} + \kappa_2 \frac{d^3 v}{dt^3} + \dots, \quad (19)$$

where τ is the shear stress in liquids, $E, \eta, \varsigma_1, \varsigma_2, \varsigma_3, \dots, \kappa_1, \kappa_2, \dots$ are the rheological coefficients that must be identified from a comparative study of the ‘mathematical’ experiments on the rheological models and the measured experimental curves.

The relationships (18), (19), that were derived from the discrete springs and dampers rheological models can be also re-written in the tensor form for the continual media. For example, the uniform isotropic Voigt body with the rheological equation (7) will have the form

$$\sigma_{ik} = \lambda u_{||} \delta_{ik} + 2\mu \varepsilon_{ik} + \eta \frac{d\varepsilon_{ik}}{dt} \quad (20)$$

where λ and μ are Lamé coefficients.

The equation (20) must be substituted in the momentum equation

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} = \text{div}(\hat{\sigma}) + \rho \vec{f},$$

that gives the equation

$$\rho \frac{\partial^2 \vec{u}}{\partial t^2} - \eta \Delta \frac{d\vec{u}}{dt} = \mu \Delta \vec{u} + \left(\lambda + \frac{\mu}{3} \right) \text{div}(\vec{u}) + \rho \vec{f}, \quad (21)$$

which coincides with the classical momentum equation of solid mechanics at $\eta = 0$.

For the viscoelastic liquid materials their rheological models must be substituted into the Navier–Stokes equations in their general form

$$\text{div}(\vec{v}) = 0, \quad \rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \nabla) \vec{v} = -\nabla p + \text{div}(\hat{\tau}) + \rho \vec{f}. \quad (22)$$

For example, when one uses the continual version of Zener’s body

$$\tau_{ik} = \left[I + \varsigma_1 \frac{d}{dt} \right]^{-1} \left(2\eta + \kappa_1 \frac{d}{dt} \right) v_{ik},$$

the momentum equation will be

$$\left[I + \varsigma_1 \frac{d}{dt} \right] \left(\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \nabla) \vec{v} + \nabla p \right) - \frac{\kappa_1}{2} \frac{d}{dt} \Delta \vec{v} = \eta \Delta \vec{v} + \rho \vec{f} + \varsigma_1 \rho \frac{d\vec{f}}{dt}. \quad (23)$$

Therefore, the momentum equations for viscoelastic materials have the time derivatives of higher order in comparison to the classical equations and additional initial conditions for the derivatives of the displacements or velocities are needed. The corresponding theorems of existence and uniqueness of their solutions are still not proven but there are thermodynamic estimations based on the second law that restricts the values of the model parameters.

6. CLASSIFICATION OF RHEOLOGICAL MODELS OF NON-NEWTONIAN FLUIDS

Newtonian fluids exhibit the linear dependence $\tau_{ik} = 2\eta v_{ik}$ between their stress and strain rate tensors. The viscosity of such liquids $\eta = \eta(T, C_j)$ only depends on temperature T and, possibly, on the concentration of some dissolved substances with concentrations C_j , which could significantly change the viscosity of the suspension at even very low concentrations [7]. In this case, the viscosity remains independent of the shear rate, exposure time and other factors. The examples of the Newtonian fluids are: water, aqueous solutions of mineral components, vegetable oils, milk, purified juices, alcohols, air, gas and many others.

Materials for which the dependence $\tau_{ik}(v_{ik})$ is different from the linear one are called non-Newtonian, and there are various types of non-Newtonian behavior. Examples of the non-Newtonian liquids: polymer melts, suspensions of hard and soft particles, lubricants, food masses and many others (§1 and Fig. 4).

6.1. Liquids with transverse viscosity

In such liquids, the dependence $\tau_{ik}(v_{ik})$ is nonlinear due to the appearance of additional nonlinear terms, for example, second power of the tensor v_{ik}

$$\tau_{ik} = 2\eta v_{ik} + \tilde{\mu} v_{il} v_{lk} \quad \text{or} \quad \hat{\tau} = 2\eta \hat{v} + \tilde{\mu} \hat{v}^2 \quad (24)$$

where $\tilde{\mu}$ is the transverse viscosity. For the liquids with transverse viscosity, the normal stresses appear in purely shear flows. For example, in the Couette flow of such a liquid (Fig. 17a), the velocity vector $\vec{v} = (v(y), 0, 0)$ and the strain rate tensor have nonzero components $v_{12} = v_{21} = dv/dy$. Then (24) gives

$$\begin{aligned} \tau_{11} &= 2\eta v_{11} + \tilde{\mu} v_{21} v_{12} = \tilde{\mu} v_{12}^2 \neq 0, \\ \tau_{22} &= 2\eta v_{22} + \tilde{\mu} v_{21} v_{12} = \tilde{\mu} v_{12}^2 \neq 0, \\ \tau_{12} &= 2\eta v_{12} = \tau_{21} \neq 0. \end{aligned}$$

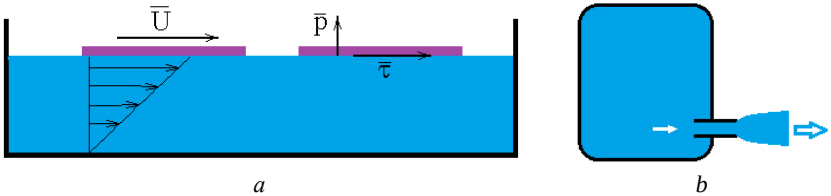


Fig. 17. Couette flow with normal and shear forces (a)
and expansion of the jet (b)

Thus, not only tangential, but also normal stresses τ_{11} , τ_{22} arise in such a liquid. Some paints have transverse viscosity, and their jets at the outlet of the spray gun is expanded due to the normal stress effect, thus covering a larger area (Fig. 17b).

