Research Article

Bouncing Liquids and Flowing Solids

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Summary: *Many materials, such as blood, emulsion paints, modern lubricating oils, plastics of all kinds, and so on, have properties which are different from those of ordinary liquids and solids. The response to stress of some of these materials can be spectacularly different from that of viscous liquids and elastic solids; they can exhibit behaviour which cannot be adequately explained by the simple mathematical laws of classical theories. This behaviour is the concern of rheologists.*
The unusual behaviour of these materials is discussed and a brief review is made of some fairly recent developments in the formulation of mathematical equations which can explain such behaviour.

Keywords: *Rheology, deformation, flow, stress, strain, non-Newtonian liquids, non-Hookean solids*

Introduction

The best example of a bouncing object is a rubber ball or a billiard ball. Both these are made of solid material and can be classified as *bouncing solids*. On the other hand, water and beer are good examples of *flowing liquids*. This 'normal' behaviour of solids and liquids can be mathematically explained by the classical theories of **solid deformation** (Hooke's law of elasticity) or **liquid flow** (Newton's law of viscosity). Here we exclude gaseous materials.

However, the behaviour suggested by the title of this article is rather different from that of our daily experience. Indeed many modern materials exhibit behaviour which cannot be adequately explained by any of the classical theories of solid deformation or liquid flow. The field of study which deals with such behaviour is **rheology**. The word rheology comes from the Greek ῥειν meaning 'to flow' and it is applied to the study of deformation and flow of materials *which do not conform to simple mechanical laws*. In rheology we generally distinguish between liquids and solids as those materials which change, or do not change, their shape continually when subjected to forces however small; that is, *a liquid is one which changes, while a solid is one which does not change, its shape under its own weight*; thus, for example, ordinary table jelly is a solid, though when shaken it shows the appearance of a mobile liquid. Here we are in a field where the boundary between liquids and solids is not very sharp. Indeed certain materials exhibit some of the properties of ordinary solids and some of the properties usually associated with ordinary liquids – they have both elasticity and viscosity in varying degrees.

Rheological Study Cycle

Our aim is to construct precise unambiguous statement of all the deformation and flow properties of real physical continuous materials which ideally describe the behaviour of the material under all conditions of motion and of stress. One way of achieving this is to combine the effort of the experimental and the theoretical rheologists working in close collaboration in a study cycle consisting of four important linked stages:

(i) Observation of behaviour of material experimentally;

(ii) Formulation of mathematical laws to explain observed behaviour;

(iii) Use of formulation to predict behaviour under new conditions of stress;

(iv) Back to the laboratory to confirm (or otherwise) predicted behaviour.

Prediction should be the basis on which crucial experiment is planned to test the validity of the new formulation. Any discrepancy between prediction and experimental observation requires a repetition of the cycle according to the following flow diagram:

Study Cycle

Experimental	Observation of behaviour	← Confirmation of predictions
	↓	↑
Theoretical	Formulation of Mathematical laws	→ Prediction of new behaviour
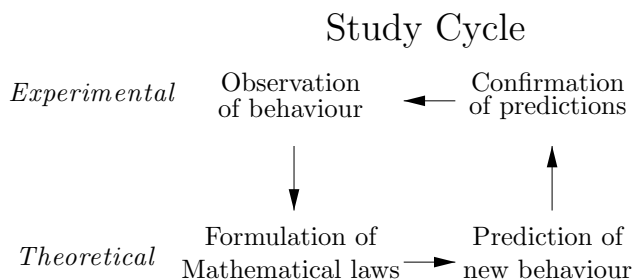
Idealized Materials with Simple Properties

In our day to day experience with ordinary liquids and solids we observe behaviour which lead to the formulation of simple mathematical laws known as the *equations of state* for the materials.

Liquids

- Flow or change shape under their own weight. They need to be kept in containers;
- Do not have inherent elasticity;
- When disturbed they settle down slowly while the applied energy is dissipated into heat;
- Easily divided into parts or droplets which do not show sharp edges.

