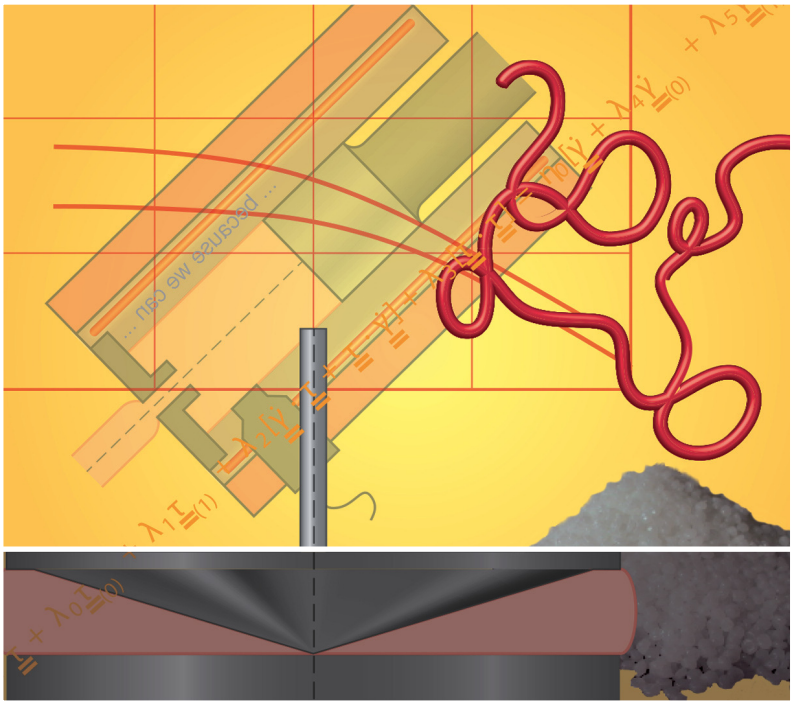
Tim A. Osswald
Natalie Rudolph

Polymer Rheology

Fundamentals and Applications



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Dedication

We dedicate this book to our friend, colleague, and mentor Professor Dr.-Ing. Dr. h.c. Gottfried W. Ehrenstein. His lifelong commitment to learning, teaching, and research has inspired more than a generation of students and engineers, and has resulted in a continuous flow of ideas and innovation in plastics technology.

Preface

Designed to provide a polymer rheology background to both engineering students and practicing engineers, this book is written at an intermediate level with the technical information and practical examples required to enable the reader to understand the complex rheological behavior of polymers and its far-reaching consequences. It also provides the necessary decision-making tools for the appropriate choice of rheological testing methods, and the means to troubleshoot rheology related problems encountered in polymer processing. The organization of Polymer Rheology – Fundamentals and Applications and the practical examples throughout the book make it an ideal textbook and reference book, and the information provided is particularly valuable to processors and raw materials suppliers.

The authors would like to acknowledge the invaluable help of many during the preparation of this manuscript: our colleagues at the Polymer Engineering Center at the University of Wisconsin-Madison and at the Institute for Polymer Technology at the Friedrich-Alexander-University in Erlangen, Germany. In particular we would like to thank Dr. Andrew Schmalzer for serving as a sounding board and for his input, John Puentes for helping with the example problems in Chapter 4, Chuanchom Aumnate for the measurements used in the examples in Chapters 2 and 5, and Camilo Perez for reviewing Chapter 3. We are grateful to Tobias Mattner for his outstanding job in not only drawing the figures, but also making excellent suggestions on how to more clearly present the information. Thanks are due to Dr. Christine Strohm for her valuable expertise in editing this book. Dr. Nadine Warkotsch, Dr. Mark Smith and Jörg Strohbach of Carl Hanser Verlag in Munich are thanked for their support throughout this project. Above all, the authors would like to thank their families for their continued support of their work and their input throughout the writing of this book.

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Contents

1 Introduction to Rheology

On December 9th of 1929, a little over a month after the Wall Street crash, and seven years after he published his book *Fluidity and Plasticity* [1], Eugene Bingham (Fig. 1.1), a chemistry professor at Lafayette College in Easton, Pennsylvania, and a group of chemists, engineers, and physicists met for the first time in Washington D.C.; they called themselves the *Society of Rheology*. Hence, for the first time the word rheology, coined by Markus Reiner and Eugene Bingham in 1920, was officially used[1].

