

Theory of the rheological properties of dispersions†

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A theory of flow of substances showing elastic recovery is developed. It leads to a set of differential equations which contain three parameters. In the case of dispersions these parameters can be derived from the properties and the composition of the components.

1. INTRODUCTION

In the mechanics of continua the theories of two types of substances have been mainly considered, those of Hookean elastic solids and of Newtonian fluids. It is common knowledge that there are many substances of great importance which cannot be classified under either heading. Some of these substances exhibit both elastic and viscous properties; they flow under the influence of applied stresses, but on removal of stress part of their deformation is gradually recovered, a phenomenon known as elastic recovery.

The aim of the present paper is twofold. First, we shall derive a set of fundamental differential equations which describe the properties of flow of substances which show elastic recovery. These equations contain a number of parameters, and it is the second aim of this paper to relate these parameters to structural properties of such materials. Many of the substances which exhibit elastic recovery are two-phase systems forming colloidal sols, or dispersions consisting of independent solid micelles embedded in a viscous fluid. They can be represented by a simplified physical model in which the micelles are considered to be elastic spheres, while the fluid is treated according to the classical theory of hydrodynamics. This is a model which we were able to treat without undue mathematical difficulties, while on the other hand sols are also of considerable experimental interest.

Although we shall restrict ourselves to dispersions, the resulting equations of flow are of a very general nature if we do not specify the parameters by the expressions which connect them with the structure of the dispersions. We, therefore, hope that these equations may also be applicable to other substances. On the other hand, we are aware that they can be generalized in various ways, but in the present paper it is our intention to present them in their simplest form.

2. STRUCTURE AND METHOD

First, then, consider a substance consisting of equal elastic spheres dispersed in a Newtonian fluid of viscosity η . To simplify calculations a unit length is chosen such that on an average there is one solid sphere contained in the volume $4\pi/3$, i.e. in a

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sphere of unit radius. If a is the radius of the elastic spheres measured in this unit, a^3 is the relative volume occupied by the dispersed particles compared to the total volume of the mixture. By definition

$$a^3 < 1. \quad (1)$$

It will be assumed that the fluid adheres to the surface of the spheres, which means that the velocity of flow at such a surface is the same for the fluid as for the elastic sphere. It is easy to consider qualitatively the rheological properties of such a substance. Consider first the spheres as rigid. As has been shown by Einstein (1906, 1911) such a system behaves like a fluid with an effective viscosity

$$\eta^* = \eta(1 + \frac{5}{2}a^3), \quad (2)$$

provided

$$a^3 \ll 1. \quad (3)$$

Actually the spheres are not rigid, which means that on application of a stress they are deformed. In view of the adherence of the fluid to the sphere this deformation requires a certain time which depends on the viscosity η . Thus on application of an external stress to our substance one would expect a flow whose velocity gradually decreases, and which ultimately reaches a value determined by the effective viscosity η^* . On removal of the external stress the spheres, in view of their interaction with

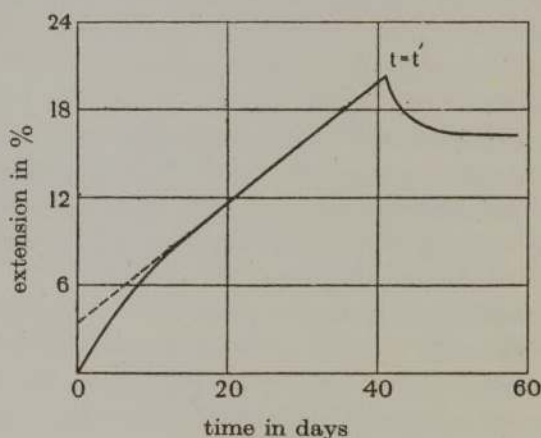


FIGURE 1. Experimental strain-time curve of a bitumen according to Lethersich (1942). A constant load is applied at the time $t = 0$ and removed at $t = t'$.

the surrounding fluid, will again require some time to go back to their undeformed shape. This gives rise to an elastic recovery. A behaviour of the type described just now is displayed by many substances. As an example figure 1 shows the experimental strain-time relation of a bitumen of the sol type.

