Introduction. Rheology: Subject and Goals

Rheology, as an independent branch of natural sciences, emerged more than 70 years ago. It originated from observations of "strange" or abnormal behavior of many well-known materials and difficulties in answering some "simple" questions. For example:

- paints are evidently liquids because they can be poured into containers, but why do they remain on vertical walls without sagging down, unlike many other liquids?
- clays look solid but they can be molded into a shape; they may occupy vessels the way any liquid does; why do clays behave like many liquids?
- yogurt does not flow out of a container (it has high viscosity), but after intensive mixing its viscosity decreases, and then increases again when left to rest, so which value of viscosity should be considered?
- concrete mix appears to be solid and rigid, but when subjected to an external force it changes its shape similar to liquids; what are the reasons for such behavior?
- parts made out of polymeric materials (plastics) look solid and hard, similar to parts made out of metal, but they are noticeably different: when force is applied to a metallic part it slightly changes its shape and maintains its new shape for a long time; this is not the case with plastics which also change their shape after force is applied but they continue to change shape; if this material is solid, why does it "creep"?
- pharmaceutical pastes (for example, toothpaste or body lotion) must be "liquids" when applied and they should immediately become "solids" to remain on skin; are they liquids or solids?
- sealants widely used in construction must be fluid-like to seal all spaces and to fill cavities, but then sealant must rapidly "solidify" to prevent sagging; is sealant liquid or solid?
- metals are definitely solids, but how is it possible to change their initial form by punching and stamping as if metal was liquid?

These are just few examples. It is common for them that they represent properties of many real materials and that they exhibit a mixture of *liquid-like* and *solid-like* properties. This shows that commonly used words "liquid" and "solid" are insufficient to describe their properties, and *new concepts* are need to understand properties of many real materials. A *new terminology* emerges from discoveries and description of new features of materials. *New methods* are needed to characterize and measure their properties. *New fields of application* can be expected from the application of new concepts and the results of studies. All these are the essence of *rheology.*

Superposition of liquid-like and solid-like features in behavior of technological materials is directly regarded as the consequence of *time effects*, i.e., the results of observations depend on a *time scale*. Possibly, this is the most common feature of the materials, which were listed above. Time by itself has no meaning, but time is a reflection of changes in material structure taking place during the period of observation (or experiment).

The main method of rheology consists of constructing *models*, which are useful in qualitative or (better) quantitative description of experimental results of mechanical behavior of different materials. Any natural science pretends to deal with reality and does so by means of *phenomenological models*. Any model is created not to reflect all, but the most important, characteristic features of an object. The concepts of *liquids* and *solids* are also models and their formal (mathematical) representation originated from the classical works by Isaac Newton and Robert Hooke.

Newton (1687) reflected upon a resistance of liquids to a cylinder rotating in a vessel. His ideas were converted to a more accurate form by Stokes, who formulated a general law of liquid-like behavior, known as the Newton-Stokes law. According to this concept, the deformation rate is expected to be proportional to stress and the constant coefficient of proportionality is called viscosity, which is a material parameter of liquid. This law assumes that, in flow of liquids, a force (or resistance to flow) is proportional to a velocity (of movement).

Hooke (1676) formulated a similar proposal concerning properties of solids. The law, named after him, was translated to modern form by Bernoulli and then by Euler. *Hooke's law* states that in deformation of solids, stress is proportional to deformation. The coefficient of proportionality is called *Young's modulus*.

Both models represent properties of many real materials and work well in describing their behavior with a considerably high degree of accuracy. However, there are many other materials which *are not described* by the Newton-Stokes and the Hooke laws. Rheology relies on the concept that *non-Newtonian* and *non-Hookean* materials exist in reality. These materials are interesting from both theoretical and applied aspects, and that is why such materials must be the objects of investigation.

It is important to emphasize that every model describes properties of real materials with a different degree of approximation. The Newton-Stokes and Hooke laws are not exceptions, and more strict and complex laws and equations give much better approximation of reality than the classical Newton-Stokes and Hooke laws known from school years.