Equation of state is Newton's law of viscosity *stress $\propto$ rate-of-strain* or

$$p = \eta e, \qquad (1)$$

if incompressible, where η is the (constant) coefficient of viscosity.

Solids

- Do not flow but keep their shape, and do not deform under their own weight;
- Elastic – some very extensible (rubber), some not very extensible (steel);
- Spontaneously resume their shape after dilatation. The applied energy is stored as elastic energy and is recovered immediately;
- When broken by large forces, they show sharp edges (bottle neck effect);

Equation of state is Hooke's law of elasticity *stress $\propto$ strain* or

$$p = \mu E, \qquad (2)$$

where μ is the (constant) modulus of elasticity.

Three Dimensional Stressing

In general, we take a set of Cartesian coordinate axes Ox_1, Ox_2, Ox_3 using suffixes $1, 2, 3$ instead of writing Ox, Oy, Oz (see, for example, *Vector Analysis*, Camilleri, 1994) to combine the different equations corresponding to shearing in different planes and write invariant equations involving the stress tensor p_{ik} ($i, k = 1, 2, 3$) and the rate-of-strain tensor e_{ik} or strain tensor E_{ik}.

Equations of state (1) and (2) then take Cartesian tensor form

$$p_{ik} = \eta e_{ik} \qquad \text{and} \qquad p_{ik} = \mu E_{ik}. \qquad (3)$$

In both cases the equations of state are *linear algebraic* relations involving second-order symmetric ($p_{12} = p_{21}$, etc.) tensors and physical constants. Hence each of relations (3) represent nine equations, of which only six are different. Using these simple equations engineers have managed over the years to build ships, bridges, dams, cathedrals, towers, etc.

Materials with Complicated Properties

There are other materials whose behaviour under stress is spectacularly different from that of classical idealized materials. The following are a few examples of easily observed violations of the more familiar behaviour.
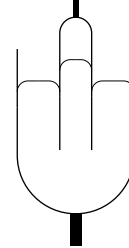
(a) Blood is non-Newtonian
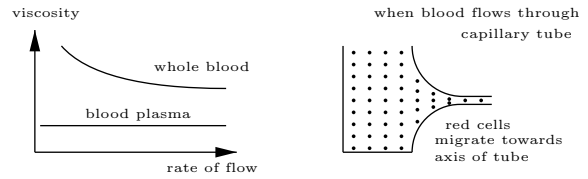
(b) Merrington Effect   (c) Weissenberg Effect
Rubber Solution is non-Newtonian

(a) While the viscosity of blood plasma is constant for all rates of flow, the *viscosity of "whole blood" is not constant but decreases as the rate of flow increases.* Also, when blood flows through a capillary tube the red cells migrate towards the axis of the tube reducing the effective viscosity. This is very fortunate indeed, otherwise we would need far more powerful heart pumps.

(b) Merrington (1943) observed that *rubber solution 'swells radially outwards' on emerging from a capillary tube* whereas Newtonian liquids exhibit the opposite effect known as 'vena contracta'.

(c) Weissenberg (1947, 1948, 1950) observed that *when certain liquids* (such as sweetened condensed milk) *are sheared between rotating coaxial cylinders they tend to migrate towards the inner cylinder* resulting in a higher level there. When stirred with a rod condenced milk tends to 'climb' the rod; it has been suggested to use condensed milk to catch mice, since the poor mouse which finds itself in a shallow pool of such a liquid would get more entangled the harder it tries to get away. On the other hand, when a Newtonian liquid is stirred with a rod it tends to move away from the rod leaving a hollow there.

(d) Again *when the stirring rod is removed certain liquids, such as polymer solutions, tend to 'recoil back' and part of their deformation is gradually recovered* – they are said to have an **elastic memory**. Newtonian liquids would continue to rotate until all energy is dissipated into heat.