The next task is to develop the above consideration into a quantitative theory. This will be done for those substances for which the volume occupied by all the spheres is small compared with the total volume of the substance, i.e. for which

condition (3) is valid. The spheres as well as the fluid will be assumed to be incompressible and isotropic, and that their inertia can be neglected, i.e. oscillations will not be considered. The elastic behaviour of the spheres can thus be described by a single elastic constant, e.g. the modulus of rigidity k , which means that a shear stress S_{ik} produces a shear strain d_{ik} given by

$$S_{ik} = 2kd_{ik}. \quad (4)$$

The fluid obeys the following equations (cf. text-books on hydrodynamics). Let \mathbf{u} be the velocity of flow with the components u_i ($i = 1, 2, 3$) in rectangular co-ordinates. Then the condition for incompressibility is

$$\text{div } \mathbf{u} = 0. \quad (5)$$

Furthermore, if S_{ik} ($i, k = 1, 2, 3$) are the stress components in rectangular co-ordinates,

$$S_{ik} = -p\delta_{ik} + \eta \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right), \quad (i, k = 1, 2, 3), \quad (6)$$

where p is the hydrostatic pressure while

$$\delta_{ik} = \begin{cases} 0, & \text{if } i \neq k, \\ 1, & \text{if } i = k. \end{cases}$$

Clearly, using (5) and (6), $S_{11} + S_{22} + S_{33} = -3p$. (7)

Assuming that there are no external volume forces, general principles of mechanics if applied to (6) lead to the well-known differential equations

$$\eta \Delta u_i - \frac{\partial p}{\partial x_i} = 0 \quad (i = 1, 2, 3). \quad (8)$$

A method must now be found to derive the macroscopic rheological properties of our substance from the behaviour of its components. For this purpose a method has been generalized which has been used to calculate from the behaviour of a single dipole the macroscopic dielectric polarization of a dipolar substance in an external electric field. A 'unit cell' is chosen consisting of one sphere and some fluid and the whole medium treated outside the unit cell as a macroscopic continuum. Then it is demanded that the macroscopic flow remains unchanged if the unit cell too be replaced by the macroscopic medium. This will lead to the conditions from which the macroscopic properties of flow can be deduced.

Einstein (1906, 1911) used a different method for his case of rigid spheres which can also be generalized and applied to the case of elastic spheres. In view of (3) both methods consider the influence of the spheres as a perturbation of the viscous flow of the fluid and should, therefore, lead to the same result. We have satisfied ourselves that this is actually the case, although the mathematical treatment is different. In the following we shall present the calculations according to our method which we think, in the present case, leads in a more direct way to the macroscopic rheological properties.

To bring the present method into a mathematically convenient form it will be noticed that the equations (4)–(8) for the components of our substance connect stresses in a linear way with deformations and their time derivatives. Therefore, in view of the incompressibility and of the isotropy of our substance, any suitable system of external stresses and any suitable macroscopic shape of the substance may be chosen in order to calculate its flow. Its behaviour under another system of stresses or when its macroscopic shape is different will then follow from symmetry.

A cube of our substance will be chosen whose centre coincides with the origin of the co-ordinate system, and whose surfaces are perpendicular to the co-ordinate axes x_i . At the surfaces perpendicular to x_1 a uniaxial stress $3T$ is applied. Instead, in view of the incompressibility at the cube, the following equivalent system of tensile stresses may be applied:

$$S_{11} = 2T, \quad S_{22} = S_{33} = -T, \quad \text{i.e. } p = 0, \quad (9)$$

which differs from the uniaxial stress only by adding the hydrostatic pressure T . Although the properties of flow of our substance are not known, its incompressibility and isotropy in conjunction with the linearity of equations (4)–(8) require the following spacial distribution of flow:

$$u_1 = 2\gamma x_1, \quad u_2 = -\gamma x_2, \quad u_3 = -\gamma x_3, \quad (10)$$

where γ depends on the stress, T , but is independent of the co-ordinates x_i . For the same reasons the stresses inside the substance are also given by (9), i.e. they are independent of the co-ordinates x_i . γ may, and in general will, however, depend on time, and the calculation of this time dependence is our main task.

The subsequent consideration of the macroscopic structure will give rise to axial symmetry. We shall consider within our substance a macroscopic sphere of radius $R \gg 1$. If polar co-ordinates (r, θ, ϕ) with the 1-direction as axis be chosen, the stress system (9) is given by

$$S_{rr} = 2TP_2(\cos \theta), \quad S_{r\theta} = TP'_2(\cos \theta), \quad S_{r\phi} = 0, \quad p = 0, \quad (11)$$

while the components of the flow (10) are now

$$u_r = 2\gamma r P_2, \quad u_\theta = \gamma r P'_2, \quad u_\phi = 0, \quad (12)$$

where P_2 is the second Legendre polynomial, i.e.

$$P_2(\cos \theta) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}, \quad P'_2(\cos \theta) = -3 \cos \theta \sin \theta. \quad (13)$$

The suffixes r, θ, ϕ of S and u refer to the r, θ and ϕ components respectively.