Both basic phenomenological (i.e., taken as probable *assumptions*, but only assumptions) relationships (the Newton-Stokes and Hooke laws) do not include inherent structure of matter. Because matter consists of molecules and intermolecular empty spaces, every material is heterogeneous. At the same time, an observer sees a body as a homogeneous continuous mass without holes and empty spaces. The obvious way out of these contradictory evidences lies in the idea of the *space scale of observation*. This scale can be small enough to distinguish individual molecules or their parts. Then, molecules can be combined in regular arrangements, such as crystals, and then crystals can be organized in super-crystalline (or super-molecular) arrangements. All this leads to the concept of material *structure*, i.e., more or less well-organized and regularly spaced shapes. The structure might be well determined. This is the case, for example, of reinforced plastics and monocrystals. In other cases, "structure" can mean complex intermolecular interactions, which cannot be observed by direct methods. Rheology is specially interested in structured materials, because their properties change due to the influence of applied forces on the structure of matter.

The definition of rheology as a branch of natural science and the subject of rheological studies can be formulated based on the following argument. Traditionally, rheology is defined as "the study of deformations and flow of matter" (College Dictionary). However, this definition is ambiguous. The definition is close to mechanics of continuum, and does not distinguish special features of rheology.

The following points should be emphasized:

- Rheological studies are not about "deformation and flow" but about *properties* of matter determining its *behavior*, i.e., its reaction to deformation and flow.
- Rheology deals with materials having properties not described by the models of Newton-Stokes and Hooke. It is a negative statement (the rule of contraries). The positive statement is that rheology studies materials having properties described by *any* relationship between force and deformation. In this sense, the Newton-Stokes and Hooke laws are limiting cases formally lying on the border of rheology. The subject of rheology is not about all matters, but only those for which *non-linear* dependencies between forces and deformations or rates of deformations are main characteristics.
- Rheology is interested in materials, deformation of which results in *superposition* of *viscous and elastic* effects.
- Rheology studies materials with *structure changes* under the influence of applied forces.

One of the key words in rheology is the behavior of various real continuous media. What is the meaning of: "*behavior*"? For a body of finite size, it is a relationship between external action (forces applied to a body) and internal reaction (changes of a body shape). For continuous media this approach is extrapolated to a point and the relationship between forces and deformations at this point (i.e., changes of distance between two arbitrary points in a body) is examined. Thus, by discussing what happens in a body *at a point of reference*, the problem of a geometrical form of a body as such is avoided, but the subject of investigations are only its substantial, inherent properties.

The *first* main *goal* of rheology consists of establishing the relationship between applied forces and geometrical effects induced by these forces at a point. The mathematical form of this relationship is called the *rheological equation of state*, or the *constitutive equation*. The Newton-Stokes and Hooke laws are the simplest examples of such equations. Rheological equations of state can be (and they are!) very different for numerous real materials. The rheological equations of state found for different materials are used to solve macroscopic problems related to continuum mechanics of these materials. Any equation is just a model of physical reality.

The independent *second goal* of rheology consists of establishing relationships between rheological properties of material and its molecular structure (composition). This is related to estimating quality of materials, understanding laws of molecular movements

