The Origins of Rheology: A Short Historical Excursion

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I. Prelude to rheology

This article provides a brief historical perspective on the evolution of rheology and the long gestation period before the birth of the subject. It is not intended to be a comprehensive state-of-the-art review but rather to capture key events in the historical progression of the discipline, which was far from monotonic, and the significant contributions from a variety of specialists. Considerable liberty has been taken in identifying key players and avoiding repetitive mention of different efforts by the same workers in order to emphasize the diversity of influences and individuals who have molded the discipline, and to satisfy severe space constraints. Some valuable resources for the historical aspects of rheology are Bingham (1922), Scott Blair (1949), Markowitz (1968), Bird et al. (1987a,b), White (1990), and Tanner and Walters (1998), and the reader is referred to these works for further details.

As per the strict definition, rheology is concerned with the description of the flow behavior of all types of matter. By convention, however, rheologists' main interests are restricted to industrially relevant materials with properties intermediate between those of ideal solids and liquids. A useful engineering definition of rheology is the description of materials using "constitutive equations" between the stress history and the strain history. Table 1 provides a convenient reference for the accompanying discussion regarding the period prior to the formal creation of the discipline of rheology in 1929.

Table 1: Significant rheological works prior to the formal inception of rheology in 1929

#	FLUIDS/MODELS CLASS		KEY TIME	REPRESENTATIVE WORKS
1	Ideal materials	a) Perfect, · rigid bodies	Antiquity	Archimedes (~250 BCE), Newton (1687)
		b) Ideal elastic solids	1600s	Boyle (1660), Hooke (1678), Young (1807), Cauchy (1827)
		c) Inviscid fluids	1700s	Pascal (1663), Bernoulli (1738), Euler (1755)
		d) Newtonian liquids	Early 1800s	Newton (1687), Navier (1823), Stokes (1845), Hagen (1839), Poiseuille(1841), Weidemann (1856)
2	Linear viscoelasticity		Mid 1800s	Weber (1835), Kohlrausch (1863), Wiechert (1893), Maxwell (1867), Boltzmann (1878), Poynting & Thomson (1902)
3	Generalized Newtonian (viscous) liquids		Late 1800s-Early 1900s	Schwedoff (1890), Trouton & Andrews (1904), Hatchek (1913), Bingham(1922), Ostwald (1925) - de Waele (1923), Herschel & Bulkley (1926)
4	Non-linear viscoelasticity		Early 1900s	Poynting (1913), Zaremba (1903), Jaumann (1905), Hencky (1929)
5	Key material descriptions	a) Suspensions	Early 1900s	Einstein (1906), Jeffrey (1922)
		b) Polymers		Schonbein (1847), Baekeland (1909), Staudinger (1920), Carothers (1929)
		c) Extensional viscosity		Barus (1893), Trouton (1906), Fano (1908), Tamman & Jenckel (1930)
6	The genesis of rheology		1929	Bingham, Reiner and others

1) Ideal materials

a) *Rigid solids*: The entire subject of general mechanics deals with ideal "Euclidean" bodies where only the mass (or density) of the bodies is relevant (Euclidean geometry is based on rigid bodies which do not undergo deformation). In fact, Newton's "Principia" was primarily concerned with rigid body mechanics and his comment on viscosity was only a corollary of his prescient mind. Solid mechanics is the oldest branch of the physical sciences and it is appropriate to recall the apocryphal, if time worn, story of Archimedes (~250 BCE) who claimed that he could move the world if he were provided the right leverage.

b) *Elastic solids*: At the other end of the spectrum, where pure elastic solid-like behavior is concerned, Robert Hooke (Hooke (1678)) proposed that "the power of any spring is in the same proportion with the tension thereof" (i.e., the stress is proportional to the strain). It is worth noting that Robert Boyle had actually come up with a similar rule related to a "spring of air" as far back as1660. The constant of proportionality was later identified as an intrinsic property of the material – the elastic (or Young's) modulus – by the great English polymath Thomas Young in 1807 (see Markowitz (1968)). Cauchy set up the first fundamental equations of classical (small deformation) elasticity in 1827 based largely on the work of investigators like C. L. M. H. Navier, C. A. Coulomb and S. D. Poisson.