(e) A material known as 'bouncing putty' looks and feels very much like ordinary plasticine. Yet it is mobile enough to flow under its own weight and must therefore be classified as a liquid. A piece of this material flows into a pool with a smooth upper surface within minutes of being placed on a table, yet it may be bounced on the table like a rubber ball with no visible flattening at its point of contact with the table. *It shows very different response to slow and to rapid shearing*; when handled slowly it flows even through a fine mesh, but when snapped suddenly it feels elastic and shows sharp edges (bottle neck effect) where it breaks.

In fact we have a whole spectrum of materials which exhibit both viscous and elastic properties in varying degrees. In formulating the equations of state, here we consider a model of the material called a **disperse system** which in the simplest form consists of two uniform component materials.

Disperse Systems Model
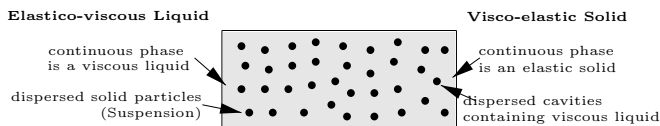
The first material, the disperse phase, which may be solid or liquid, is made up of small bits dispersed at random in the second, the continuous phase, which may also be liquid or solid and which fills all the space between the dispersed bits of the first phase. If both phases are liquid they are taken to be immiscible, one of which or both having elastic properties and the dispersion is referred to as an **emulsion**.

If the continuous phase of the dispersion is a liquid and the dispersed phase consists of solid particles it is referred to as a **suspension**. In this case the dispersion as a whole is essentially a liquid and we talk about an **elastico-viscous liquid**. On the other hand, if the continuous phase of the dispersion is a solid with dispersed cavities filled with viscous liquid, the dispersion as a whole is essentially a solid and we talk about a **visco-elastic solid**.

Elastico-Viscous Liquids

For our purpose here it easiest to consider mainly dipersions having continuous liquid phase i.e. elastico-viscous liquids. The case of essentially solid dispersions or visco-elastic solids follow analogous arguements.

Slow, Steady Rates of Deformation

Einstein (1906, 1911) considered a suspension of *inelastic* solid spherical particles, of concentration c, in a Newtonian liquid of viscosity η and found that

at *very small, steady (time-independent)* rates of shear it behaves as a liquid of viscosity η_0 given by

$$\eta_0 = \eta(1 + 2.5c). \qquad (4)$$

Taylor (1932) found that, again at *very small, steady* rates of shear, the viscosity of an emulsion of liquid droplets of viscosity η', with concentration c, in a liquid of viscosity η is

$$\eta_0 = \eta\left(1 + \frac{\eta + 2.5\eta'}{\eta + \eta'}c\right). \qquad (5)$$

The equation of state for these 'hypothetical liquids' is

$$p_{ik} = 2\eta_0 e_{ik}, \qquad (6)$$

which is still a linear algebraic equation and the liquids are characterized by *one* physical constant η_0 which is, of course, a function of the constants of the component materials and the concentration c. Note that (4) is a special case of (5) as $\eta/\eta' \to 0$. The models of Einstein and Taylor exhibit no elasticity of shape at all (all component materials assumed inelastic) so that when all deforming forces are suddenly released such materials retain their shape without recoil.

Small, Variable Deformation

Fröhlich and Sack (1946) considered a suspension of Hookean elastic solid spheres of elastic modulus μ uniformly dispersed in a Newtonian liquid of viscosity η, and showed that, at *small variable* rates of shear, the equation of state relating the viscous stress p_{ik} to the rate-of-strain e_{ik} takes the form

$$\left(1 + \lambda_1\frac{\partial}{\partial t}\right)p_{ik} = 2\eta_0\left(1 + \lambda_2\frac{\partial}{\partial t}\right)e_{ik} \qquad (7)$$

with $\quad (\lambda_1 > \lambda_2 > 0), \quad$ where $\quad \eta_0 = \eta(1 + 2.5c)$,

$$\lambda_1 = \frac{\eta(3 + 5c)}{2\mu}, \qquad \lambda_2 = \frac{\eta(3 - 7.5c)}{2\mu}.$$

It is to be noted that the equations are now *linear differential* equations involving rate-of-change with respect to time, i.e. they are time-dependent. The class of liquids characterized by (7) are referred to as **liquids of type1** since the equation involves *first* derivatives. It is characterized by *three* physical constants; a relaxation time λ_1, a retardation time λ_2, and viscosity η_0. These materials exhibit both viscous and elastic properties. On the application of external stresses the suspended elastic particles will now be deformed absorbing some energy, but the deformation requires time which depends on the viscosity of the continuous liquid phase. On removal of the external stress, the particles require time to recover their undeformed shape and release the stored elastic energy.

