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Review

HISTORICAL PERSPECTIVES ON THE ELASTICITY OF LIQUIDS

DANIEL D. JOSEPH

Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)

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1. Elasticity and viscosity

The existence of normal stresses, shear thinning and recoil in polymeric solutions and undiluted polymers (melts) makes it impossible to believe that every liquid is Newtonian. There are recurrent arguments starting with Poisson [1829], stimulated by Maxwell [1873], which suggest that every liquid should have some instantaneous elasticity. Indeed, important constitutive theories, like those of Maxwell, or Boltzmann [1874] are founded on the idea that liquids will accommodate short lived elastic responses. This idea runs against the commonly accepted notion that liquids like water and glycerin have a purely viscous response, without elasticity. Another idea is that liquids possess both elasticity and viscosity in varying amounts.

H. Jeffrey's [1929] was the first to propose a constitutive equation with both viscosity and elasticity. In one dimension his equation is

$$\lambda\frac{\partial \tau}{\partial t} + \tau = \eta\frac{\partial u}{\partial x} + \lambda\mu\frac{\partial^2 u}{\partial x \partial t}, \tag{1}$$

where τ is the shear stress, λ is a relaxation time, η is the elastic viscosity and μ is the Newtonian viscosity. This equation reduces to Maxwell's when $\mu = 0$. In three dimensions, $\boldsymbol{\tau}$ is a second order symmetric tensor and $2\boldsymbol{D}$ replaces $\partial u/\partial x$, where $\boldsymbol{D}[\boldsymbol{u}]$ is the symmetric part of the velocity gradient.

In models of the Jeffreys type, the Newtonian viscosity $\mu = \mu\lambda_2/\lambda$ is expressed in terms of a retardation time λ_2 and the relaxing elastic effects are associated with a relaxation time λ. An invariant formulation of rate equations containing relaxation without retardation was given by Zaremba [1903]. An invariant formulation of rate equations containing relaxation and retardation (Newtonian viscosity) effects evidently first appears in the celebrated 1950 paper of Oldroyd. Green and Rivlin [1960] appear to have been the first to introduce Newtonian viscosity into integral models. They get rate terms from integrals by allowing delta functions and their derivatives in the

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kernels. Saut and Joseph [1983] derived integral expressions of the type introduced by Green and Rivlin from a theory of fading memory in which the ensemble of all possible linearized stresses coincides with a certain topological dual of a domain space (say, a Sobolev space) for allowed deformations.

Maxwell models and the generalization of these embodied in the theory of fading memory of Coleman and Noll cannot contain a Newtonian viscosity. These models are all instantaneously elastic.

Ludwig Boltzmann [1874] introduced a linear integral representation for stress in viscoelastic solids. He was motivated by experiments on creep of silk fibers by Weber [1835] and on glass fibers by F. Kohlrausch [1863,1866]. Boltzmann did not apply his equations to liquids but he thought his equation might apply to soft or viscous materials. An excellent review of Boltzmann's work has been written by H. Markovitz [1977]. When applied to fluids in the one dimensional case, Boltzmann's equation becomes

$$\tau=\int_{-\infty}^{t} G(t-t')\frac{\partial u(x,t')}{\partial x}\mathrm{d}t'. \tag{2}$$

This type of representation for the stress also gives rise to instantaneous elasticity. Maxwell's equation ((eqn. 1) with $\mu=0$) is a special case of Boltzmann's with

$$\mathrm{G(s)}=\frac{\eta}{\lambda}\mathrm{e}^{-s/\lambda}.$$

In Maxwell's 1878 article on the "Constitution of Bodies" he quoted Boltzmann's integral representation and ignored his own. Perhaps because the article was published in the famous 9th edition of the *Encyclopedia Brittanica*, Maxwell's first-order differential equation continued to exert a much greater influence on the future development of rheology than did Bolzmann's more encompassing theory.