c) *Inviscid fluids*: A class of ideal materials is the so-called Pascalian (or inviscid) fluids which exhibit no resistance to flow. Blaise Pascal in 1663 first made the equivalent statement that the pressure in a liquid is the same in all directions (although the principle of the ideal fluid was conceived by Archimedes in classical times). The related field of hydrodynamics which formally deals with the motion of fluids where viscosity effects are absent was well developed at the turn of the 18^{th} century thanks largely to the classic studies of workers like Bernoulli (1738) and Euler (1755).

d) *Newtonian fluids*: Tracing the genealogy of any discipline to the "Principia" of Sir Isaac Newton serves to enhance the "gravity" of any subject, no pun intended. In his masterpiece, Newton stated his famous definition of the resistance of an ideal fluid (what we today call viscosity) which is the key property of relevance to rheology (Newton, 1687): "The resistance which arises from the lack of slipperiness originating in a fluid – other things being equal – is proportional to the velocity by which the parts of the fluid are being separated from each other."

The earliest quantitative application of "real fluid" or viscosity effects (albeit empirical) was by the ancient Egyptian scientist Amenemhet (~1600 BCE) (Scott Blair (1949)) who might perhaps be called the first "rheologist." Amenemhet made a 7 degree correction to the drainage angle of a water clock to account for the viscosity change of water with temperature (which can be significant between day and night in the tropics).

Hagen's work in 1839 was the first clear recorded study of the viscosity of a liquid; he determined that the pressure drop for capillary flow is the sum of two quantities: a viscosity term and a kinetic energy correction. The next key research related to capillary was the painstaking work of Poiseuille (1841). These were both entirely empirical studies in narrow tubes and showed that the flow rate was proportional to the pressure gradient and the fourth power of the radius. Pioneering work on the laws of motion for real fluids (with finite viscosities) was carried out by Navier (1823) which was followed up on by Stokes (1845). The celebrated Navier-Stokes equations enabled, for example, prediction of velocity distributions and flow between rotating cylinders and cylindrical tubes. Stokes was apparently not able to show experimental validity of his result for discharge through tubes (Markowitz (1968)); Wiedemann (1856) first showed agreement between the Hagen-Poiseuille data and the Navier-Stokes prediction. It was finally left to M. M. Couette to show that the viscosity value obtained using a special concentric cylinder set-up (to avoid end-effects) and in tube flow were identical – first establishing that the viscosity was an intrinsic property of the material (see, for e. g., Piau et al. (1994)).

2) Linear viscoelasticity

Initial work on viscoelasticity was primarily targeted towards creep and relaxation behavior of metals until the explosive growth of the polymers industry. The earliest systematic study of materials that were neither Hookean nor Newtonian was carried out by Weber (1835) using silk threads (because of their application in electromagnetic instruments). The removal of an extensional load led to an immediate contraction followed by further gradual contraction until the initial (pre-loaded) length was attained – he had identified the phenomenon of stress relaxation (which he called "the after effect"). Thus Weber had qualitatively captured the phenomenon of viscoelasticity even before Poiseuelle's results on tube flow and Stoke's work on viscous liquids. Kohlrausch (who extended his father's work) then experimentally established the linearity of the phenomenon in 1863 based on his work with glass. During this same period a major contribution to rheology came from Maxwell (1867) who postulated his famous first-order empirical differential equation relating the shear stress to the deformation and the accompanying simple exponential stress relaxation.

The results of Weber and Kohlrausch enabled Ludwig Boltzmann (1878) to arrive at his "principle of superposition:" "The value of a characteristic function of a system is equal to the sum of all changes induced in the system by the driving functions which have been applied to it throughout its history." He arrived at an integral representation of linear viscoelasticity in its full 3-D generality. The next major modification was by Wiechert (1893) and Thomson (1888), who independently introduced the concept of a distribution of relaxation times. The well-known "spring-and-dashpot" analogy for the Maxwell model was not introduced until 1902 by Poynting and Thomson.