Oldroyd (1953) showed that the properties of an idealized dilute emulsion with liquid droplets replacing the elastic spheres are quantitatively the same

as for the corresponding suspension. The investigations were extended by Oldroyd (1955) to include the effect of an interfacial film everywhere between the boundaries of the two phases, such as that introduced when a trace of stabilizer is added to an emulsion. He found that, if the film has any inherent elasticity, the equation for p_{ik} (again for slow, variable deformation) takes the form

$$\left(1 + \lambda_1 \frac{\partial}{\partial t} + \nu_1 \frac{\partial^2}{\partial t^2}\right) p_{ik} = 2\eta_o \left(1 + \lambda_2 \frac{\partial}{\partial t} + \nu_2 \frac{\partial^2}{\partial t^2}\right) e_{ik} \tag{8}$$

possibly with more additional derived terms on each side. The class of liquids characterized by (8) are referred to as **liquids of type 2** since the equation involves *second* derivatives. These liquids are characterized by 5 physical constants $\lambda_1, \lambda_2, \nu_1, \nu_2$ and η_0. Liquids characterized by an equation of the form

$$\left(1 + \alpha_1 \frac{\partial}{\partial t} + \alpha_2 \frac{\partial^2}{\partial t^2} + \ldots + \alpha_N \frac{\partial^N}{\partial t^N}\right) p_{ik}$$

$$= 2\eta_o \left(1 + \beta_1 \frac{\partial}{\partial t} + \beta_2 \frac{\partial^2}{\partial t^2} + \ldots + \beta_N \frac{\partial^N}{\partial t^N}\right) e_{ik}, \tag{9}$$

where the constant η_0 is the limiting viscosity at small rates of shear and $\alpha_1, \beta_1 \alpha_2, \beta_2, \ldots, \alpha_N, \beta_N$ are constants such that α_N and β_N do not both vanish, are referred to as **liquids of type** N. Oldroyd (1962) showed that in general, a dilute emulsion consisting of a liquid of type M dispersed in a liquid of type N, with constant interfacial tension between the two components is an elastico-viscous liquid of type (at most) $1 + 2M + 3N$.

Linear differential equations of the forms (7) to (9) may also be simulated by mechanical models consisting of springs and dashpots in series and in parallel – see, for example, *Hydrodynamics of Elastico-Viscous Liquids*, Camilleri (1965).

It is noted that for *slow steady* shearing equations (7) to (9) would reduce to the Newtonian viscosity relation (6).

Finite Rates of Deformation

In obtaining the equations of state (7) to (9) we restricted attention to *small* variable rates of deformation and it is found that these equations are not adequate to describe behaviour at finite rates of deformation. Any quantity associated locally with a fluid, such as the temperature of the fluid, or a stress or rate-of-strain component, changes in general at a different rate according to whether we measure it at a fixed point in space over an interval of time, or measure it in a certain macroscopic element of fluid (which is moving in space) over the same instant of time. In ordinary hydrodynamics we distinguish between the rate of change with respect to time at a fixed point ($\partial/\partial t$) and the rate of change with respect to time following the material particle (D/Dt).

Thus for the scalar density ρ we have

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + v_i \frac{\partial \rho}{\partial x_i}, \tag{10}$$

where v_i ($= v_1, v_2, v_3$) is the velocity of the element and summation is understood over the repeated suffix i according to the usual summation convention.