Under the influence of stresses of the type (11), such a macroscopic sphere will be transformed into a spheroid. It will be considered as long as it can be approximated by the original sphere, and the flow compared at its surface $r = R$ with that of another sphere which has the same radius R but in which a 'unit cell' of the substance near the centre has been replaced by its microscopic structure. This second representation of our substance (cf. figure 2) consists of three concentric spheres of radius $a < 1$, 1, and $R \gg 1$. The inner sphere contains the elastic material described by the modulus of

rigidity k , the shell between $r = a$ and $r = 1$ is filled with the fluid with the viscosity η , while the shell outside $r = 1$ contains the continuum with the macroscopic properties which is to be calculated. For both inner surfaces $r = a$ and $r = 1$ continuity of stress and flow will be demanded. At the outer surface $r = R$, the stress system (11) will be applied and the flow at this surface must be calculated considering the condition (3). This flow will then be equated to the flow at the surface of the first (homogeneous) sphere of radius R which is given by equation (12) if $r = R$ is inserted. It may be expected that this is possible only if $R \gg 1$. In this case the two macroscopic spheres, i.e. the homogeneous one and the one containing the unit cell, are equal except for the parts within the radius $r = 1$. The influence of the substance inside this radius upon the flow at the external surface $r = R$ must be of the order of the ratio of the volumes, i.e. $\sim 1/R^3$. It will, therefore, be demanded that the ratio of the flow at the surfaces $r = R$ of the two large spheres must be unity if terms up to the third power in $1/R$ are considered,

$$\frac{\text{flow of sphere with structure of figure 2}}{\text{flow of homogeneous sphere}} = 1 + \sum_{n>3} \frac{\text{const.}}{R^n} \quad \text{at } r = R. \quad (14)$$

This will allow the calculation of γ .

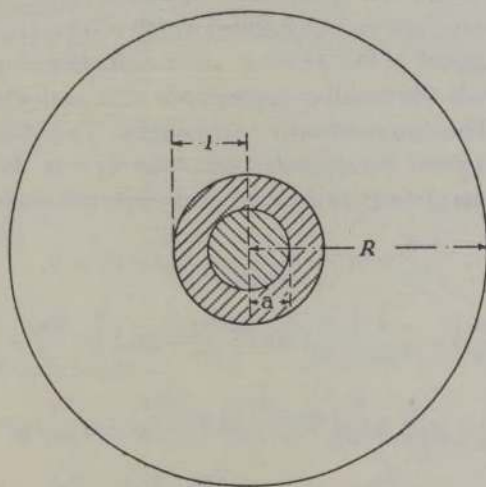


FIGURE 2. Structure of a sphere consisting of an elastic body ($r < a$), a Newtonian fluid ($a < r < 1$), and a continuum with the macroscopic properties of our substance ($1 < r < R$, $R \gg 1$).

3. CALCULATIONS

The following calculations will be greatly simplified if the case in which the spheres of radius a are rigid is considered first. This will not lead to any result beyond (2). The calculations will, however, be given in some detail, because they will be required for the case of elastic spheres which is the main interest. In view of (3) the higher powers in a than a^3 will be neglected throughout.

A. Rigid spheres

In this case the macroscopic substance can be assumed to be a fluid with the unknown viscosity η^* . The value of η^* must follow as a result of the calculations. One requires:

(i) The flow of the homogeneous macroscopic sphere consisting of fluid of the viscosity η^* . With the stress system (11) (or (9)) it is well known to be given by (12) (or (10)), where

$$\gamma = \frac{T}{2\eta^*}. \quad (15)$$

(ii) The flow of the second big sphere which is made up as shown in figure 2. In the present case it consists of a shell between $r = a$ and $r = 1$, containing fluid with a viscosity η which has to satisfy equations (5)–(8), and of a shell between $r = 1$ and $r = R$ containing fluid with a viscosity η^* which has also to satisfy (5)–(8), if η be replaced by η^* . Moreover, the following boundary conditions have to be fulfilled:

$$u_r = 0, \quad u_\theta = 0 \quad \text{at } r = a, \quad (16)$$

$$u_r \text{ and } u_\theta \text{ continuous} \quad \text{at } r = 1, \quad (17)$$

$$S_{rr} \text{ and } S_{r\theta} \text{ continuous} \quad \text{at } r = 1, \quad (18)$$

while at $r = R$, S_{rr} and $S_{r\theta}$ must be given by equation (11).