Obviously, the addition in (24) of higher order terms like

$$\hat{\tau} = 2\eta\hat{v} + \tilde{\mu}\hat{v}^2 + \tilde{\mu}\hat{v}^3 + \dots \quad (25)$$

does not lead to new rheological models because according to the Hamilton–Cayley theorem any power $n > 2$ of a tensor is expressed in its first and second powers. Therefore, the rheological law (24) is the most general form of power dependencies. The fractional powers $\hat{\tau}^\alpha = 2\eta\hat{v}^\alpha + \tilde{\mu}\hat{v}^\beta$ are also presented in rheology for specific materials as approximations of the corresponding experimental curves [8, 9].

Another possibility to introduce nonlinearity into the dependence $\tau_{ik}(v_{ik})$ is to set the dependence of viscosity on the v_{ik} components. Since the scalar quantity η cannot depend on the components of the tensor (why?) and only depend on some combinations of the components called invariants, the dependence $\tau_{ik} = 2\eta(T, C_j, v_{ik})v_{ik}$ can be written in the only form $\eta = \eta(I_{1v}, I_{2v}, I_{3v})$ where

$$I_{1v} = \text{Tr}\{v_{ik}\} = v_{kk}, \quad I_{2v} = v_{xx}v_{yy} + v_{yy}v_{zz} + v_{xx}v_{zz} - v_{xy}^2 - v_{yz}^2 - v_{xz}^2, \quad I_{3v} = \det|v_{ik}|$$

are invariants of the tensor of the 2nd rank v_{ik} . For incompressible media, it is sufficient to leave the dependence $\eta = \eta(I_{2v})$ (why?), and it is convenient to redefine

$$I_{2v} \text{ as } \tilde{I}_2 = \sqrt{2(I_{1v}^2 - 2I_{2v})} = \sqrt{2(v_{xx}^2 + v_{yy}^2 + v_{zz}^2 + 2(v_{xy}^2 + v_{yz}^2 + v_{xz}^2))} = \sqrt{2v_{ik}v_{ik}},$$

then for laminar flows we get $\tilde{I}_2 = \dot{\gamma}$ – shear rate (check!).

For the dependence $\eta(\dot{\gamma})$, two rheologically different behaviors are possible: $\partial\eta/\partial\dot{\gamma} > 0$ or $\partial\eta/\partial\dot{\gamma} < 0$.

6.2. Shear–thickening liquids

Shear–thickening (or dilatant) fluids are media in which viscosity increases with increasing the shear rate ($\partial\eta/\partial\dot{\gamma} > 0$). Suspensions of hard non–smooth particles exhibit shear–thickening properties. The dilatancy mechanisms are particle interaction, collisions and dry friction between them that significantly increase at higher shear rates. The examples are particles of ore or sand in washing solutions, quicksand and similar natural and technical fluids. Another mechanism of shear–thickening is electrostatic or chemical interaction between the particles (Fig. 18), which leads to loss of flow energy and results in an increase in viscosity.

An increase in viscosity with an increase in shear rate depends on the concentration, size, shape and nature of the particles. Examples of dilatant media are also colloidal systems, chocolate masses and others.

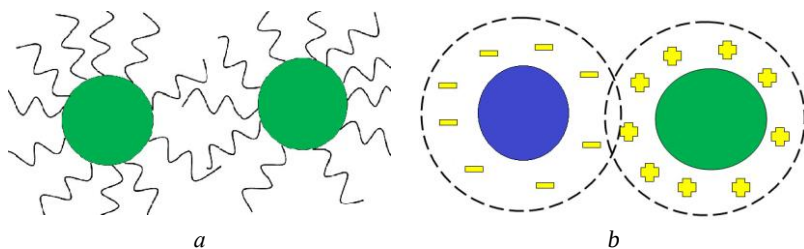


Fig. 18. A schematic representation of the chemical (a) and electrostatic (b) interaction of particles in shear-thickening suspensions

Recently, much attention has been paid to the development of effective “liquid armor” – a dilatant medium that exhibits fluidity at low impact forces, but at large forces (hit by a bullet or dagger) immediately undergoes a phase transition and becomes a solid body. One type of armor is based on silicone nanoparticles suspended in polyethylene glycol. This material is very light, with high ability for plastic deformations (Fig. 19a). At high strain rates (impact, bullet, dagger), the nanoparticles adhere, forming a microstructure with high strength (Fig. 19b).

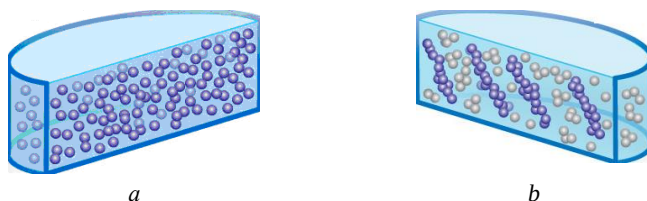


Fig. 19. A schematic representation of “liquid armor” before (a) and after (b) the phase transition, which is associated with structure formation upon absorption of impact energy

In connection with the progressive development of nanotechnology, such materials with unique rheological properties are being developed in a wide variety and are commercially available, including the laboratory research purposes.