The derivative D/Dt measures the rate of change with respect to time relative to a *moving coordinate system* whose origin is moving with the material particle. It allows for the translation of the material element and is sufficient when differentiating scalar quantities. When it comes to vector or tensor quantities (which are associated with directions) we must take a rate of change of the components relative to a *rotating coordiate system* which is moving and rotating with the material element.

A time derivative of a tensor p_{ik} that corrects for the translation as well as the rotation of the fluid element is **Oldroyd material derivative** $\mathcal{D}/\mathcal{D}t$, given by (Oldroyd, 1958)

$$\frac{\mathcal{D}}{\mathcal{D}t} p_{ik} = \frac{\partial}{\partial t} p_{ik} + v_j \frac{\partial}{\partial x_j} p_{ik} + \omega_{ij} p_{jk} + \omega_{kj} p_{ij} \tag{11}$$

where the linear motion of the fluid element is accounted for by its velocity vector v_i and the angular motion by the vorticity tensor ω_{ik} measured by

$$\omega_{ik} = \frac{1}{2}\left(\frac{\partial v_k}{\partial x_i} - \frac{\partial v_i}{\partial x_k}\right). \tag{12}$$

A time derivative of a tensor p_{ik} relative to a *convected coordinate system* which moves, rotates and deforms with the material is **Oldroyd convected derivative** $\mathcal{V}/\mathcal{V}t$, defined by (Oldroyd, 1950)

$$\frac{\mathcal{V}}{\mathcal{V}t} p_{ik} = \frac{\mathcal{D}}{\mathcal{D}t} p_{ik} + e_{ij} p_{jk} - e_{kj} p_{ij}. \tag{13}$$

This corrects also for the *straining* of the material which is measured by the rate-of-strain tensor

$$e_{ik} = \frac{1}{2}\left(\frac{\partial v_k}{\partial x_i} + \frac{\partial v_i}{\partial x_k}\right). \tag{14}$$

For a tensor p_{ik}, the derivative $\mathcal{V}/\mathcal{V}t$ differs from $\mathcal{D}/\mathcal{D}t$ only in the addition of simple products of p_{ik} and e_{ik}. It can be shown (see *Tensor Analysis*, Camilleri, 1999) that we may obtain universally valid constitutive equations of state – that is, equations with a physical significance for the material independent of any particular frame of reference and independent of the motion of the material as a whole in space – if we replace the partial time-derivative $\partial/\partial t$ in equations of state (7) to (9) by the convected time-derivative $\mathcal{V}/\mathcal{V}t$ or the material time-derivative $\mathcal{D}/\mathcal{D}t$, both of which are eligible for inclusion into

constitutive equations. The simplest possible generalization of equation (9) which is valid for all conditions of motion and stress takes the form

$$\left(1 + \alpha_1 \frac{\mathcal{D}}{\mathcal{D}t} + \alpha_2 \frac{\mathcal{D}^2}{\mathcal{D}t^2} + \ldots + \alpha_N \frac{\mathcal{D}^N}{\mathcal{D}t^N}\right) p_{ik}$$
$$= 2\eta_o \left(1 + \beta_1 \frac{\mathcal{D}}{\mathcal{D}t} + \beta_2 \frac{\mathcal{D}^2}{\mathcal{D}t^2} + \ldots + \beta_N \frac{\mathcal{D}^N}{\mathcal{D}t^N}\right) e_{ik}. \tag{15}$$

The equations of state (7) to (9) are linear differential equations and liquids characterized by them are often referred to as **linear** elastico-viscous liquids. But, in view of relation (11), the material derivative destroys the linear nature of equation (15). The first material derivative involves simple contracted products of the rate-of-strain with itself and with stresses, and higher material derivatives involve products of higher degree in stress and rate-of-strain taken together. Other generalizations of equation (15) involve such products of degree up to $(N + 1)$. In particular the most general constitutive equation of state for liquids of type *1* is