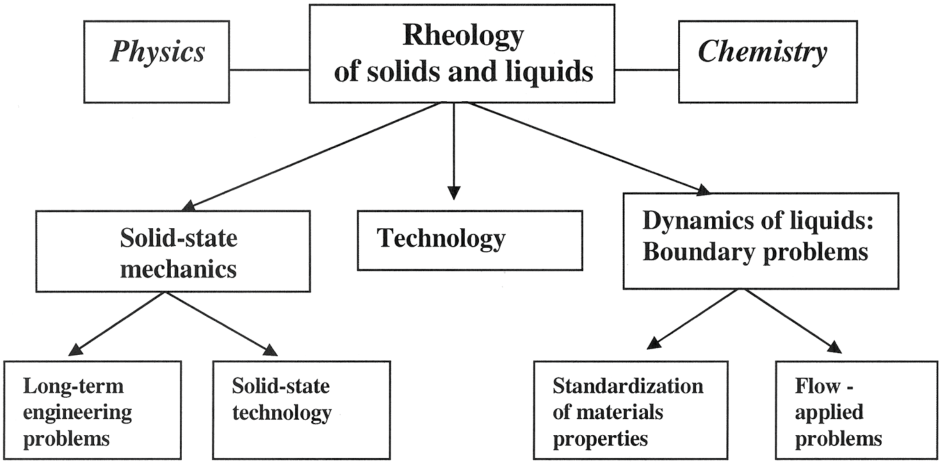

Fig. 1. Rheology as an interdisciplinary science – its place among other sciences.

and intermolecular interactions. The term *microrheology*, related to classical works by Einstein (1906, 1911), devoted to viscous properties of suspensions, is sometimes used in this line of thought. It means that the key interest is devoted not only to movements of physical points but also to what happens inside a point during deformation of medium. Therefore, it is a search for rheological equations of state of different materials based on the basic physical concepts. Then, the constants entering these models are related to various molecular parameters of material.

In its origin, the term "rheology" applies to flowing media, since the main root of the word means "to flow" (*rheo* in Greek). But it is very difficult to classify material as solid or fluid and, therefore, this term is now used for any material. As a result, many analytical methods used for solids and liquids are very similar. The majority of publications devoted to rheology and, consequently, the largest part of this book deal with flowing materials, whereas rheology of solids is frequently treated as a part of the mechanics of solids and discussed as a separate branch of science.

The place of rheology among other natural sciences and applied problems is shown in Figure 1. Rheology is a multi-disciplinary science having many relationships with fundamental physics and chemistry, as well as many applications in technology and engineering of materials and many fields of biological sciences.

Indeed, the connection between *rheology* and *physics* consists of explanation and predictions of rheological properties, based on knowledge of molecular structure and fundamental laws of physics (molecular physics, statistical physics, thermodynamics, and so on). The connection between *rheology* and *chemistry* consists of existing experimental evidences of direct correlation between chemical parameters (molecular mass and molecular mass distribution, chemical structure, intermolecular interactions, etc.) and rheological properties; therefore, it is possible to synthesize materials with desirable properties.

The second layer of interrelations consists of connection between *rheology* and *mechanics of continuum*. The results of rheological studies give the background for formulation of boundary problems in solid-state mechanics as well as in dynamics of liquids.

This includes governing equations and their solutions to find numerical values of macro-parameters, such as pressure, forces, displacements, etc.

In the framework of solid-state mechanics, such effects as a long-term behavior, engineering properties of materials as well as their technological properties are the direct objects of rheological analysis. Solutions of boundary problems in dynamics of liquids are used for analysis of flow in technology (calculation of pressure and output, resistance to movement of solid bodies in liquids, and so on), as well as for standardization of the methods of quality control in technology of liquid products.

It is worthwhile to list materials, for which the rheological analysis is the most important. In fact, such a list should include all materials, because the Newton-Stokes and Hooke laws are the limiting cases only. However, the following list gives an impression of fields that cannot be developed without participation of rheological studies:

- metals, alloys, and composites at large deformations and different technological operations
- concrete, ceramics, glass, and rigid plastics (including reinforced plastics) at long periods of loading
- polymer melts and solutions, including filled composites, rubbers
- foodstuffs
- lubricants, greases, sealants
- pharmaceuticals and cosmetics
- colloid systems including emulsions and detergents of any types
- paints and printing inks
- mud, coal, mineral dispersions, and pulps
- soils, glaciers and other geological formations
- biological materials such as bones, muscles and body liquids (blood, saliva, synovial liquid, and others).

It is worth mentioning that polymers and plastics continue to be the main object of rheological studies, and at least half of the publications on rheology are devoted to them.

To recapitulate, it seems useful to point out that the main ideas of the *Introduction* permit us to compose a dictionary of rheology.