Using Boltzmann's equation we may define the elastic viscosity

$$\eta=\int_{0}^{\infty} G(s)\mathrm{d}s \tag{3}$$

generally as the area under the relaxation curve. We may, in fact, write a generalization of Jeffreys' equation in the spirit of Boltzmann. Thus

$$\tau=\mu\frac{\partial u}{\partial x}+\int_{-\infty}^{t} G(t-t')\frac{\partial u(x,t')}{\partial x}\mathrm{d}t'. \tag{4}$$

In this case the viscosity $\tilde{\mu}$ which viscometers measure at low rates of shear would be given by

$$\tilde{\mu}=\mu+\eta. \tag{5}$$

The rigidity or elasticity of a liquid is the instantaneous value $G(0)$ of the shear relaxation function $G(s)$. For a Maxwell model $G(0) = \eta/\lambda$. The effective rigidity of many different liquids have recently been measured by Joseph, Riccius and Arney [1985] using a wave speed meter.

To decide about elasticity and viscosity we could consider ever more dilute solutions of polymer chains of large molecules in solvents which are thought to be Newtonian. What happens when we reduce the amount of polymer? There are two good ideas about this which are in collision. The first (Jeffreys') idea says that there is always a viscosity and some elasticity with an ever greater viscous contribution as the amount of polymer is reduced. The theories of Rouse and Zimm adopt this view. On the other hand we may suppose that the liquid is elastic so that $\mu = 0$ and the static viscosity $\tilde{\mu} = \eta$ is the area under the graph of the relaxation function. Since η is finite in all liquids, we have $\eta = G(0)\bar{\lambda}$, where $\bar{\lambda}$ is a mean relaxation time. Maxwell's idea is that the limit of extreme dilution is such that the rigidity $G(0)$ tends to infinity and $\bar{\lambda}$ to zero in such a way that their product η is finite. Ultimately, when the polymer is gone, we are left with an elastic liquid with an enormously high rigidity. This idea apparently requires anomalous behavior because $G(0)$ appears to decrease with polymer concentration when the concentration is finite. The elastic response promotes hyperbolicity and denotes diffusion in the dynamics governing fluid motions.

The contradiction between the two foregoing ideas and the apparent anomaly can be ameliorated by replacing the notion of a single mean relaxation time with a distribution of relaxation times. This notion is well grounded in structural theories of liquids in which different times of relaxation correspond to different modes of molecular relaxation. It is convenient again to think of polymers in a solvent, but now we can imagine that the solvent is elastic, but with an enormously high rigidity. In fact many of the so called Newtonian solvents have a rigidity of the order 10^9 Pascals, which is characteristic of glass, independent of variations of the chemical characteristics among the different liquids (for example, see Harrison, 1976). To find this glassy modulus it is necessary to use high frequency devices operating in the range of 10^9 Hertz. These devices were first introduced by Mason [1947] and Mason, Baker, McSkimin and Hess [1948] at Bell labs. To measure the glassy modulus in low molecular weight liquids it is also necessary to supercool them to temperatures near the glassy state. In these circumstances the liquid acts like a glassy solid, the molecular configurations cannot follow the rapid oscillations of stress, the liquid cannot flow. For slower processes it is possible for the liquid to flow and if the relaxation is sufficiently fast the liquid will appear to be Newtonian in more normal flow. For practical purposes there is no difference between Newtonian liquids and liquids with rigidities of order 10^9 and mean relaxation time of 10^{-10} seconds or so. In fact it is convenient to regard such liquids as Newtonian, even though $\mu = 0$ and $\tilde{\mu} = \eta$.

The presence of polymers would not allow the liquid to enter the region of viscous relaxation at such early times. Instead much slower relaxation processes associated with the polymers would be induced (cf. Mason, et al., op. cit.). The second slower regime of relaxation starts in a neighborhood of small times which terminate fast relaxations from the glassy state. A value representative of $G(t)$ at these early times can be said to loosely define a second smaller modulus, the effective modulus. For many polymer solutions the effective modulus defines the effective rigidity of the solution against changes of configuration of chains of polymers. It can be said that the effective modulus is associated with the longest relaxation times whenever it can be defined. If the shorter time or times of relaxation outside the range of practical interest are represented by a Newtonian viscosity, as in (4), then the effective modulus is $G(0)$, call it $G_\mu(0)$; $G(0)$ with $\mu = 0$ is the glassy modulus.