3) Generalized Newtonian materials

Schwedoff's (1890) experimental work on colloidal gelatin solutions using a Couette device was one of the first results on non-Newtonian systems. His data indicated a non-linearity of torque-angular velocity data in a Couette instrument; he also had to incorporate a yield value to describe his results. Hess (1910) and Hatchek (1913) were some of the other early pioneers who postulated that the viscosity was a function of the rate of shear based on results analogous to those of Schwedoff for gelatin sols. Trouton and Andrews (1904), in their studies on pitch, had to subtract a small "initial stress" in order to obtain a flow rate proportional to the stress. This type of fluid behavior is now associated with Bingham (1922), who proposed a "yield stress" to describe the flow of paints. Equations for shear rate-dependent viscosities were proposed by Ostwald (1925)-de Waele(1923), and Herschel and Bulkley (1926).

4) Non-linear viscoelasticity prior to 1929

Poynting (1913) performed some very elegant experiments in non-linear elasticity. He determined that loaded wires increased by a length that was proportional to the square of the twist against all expectations of linear elasticity theory. Zaremba (1903) extended linear viscoelasticity theory to the non-linear regime by introducing a corotational derivative to incorporate a frame of reference that was translating and rotating with the material. Similar work was done by Jaumann (1905) and, despite Zaremba's precedence, the derivatives are referred to as "Jaumann derivatives." Hencky (1929) whose name is identified with the "logarithmic" (or instantaneous strain) also proposed analogous ideas.

5) Some key material descriptions prior to 1929

a) *Suspensions*: Dispersions and suspensions have always been of great interest as typified by the importance of ink, blood, paints, and the silting of harbors. Thomas Graham (1805-1869) is regarded as the founder of the term colloidal dispersions (comprising particles with diameters less than 1 μ). Einstein (1906) was the first worker to develop an equation for the effective viscosity of dilute suspensions (< ~5%) and work has since expanded to cover a wide range of particle concentrations, sizes and shapes. Jeffrey's (1922) seminal work on the orbits of elongated particles and fibers in dilute suspensions has been the basis for many later studies in suspension rheology.

b) *Polymers*: The ability to define the structure of macromolecules was a relatively recent occurrence in human history in spite of our reliance on such materials (like cotton, silk, gums and resins) since ancient times. Some significant events in the development of industrial materials of relevance to rheology are (see, e. g., White (1990)): the development of a rubber industry based on coagulated rubber latex, procedures for vulcanizing (modifying) rubber with sulfur and heat, the development of cellulose nitrate and xanthate (Schonbein (1847)), and the development of gutta percha. One of the early founders of polymer chemistry was Staudinger (1920) who first proposed the now familiar "chain formula" for these large molecules. Carothers (1929) at the DuPont Company began synthesizing polyesters and polyamides in the 1930s which provided an impetus for the polymer industry in the U.S. Parallel efforts were initiated by Baekeland (1909) for phenol-formaldehyde resins and by Fritz Hofmann at Farbenfabriken Bayer (see, for example, Weil (1926)). During the Second World War the requirement to develop materials for flame throwers, which were known to be viscoelastic, triggered further interest in rheology.

c) *Extensional viscosity effects*: The origins of elongational flow measurements are largely due to Trouton (1906) who considered the uniaxial stretching of pitch and "shoemaker's wax." The next major study was by Tamman and Jenckel (1930) on elongational flow of molten glass filaments. Extrudate or die swell was first correctly identified with "stretching" by Merington (1943) although Barus (1893) had reported an analogous phenomenon much earlier which he attributed to shear recovery. Because of high extensional viscosities, polymer solutions can be drawn up through a nozzle even if it is raised above the free surface. This phenomenon is referred to as Fano flow because of his initial investigation on the subject (Fano (1908)). This effect appears to have been used as early as ca.55 C.E. to harvest bitumen from the Dead Sea (as concluded by Bird et al. (1987a) based on the Complete Works of Tacitus).