6.3. Shear-thinning liquids

The viscosity of shear-thinning (or pseudoplastic) fluids decreases with increasing shear rate ($\partial\eta/\partial\dot{\gamma} < 0$). The mechanisms of shear-thinning behavior are unwinding of long molecular chains by the flow, orientation and stretching of polymer molecules in the flow. If pseudoplastic fluids contain elongated particles or polymer fibers, then in the flow they are oriented along streamlines, which leads to a decrease in friction between them, and to improved streamlining, i.e. to a decrease in viscosity with an increase in shear rate. Examples of such liquids are: polymer solutions, ketchup, blood, paints, juices with pulp, vegetable purees, paper pulp. Schematically, the change in the orientation of the particles of the pseudoplastic fluid in the flow at different

shear rates is shown in Fig. 20a. The rounded particles of such media are arranged in longitudinal chains (Fig. 20b in the center), in contrast to non-interacting particles (Fig. 20b, above), and dilatant media that form a microstructure (Fig. 20 b, below).

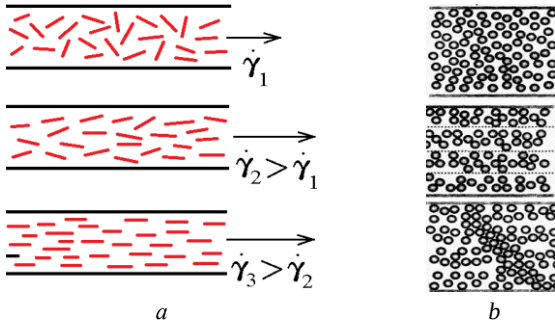


Fig. 20. The patterns of elongated (a) and rounded (b) particles in shear-thinning suspensions at different flow rates

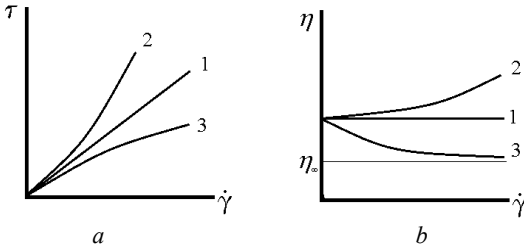


Fig. 21. The dependences $\tau(\dot{\gamma})$ (a) and $\eta(\dot{\gamma})$ (b) for Newtonian (1), shear-thickening (2) and shear-thinning (3) liquids; η_∞ is the asymptotic viscosity

In 1909, Ostwald proposed a power-law rheological model in the form $\tau = k(\dot{\gamma})^n$. Here, viscosity $\mu \equiv \tau / \dot{\gamma} = k(\dot{\gamma})^{n-1}$ is a power function of shear rate. When $n=1$ we have Newtonian fluid, when $n>1$ – it is shear-thickening, and when $0 < n < 1$ – it is shear thinning.

To compare their behavior, the

diagrams $\tau(\dot{\gamma})$ and $\eta(\dot{\gamma})$ are plotted in Fig. 21a and Fig. 21b, respectively.

6.4. Viscoplastic liquids

Viscoplastic liquids begin to flow only when the shear stress applied exceeds a certain critical value τ_0 , which is called the initial yield stress, i.e. $\dot{\gamma}=0$ when $\tau < \tau_0$ and $\dot{\gamma} > 0$ when $\tau > \tau_0$. The mechanism of viscoplasticity is associated with the presence of bonds between the particles at low or zero strain rates, due to which they can form a microstructure at rest (Fig. 22a). To destruction the microstructure and start the flow, a stress $\tau > \tau_0$ must be applied. Examples of such liquids are blood (Fig. 22b), toothpaste, tomato paste, solidifying or polymerizing solutions, etc.

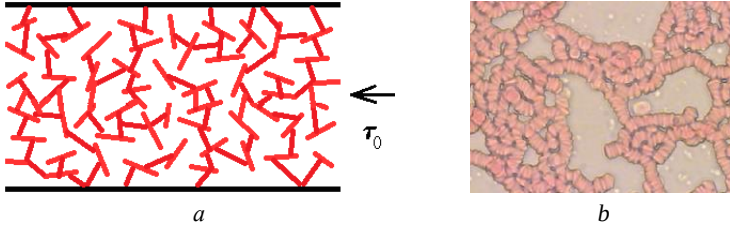


Fig. 22. A sketch of the microstructure formed by elongated particles (a) and the microstructure formed by the erythrocytes in blood (b) at rest

The simplest linear model of a viscoplastic liquid (the Bingham model, §2) is

$$\begin{aligned} \tau &= \tau_0 + \eta \dot{\gamma} & \text{at } \tau > \tau_0, \\ \dot{\gamma} &= 0 & \text{at } \tau < \tau_0, \end{aligned}$$

or in the tensor form
$$\tau_{ik} = 2 \left(\frac{\tau_0}{I_{2\tau}} + \eta \right) v_{ik}, \quad I_{2\tau} > 2\tau_0.$$

The first nonlinear model was proposed by Caisson in his experiments on a suspension of soot particles in water and has the form

$$\begin{aligned} \sqrt{\tau} &= \sqrt{\tau_0} + \sqrt{\eta \dot{\gamma}} & \text{at } \tau > \tau_0, \\ \dot{\gamma} &= 0 & \text{at } \tau < \tau_0, \end{aligned}$$

or in the tensor form
$$\tau_{ik} = 2 \left(\sqrt{\frac{\tau_0}{I_{2\tau}}} + \sqrt{\mu} \right)^2 v_{ik}, \quad I_{2\tau} > 2\tau_0.$$

A generalization of Caisson model was proposed by Schulman in the form $\tau^m = \tau_0^m + k \dot{\gamma}^n$, where $\eta = k \dot{\gamma}^{n/m}$ is the viscosity for the Ostwald power fluid.