Rheology is a science concerned with mechanical properties of various solid-like, liquid-like, and intermediate technological and natural products. It accomplishes its goals by means of *models* representing principal peculiarities of *behavior* of these materials. The behavior of material is a *relationship* between forces and changes of shape. A model gives a mathematical formulation of such relationship. *Rheological properties* are expressed by the model structure (i.e., its mathematical image) and values of constants included in the model are characteristics of material.

Rheological models are related to *a point*, which is a physical object including a sufficient number of molecules in order to neglect the molecular structure of matter and to treat it as a continuum. The rheological analysis is based on the use of *continuum* theories, meaning that the following is assumed:

- there is no discontinuity in transition from one geometrical point to another, and the mathematical analysis of infinitesimal quantities can be used; discontinuities appear only at boundaries

- properties of material may change in space (due to the gradient of concentration in multi-component mixtures, temperature distribution, or other reasons) but such changes occur gradually; these changes are reflected in space dependencies of material properties entering equations of continuum theories which must be formulated separately for any part of material surrounded by the boundary surfaces at which discontinuity takes place
- continuity theories may include an idea of anisotropy of properties of material along different directions.

Rheological behavior of material depends on *time* and *space scales* of observation (experiment). The former is important as a measure of the ratio of the (time) rate of inherent processes in a material to the time of experiment and/or observation; the latter determines the necessity to treat a material as homo- or heterogeneous.

The results of macroscopic description of behavior of real engineering and biological media, based on their rheological properties, are used in numerous applications related to technology of synthesis, processing, and shaping various materials listed above.

LITERATURE

Many books devoted to rheology were published during the 70 year history of this science. It is not possible to list all of them. The most important books which gave the input to development of rheology and reviewed results of principal rheological schools are cited in the text of this book. The same concerns many historically important and original publications.

The modern history of rheology began with the publication of several books in the 1940s which had a great impact on the education of future generations of rheologists. Among them it is necessary to recall:

T. Alfrey, **Mechanical Behavior of High Polymers**, *Interscience*, N.Y. 1948.
M. Reiner, **Twelve Lectures on Theoretical Rheology**, *North Holland Publ. Co.,* Amsterdam. 1949.
G.W. Scott Blair, **A Survey of General and Applied Rheology**, *Pitman*, London, 1949.

Those who are interested in special aspects of rheology may like to pay attention to the following books published more recently.

1 Deepak Doraiswamy, The origin of rheology: For a short historical excursion see http://sydney.edu.au/engineering/aeromech/rheology/Origin_of_Rheology.pdf
The development of rheology including sketches devoted to people who played the most important role in rheology can be found in a monograph:
R.I. Tanner, K. Walters, **Rheology: A Historical Perspective**, *Elsevier*, Amsterdam, 1998.

2 The state of rheology and the main results obtained until 1969 were summarized in a five volume book **Rheology. Theory and Applications**, Ed. F.R. Eirich, v. 1-5, *Academic Press*, London, 1956-1959.
One can find comprehensive analysis of rheology in the following books:
J. D. Ferry, **Viscoelastic Properties of Polymers**, *Wiley*, NY, 1980.
C.W. Macosko, **Rheology: Principles. Measurements and Applications**, *VCH*, New York, 1993.
F.A. Morrison, **Understanding Rheology**, *Oxford University Press*, New York, 2001.