II. The genesis of rheology

Rheology is one of the very few disciplines whose coinage can be traced to an exact date: April 29, 1929 (Bingham (1944), Scott Blair (1949)); the first reference to a related term "microrheometer" actually appeared as far back as 1879 (Hannay, 1879). A Plasticity Symposium (to study viscosity) was held on October 17, 1924 as part of the 50^{th} anniversary celebration of the career of a Prof. Edward Hart at Lafayette College, Penn. The high level of interest expressed in this subject eventually led to a Third Plasticity Symposium in 1929 at which a decision was made to form a permanent organization for the development of the new discipline of rheology. The preliminary scope of The Society of Rheology was set up by a committee which then met on April 29, 1929 at Columbus, Ohio[1] and some of the luminaries who participated in this pioneering event included Eugene C. Bingham, Winslow H. Herschel, Marcel Brillouin, Herbert Freundlich, Wolfgang Ostwald, Ludwig Prandtl and Markus Reiner. The name "rheology" was proposed to describe "the study of the flow and deformation of all forms of matter" by E .C. Bingham and M. Reiner; Heraclitus' quote "παντα ρει" or "everything flows" was taken to be the motto of the subject (Reiner (1964)).

III. Rheology since its inception

Table 2 provides a convenient reference for key developments in rheology related to the post-inception period.

1) Constitutive equations

a) *Differential models*: Initial theoretical work on rheology after its formal inception was largely concerned with continuum mechanics formulations to enable characterization and description of material flow behavior for commercial applications. A major advancement was J. G. Oldroyd's work in 1950 on convected derivatives based on application of "the invariance of material properties with respect to the frame of reference;" this represented the culmination of a number of earlier efforts relating to complex derivatives of the stress. Some notable differential models are the "retarded-motion expansions" (e. g., Rivlin and Ericksen (1955) and Giesekus (1962)) in which the stress is expressed as a power series

[1] The first official meeting of The Society of Rheology was held at the National Bureau of Standards on December 19, 1929 at which a formal committee was appointed on definitions and action was taken for securing an improved absolute viscosity standard; the Journal of Rheology was also started as a quarterly.

involving increasing powers of the rate-of-strain tensor and increasing orders of partial time derivatives.

b) *Integral-type models*: Another slightly later development was the complementary effort of Green and Rivlin (1957), and Coleman and Noll (1961) who used integral formulations whereby the stress at any location and time depended on the entire past history of the local deformation. The entire subject of constitutive equations and their development have been discussed in great detail by Bird et al (1987a,b), Larson (1988) and more recently by Tanner (2001).

c) *Network theories*: The early work by Green and Tobolsky (1946) was one of the first attempts to describe relaxation processes in networked polymers. The network theory for rubber-like fluids developed independently by Lodge (1956) and Yamamoto (1956) was the next major advance in the field. The permanent chemical junctions in rubber are assumed to be replaced by temporary physical junctions whose kinetics have to be described. An extension of the Lodge model is the K-BKZ model (Kaye (1962), Bernstein, Kearsley and Zapas (1963)) whereby a more general form was sought by redefining the kernel function in the Lodge integral formulation.

d) *Reptation theories*: A "tube model" was first proposed by Edwards (1967) for rubbers. The Doi-Edwards model (1978, 1986) based on the reptation theory of de Gennes (1971) was another significant advancement in the field whereby the tube model was extended to melts and concentrated solutions. The polymer chain is constrained to move in a "tube" because of the presence of neighbouring molecules and the tube itself evolves in time as the chain crawls or "reptates."

e) *Molecular models*: Kuhn (1934) first addressed the characterization of the configuration of polymer molecules using a random coil model. Starting with this work and progressing with the landmark kinetic theory papers of Kramers (1944), Rouse (1953), Zimm (1956) and Kirkwood (1967), it was becoming increasingly apparent that material equations should reflect the polymer structure to facilitate processing and development of new materials. This approach culminated in the major effort by Bird et al. (1987b) which summarized the state-of the-art in the field (this work includes the so-called generalized phase-space kinetic theory which incorporates both the velocities and positions of the "beads" in the bead-spring models).