$$\left(1 + \lambda_1 \frac{\mathcal{D}}{\mathcal{D}t}\right) p_{ik} + \kappa_1 e_{ik} p_{jj} + \kappa_2 (e_{ij} p_{jk} + e_{kj} p_{ij})$$
$$+ \kappa_3 e_{jn} p_{jn} \delta_{ik}$$
$$= 2\eta_0 \left(e_{ik} + \lambda_2 \frac{\mathcal{D}e_{ik}}{\mathcal{D}t} + 2\kappa_4 e_{ij} e_{jk} + \kappa_5 e_{jn} e_{jn} \delta_{ik}\right), \tag{16}$$

first suggested by Oldroyd (1958), which involves *eight* physical constants characterizing a wide spectrum of materials. The corresponding generalization for liquids of type *2* which include third-order products in stress/rate-of-strain taken together was obtained by Camilleri (1965) and involves no less than *thirty* physical constants.

The class of liquids characterized by constitutive equations of state (16) are capable of exhibiting the kind of non-Newtonian behaviour that is often observed in real liquids as, for example, a variation of apparent viscosity with the rate of steady shearing (Oldroyd, Strawbridge & Toms, 1950), the Weissenberg climbing effect (Lux-Weiner & Scoenfield-Reiner, 1952), a distribution of normal stresses corresponding to an extra tension along the streamlines (Roberts, 1954), and secondary transverse circulatory flow in the section between non-intersecting cylinders of various shapes (Camilleri & Jones, 1965, 1966).

Visco-Elastic Solids

In an analogous way, dispersions which are essentially solid, having a solid continuous phase in which spherical cavities, filled with liquid or with solid of another material, are characterized by a single shear modulus μ_0 if examined in equilibrium or at sufficiently small rates of shear.

Mackenzie (1950) considered the case of a continuous phase with shear modulus μ and bulk modulus κ and found that the presence of scattered small holes results in a disperse system of shear modulus

$$\mu_0 = \mu \left[1 - \frac{5(3\kappa + 4\mu)c}{9\kappa + 8\mu}\right].$$

Hashin (1955) considered the presence, instead, of scattered small rigid spherical inclusions which resulted in an increased shear modulus

$$\mu_0 = \mu \left[1 + \frac{5(3\kappa + 4\mu)c}{6(\kappa + 2\mu)}\right].$$

Oldroyd (1956) found that for small variable rates of shear the equation of state for visco-elastic disperse systems is of the form

$$\left(1 + \alpha_1 \frac{\partial}{\partial t} + \alpha_2 \frac{\partial^2}{\partial t^2} + \ldots + \alpha_N \frac{\partial^N}{\partial t^N}\right) p_{ik}$$
$$= 2\mu_o \left(1 + \beta_1 \frac{\partial}{\partial t} + \beta_2 \frac{\partial^2}{\partial t^2} + \ldots + \beta_N \frac{\partial^N}{\partial t^N}\right) E_{ik}, \tag{17}$$

replacing the equation $p_{ik} = \mu_0 E_{ik}$, representing Hooke's law, which in this system is valid only in equilibrium. Equation (17) may be generalized to a universally valid constitutive equation by replacing the partial derivatives with the material or convected derivatives, the simplest generalization being

$$\left(1 + \alpha_1 \frac{\mathcal{D}}{\mathcal{D}t} + \alpha_2 \frac{\mathcal{D}^2}{\mathcal{D}t^2} + \ldots + \alpha_N \frac{\mathcal{D}^N}{\mathcal{D}t^N}\right) p_{ik}$$
$$= 2\mu_o \left(1 + \beta_1 \frac{\mathcal{D}}{\mathcal{D}t} + \beta_2 \frac{\mathcal{D}^2}{\mathcal{D}t^2} + \ldots + \beta_N \frac{\mathcal{D}^N}{\mathcal{D}t^N}\right) E_{ik}, \tag{18}$$

To conclude, we shall expect a wide range of materials to be characterized by differential constitutive equations of the form (15) representing what is fundamentally liquid behaviour, or of the form (18) representing basically solid behaviour. The physical constants in the equations will distinguish between different materials of the same class. In *steady* flow at small rates of shear or at *constant* small shear (that is, at constant shear stress in either case), the differential equations will reduce to those for the corresponding classical idealized material.

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