To compare the rheological properties of the above discussed fluids, their dependencies $\tau(\dot{\gamma})$ and $\eta(\dot{\gamma})$ are plotted in Fig. 22a and Fig. 22b, respectively.

Similar to the power-law model, a generalized Hershel–Bulkley viscoplastic fluid model was proposed in the form $\hat{\tau} = 2\eta(I_{2v})\hat{\gamma}$, $\eta(I_{2v}) = kI_{2v}^{n-1} + \frac{\tau_0}{I_{2v}}$.

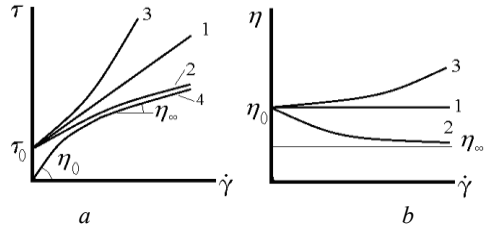


Fig. 22. Sketches of the dependences $\tau(\dot{\gamma})$ (a) and $\eta(\dot{\gamma})$ (b) for viscoplastic Bingham (1), Caisson (2), Schulman (3) and shear-thickening fluid (4)

In the case $\tau_0 = 0$, $n = 1$, it gives a Newtonian fluid; in the case $\tau_0 > 0$, $n = 1$ it is the linear Bingham plastic fluid; at $\tau_0 = 0$, $0 < n < 1$ it is a shear-thickening fluid, at $\tau_0 = 0$, $n > 1$ it is a shear-thinning fluid; in the case $\tau_0 \neq 0$, $n > 1$ it is a visco-

plastic fluid with shear–thickening behavior, and in the case $\tau_0 \neq 0$, $0 < n < 1$ it is a viscoplastic fluid with shear–thinning behavior.

The presented models allow us to conduct not only isometric and isotonic experiments with materials, but also dynamic experiments (§5) and solve steady and non–steady fluid mechanics problems [8, 9].

To build more complex models of viscoplastic media, discrete rheological models (see §5) are used with further replacement of the scalar variables by their tensor equivalents (see §6.5).

A number of very specific models obtained in experiments with various nonlinearly viscous liquids is presented in literature, such as the Ellis rheological model $\tau = \mu_0 \dot{\gamma} + k \dot{\gamma}^n$, the Steiger model $\tau = \frac{\dot{\gamma}}{k_1 + k_2 \tau^2}$, the Reiner–Phillipov

model $\tau = \left(\mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + (\tau / A)^2} \right)$, the Eyring model $\tau = k_1 \dot{\gamma} + k_2 \sin(\tau / A)$, the

Williams model $\tau = \mu_\infty \dot{\gamma} + \frac{k_1 \dot{\gamma}}{k_2 + \dot{\gamma}}$, the Haven model $\tau = \frac{\mu_0 \dot{\gamma}}{1 + k_3 \tau^n}$, where $A, k_{1,2,3}$

are additional empirical rheological coefficients.

6.5. Viscoelastic liquids

Viscoelastic fluids exhibit liquid properties at slow deformations (shear loads), while they behave as elastic solids at fast (impulse) loads. Therefore, viscoelastic materials exhibit both elastic and viscous properties at different ranges of the external loads and their rheological law can be written in the most general form as

$$F(\dot{\gamma}, \ddot{\gamma}, \ddot{\gamma}, \dots, \tau, \dot{\tau}, \ddot{\tau}, \dots) = 0.$$

Viscoelasticity is associated with the presence of elastic particles of various shapes or large molecules and molecular complexes (micro/nanostructures). The models of viscoelastic liquids consisting of springs and dampers are considered in detail §5. It should be noted that the rheological properties of real liquids are much

richer and more interesting [8–10], therefore, other types of elements of rheological models were introduced (Fig. 23). To model the initial yield stress effects, the Saint–Venant element (1870) which imitates the rest friction can be used (Fig. 23a).

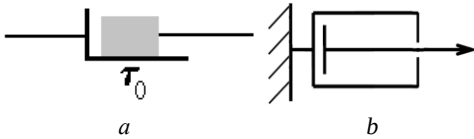


Fig. 23. Saint–Venant sliding element (a) and Pellet element (b)

It is depicted as a block lying on the rough surface. To bring the element into motion, it is necessary to apply a force exceeding the static friction stress (τ_0). The Pellet element is a viscous element with a deformation restriction (Fig. 23b). It describes an abrupt or monotonous change in the conformation of polymer molecules (unwinding

and straightening of their chains), after which the deformation stops. It is depicted as a piston in a closed tube filled with a viscous, exponential, or other fluid inside.

A parallel connection of the Saint–Venant element with a viscous one gives the Bingham model (Fig. 24a at $k = \eta$) or the model of a viscoplastic power fluid

$$\dot{\gamma} = \left(\frac{\tau - \tau_0}{k} \right)^{1/n}, \quad \tau > \tau_0; \quad \dot{\gamma} = 0, \quad \tau < \tau_0.$$

A combination of the Saint–Venant element with the Maxwell body gives the Bingham–Maxwell model (Fig. 24b)

$$\dot{\varepsilon} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 = \frac{\dot{\tau}}{E} + \frac{\tau - \tau_0}{\eta}, \quad \tau > \tau_0.$$

Note that when the friction element is connected in parallel with the spring, the latter, after unloading, will only partially return to its initial state until the stresses in the system become $\tau < \tau_0$, after which the spring remains in a state with permanent deformation, i.e. the friction element provides inelastic behavior of a number of the elastic elements.