2) Experimental advances and rheological characterizations

The early decades of rheology were marked by investigations into a number of experimental phenomena.

a) *Shear flows and the no-slip boundary condition*: Stokes (1845) was the first to establish the no-slip boundary condition

Table 2: Rheology since its inception in 1929

#	AREA OF ACTIVITY		REPRESENTATIVE WORKS
1	Constitutive equations	a) Differential models	Oldroyd (1950), Truesdell (1952), Rivlin and Ericksen (1955), Giesekus (1962), White-Metzner (1963)
		b) Integral models	Green & Rivlin (1957), Coleman & Noll (1961)
		c) Network models	Green & Tobolsky (1946), Lodge(1956), Yamamoto (1956), Kaye (1962) - Bernstein et al. (1963)
		d) Reptation models	Edwards (1967), De Gennes (1971), Doi & Edwards (1978, 1986)
		e) Molecular models	Kuhn (1934), Rouse (1953), Zimm (1956), Kirkwood (1967), Bird et al. (1987)
2	Experimental advances and rheological descriptions	a) Shear flows and the no-slip boundary condition	Eisenschitz et al. (1929), Mooney (1931,1936), Schofield & Blair (1930), Pearson & Petrie (1968), Graessley (1977), Ramamurthy (1986)
		b) Normal stresses and rod-climbing effects	Lander (1945), Weissenberg (1947), Markowitz (1957), Philippoff (1957), Ginn & Metzner (1969), Binnington & Boger (1985)
		c) Dynamic studies	Eisenschitz & Philippoff (1933), Schofield & Scott Blair (1932), Leaderman (1943), Cox-Merz (1958), Doraiswamy et al. (1991)
		d) Thixotropy	Freundlich & Bircumshaw (1926), Cheng & Evans (1965), Mewis (1979), Barnes (1997)
		e) Flow Instabilities	Nason (1945), Tordella (1958), Petrie & Denn (1976), Bousfield et al. (1986)
		f) Turbulent drag reduction	Toms (1949), Agoston et al. (1954), Hershey & Zakin (1967), Seyer & Metzner (1967)
		g) Optical studies/ birefringence	Adams et al. (1965), Carothers & Hill (1932), Hermans & Platzek (1939), Janeschitz-Kriegl (1983), Fuller (1985)
		h) Time-temp. superposition	Williams et al. (1955), Ferry (1970)
		i) Extensional behavior	Merrington (1943), Treolar (1944), Ballman (1965), Cogswell (1969), Metzner (1968), Meissner (1969), Dealy et al. (1976), Spearot & Metzner (1972), Laun & Munstedt (1978), Sridhar & Gupta (1985)
3	Advanced materials	a) LCPs	Leslie (1968)-Ericksen (1961),Doi (1981), Wissbrun (1985), Doraiswamy & Metzner (1986), Marrucci & Greco (1992)
		b) Composites and two-phase systems	Taylor (1934), Krieger-Dougherty (1959), Rumscheidt & Mason (1961), Leal (1975), Batchelor (1977), Folgar & Tucker (1984), Heller & Kuntamukkula (1987), Khan & Armstrong (1986), Acrivos & Shaqfeh (1988), Mewis et al. (1989), Dennis et al. (2001)
		c) ER/MR fluids	Winslow (1949), Parthasarthy & Klingenberg (1996)
4	Computational rheology	a) Continuum simulations	Turner et al. (1956), Gottlieb & Orzag (1977), Cruse & Risso (1968), Yoo & Joseph (1985), Beris et al. (1987), Walters & Tanner (1992), Crochet & Walters (1993)
		b) Molecular dynamic simulations	Adler & Wainright (1957), Ashurst & Hoover, (1975), Evans & Morriss (1988), Davis & Todd (1998)

at solid walls. The "problem" of slip was addressed by Schofield and Scott Blair (1932) and Mooney (1931). Pearson and Petrie (1968) showed that for slip to occur the molecular size must be greater than the wall roughness scale. Ramamurthy (1986) conclusively established that slip can occur during extrusion of polymer melts. Mooney's 1936 study on natural rubber was perhaps the first careful characterization of the viscosity-shear rate behavior of a bulk polymer. The culmination of obtaining shear-stress- shear rate data without assuming any functional form for the viscosity was reached by Eisenschitz-Rabinowitch-Weissenberg (1929), and Mooney (1931). Important work on the effect of polymer entanglement and architecture on viscosity was done by Graessley (1977). The flexible five-parameter Carreau model was postulated in 1968 to describe a wide variety of flow behavior (see, for e. g., Bird (1987a)).