3 The following books are devoted to the general theoretical background of rheology:
G. Astarita, G. Marucci, **Principles of Non-Newtonian Fluid Mechanics**, *McGraw-Hill*, New York, 1974.
R.B. Bird, R.C. Armstrong, O. Hassager, **Dynamics of Polymeric Liquids**, v. 1-2, *Wiley*, New York, 1987.
M. Doi, S.F. Edwards, **The Theory of Polymer Dynamics**, *Oxford Science Publisher*, Oxford, 1986.
J. Furukawa, **Physical Chemistry of Polymer Rheology**, *Springer*, Berlin, 2003.
H. Giesekus, **Phänomenologische Rheologie: Eine einführung**, *Springer*, Berlin, 1995.
R.R. Huilgol, N. Phan-Thien, **Fluid Mechanics of Viscoelasticity**, *Elsevier*, Amsterdam, 1997.
G.D.C. Kuiken, **Thermodynamics of Irreversible Processes: Application to Diffusion and Rheology**, *Wiley*, New York, 1994.
R.G. Larson, **Constitutive Equations for Polymer Melts and Solutions**, *Butterworths*, Boston, 1988.
R.G. Larson, **The Structure and Rheology of Complex Fluids**, *Oxford University Press*, New York, 1999.
A.I. Leonov, A.N. Prokunin, **Nonlinear Phenomena in Flows of Viscoelastic Polymer Fluids**, *Chapman and Hall*, London, 1994.
A.S. Lodge, **Elastic Liquids**, *Academic Press*, London, 1960.
H.C. Öttinger, **Stochastic Processes in Polymer Fluids**, *Springer*, Berlin, 1996.

W. R. Schowalter, **Mechanics of Non-Newtonian Fluids**, *Pergamon*, 1978.
N.W. Tschoegl, **The Phenomenological Theory of Linear Viscoelasticity**, *Springer*, Berlin, 1989.
A.S. Wineman, K.R. Rajagopal, **Mechanical Response of Polymers: Introduction**, *Cambridge University Press*, Cambridge, 2000.
4 The following monographs were devoted to different materials extensively studied by rheological methods:
D. Acierno, A.A. Collyer (Eds.), **Rheology and Processing of Liquid Crystal Polymers**, *Chapman and Hall*, London, 1996.
J.M.V. Blanshard, P. Lillford, **Food Structure and Behavior**, *Academic Press*, London, 1987.
O.E. Briskoe, **Asphalt Rheology: Relationship to Mixture**, *ASTM*, Philadelphia, 1987.
P. Coussot, **Mudflow Rheology and Dynamics**, *A.A. Balkema*, Rotterdam, 1997.
D.A. Drew, D.D. Joseph, S.L. Pasman (Eds.), **Particulate Flows: Processing and Rheology**, *Springer*, New York, 1998.
H.A. Faradi, J.M. Faubion (Eds.), **Dough Rheology and Baked Products Texture**, *Van Nostrand Reinhold*, New York, 1990.
Y.C. Fung, **Biomechanics: Mechanical Properties of Living Tissues**, *Springer*, New York, 1993.
R.K. Gupta, **Polymer and Composite Rheology**, *Marcel Dekker*, New York, 2000.
B.G. Higgins, **Coating Fundamentals: Suspension Rheology for Coating**, *TAPPI Press*, Atlanta, 1988.
M.J. Keedwell, **Rheology and Soil Mechanics**, *Elsevier Science*, London, 1984.
D. Laba (Ed.), **Rheological Properties of Cosmetics and Toiletries**, *Marcel Dekker*, New York, 1993.
G.D.O Lowe (Ed.), **Clinical Blood Rheology**, *CRC Press*, Boca Raton, 1988.
J.M. Mazumdar, **Biofluids Mechanics**, *World Scientific*, Singapore, 1992.
W.B. Russel, D.A. Saville, W.R. Schowalter, **Colloidal Dispersion**, *Cambridge University Press*, Cambridge, 1989.
A.V. Shenoy, **Rheology of Filled Polymer Systems**, *Kluwer*, Dordrecht, 1999.
G.V. Vinogradov, A.Ya. Malkin, **Rheology of Polymers**, *Springer*, Berlin, 1980.
5 Applied problems of rheology are presented (in addition to the above listed monographs) in the books:
V. Capasso, **Mathematical Modeling of Polymer Processing**, *Springer*, Berlin, 2003.
J.M. Dealy, K.F. Wissbrun, **Melt Rheology and Its Role in Plastics Processing**, Van Nostrand, New York, 1990.
C.D. Han, **Rheology in Polymer Processing**, *Academic Press*, NY, 1976.