2. Elasticity of liquids—historical account

In this section I collect and organize the old literature on the elasticity (rigidity) of liquids. Most recent(> 1940) accounts of the history of constitutive equations for liquids ignore the questions raised in this paper. They treat the history of Newtonian and non-Newtonian fluids, presuming implicitly that it is possible to hold a strict division between these two types of fluids. Moreover, the non-Newtonian fluids are either assumed to be entirely viscous (Stokesian power law fluids) or entirely (instantaneously) elastic, without viscosity. Models of the Jeffreys type are not considered.

I learned of the existence of an old literature by reading section 9.2 on "the stiffness of a fluid" by Harry Bateman in the well-known and even celebrated book on hydrodynamics by Bateman, Dryden and Murnaghan [1932]. A very good description of the physical basis for elasticity in liquids is given in an article on phenomenological theories of relaxation and of viscosity by J.M. Burgers [1939]. Two fine reviews of different aspects of the history of rheology by H. Markovitz have appeared recently [1968,1977].

My present purpose is best satisfied with the following long citation from the article by Burgers:

> The formation of an adequate picture of the internal structure of a liquid is a problem of great difficulty. It has been pointed out by many physicists that the structure must have much more in common with that of solid matter, than with that of a gas. The following exposition of this view may be taken over from Poynting [37]: "A liquid may be imagined to be, in the

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[37] J.H. Poynting, Philos. Magaz. (V) **42**, p. 289, 1896 (the paper is concerned mainly with the theory of osmotic pressure).

main, a solid structure in as much as the molecules cohere and resist strain of any kind. But the molecules have so much energy, potential or kinetic or both, that they are not very far from instability. In a mass of connected molecules irregularly vibrating, concentrations of energy must occur, and at the points of concentration individual molecules may receive so much energy that they are able to do the work needed to free them from their immediate surroundings. Thus the solid structure is continually breaking down and renewing itself." Poynting then continues with an explanation of the phenomenon of viscosity on the general lines already exposed before: "If we impose a shear strain on the structure, the strain will of course disappear with the structure in which it is produced. But the breaking down will always lag slightly behind the imposition of the shear, and the still surviving shear strain will be accompanied by a resistance the same in kind as the resistance to shear in a solid, though in a liquid it is only recognized as viscosity. This is the view first set forth by Poisson and developed by Maxwell." By introducing a factor expressing the fraction of the molecules which are set free (or, "mobilized") per second, the coefficient of viscosity is then obtained as the quotient of the modulus of rigidity and this factor.

The view that in a liquid there is not an absolute random arrangement of the molecules, but a type of local structure, has in later years received much support both from the results of the examination of X-ray diffraction patterns obtained with liquids, and from the study of the so-called crystalline liquids ("liquid crystals"). It may be considered as highly probable that not only in crystalline liquids, but also in ordinary isotropic liquids the molecules may associate to groups. This association, i.e. the formation of certain regular arrangements with more or less determined relative orientations, is produced by the fact that the molecules in many cases are polarized bodies, and consequently can be bound together to complexes of some extent. These complexes or groups might be considered as a kind of very imperfect crystals. It must be assumed that the groups have no sharp boundaries; in the neighborhood of the boundaries the orientation probably will become less regular, and a more or less gradual transition may be supposed to exist in the orientation when we pass from one group to another. The forces between the molecules in the neighborhood of the transition layer then will be smaller than those between the fully orientated molecules in the interior of a group, and in this way it may be explained that the various groups easily can slide over each other, thus making the substance into something different from a fully crystallized solid. It must also be assumed that the molecules lying in the neighborhood of a transition layer may easily change their citizenship from one group to another. The whole picture thus is continually in a state of change, as is necessary to produce the appearance of a homogeneous, isotropic "liquid". This state of a partial arrangement is called by Stewart: cybotaxis [38]; for the groups themselves the name cyboma's has been proposed by Kistler. As Kistler remarks a single cyboma may progress through the liquid by growth on one side and decay on the other. It may branch out and the branches quickly split off or it may liquefy as a whole [39].