Figure 1.1
Professor Eugene Bingham, in 1945 shortly before his death (Courtesy of Special Collections & College Archives, Skillman Library, Lafayette College)

[1] The roots of the word rheology are the Greek "reo" (flow) and "logos" (study).

However, the history of the field of rheology goes back centuries prior to Bingham and Reiner. A historical review is not complete until the more important events and discoveries through time, and the people who made those events and discoveries possible, have been identified. In Table 1.1 we list these events, discoveries, and important publications. If we inadvertently left out some, we apologize.

Table 1.1 Historical overview of the field of rheology

When	Who	What	Ref
1663	B. Pascal	Published works on inviscid fluids	[2]
1678	R. Hooke	Published work on elastic springs	[3]
1687	I. S. Newton	Published work on viscous fluids	[4]
1705	Bernoulli brothers	Publish the Bernoulli equation	[5]
1807	T. Young	Proposes the elastic (Young's) modulus	[6]
1820	C. Navier	Describes behavior of Newtonian fluids which eventually becomes the Navier-Stokes equation	[7]
1822	A. Cauchy	Describes stress and strain and formulates the Cauchy deformation tensor	[7]
1829	S. Poisson	Describes Poisson's ratio, ν	[8]
1839	G. Hagen	Builds the first capillary viscometer	[9]
1840	J. L. M. Poiseuille	Studies the rheology of blood and builds a capillary viscometer	[10]
1845	G. G. Stokes	Formulates a three dimensional Newtonian fluid model	[11]
1849	G. G. Stokes	Studies the parabolic velocity distribution in a capillary	[5]
1851	G. G. Stokes	Sphere fall experiments	[12]
1859	A. V. Lourenço	Observes viscosity increase with an increase in molecular weight	[13]
1861	A. Lipowitz	Builds a penetrometer to measure the hardness of a gel with a sinking weight	[14]
1861	T. Graham	Coins the word "Colloid"	[15]
1867	J. C. Maxwell	Formulates the viscoelastic Maxwell model	[16]
1873	J. D. Van der Waals	Publishes work on intramolecular forces	[17]
1874	L. Boltzmann	Publishes the superposition principle	[18]
1876	L. Boltzmann	Publishes work on the memory function	[19]
1881	M. Margules	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[20]
1886	M. M. Couette	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[21]
1888	M. M. Couette	Builds the first concentric cylinder system to measure viscosity; the drag flow viscometer or the Couette device	[22]
1890	W. Thomson-Kelvin	Describes a "solid viscosity", meaning a viscoelastic solid, known today as the Kelvin model	[5]
1890	W. Voigt	Publishes experiments on viscoelastic solids	[23]
1891	W. Ostwald	Builds a capillary viscometer, Ostwald viscosimeter	[14]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1894	J. Finger	Formulates the Finger-Strain Tensor for shear and elongational deformation test specimens	[24]
1905	F. T. Trouton	Derives the equation $\mu_E = 3\mu_S$, which describes the relation between elongational and shear viscosities, known today as the Trouton viscosity	[25]
1906	A. Einstein	Derives the equation $\mu = \mu_0\left(1+2.5\phi\right)$, which defines the viscosity of a suspension as a function of the volume fraction of solid particles	[26]
1916	E. Bingham	Describes fluids with a yield stress; the Bingham fluid	[27]
1920	H. Staudinger	Describes polymers as rigid rods that he calls macromolecules	[28]
1922	E. Bingham	Publishes his book "Fluidity and Plasticity"	[29]
1923	A. de Waele	Derives a power relation between viscosity and rate of deformation; the power-law model.	[30]
1925	W. Ostwald	Two years after de Waele, derives the power relation between viscosity and rate of deformation; the power-law model or the Ostwald-de Waele model	[31]
1927	S. B. Ellis	Publishes work on flow behavior	[5]
1928	E. Hatschek	Publishes his book "The Viscosity of Liquids"	[32]