Similarly, a composition of the Saint–Venant element with the Voigt body gives the Bingham–Voigt model. It is shown in Fig. 24c with the Ostwald liquid instead of Newtonian one in the viscous element. Its rheological relation is

$$\tau = \tau_1 + \tau_2 = E\varepsilon + \frac{\dot{\tau}}{E} + \tau_0 + k\dot{\gamma}^n, \quad \tau > \tau_0.$$

A combination of the Saint–Venant element with the Burgers body gives the popular Sheffield–Scott–Blair model (Fig. 24d) with the rheological relation

$$\dot{\gamma} = \frac{\dot{\tau}}{E_1} + \frac{\tau}{\eta_2} \exp\left(-\frac{E}{\eta_1} t\right) + \frac{\tau - \tau_0}{\eta_1}, \quad \tau > \tau_0.$$

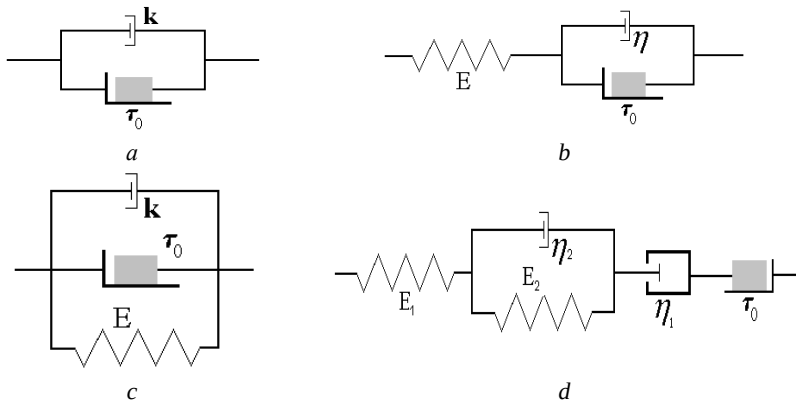


Fig. 24. Ostwald viscoplastic (a), Bingham–Maxwell (b), Bingham–Voigt (c), and Sheffield–Scott–Blair (d) discrete rheological models

The latter model describes well the rheology of baked bread and is used for elaboration, improvement and optimization mechanical tools for its slicing and processing. The criterion for tool optimization is to achieve the condition $\tau > \tau_0$ with the least plastic deformations of the sample is achieved [10].

6.6. Thixotropic liquids

Thixotropic fluids are an example of another class of non-Newtonian behavior that demonstrates the temporary effects. Thixotropy is the property of some liquids to change their viscosity over time under the influence of mechanical (stirring, shaking), thermal (heating, cooling), chemical, and some other influences. After the cessation of external load, the viscosity of such liquids increases with time [8–10]. In thixotropic fluid models, viscosity depends on some parameter(s) characterizing the microstructure of the medium and obeying additional evolutionary equation(s).

Examples of thixotropic liquids: blood, biogels, yogurt, kefir, honey, gelatin.

Thixotropy mechanism: the interaction of system components with a gradual change in the phase state. For example, honey or solution of gelatin exhibit slow increase in viscosity with time right up to final solidification. When they are heated, their viscosity decreases due to the phase transition and destruction of their microstructure. Yogurt or kefir at rest go into the state of a viscoelastic solid, but with mechanical stirring their viscosity decreases. Ketchup flows out of the container only after vigorous shaking.

The state of the microstructure of thixotropic liquids can be described by internal variable(s), like the length L_{ms} of the chains or fibers, the number N of particles in them, their relative shape, etc. Then, to say, $\tau_{ik} = 2\mu(T, L_{ms}(\dot{\gamma}))v_{ik}$. Upon substitution of this relation into (22), one will obtain an unclosed system of Navier–Stokes equations (4 equations with 5 variables). To close the system, one needs the corresponding evolution equation in the form

$$\zeta \frac{dL}{dt} = f(L, \dot{\gamma}) \quad \text{or} \quad \xi \frac{dN}{dt} = K^+(N, \dot{\gamma}) - K^-(N, \dot{\gamma}), \quad (26)$$

where the function $f(L, \dot{\gamma})$ is set from physical conditions, statistical mechanics, experimental results, etc., and ζ is the characteristic time of the microstructure change.

If $\zeta \ll T$, where T is the characteristic time, then in (26) we can neglect the left-hand side and get the expression $L = L(\dot{\gamma})$ from the condition $f(L, \dot{\gamma}) = 0$. In this case, thixotropy is reduced to viscoplasticity, and the internal variable disappears.

As a basis for constructing equations (26), a discrete model can be used. The very first formulation of such a model was done by M. Smoluchowski in 1916. He considered Brownian coagulation in colloids. At the initial time, the dispersed system is spatially homogeneous and contains aggregates of various masses composed from single particles. If the aggregate consists of k particles, then its mass $m_k = km_0$. Due to Brownian fluctuations, the aggregates approach each other and stick together,

forming new particles with a mass equal to the sum of the masses of the colliding particles. Paired collisions can lead to the formation of an aggregate of k particles if aggregates of $k-p$ and p particles collide and stick together (Fig. 25a,b). There are also negative sources when the k -particle aggregate sticks to the p -particle aggregate forming a new $(k+p)$ -particle aggregate. The Smoluchowski kinetic equation for pair interactions is

$$\frac{dN_k}{dt} = \frac{1}{2} \sum_{p=1}^{k-1} K(k-p, p) N_{k-p} N_p - \sum_{p=1}^{\infty} K(k, p) N_k N_p, \quad (27)$$

where $K(k-p, p) = K(p, k-p)$ is the core of the kinetic equation of coagulation, corresponding to the probability of collision and coalescence of the $(k-p)$ - and p -particle aggregates.