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38 G.W. Stewart and R.M. Morrow, Physical Review **30**, p. 232, 1927. G.W. Stewart, Chem. Reviews **6**, p. 483, 1929; Reviews of Modern Physics **2**, p. 116, 1930; Nature **128**, p. 727, 1931. See also: E. Gross and M. Vuks, Nature **135**, p. 100, 1935. For a criticism of the conception of cybotaxis compare Second Report, p 34.

39 S.S. Kistler, Journ. of physic. Chemistry **36** (2), p. 2948, 1932 (this paper is more especially concerned with the explanation of certain properties of colloidal systems on the assumption of cybotaxis in the dispersing liquid).

> The fact that these groups or cyboma's possess a certain mean life time can be inferred from measurements of the dielectric constant of liquids with alternating fields, It is found that the dielectric constant shows a kind of anomalous dispersions and exhibits a rapid change in the vicinity of some critical frequency. The critical frequency is a function of the temperature; it increases with increasing temperature. Apparently its inverse may be considered as a measure of the relaxation time in Maxwell's and Poynting's deductions [40].

A critical review of the concept of cybotaxis can be found in the article of F.M. Jaeger [1938].

Experimental verifications of the presence of elasticity in liquids have proceeded by methods involving.

(1) experiments using polarized light,
(2) experiments on stress relaxation between rotating cylinders and spheres,
(3) recoil experiments,
(4) experiments using sinusoidal oscillations,
(5) experiments using cone and plate devices,
(6) photographs of shear waves using tracers,
(7) experiments based on measuring the speed of propagation of shear waves into liquids at rest.

Experiments of type (1) through (4) appear already in the old literature, but (1) and (4) have undergone rapid development in more recent times. In fact both types of experiments use sinusoidal oscillations. Using the optical birefringence induced by sinusoidal shearing it is possible to carry out direct quantitative measurements of a complex propagation constant from which the complex viscosity can be derived (Thurston and Schrag, 1963). The complex viscosity

$$\eta^*(\omega) = \mu + \int_0^\omega G(s)\, e^{-i\omega s} ds$$

or the equivalent rigidity $G^* = i\omega\eta^*$ are also measured by sinusoidal oscillations on standard cone and plate machines as well as on the high frequency devices pioneered by Mason, et al., op. cit. Experiments of type (5) are widely used for polymer solutions and melts. There is only one experiment of type (6), reported in the Ph.D. thesis [1975] of E.H. Lieb. Two photographs using tracers appear to exhibit propagation of shear waves in one polymeric liquid. Experiments of type (7) were introduced recently by Joseph, Riccius and Arney [1985].

In 1866, Clerk Maxwell [1873], the celebrated Professor of experimental physics, motivated by Poisson's theory of the internal friction of fluids, made

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[40] See P. Debije, Trans. Farad. Society **30**, p. 679, 1934 and other papers.

some attempts to ascertain whether the state of strain in a viscous fluid in motion could be detected by its action on polarized light. He says that

> I have enumerated these instances of the application of polarized light to the study of the structure of solid bodies as suggestions with respect to the application of the same method to liquids so as to determine whether a given liquid differs from a solid in having a very small "rigidity", but a sensible "time of relaxation", or in both ways. Those which, like Canada balsam, act strongly on polarized light, have probably a small "rigidity," but a sensible "time of relaxation." Those which do not show this action are probably much more "rigid," and owe their fluidity to the smallness of their "time of relaxation".

Maxwell's constitutive theory, derived in his 1867 treatise on gases introduces the stress relaxation function (3). It appears that Maxwell thought his equation should apply to liquids and gases. He says that the "phenomenon" of viscosity in all bodies may be described independently of hypothesis by rate equations of the prescribed form. Markovitz [1968] notes that

> In his writings on states of matter, Maxwell drew a careful distinction between solids and fluids and, in many of his publications, pointed out that materials such as pitch are fluids:
>
> "If, therefore, we define a fluid as a substance which cannot remain in permanent equilibrium under a stress not equal in all directions", we must call these substances (cold pitch and asphalt) fluids, though they are so viscous that we can walk on them without leaving any footprints. What is required to alter the form of a soft solid is a sufficient force and this, when applied, produces its effect at once. In the case of a viscous fluid it is "time" which is required, and if enough time is given, the very smallest force will produce a sensible effect".