b) *Normal stresses and the rod climbing effect*: Normal stresses play a major role in a number of industrial processes like extrusion, fiber spinning and impeller-mixing. The rod-climbing effect (which refers to the rising of the free surface up a rotating rod) appears to have arisen from work on saponified hydrocarbon gels for use as flame throwers in World War II. (e. g., Garner et al. (1950) and Lander (1945)). Weissenberg (1947) appears to have been the first to attribute this phenomenon to the first normal stress and it is not incongruous that this effect is now named after him. Some pioneering work in this area was done by Philippoff (e.g., 1957)) and Markowitz (1957). The second normal stress difference is typically considered to be negative and a small fraction of the first normal stress difference for typical polymeric systems (the Ginn and Metzner (1969) paper is a representative result). Anomalous "hole-pressure" effects in devices related to normal stress measurements have been reviewed by Tanner and Walters (1998). An important test fluid was developed by Binnington and Boger (1985) which had the advantage of being highly elastic but yet having a constant viscosity, thus lending itself to a number of useful academic and industrial studies.

c) *Dynamic studies*: Small-strain dynamic studies of polymers and polymer solutions date to the 1930s (e. g., Eisenschitz and Philippoff (1933), Philippof (1934)). Andrews et al. (1948) and Leaderman (1943) were some of the pioneers in this field. Stress relaxation studies were also carried out in the same period by Schofield and Scott Blair (1932) on flour dough. The Cox-Merz rule (1958) (an empiricism predicting an equivalence of the complex viscosity and the viscosity at the corresponding values of frequency and shear rate) has been a very useful method for correlating linear viscoelastic properties with the viscosity behavior. This work was extended in the form of the Delaware-Rutgers rule (Doraiswamy et al. (1991)) for suspensions using a Herschel-Bulkley-type formulation with a recoverable strain.

d) *Thixotropy*: Thixotropy may be defined as the decrease in apparent viscosity with time under stress and this behavior appears to have first been formally named by Freundlich based on their work on suspensions (see, e. g., Freundlich and Bircumshaw (1926)). The earliest reference to thixotropy is by von Kuhne in 1863 during his observation of the wandering of a nematode through a muscle cell without any apparent effort: "The movement seemed to liquify the striations, but they set anew after the nematode had passed." The opposite but analogous time-dependent effect related to viscosity increase with time was termed "rheopexy" by Freundlich and Juliusberger in 1935 based on studies with colloidal systems. Some illustrative works in this field are Cheng and Evans (1965), Mewis (1979) and Barnes (1997).

e) *Flow instabilities*: Because of elasticity, normal-stress and shear-thinning effects, non-Newtonian materials show a wide variety of unstable behavior. In extensional flows, it is possible to have effects like draw-resonance (where sinusoidal fluctuations in fiber diameter are amplified along the length), shark-skin behavior (where filament roughness occurs) and "melt fracture" (where a helical, distorted, extrudate forms); distorted extrudates were reported as far back as 1945 by Nason. Some key studies in this field are those of Tordella (1958) and Petrie and Denn (1976). Viscoelasticity was shown to suppress jet break-up as indicated by the relatively recent work of Bousfield et al. (1986).

f) *Turbulent drag reduction*: Turbulent drag reduction is a phenomenon whereby use of a (polymeric) additive results in a lower pressure drop for flow through a pipe. Much of this work was done by various independent groups during the war and did not appear in open literature until much later. Key initial workers in the field were Toms (1949) and Agoston et al. (1954). This matter was followed up in earnest only in the 60s by researchers like Hershey and Zakin (1967). One of the likely mechanisms for this phenomenon was proposed by Seyer and Metzner (1967) and was attributed to the large extensional viscosity of the additives which could damp out secondary flows (or vortices) associated with turbulence.