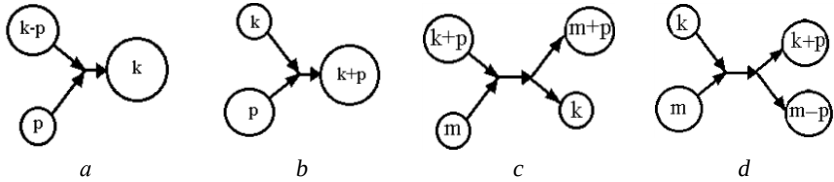


Fig. 25. Positive (a, c) and negative (b, d) adhesion of aggregates (a, b) and exchange interactions (c, d)

The continuous analogue of (27) can be written in the form

$$\frac{dN}{dt} = K^+(C, N, \dot{\gamma}) - K^-(C, N, \dot{\gamma}) - \text{div}(\vec{J}_N).$$

where $\vec{J}_N$ is the diffusion flux of aggregates [8,9].

There are also **anti-thixotropic** (or **rheopectic**) fluids, which, on the contrary, behave as fluids at low strain rates and as viscoelastic solids – at rapid loads (deformations). Such fluids can flow out of a slightly inclined vessel. The stress-strain curves for thixotropic and anti-thixotropic fluids at periodical loadings are presented in (Fig. 26 a–c).

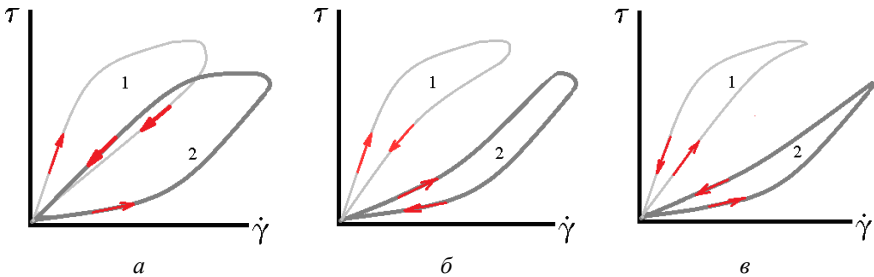


Fig. 26. Curves $\tau(\dot{\gamma})$ for thixotropic (1) and rheopectic (2) liquids during loading–unloading (a), absorption (b) and release (c) of energy

6.7. Fluids with internal degrees of freedom

6.7.1. Oriented fluids

An example of oriented fluids is liquid crystals (LC) which possess rheological properties of either liquids (fluidity, Fig. 27c) or crystals (anisotropy, Fig. 27a). LC consist of elongated, disk-, rod-shaped or more complex molecules that are ordered in a certain way (Fig. 27b,d,e,g). The orientation of the molecules is determined by the vector $\vec{n}$, which is called director (Fig. 27e,f). Due to thermal motion the particles oscillate around the direction $\vec{n}$ (Fig. 27b). Additional heating destroys the order and LC became a liquid (Fig. 27c).

LC can be divided into nematic (Fig. 27d), smectic (Fig. 27e,f) and cholesteric (Fig. 27g) types. External physical fields like electric or magnetic fields, can change the orientation of particles, which leads to a change in the optical and other physical properties of LC, that is widely used in different devices and technologies (displays, monitors, switches, sensors, etc.).

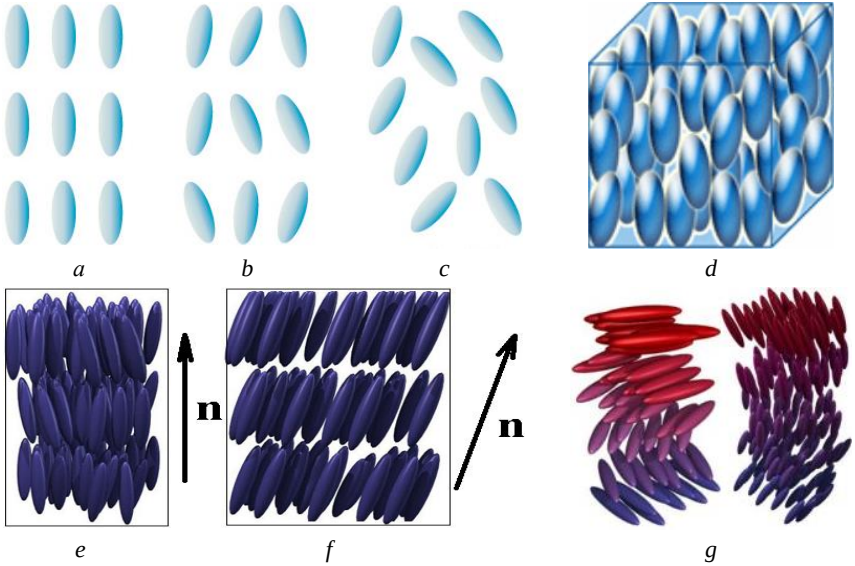


Fig. 27. The structure of solids (a), LC (b), liquids (c), nematics (d), smectics of type A (e) and type C (f) and cholesterics (g)