Maxwell's idea that fluids may be described as relaxing elastic solids is in conflict with the instantaneous changes of configuration required by the Newtonian fluids embraced by Maxwell's friend, Stokes. Maxwell evidently felt a need to show how his theory could be reconciled with Stokes. He writes [Larmor, 1907]

> GLENLAIR, DALBEATTIE.
>
> 25 Sept. 1875.
>
> MY DEAR STOKES,
>
> I quite concur with you that Mr. Gore's paper should now be printed *in extenso* in the proceedings.
>
> Mrs. Maxwell has been keeping pretty well and has been able to get out on her pony.
>
> Would you agree with the following statements about elasticity and viscosity, as related to a molecular theory?
>
> When after being strained the groups of molecules in a body tend to return to the same stable configurations as when unstrained, the body is elastic. If at corresponding stages of the straining and restitution the stresses are the same, the body is perfectly elastic. If the stress during restitution is less than that during deformation the elasticity is imperfect.
>
> If, when the strain exceeds a certain value, complete restitution does not occur, this value is called the limiting strain and the stress the limiting stress of elasticity.

If, when the stress is removed, the body does not completely return to its original form the body is said to be plastic or viscous. A viscous body, if kept strained long enough, loses all tendency to change its form. A plastic body does not permanently change its form unless the stress exceeds a certain value, and if kept strained it never loses all stress.

THEORY

In an elastic solid the thermal agitation of the molecules does not carry them beyond the limits of oscillating about stable configurations.

But as the thermal agitation increases so many molecules per second are thrown out and oscillate about a new configuration, the nature of which is determined by the present form of the body and not by its unstrained form. The greater the strain it is probable that more molecules will be so thrown out; but the number is not proportional to the strain, but varies very little for small strains, and suddenly rises enormously for breaking strains.

If $1/l$ of the molecules are thrown out in unit of time from a state of strain represented by e, f, g, a, b, c, see Thomson and Tait, and if these molecules enter into the state $\frac{1}{3}\theta$, $\frac{1}{3}\theta$, $\frac{1}{3}\theta$, 0, 0, 0, where

$$\theta = e + f + g,$$

then *

$$\frac{de}{dt} = \frac{1}{l}\left[e - \tfrac{1}{3}\theta\right] + \frac{du}{dx},$$

$$\frac{da}{dt} = -\frac{1}{l}a + \frac{dv}{dz} + \frac{dw}{dy};$$

and if k and n are the coefficients of elasticity so that

$$P = \left(k - \tfrac{2}{3}\mathrm{n}\right)\theta + 2ne \text{ and } S = na,$$

the equations of motion will be of the form

$$\frac{1}{\dfrac{1}{l} + \dfrac{d}{dt}}\left[\left[\frac{k}{l} + \left[k + \frac{n}{3}\right]\frac{d}{dt}\right]\frac{d\theta}{dx} - n\nabla^2 u\right] + X - \rho\frac{Du}{Dt} = 0,$$

with 2 others and

$$\frac{d\theta}{dt} = \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}.$$

If l is small we may put

$$p = C - k\theta \text{ and } nl = \mu$$

and the equation becomes

$$-\frac{dp}{dx} - \mu\nabla^2 u + X - \rho\frac{Du}{Dt} = 0.$$

Yours very truly,
J. CLERK MAXWELL

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* Here (u, v, w) is velocity. The signs of the terms involving $\nabla^2 u$ below should be changed, unless $\nabla^2 u$ has itself the quakernionic sign.