1929	E. Bingham	Founds the Society of Rheology	[33]
1929	R. Eisenschitz, B. Rabinowitsch and K. Weissenberg	Propose the rheological energy triangle	[34]
1929	B. Rabinowitsch	Derives a correction factor for the shear rate of non-Newtonian fluids in capillary viscometers	[35]
1929	H. Jeffreys	Publishes his book "The Earth", in which he describes "elastoviscous" (viscoelastic fluids) materials	[36]
1930	C. W. Brabender	Builds a dough kneader; Farinograph or Extensograph	[14]
1931	A. Nadai	Publishes his book "Plasticity"	[37]
1934	M. Mooney	Proposes a "shearing disc viscometer" or parallel disc viscometer	[38]
1934	M. Mooney and R. H. Ewart	For the first time use a cone-and-plate rheometer	[39]
1935	H. Freundlich	Coins the word "Thixotropy" to describe changes in fluid behavior caused by movement	[40]
1935	J. M. Burgers	Develops a viscoelastic model by combining the Maxwell and the Kelvin-Voigt models	[41]
1936	E. Guth and R. Simha	Modify Einstein's 1906 equation to $\mu = \mu_0\left(1+2.5\phi+14.1\phi^2\right)$ for the viscosity of a suspension	[42]
1938	G. W. S. Blair	Publishes his book "An Introduction to Industrial Rheology", for the first time using the word "rheology" in the title of a book	[43]
1940	M. Mooney	Publishes work on rubber elasticity	[44]
1945	M. Reiner	Proposes that the theories of fluid viscosity also apply to polymer melts	[45]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1945	Brookfield Company	First Brookfield rotational viscometer is marketed in Stoughton, Massachusetts	[46]
1946	M. S. Green and A. V. Tobolsky	Propose the Transient Network Model for uncross-linked polymers	[47]
1946	R. J. Russell	Measures normal stresses using parallel disc and cone-and-plate rheometers	[48]
1947	K. Weissenberg	Discovers the rod climbing effect, today known as the Weissenberg Effect	[49]
1948	R. S. Rivlin	Applies theories of fluid viscosity to polymer melts	[50]
1948	G. W. S. Blair	First International Congress on Rheology	[51]
1953	P. E. J. Rouse	Proposes a bead-spring model for cross-linked polymers; known as the Rouse model	[52]
1955	M. L. Williams, R. F. Landel and J. D. Ferry	Propose the time-temperature superposition principle	[53]
1955	Haake Company	Rotational viscometer is marketed in Berlin and Karlsruhe, Germany	[46]
1956	B. H. Zimm	Includes hydrodynamic interactions in the Rouse model for dilute polymeric suspensions: Rouse-Zimm model.	[54]
1956	A. Lodge	Expands the Transient Network Model by Green and Tobolsky	[55]
1956	F. R. Eyrich	Publishes his book “Rheology – Theory and Applications”	[56]
1957	E. B. Bagley	Derives the entrance pressure corrections for capillary viscometers, known today as Bagley end correction factor	[57]
1958	W. P. Cox and E. H. Merz	Propose a relation between frequency in the oscillatory test and rate of deformation in the rotational viscometer (Cox-Mertz relation)	[58]
1960	R. B. Bird, W. E. Stewart and E. Lightfoot	Publish their book “Transport Phenomena”, nicknamed “BSL”	[59]
1960	A. S. Lodge	Publishes his book “Elastic Liquids”	[60]
1960	M. Reiner	Publishes his book” Deformation, Strain and Flow”	[61]
1962	A. Kaye	Develops the integral viscoelastic model that later became known as the K-BKZ model	[62]
1963	B. Bernstein, E. Kearsley and L. Zapas	Develop the integral viscoelastic model that Kaye published 2 years earlier. The model became known as the K-BKZ model	[63]
1965	M. M. Cross	Proposes the Cross model for shear-thinning fluids with a small shear rate Newtonian plateau	[64]
1966	H. Giesekus	Develops the differential viscoelastic model that became known as the Giesekus model	[65]
1967	S. F. Edwards	Proposes Entanglement Theory for polymers	[66]
1968	P. J. Carreau	Proposes a viscosity model with a small and large shear rate Newtonian plateau; Bird-Carreau Model	[67]