C.D. Han, **Multiphase Flow in Polymer Processing**, *Academic Press*, NY, 1981.
A.I. Isayev (Ed.), **Injection and Compression Molding Fundamentals**, *Marcel Dekker*, New York, 1987.
A.I. Isayev (Ed.), **Modeling of Polymer Processing. Recent Developments**, *Hanser*, Munich, 1991.
J.M. Piau, J.F. Agassant (Eds), **Rheology for Polymer Melt Processing**, *Elsevier*, Amsterdam, 1996.
R.I. Tanner, **Engineering Rheology**, 2nd Edition, *Oxford University Press*, Oxford, 2000.
M.R. Kamal, A.I. Isayev and S.-J. Liu (Eds.), **Injection Molding Technology and Fundamentals,** *Hanser*, Munich, 2009.
J.F. Steffe, **Rheological Methods in Food Process Engineering**, 2nd Edition, *Freeman Press*, East Lansing, 1996.
J.L. White, **Principles of Polymer Engineering Rheology**, *Wiley*, New York, 1990.
6 Experimental methods of rheology are discussed in the following books:
H.A. Barnes, J. F. Hutton, K. Walter, **An Introduction to Rheology**, *Elsevier*, Amsterdam, 1989.
D.V. Boger, K. Walters, **Rheological Phenomena in Focus**, *Elsevier*, Amsterdam, 1993.
A. Collyer, D.W. Clegg (Eds), **Rheological Measurement**, *Chapman and Hall,* London, 1998.
A. Collyer (Ed.), **Techniques in Rheological Measurement**, *Chapman and Hall*, London, 1993.
J.M. Dealy, **Rheometers for Molten Plastics. A Practical Guide to Testing and Property Measurement**, *Van Nostrand Reinhold,* New York, 1982.
J.M. Dealy, P.C. Saucier, **Rheology in Plastics Quality Control**, *Hanser*, Munich, 2000.
G.F. Fuller, **Optical Rheometry of Complex Liquids**, *Oxford University Press*, New York, 1995.
H. Janeschitz-Kriegl, **Polymer Melt Rheology and Flow Birefringence**, *Springer*, Berlin, 1983.
W.-M. Kulicke, B.C. Clasen, **Viscometry in Polymers and Polyelectrolytes**, *Springer*, Berlin, 2004.
V.I. Levitas, **Large Deformation of Materials with Complex Rheological Properties at Normal and High Pressures**, *Nova Science*, New York, 1996.
A.Ya. Malkin, A.A. Askadsky, V.V. Kovriga, A.E. Chalykh, **Experimental Methods of Polymer Physics**, *Prentice-Hall*, Englewood Cliffs, 1983.
K. Walters, **Rheometry**, *Chapman and Hall*, London, 1975.
R.W. Whorlow, **Rheological Techniques**, *Ellis Harwood*, New York, 1992.
7 Computational methods are very important in applications of rheology, because of rather complicated equations used in calculation. However, although many papers in journals have been published only a very limited number of books are devoted to this problem, for example:

T. J. Chung, **Computational Fluid Dynamics**, *Cambridge University Press*, New York, 2002.
M. J. Crochet, A. R. Davies, K. Walters, **Numerical Stimulation of Non-Newtonian Flow**, *Elsevier*, Amsterdam, 1984.
R.G. Owens, T.N. Phillips, **Computational Rheology**, *Imperial College Press*, London, 2002.
J.R.A. Pearson, S.M. Richardson (Eds), **Computational Analysis in Polymer Processing**, *Applied Science Publishers*, London, 1983.
C. Pozdrikidis, **Fluid Dynamics. Theory, Computation and Numerical Simulation**, *Kluwer Academic Publisher*, Dordrecht, 2001.
C.L. Tucker (Ed.), **Computer Modeling for Polymer Processing**, *Hanser*, Munich, 1989.

Papers devoted to rheology appear in a large number of journals, but there are six special journals devoted to rheology, as follows:
Journal of Rheology
Journal of Non-Newtonian Fluid Mechanics
Nihon Reorogi Gakkaishi (Journal of Society of Rheology Japan)
Rheologica Acta
Applied Rheology
Korea-Australia Rheology Journal
New results in different branches of rheology can be found in these journals.