(iii) Then the condition (14) must be fulfilled which will lead to a determination of η^* .

In view of the symmetry of the problem the ϕ -component of the flow, u_ϕ , will be expected to vanish while the angular dependence of u_r and p should be given by P_2 , and that of u_θ by P'_2 . This leads actually to a solution. To obtain it, it is necessary to transform (5)–(8) into polar co-ordinates and take $u_\phi = 0$. In equations (16)–(18), this latter condition has already been used. One thus obtains from (5)

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (u_\theta \sin \theta) = 0, \quad (19)$$

$$\text{from (8)} \quad \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u_r}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \left(\frac{\partial u_r}{\partial \theta} - 2u_\theta \right) \right] - \frac{2u_r}{r^2} - \frac{1}{\eta} \frac{\partial p}{\partial r} = 0, \quad (20)$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u_\theta}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u_\theta}{\partial \theta} \right) + \frac{2}{r^2} \frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{r^2 \sin^2 \theta} - \frac{1}{\eta} \frac{1}{r} \frac{\partial p}{\partial \theta} = 0, \quad (21)$$

$$\text{and from (6)} \quad S_{rr} = -p + 2\eta \frac{\partial u_r}{\partial r}, \quad S_{r\theta} = \eta \left(\frac{\partial u_\theta}{\partial r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{r} \right), \quad S_{r\phi} = 0. \quad (22)$$

The most general solution of (19)–(21) with a P_2 symmetry contains four constants A, B, C, D and has the form,

$$u_r = \left(\frac{Ar^3}{7} + \frac{B}{2r^2} + 2Cr - \frac{3D}{r^4} \right) P_2, \quad (23)$$

$$u_\theta = \left(\frac{5Ar^3}{42} + Cr + \frac{D}{r^4} \right) P'_2, \quad (24)$$

$$p = \eta \left(Ar^2 + \frac{B}{r^3} \right) P_2. \quad (25)$$

Inserting these solutions into (22) one finds

$$S_{rr} = \eta \left(-\frac{Ar^2}{7} - \frac{3B}{r^3} + 4C + \frac{24D}{r^5} \right) P_2, \quad (26)$$

$$S_{r\theta} = \eta \left(\frac{8Ar^2}{21} + \frac{B}{2r^3} + 2C - \frac{8D}{r^5} \right) P'_2. \quad (27)$$

These solutions refer to $a < r < 1$. The solutions in $1 < r < R$ are the same if η be replaced by η^* and the four constants A, B, C, D by four other constants A_1, B_1, C_1, D_1 . Assuming that η and η^* are given, the solution thus contains eight constants. To determine them one has six homogeneous equations from the boundary conditions (16), (17), (18) together with the two inhomogeneous equations at $r = R$ required to give S_{rr} and $S_{r\theta}$ the values (11). These are just sufficient equations to determine all the eight constants. It is thus seen that the flow of a sphere with the structure of figure 2 can be calculated for any value of η and η^* in terms of the external stress. To determine η^* it is necessary, in addition, to fulfil equation (14), i.e. one must equate the flow at the surface $r = R$ of the sphere (given by (23) and (24) if A, B, C, D are replaced by A_1, B_1, C_1, D_1) to the flow at the surface $r = R$ of a homogeneous sphere of fluid with the viscosity η^* which is given by (12) and (15). For $R \gg 1$, this condition must be fulfilled independently of R . It therefore includes the condition according to which the stress at $r = R$ must be given by (11). Equation (14) thus means for u_r

$$\frac{u_r(R)}{2\gamma R P'_2} = \frac{C_1}{\gamma} \left(1 + \frac{A_1}{14C_1} R^2 + \frac{B_1}{4C_1} \frac{1}{R^3} - \frac{3D_1}{2C_1} \frac{1}{R^5} \right) = 1 + \sum_{n>3} \frac{\text{const.}}{R^n},$$

and for u_θ

$$\frac{u_\theta(R)}{\gamma R P'_2} = \frac{C_1}{\gamma} \left(1 + \frac{5A_1}{42C_1} R^2 + \frac{D_1}{C_1} \frac{1}{R^5} \right) = 1 + \sum_{n>3} \frac{\text{const.}}{R^n}.$$