g) *Birefringence*: Brewster (1813) was one of the first scientists to show that birefringence (variation of refractive index with direction) could be induced by application of stress in materials like glass and gels. Maxwell (1853) postulated that the birefringence varied linearly and isotropically with the applied stress. Birefringence was related to molecular orientation as far back as 1932 (e.g., Carothers and Hill) and this effect was first quantified by Hermans and Platzek (1939). These historical aspects of birefringence as well as later investigations on suspensions, solutions and melts have been reviewed by White (1990). The birefringence method has been used to determine stress fields in complex flows (e.g., Adams et al. (1965)). The stress-optical law which states that there is a linear relationship between the stress tensor and the

deviatoric components of the refractive index tensor was formally verified by Janeschitz-Kriegl (1983).
A number of rheo-optical techniques have been developed and summarized by Fuller (1985).

h) *Time-temperature superposition*: Time-Temperature Superposition and the Method of Reduced Variables are two empirical techniques that make use of normalized variables to plot data in the form of universal curves; these were developed primarily by Williams et al. (1955) and Ferry (1970) in the form of the W-L-F procedure, and facilitate data collection and extending their range of application.

i) *Extensional behavior*: Merrington (1943) attributed his observations on extrudate swell in rubber solutions to elastic recovery. Modern investigation of the extensional viscosity of polymer systems dates to Ballman in 1965. An early experiment by Metzner (1968) demonstrated that if the extensional stresses are sufficiently high they can cause the splash induced by striking a pool of liquid to retract so that the initial fluid position is almost attained. This was followed by a number of elongational flow studies on molten polymer systems like, for example, Meissner (1969), Vonogradov et al. (1970), and Laun and Munstedt (1978). The extensional behavior is frequently termed "extensional viscosity" in the literature, an appellation which, unfortunately, obscures the importance of strain, as well as strain rate (see Spearot and Metzner (1972)). Cogswell (1969) was one of the first to propose the use of pressure losses through orifice dies to determine the elongational behavior. This semi-quantitative approach was used to measure one of the highest reported ratios of extensional viscosity to shear viscosity (~30,000) (Metzner and Metzner (1970)). The earliest experiment for biaxial and planar extension is due to Treloar (1944) and involved rubber. Instruments for such studies were also developed by Denson and Gallo (1971) and Dealy et al.(1976). Winter et al. (1979) first developed an orthogonal stagnation flow. An extensional rheometer was developed by Sridhar and Gupta (1985) for measurements on very low viscosity polymer solutions (~5 cP).

3) Advanced materials

The technological need to describe the behavior of advanced materials like liquid crystals, electro- rheological fluids and composites spawned a range of related research problems and some of the efforts are summarized below:

a) *Liquid crystalline polymers*: Some of the earliest work on anisotropic fluids was by Oseen (1925) which was eventually followed by the Leslie(1968) -Ericksen (1961) formulation based on continuum theory where a unit vector termed the director was used to incorporate the anisotropy of the system; these formulations are better suited to describe the flow behavior of low molecular weight liquid crystals. The molecular theory of Doi and Edwards for rigid back-bone macromolecules (1978) was the next major advancement in the description of these systems. Domain structures are often formed in these systems and one of the early attempts to describe these systems is typified by the work of Wissbrun (1985). Kiss and Porter (1978) first reported the unusual phenomenon of negative normal stresses for these materials.

b) *Composites and other two-phase systems*: The importance of fiber reinforced plastics and ceramics has triggered enormous interest in the processing of composite materials and suspensions in recent years. Batchelor (1977) extended the Einstein (1905) equation to higher concentrations by incorporating interaction between "hard spheres." A number of equations have been postulated to describe the rheology of a variety of colloidal and non-colloidal additives like the Krieger-Dougherty (1959) expression of anisotropic particles and the equation of Russel et al. (1989) for "hairy" particles. Batchelor (1971) calculated the stresses during the flow of suspensions of parallel fibers. Leal (1975), and Acrivos and Shaqfeh (1988) developed theories to describe fiber suspension behavior employing a second-order fluid model and an effective medium approach, respectively. Folgar and Tucker (1984) developed a constitutive equation for the flow of fiber/polymer systems. The recent interest in optimizing the dispersion of nano-size particles (like clay or carbon nanotubes) in polymers (like nylon-6) because of their unusual properties like decreased diffusivity, and increased tensile modulus and flame resistance has triggered new rheological investigations on these new systems (see, e. g., Dennis et al. (2001)).