The rheological relation for LC has the form $\hat{\tau} = 2\mu\hat{v} + \hat{T}(\vec{n})$ where the tensor $\hat{T}(\vec{n})$ is constructed based on the properties of the material. For oriented fluids, the simplest way to build this additional tensor is $\hat{T}(\vec{n}) = \alpha\vec{n} \otimes \vec{n}$ (or $T_{ik} = \alpha n_i n_k$), where $\alpha = \alpha(T, \dots)$. The system of Navier–Stokes equations (22) must be completed

by the rheological relation for LC and the equation of evolution of the vector $\vec{n}$, which leads to a closed system of equations

$$\begin{aligned}\operatorname{div}(\vec{v}) &= 0, & \rho \frac{d\vec{v}}{dt} &= -\nabla p + \mu \nabla^2 \vec{v} + \operatorname{div}(\hat{T}(\vec{n})) + \rho \vec{f}, \\ \frac{d\vec{n}}{dt} &= G(\vec{n}, \vec{v}, \vec{f}, \dots)\end{aligned}$$

In cholesterics $\vec{n} = \vec{n}(z)$, where the Oz axis is the axis around which the particles are packed in a spiral (it is orthogonal to the plane of Fig. 27g).

6.7.2. Micropolar fluids

The particles of **micropolar fluids** can rotate (Fig. 28a) in space with an angular velocity $\vec{\omega}$ that differs from the speed of rotation of the liquid $\vec{\Omega} = \operatorname{rot}(\vec{v})$ due to slippage or active mechanisms. **Examples:** bacterial suspensions (Fig. 28b), micromotors, granular media.

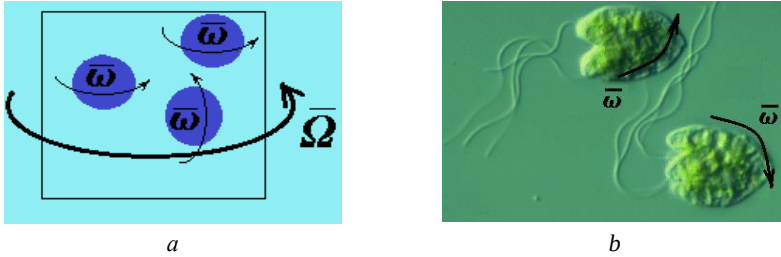


Fig. 28. The structure of a micropolar liquid (a) and a bacterial suspension with actively rotating cells (b)

The rheological law for micropolar liquids has the form $\hat{\tau} = 2\mu\hat{v} + \hat{T}(\vec{\omega} - \vec{\Omega})$. The tensor of active rotations $\hat{T}$ is constructed according to experimental data. Accordingly, the governing mass, momentum and energy equations must be completed by the equations for internal rotations, for example, in the form

$$\begin{aligned}\rho \frac{d\vec{v}}{dt} &= -\nabla p + \mu \nabla^2 \vec{v} + \operatorname{div}(\hat{T}(\vec{\omega} - \vec{\Omega})) + \rho \vec{f}, \\ \frac{d\vec{\omega}}{dt} &= G(\vec{\omega}, \vec{v}, \vec{f}, \dots).\end{aligned}$$

For the active micropolar liquids autocatalytic chemical reactions, energy absorption, and its conversion from chemical to mechanical energy (for living cells) must be taken into account in the function G .

6.7.3. Micromorphic fluids

These fluids are suspensions of deformable particles. In the course of fluid flows some part of the flow energy is spent on deformations of the particles appeared due to their inelastic collisions. The loss of energy resulted in the increase in effective viscosity in comparison with the basic fluid. **Examples:** cellular suspensions, blood, polymer solutions, suspensions of elastic capsules. The rheological law for such fluids has the form $\hat{\tau} = 2\mu\hat{\nu} + \hat{T}(\hat{W})$, where $\hat{W}$ is the tensor of microdeformations of particles [8–11].

To construct this tensor, a coordinate system associated with the particle's surface must be introduced and the mechanics of the surface deformation as a membrane, thin or thick shell, etc. must be formalized (Fig. 29a). Effective modeling for a small number of particles can be carried out by the finite element method (Fig. 29b). The model parameters must be then identified by the comparative study of the numerical simulations and experimental data.

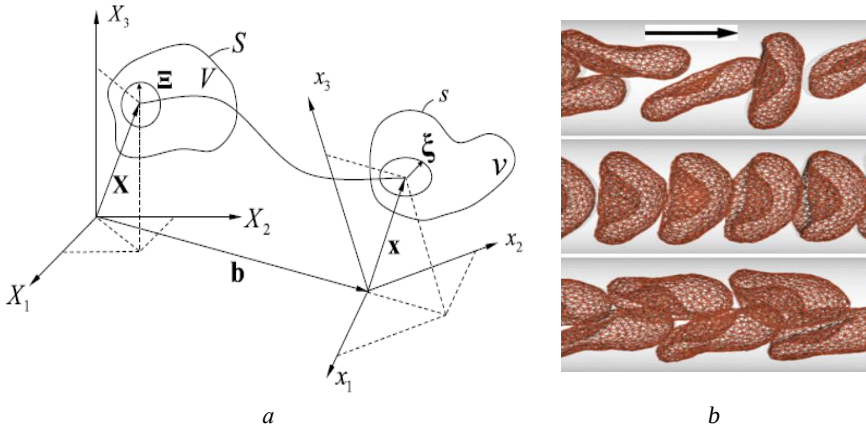


Fig. 29. Mechanics of microdeformations of one (a) and a group (b) of soft particles on the example of red blood cells

6.8. Models with integral operators

6.8.1. Materials with memory

In the materials with memory the stress state at a given moment is determined by the history of deformation. Such materials can be viscoelastic solid/fluid with different rheological behavior (shear-thinning or thickening, etc.). They are able to “remember” their stress-strain state and restore it later (Fig. 30a). **Examples:** memory alloys (Cu–Al–Ni, Ni–Ti, Fe–Mn–Si, Cu–Zn–Al, Cu–Al–Ni), memory polymers (polyurethanes, polystyrenes, and many others). Under certain conditions, such materials experience plastic and viscoplastic deformations (flow).