Table 1.1 (*continued*) Historical overview of the field of rheology

When	Who	What	Ref
1969	J. Meissner	Designs the uniaxial elongational rheometer	[68]
1971	P. G. DeGennes	Proposes the Reptation Model for polymer molecules	[69]
1977	R. B. Bird, R. C. Armstrong and O. Hassager	Publish their book "Dynamics of Polymeric Liquids"	[70]
1977	R. B. Bird, O. Hassager, R. C. Armstrong and C. F. Curtis	Publish their book "Kinetic Theory"	[71]
1982	J. M. Dealy	Publishes his book "Rheometers for Molten Plastics"	[72]
1985	R. B. Bird and H. Giesekus	Develop model for non-linear deformation behavior	[46]
1986	M. Doi and S. F. Edwards	Further develop the Reptation model	[73]
1990	J. M. Dealy and K. F. Wissbrun	Publish their book "Melt Rheology and Its Role in Plastics Processing"	[74]
1994	C. W. Macosko	Publishes his book "Rheology: Principles, Measurements and Applications"	[75]
1997	P. J. Carreau, D. C. R. DeKee and R. P. Chhabra	Publish their book "Rheology of Polymeric Systems – Principles and Applications"	[76]

1.1 The Field of Rheology

While the motto of the Society of Rheology has always been the quote by Simplicius and Heraclitus "Πάντα ῥεῖ" (Panta rei) [77–81] or "everything flows," the field of rheology covers the behavior of perfectly viscous liquid (Newtonian fluid) materials and perfectly elastic solid (Hookean solid) materials, as depicted in the diagram in Fig. 1.2. From the outside, rheology is framed by the rigid solid, or Euclidean solid, and the ideal inviscid fluid, or Pascalian fluid. The Euclidean solid and Pascalian fluid are both mathematical idealizations. In the case of the Euclidean solid we assume that the body does not deform, and when it moves, it does so by pure translation and rotation. On the other hand, the assumption for the Pascalian fluid is that the stresses acting on the fluid are only a result of pressure, or hydrostatic stresses, and not the result of deformation during flow. From a material behavior point of view, a Euclidean solid has an infinite modulus, while a Pascalian fluid exhibits zero viscosity, two unrealistic extremes.

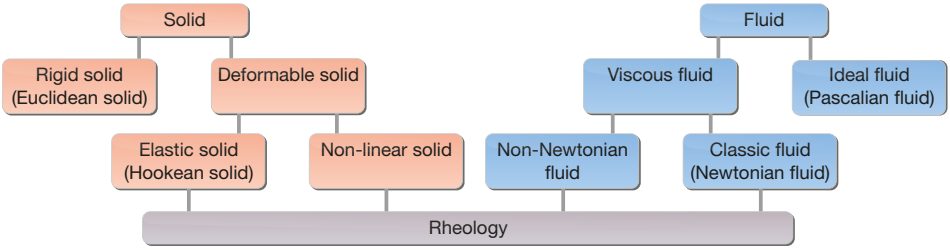

Figure 1.2 The field of rheology in perspective

While the field of rheology encompasses materials with a finite modulus and a measurable viscosity, most materials are neither perfectly viscous liquids nor perfectly elastic solids, but viscoelastic materials that can be described from a fluids or a solids point of view by a rheologist or a solid mechanician, respectively. Either way, when deforming complex materials such as polymers, there will always be a viscous and an elastic force component. To simplify our lives and make calculations and predictions possible, particularly when the flow geometry is complex, such as plastic flow during injection molding, we often drop the elastic response of plastics during flow.

In 1929, Eisenschitz, Rabinowitsch, and Weissenberg [7] proposed a triangular coordinate system (Fig. 1.3) to clarify the boundaries of the field of rheology. It represents the work or energy in all rheological phenomena in the form of kinetic energy, elastic or stored energy, and dissipated or lost energy. It is a simple and descriptive way to illustrate the interconnection between these energies or work. In most cases, the state of a body or system is represented by a point in the interior of the triangle, where the distance a is the fraction of the total energy represented by kinetic energy, b is the fraction representing elastic or stored energy, and c is the fraction representing dissipated or lost energy, such that