Maxwell made an experiment to show that fluids, in spite of the great mobility of their particles, possess a characteristic property of solid bodies, namely rigidity (elasticity). Maxwell showed that just as glass under pressure acquires the polarizing property, so also a fluid layer of Canada balsam, by suitable deformation becomes optically active and doubly refractive. Maxwell's method was applied to other liquids by A. Kundt [1881] and G. de Metz [1887] (olive oil, mixtures of olive oil and petroleum or paraffin, collodium, castor oil, Canada balsam in bencol, glue in water, almond oil, whale liver oil). They tried and failed to verify the idea suggested by Maxwell's constitutive theory that the rigidity (elasticity) would be greater in more viscous liquids. Maxwell's theory gives the instantaneous elasticity of a liquid as η/λ. It appears that "relatively" mobile liquids like Canada balsam, gelatin solution, castor oil and olive oil possess the polarizing power to a high degree but much more viscous liquids, glycerin, treacle, sugar solutions and gum arabic, even under the greatest deformation, remain inactive. In fact, Maxwell himself seems to have been persuaded that the polarizing power is great in liquids with slow relaxation, rather than high viscosity.

Schwedoff [1889], Colin [1893], Thompson and Andrews [1905], Tammann and Lauer [1908] and Tamman and Faust [1909] use direct methods involving forces and deformations.

Theodore Schwedoff was a professor of physics at the University of Odessa. He was inspired by Maxwell's ideas and sought a direct means to verify them. He says that

> On connait bien les méthodes expérimentales qui permettent de mesurer la cohésion des corps solides. Quant aux liquides, on n'en a pu mesurer que la viscosité, et, pour cette raison, leur rigidité est réputée nulle. Pourtant, la généralité des propriétés de la matière avait depuis longtemps inspiré aux physiciens l'idée que les fluides aussi, malgré l'extrême mobilité de leurs particules, doivent receler des vestiges de la rigidité. Maxwell conçut l'idée de relier la rigidité des liquides à leur viscosité par l'hypothèse suivante. La rigidité E d'un liquide serait liée au temps "t", écoulé depuis le moment de sa déformation, par la relation
>
> $$E = E_0 e^{-(t/\tau)},$$
>
> où E_0 est la rigidité du liquide au premier instant de déformation, e la base des logarithmes népériens, τ le module de relaxation, c'est-à-dire la période au bout de laquelle E tombe à $(1/e)^{\text{ième}}$ de sa valeur initiale. Cette hypothèse conduit à la loi
>
> $$\eta_1 = E_0\tau,$$
>
> où η est le coefficient de frottement du liquide.

Experiments made by Schwedoff with a solution of 5 grams of gelatin in one liter of water were performed between cylinders. The outer cylinder was stationary. The inner cylinder was set into rotation by twisting a torsion wire fixed at the center of the inner cylinder. After a certain instant, a fixed angle of twist of the inner cylinder was maintained by continuously reducing the torque, detwisting the torsion wire. The function giving the detwist as a function of time, for constant angular displacement of the inner cylinder, is the relaxation function. Schwedoff found that the apparent rigidity followed a law

$$R = E\left[\frac{\lambda}{\epsilon} + \left(1 - \frac{\lambda}{\epsilon}\right) e^{-t/\tau}\right],$$

which resembles Maxwell's but has a residual rigidity as $t \to \infty$. Schwedoff concluded that

(1) The modulus of stiffness (rigidity) is

0.535 dynes/cm^2,

consequently the fluid is 1840×10^9 times less stiff than steel.

(2) The elasticity of the fluid is perfect if the deformation does not exceed a certain amount λ and only lasts for a moment.

(3) If the deformation exceeds λ for any length of time, a deformation ρ remains over and the fluid no longer returns to its old position. Colin [1893] rediscovered the effects described by Schwedoff for a solution of gelatin of strength five gram per liter except that the rigidy was not found to vanish when the duration of the deformation was infinitely great. In Colin's experiments the angle of twist of the torsion wire is fixed, and the angle of twist of the inner cylinder is measured. Colin says that the gelatin is not a true liquid because its properties change with time. He rejects Schwedoff's law of rigidity but accepts Maxwell's, reporting some data for castor oil and claims for olive oil.

There are a number of papers on the measurement of rigidity of colloids, gels and sols. Some references for these are given in Section 9.2 of the article by Bateman [1932] and in Chap. XI of the book by Barr [1930]. The physiologist W.R. Hess [1915] did free oscillation experiments in a Couette apparatus using gelatin solutions which did not solidify. His demonstration of elasticity in these liquids was attributed to cohesive forces. Michaud [1923] found that as the concentration of jelly in water is progressively decreased the rigidity becomes zero before the concentration. He concludes that water has no rigidity.