It follows that

$$C_1 = \gamma \quad (28)$$

and

$$A_1 = 0, \quad B_1 = 0. \quad (29)$$

Solutions in $1 < r < R$ thus become

$$u_r = \left(2\gamma r - \frac{3D_1}{r^4} \right) P_2, \quad u_\theta = \left(\gamma r + \frac{D_1}{r^4} \right) P'_2, \quad (30)$$

$$p = 0, \quad S_{rr} = 4\eta^* \left(\gamma + \frac{6D_1}{r^5} \right) P_2, \quad S_{r\theta} = 2\eta^* \left(\gamma - \frac{4D_1}{r^5} \right) P'_2. \quad (31)$$

There remain the five constants A, B, C, D, D_1 and the six boundary conditions (16), (17) and (18). Since γ is known from equation (15) they lead to six inhomogeneous equations. These can be solved only if the coefficients of the equations fulfil a certain condition. This leads to the determination of η^* . One obtains from (16), using (23) and (24),

$$\left. \begin{aligned} \frac{Aa^3}{7} + \frac{B}{2a^2} + 2Ca - \frac{3D}{a^4} &= 0, \\ \frac{5Aa^3}{42} + Ca + \frac{D}{a^4} &= 0, \end{aligned} \right\} \quad (32)$$

from (17), using (23), (24) and (30),

$$\left. \begin{aligned} \frac{A}{7} + \frac{B}{2} + 2C - 3D &= 2\gamma - 3D_1, \\ \frac{5A}{42} + C + D &= \gamma + D_1, \end{aligned} \right\} \quad (33)$$

and from (18), using (26), (27) and (31),

$$\left. \begin{aligned} -\frac{A}{7} - 3B + 4C + 24D &= \frac{4\eta^*}{\eta} (\gamma + 6D_1), \\ \frac{8A}{21} + \frac{B}{2} + 2C - 8D &= \frac{2\eta^*}{\eta} (\gamma - 4D_1). \end{aligned} \right\} \quad (34)$$

The solution can easily be found by anticipating

$$A = 0. \quad (35)$$

In the final result for η^* terms of a higher order in a than a^3 will be neglected (cf. (3)). Keeping this in mind, then

$$D_1 = \gamma a^3, \quad B = -10\gamma a^3, \quad C = \gamma(1 + a^3), \quad D = -\gamma a^5, \quad (36)$$

and the value (2) for η^* .

It is of interest to calculate the stresses at the surface $r = a$ of the rigid sphere. Inserting (36) and (15) into (26) and (27) then in zero order in a

$$S_{rr} = 5TP_2, \quad S_{r\theta} = \frac{5}{2}TP'_2. \quad (37)$$

This stress system has the same symmetry as the external stress system (11), but it has $\frac{5}{2}$ times its magnitude.

B. Elastic spheres

If the spheres of radius a are considered to be elastic according to (4), a stress of the type (37) will tend to deform them into spheroids. In equilibrium the components d_r and d_θ of the displacement of the surface are thus given by

$$d_r = \frac{5T}{2k} aP_2, \quad d_\theta = \frac{5T}{4k} aP'_2. \quad (38)$$

In view of the viscosity of the fluid which adheres to the surface $r = a$, this deformation cannot be established at once on application of the external stress. Instead, a deformation of the form

$$d_r = EaP_2, \quad d_\theta = \frac{E}{2} aP'_2, \quad (39)$$

may be expected where E depends on time. Throughout, the stresses will be assumed to be weak enough to make

$$E \ll 1, \quad (40)$$

so that the deformed surface of the elastic body can be approximated by the undeformed sphere $r = a$. One thus obtains at this surface for the stress, using (4),

$$S_{rr} = 2kEP_2, \quad S_{r\theta} = kEP'_2, \quad r = a, \quad (41)$$

and for the velocity of flow

$$u_r = \dot{E}aP_2, \quad u_\theta = \frac{\dot{E}}{2}aP'_2, \quad r = a \quad (42)$$

where the dot means differentiation with respect to time.

It must be mentioned here that the most general deformation with a P_2 symmetry is not given by equation (39) but contains additional terms with one further constant F . By putting $F = 0$ we anticipate already part of the solution. Subsequently, when the constants from the boundary conditions are derived, this will lead to one super-numerary equation. The fact that this equation will be a consequence of the other equations, i.e. that it does not lead to a new incompatible condition, is a proof that assumption (39) for the deformation is correct.

In view of (40) the solution of equations (19)–(22) in the shell $a < r < 1$ is still given by (23)–(27), but the coefficients A, B, C, D may now depend on time.