$$a + b + c = 1 \tag{1.1}$$

Eisenschitz, Rabinowitsch and Weissenberg called the line AB "Elasticity," which represents a Hookean solid or perfectly elastic solid. Vertex A represents a pure Euclidean solid (or Pascalian liquid when on line AC) where all the external work is converted to kinetic energy, as would be the case for an infinitely stiff body. Furthermore, they called line AC "Viscosity," which represents a Newtonian fluid or perfectly viscous liquid where all external work is dissipated or lost. On that line, vertex A represents an infinite Reynolds number in fluid mechanics. Line BC, which they called "Relaxation," represents creeping viscoelastic flows, and is the domain where we typically see the field of rheology of highly viscous materials such as polymers. Vertex C represents a creeping flow or Stokes flow where the Reynolds number is very low. In such flows inertial effects are negligible when compared to the forces caused by viscous friction.

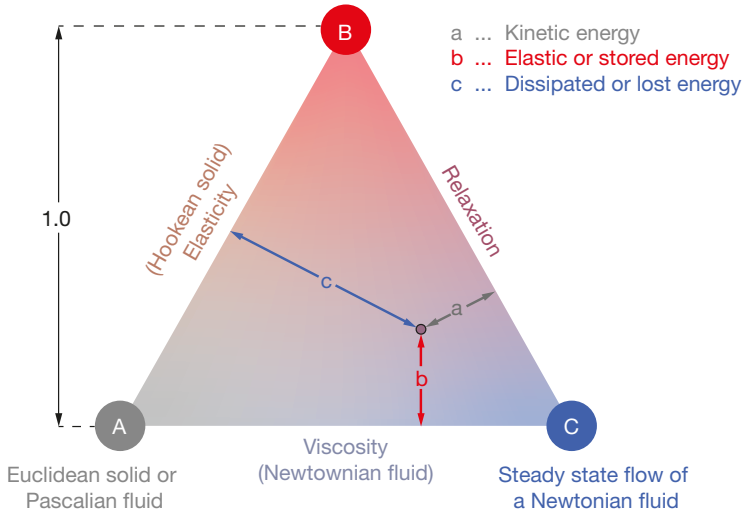

Figure 1.3 Rheological energy in triangular coordinates

1.2 Viscous Liquids or the Newtonian Fluid

Sir Isaac Newton (Fig. 1.4) was the first person to formulate a hypothesis that described the resistance to motion experienced by deforming fluids. In 1686 he published this work in Philosophiæ Naturalis Principia Mathematica [4] in a chapter titled "On the Circular Motion of Liquids". His hypothesis clearly states what we know today as a characterictic of a Newtonian fluid[2]:

That the resistance which arises from the lack of slipperiness of the parts of the fluid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another.

The phenomenon, described by Newton as "*defectu lubricitatis*," or "lack of slipperiness" between two fluid particles, was attributed to "*attritus*," meaning internal friction, or viscous friction. Since that time, the term "internal friction" and "viscous friction" have been used interchangeably. Although Newton's original work contains a mistake, corrected by Sir George Stokes [3] 150 years later, his main conclusion is still correct; it basically states that the force F required to maintain the motion between two fluid planes located at two arbitrary positions, say C and D in Newton's diagram (Fig. 1.5), is proportional to the difference between the velocity, u, of the

[2] The authors are using Emil Hatschek's translation from the Latin [2].