A different approach to the problem of rigidity of liquids was taken in England by Trouton and Andrews [1905] and in Germany by Tammann and Lauer [1908] and Tammann and Faust [1909]. H. Markovitz noted that Trouton and Andrews

> reported on their studies on hot glass, pitch and shoemakers's wax. In their apparatus they mounted a cylindrical sample of the material and performed torsional experiments. On

> applying a load they were surprised to note first that the coefficient of viscosity of bodies such as pitch is a function of the time and "second, that on removing the stress there is a flow back in the opposite direction". Thus, for the first time, we have a creep and recovery experiment on a fluid. They noted further that when they plotted the applied torque against the steady-state angular velocity they did not obtain a straight line through the origin; this was the first evidence of a shear-dependent viscosity in a fluid. Then they proceeded to perform a stress-relaxation experiment by removing weights to keep the angular deformation constant. Even now few rheological investigations are that thorough.

The German experiments of Tammann, Lauer and Faust were equally ingenious. Their apparatus is composed of concentric glass spheres, with a (large) gap of 0.65 cm. The inner cylinder is moved impulsively by a magnetic device and its motions and recoil are measured. In the 1908 paper they find that glycerin and a fluid called Betol have rigidity (elasticity) when the temperature is below a certain critical value. When the temperature is above the critical one (the viscosity is below a critical viscosity) they are unable to detect the signal which indicates the passage of the wave. They found no rigidity for water. In the 1909 paper they found that twelve out of twenty five liquids studied by them displayed rigidity when the viscosity was larger than a critical value.

This ends my survey of the contents of the old literature on the elasticity of liquids. The new literature is the literature of rheology. In the words of Marcus Reiner [1949]

> Rheology came into being as a separate branch of science as a result of the following development: Until quite recently, the technologist took his materials from nature, either as they were found, e.g. timber and stone, or refined according to methods gradually developed through thousands of years, e.g. iron and other metals. Only in a very few cases were the materials artificial products and then the method of their production had been invented ages ago and probably by chance as was the case with glass. The mechanical properties of these materials were taken as nature or chance had turned them out. Then the modern development of such industries as deal with paints, plastics, ceramics, lubricants, cellulose and rubber-products etc. necessitated the large scale production of artificial materials "which were to possess definite mechanical properties". The processes by which these materials were produced were developed by chemists. When these chemists had to investigate the mechanical properties of their materials, it became apparent that the scientific terminology which mechanics had to offer them in it theories of elasticity and viscosity was much too primitive.

I again draw attention to the 1968 review of the history of rheology by Markovitz. That review, like this, emphasizes pre-rheology. I should also like to draw attention to the personal and interesting account of the early modern history of the physics of flow of viscoelastic liquids by Ronald Rivlin [1971].

The literature of rheology is wonderfully interesting because of the bewildering variety of novel effects which may be observed. Some of the main effects, which were mentioned already in the first paragraph of this paper, are nonlinear. Among the most interesting of these nonlinear effects are those associated with normal stresses. These effects are beautifully displayed in diagrammatic sketches of seven different experiments in a paper of Weissenberg [1947], and cited repeatedly from that year to this. An interesting account of these and other special effects can be found in the book of Bird, Armstrong and Hassager [1977] and in the popular review paper of Bird and Curtiss [1984].

Nonlinear and elastic responses in fluids need not be related. In fact, fluids which depend on $\boldsymbol{D}[\boldsymbol{u}]$ alone, called Reiner–Rivlin fluids, can be very nonlinear and give rise to normal stress and other nonlinear phenomena. However, these nonlinear viscous fluids have a zero first normal stress in shear flow, contradicting experiments. Therefore the nonlinearities in fluids which have been tested so far seem to be associated with elasticity in subtle ways. For example, it can be shown that nonlinear effects associated with normal stress, shear thinning, cross-viscosity, etc. in elastic liquids are related to moments of the relaxation kernel $G(s)$. These moments can be large only if $G(s)$ does not decay too rapidly. Rapid decay would be the rule for elastic liquids which pretend to be Newtonian.

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