The rheological law for materials with memory can be written in the form

$$\hat{\tau}(t, \vec{r}) = \int_{-\infty}^t K(t, \tilde{t}) \hat{v}(\tilde{t}, \vec{r}) d\tilde{t}, \quad (29)$$

where the operator $K(t, \tilde{t})$ describes the entire history of deformation and formally corresponds to variable viscosity despite it has the dimension of stress ($[K] = \text{Pa}$). For liquids, (29) must be substituted into (22) and the momentum equation will be the integro-differential equation in the form

$$\rho \frac{d\vec{v}}{dt} = -\nabla p + \mu \nabla^2 \vec{v} + \text{div} \left(\int_{-\infty}^t K(t, \tilde{t}) \hat{v}(\tilde{t}, \vec{r}) d\tilde{t} \right) + \rho \vec{f}. \quad (30)$$

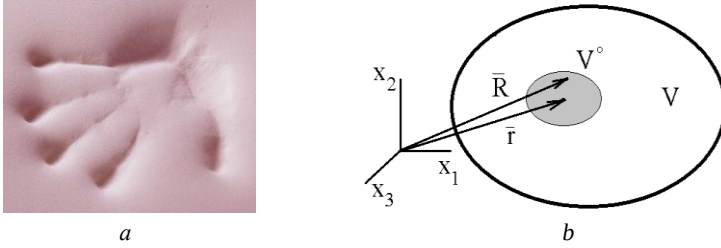


Fig. 30. A fingerprint “remembered” by a material with memory (a) and a scheme of material with nonlocal properties (b)

6.8.2. Materials with non-local properties

In such materials, the stress-strain state in each point of the medium depends on the deformations in a certain volume V° around this point (Fig. 30b), therefore, the rheological relation has the form

$$\hat{\tau}(t, \vec{r}) = \int_V K(\vec{r}, \vec{R}) \hat{v}(t, \vec{R}) d\vec{R}, \quad (31)$$

where the operator $K(\vec{r}, \vec{R})$ sets the uniform or non-uniform distribution of the influence of deformations in the point with radius-vector $\vec{R}$ on the stress in the point $\vec{r}$.

Examples: composites, biological tissues (due to nervous and chemical regulation).

7. CONCLUSION

At present, **rheology** is an actively developing field of science due to elaboration of new smart materials, synthetic polymers and composites, the development of new methods of physical and chemical processing of materials, recent studies of biological materials and their substitutes, successes in nanomaterials, nanophysics and nanoreology.

8. LIST OF REFERENCES

1. Gallegos G., Walters K. Rheology // Encyclopedia of life support systems / C. Gallegos (ed.). Vol. 1. Eloss Publ. Co., 2010. P. 1–14. URL: <https://www.eolss.net/>
2. Reiner M. Rheology // Elasticity and Plasticity. Encyclopedia of Physics, Vol. 3 / 6. / Flügge S. (ed.). Springer, Berlin, Heidelberg, 1958. P. 25–38. URL: https://doi.org/10.1007/978-3-642-45887-3_4
3. Walters K. History of rheology // Encyclopedia of life support systems / C. Gallegos (ed.). Vol. 1. Eloss Publ. Co., 2010. P. 15–30. URL: <https://www.eolss.net/>
4. Malkin A. Continuum mechanics as a ground for rheology // Encyclopedia of life support systems / C. Gallegos (ed.). Vol. 1. Eloss Publ. Co., 2010. P. 31–73. URL: <https://www.eolss.net/>
5. Sedov L. I. Mechanics of continuous media. In 2 volumes. Series in Theoretical and Applied Mechanics, ed. by R.K.T. Hseih. World Scientific Publ., 1997. URL: https://books.google.com.ua/books?id=To4GCwAAQBAJ&printsec=frontcover&hl=ru&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false
6. Landau L. D., Lifshits E. M. Theoretical Physics. Vol. 7. Theory of Elasticity. Pergamon Press, 1959. URL: https://books.google.pl/books/about/Theory_of_Elasticity.html?id=tpY-VkwCkAIC&redir_esc=y
7. Mezger Th. G. The Rheology Handbook: for users of rotational and oscillatory rheometers. Vincentz Network GmbH & Co KG, 2006. 299 p. URL: https://books.google.com.ua/books?id=N9Fdn0MEIDIC&printsec=frontcover&hl=ru&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false
8. Böhme G. Non-Newtonian Fluid Mechanics. Elsevier, 1987. 364 p. URL: <https://www.sciencedirect.com/book/9780444701862/non-newtonian-fluid-mechanics>
9. Deville M., Gatski Th. B. Mathematical Modeling for Complex Fluids and Flows. Springer Science & Business Media, 2012. 264 p. URL: <https://doi.org/10.1007/978-3-642-25295-2>
10. Christensen R. M. Theory of Viscoelasticity. An Introduction. 2–nd edition. Elsevier, 1982. URL: <https://www.sciencedirect.com/book/9780121742522/theory-of-visco-elasticity>
11. Cherevko V., Kizilova N. Complex flows of immiscible microfluids and nanofluids with velocity slip boundary conditions // Nanophysics, Nanomaterials, Interface Studies, and Applications / O. Fesenko, L. Yatsenko (eds.). Springer, 2017. P. 207–230. URL: <https://link.springer.com/book/10.1007/978-3-319-30737-4>