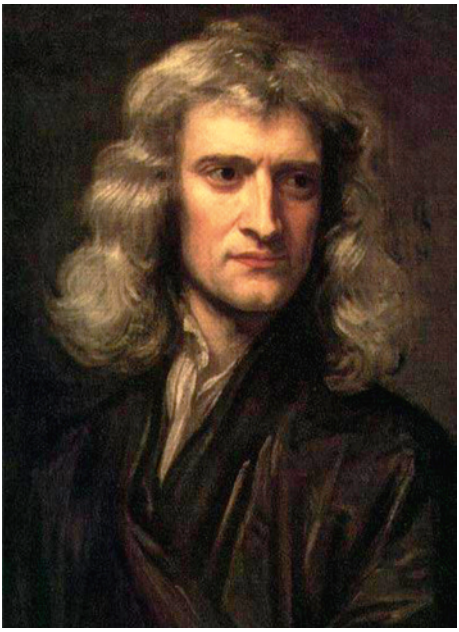

Figure 1.4
Sir Isaac Newton (1643–1727), painted in 1689 by Sir Godfrey Kneller

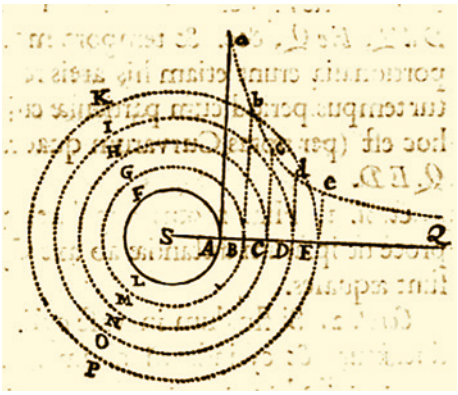

Figure 1.5
Diagram from Newton's 1686 publication [2]

two planes, and inversely proportional to the distance, r, between those two surfaces, the viscosity, η, and the area of the surfaces that separates them, A,[3]

$$F = A\eta \frac{u_\mathrm{d} - u_\mathrm{c}}{r_\mathrm{D} - r_\mathrm{C}} \tag{1.2}$$

[3] Newton used upper case A, B, C, D, etc. to describe the position of the surfaces, and lower case a, b, c, d, etc. to describe the velocity of those surfaces.

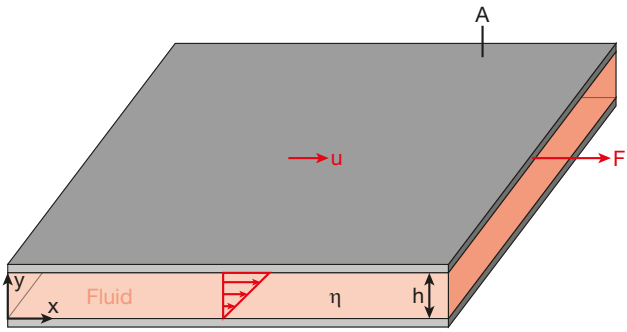

Figure 1.6 Simple shear flow with Cartesian coordinates

As shown in Newton's diagram, his analysis pertained to a rotating cylinder immersed in an infinitely large fluid body. For a more simplified system, such as the simple shear flow generated between two parallel plates presented in Fig. 1.6, Equation 1.2 can be expressed in terms of shear stress, and written as

$$F/A = \eta \frac{u}{h} \tag{1.3}$$

or

$$\tau_{xy} = \eta \dot{\gamma}_{xy} \tag{1.4}$$

where τ_{xy} is the shear stress in the x direction on a plane with its normal direction pointing in the y direction, and $\dot{\gamma}_{xy}$ is the corresponding rate of shear, or rate of deformation. The stress (here τ_{xy}) that leads to the deformation of the fluid contained within the system is also often referred to as the deviatoric stress[4].

The Newtonian model, or the viscous component of a material, is often also represented using a dashpot, shown in Fig. 1.7.

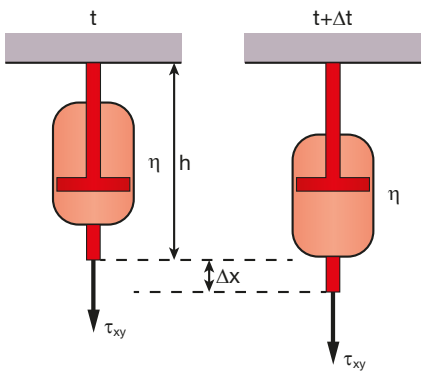

Figure 1.7 The dashpot – a schematic representation of a Newtonian fluid

[4] As will be shown in Chapter 2, which covers flow, the total stress, σ, is divided into the deviatoric stress component, τ, which causes deformation, and the hydrostatic stress component, which results from pressure, p.