Taylor (1934), and Mason (e.g., Rumscheidt and Mason (1961)) were responsible for some of the key results on deformation and break-up of liquid drops in various flow fields. Heller and Kuntumukkula (1987) concluded that much of the earlier data on foam rheology had been influenced by wall slip or stability effects; expressions have been developed to predict the rheological properties of foams but experimental determination of the material functions remains a daunting task (e.g., Khan and Armstrong (1986)).

c) *Electrorheological/Magnetorheological (ER/MR) fluids*: Electro/magneto rheological fluids offer the potential of large viscosity changes on application of an electric or magnetic field. This behavior has potential in new applications like power transmission fluids and robotics. These effects appear to have first been noted by Winslow (1949). Recent work in this area has been reviewed by Parthasarthy and Klingenberg (1996).

4) Computational rheology

a) *Continuum modeling*: The finite-difference method (FDM) was widely prevalent by the 1960s when transistor technology first came into bloom. More powerful techniques like the finite-element method (FEM) which was initiated in 1956

(Turner et al. (1956)), the boundary element method (BEM) (Cruse and Rizzo (1968)) and the spectral methods (SM) (e.g., Gottlieb and Orzag (1977)) were developed as computer technology improved. All these methods essentially reduce the PDEs of the rheological field problems to a set of simultaneous, non-linear, equations for the nodal variables. A major problem in numerical simulations was the so-called High Weissenberg Number Problem (the existence of a critical Weissenberg number above which the algorithms failed). Some significant early works in this area are Beris et al. (1987), Yoo and Joseph (1985), Walters and Tanner (1992), and Crochet and Walters (1993). An analogous finite volume method was applied to three dimensions flows by Xue et al. (1995).

b) *Molecular dynamics (MD) modeling*: MD simulations on super-computers were developed as a promising path to relating polymer microstructure to macroscopic rheological properties (see, for e.g., Ashurst and Hoover (1975), Evans and Morriss (1988), Daivis and Todd (1988)). This method, since its inception in the late 1950's (e.g., Adler and Wainwright (1957)) for studying the interactions of hard spheres, enables calculation of the time dependent behavior of a molecular system. Molecular dynamics simulations involve solution of Newton's equations of motion for a large number of particles interacting with each other via nonlinear (usually empirical) force laws. The connection between microscopic simulations and macroscopic properties is made via statistical mechanics which provides the rigorous mathematical expressions that relate macroscopic properties to the distribution and motion of the atoms and molecules. The scope of systems studied by MD is enormous and envelopes solids, liquids and gases; solvent molecules and solvated protein-DNA complexes; and simple and complex hydrodynamic flows.

IV. Concluding remarks

It should be apparent from this overview that the progression of the discipline has not been monotonic and it took over a century before contributions by scientists from widely varied fields necessarily condensed into the formal field of rheology. It also indicates that many of the major contributors to rheology acquired their lasting fame in other fields while some other rheologists may have been short-changed by history.

Starting with Amenemhet's need for a viscosity correction to improve the accuracy of his water clock in ~1600 BCE, rheology has primarily been concerned with solving practical problems. At the same time, the complexity of the issues involved (both of a physical and mathematical nature) has attracted some of the finest scientific minds. The cumulative result has been the thriving discipline we know today with contributions ranging from the empirical and phenomenological to the abstract and esoteric. Rheology as we know it now overlaps with a number of fields like reaction engineering, computational science, thermodynamics and advanced materials design to name a few. This is attested by the fact that work pertaining to rheology is reported in a wide range of journals like Macromolecules and the Journal of Chemical Physics, and is no longer limited to highly specialized journals like Rheologica Acta and the Journal of Rheology. The pioneers of our discipline which came into being four score years ago could hardly have envisioned the range of potential applications we see around us today – ranging from magneto-rheological fluids for power transmission in automobiles to the processing of nano-composites. It would perhaps be unwise to make any speculations on the depth and breadth of new material advances another four score years down the road except that rheology will almost certainly be a cornerstone in their design and processing.

V. References

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