While the schematic representation in Fig. 1.7 reflects an elongational deformation along the *x*-axis, the dashpot can also be used for shear deformation, which is written as

$$\gamma_{xy} = \frac{\Delta x}{h} \tag{1.5}$$

Figure 1.7 also shows that the deformation is time dependent and, in the case of a Newtonian fluid, the dependence between deformation and time is linear. In terms of shear strain rate, we can write

$$\gamma_{xy} = \dot{\gamma}_{xy}\,\Delta t \tag{1.6}$$

In Fig. 1.8, the strain within a Newtonian fluid, labeled as viscous strain, is presented for the case where a constant stress is applied during a time period from 0 to Δt. Once the load is released at time Δt, the material element remains deformed. This reflects point "C" in the Eisenschitz, Rabinowitsch and Weissenberg triangle, at which all energy is dissipated or lost and the deformation can no longer be recovered.

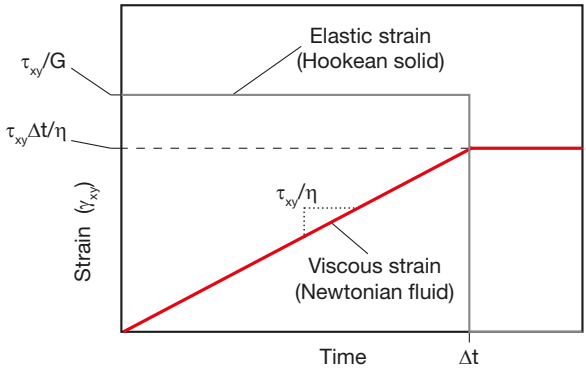

Figure 1.8 Strain response of a Newtonian fluid and a Hookean solid

1.3 Linear Elasticity or the Hookean Spring

Robert Hooke is a relatively unknown English scientist and engineer of the 17th century, who was completely overshadowed by his contemporary, Isaac Newton. In fact, an animosity between the two existed after Hooke claimed that Newton's work on gravitation was based on work he had done. As a result, Newton's obsession was to make sure that Hooke be forgotten; something he almost accomplished. Two years after Hooke's death in 1703, Newton became president of the Royal Society, and in that function made sure that every memory of Hooke was erased from the society, including his portrait and laboratory equipment, which mysteriously disappeared when the Royal Society moved to a new location after 1705.

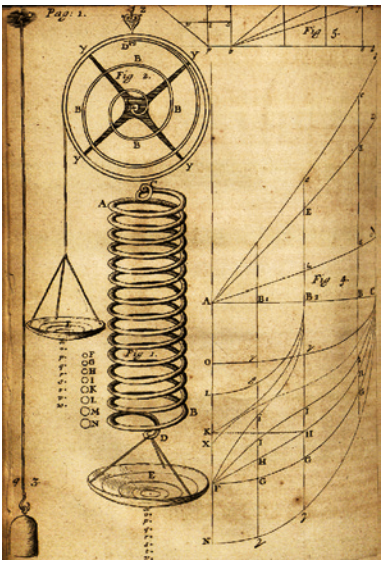

Figure 1.9 Diagram from Hooke's 1678 paper

However, while Hooke is certainly not part of popular culture in the way Newton has become, today his name remains well known among engineers who deal with solid mechanics, thanks to his theory of linear elasticity. Robert Hooke was the first person to find a relation between force and deflection in linear elastic solids, and published that work in his 1678's "*Lectures de Potentia Restitutiva*," or, "Of Spring". The basic theory behind what we today refer to as the Hookean spring (Fig. 1.9) is summarized in Latin by Hooke's words "*Ut tension sic vis*" or "*As the extension, so the force*." More simply stated, we can say that the force, F, is directly proportional to the deflection, Δx. This can be written using

$$F = k\,\Delta x \tag{1.7}$$

where k is the constant of proportionality or the spring constant, also called the stiffness. Hooke's concept was modified in 1727 by Leonhard Euler, who represented the force in terms of stress, F/A, and the displacement in terms of strain, $\Delta x/h$, where h represents the original length. The units in the constant of proportionality can be adjusted by using a modulus of elasticity or stiffness, E, or for a system that is deformed in shear, such as the one depicted in Fig. 1.10, a modulus of rigidity, G,

$$F/A = G\left(\Delta x/h\right) \tag{1.8}$$

In terms of stress and strain the above equation can be written as

$$\tau_{xy} = G\gamma_{xy} \tag{1.9}$$

where τ_{xy} is the shear stress and γ_{xy} the corresponding shear strain.