The outer shell $1 < r < R$ is now filled with a medium with unknown properties. In view of (40) and (3) it is known, however, that the mathematical expressions describing these properties can be developed into power series in a , and that the elastic terms (containing E or \dot{E}) will not appear in the zero-order terms. From this the general shape of the expressions for the flow of this substance may be derived. Consider first the homogeneous sphere of radius R which consists entirely of this substance. As discussed in § 2 its flow is given by equation (12), but γ is no longer connected with the stress by equation (15) which referred to a viscous fluid where the stress is entirely due to internal friction. For our substance this should be only so when the deformation of the elastic spheres has become stationary. Otherwise an additional term proportional to \dot{E} would be expected which means that the total velocity of flow contains one term which is proportional to the velocity of deformation of the elastic spheres. Thus, instead of (15),

$$\gamma = \frac{T}{2\eta^*} + \zeta\dot{E}, \quad (43)$$

where ζ is a constant which is expected to vanish if $a = 0$. In view of (43), the connexion between stress and flow is no longer given by

$$S_{rr} = 2TP_2 = 4\eta^*\gamma P_2, \quad S_{r\theta} = TP'_2 = 2\eta^*\gamma P'_2,$$

but by

$$S_{rr} = 4\eta^*(\gamma - \zeta\dot{E})P_2, \quad S_{r\theta} = 2\eta^*(\gamma - \zeta\dot{E})P'_2. \quad (44)$$

The following calculations have now to show that a value for ζ exists for which hypothesis (43) actually leads to a self-consistent solution, i.e. that the two big spheres of radius R will actually show the same flow at the surface (in the sense of equation (14)).

Now return to the flow in the outer shell $1 < r < R$ of the sphere described in figure 2. In the case *A* this flow was given by equation (30), i.e. it was composed of a homogeneous flow $u_r = 2\gamma r P_2$, $u_\theta = \gamma r P'_2$, and a non-homogeneous flow (D_1 -term) which represents the influence of the inner shell and which is of the first order in a^3 (cf. (36)). The influence of the elasticity of the spheres which is now considered is to change the flow considered in § A by adding terms of the first order in a^3 . Therefore, any correction of the D_1 terms in equation (30) would lead to second-order terms which are neglected here. On the other hand, γ -terms will be influenced so that expression (15) is replaced by (43). Considering this, (30) still represents the flow in the outer shell, and condition (14) is thus fulfilled in the same way as in § A. Equation (31) does, however, no longer represent the stresses but has to be supplemented in the same way as (44). Thus

$$S_{rr} = 4\eta^* \left(\gamma - \zeta \dot{E} + \frac{6D_1}{r^5} \right) P_2, \quad S_{r\theta} = 2\eta^* \left(\gamma - \zeta \dot{E} - \frac{4D_1}{r^5} \right) P'_2. \quad (45)$$

Again the D_1 terms need not be improved as they are already of the first order.

Now proceed in a similar way as in § A. The boundary conditions (17) and (18) at $r = 1$ must be fulfilled, while (16) must now be replaced by

$$u_r, u_\theta, S_{rr}, S_{r\theta} \text{ continuous at } r = a. \quad (46)$$

This leads to the following equations. From (46) using (23)–(27) and (41) and (42) follows

$$\left. \begin{aligned} \frac{Aa^3}{7} + \frac{B}{2a^2} + 2Ca - \frac{3D}{a^4} &= \dot{E}a, \\ \frac{5Aa^3}{42} + Ca + \frac{D}{a^4} &= \frac{\dot{E}a}{2}, \end{aligned} \right\} \quad (47)$$

$$\left. \begin{aligned} -\frac{Aa^2}{7} - \frac{3B}{a^3} + 4C + \frac{24D}{a^5} &= \frac{2k}{\eta} E, \\ \frac{8Aa^2}{21} + \frac{B}{2a^3} + 2C - \frac{8D}{a^5} &= \frac{k}{\eta} E. \end{aligned} \right\} \quad (48)$$

From (17) one obtains as in (33),

$$\left. \begin{aligned} \frac{A}{7} + \frac{B}{2} + 2C - 3D &= 2\gamma - 3D_1, \\ \frac{5A}{42} + C + D &= \gamma + D_1, \end{aligned} \right\} \quad (49)$$

and from (18), using (45) and the left-hand side of (34)

$$\left. \begin{aligned} -\frac{A}{7} - 3B + 4C + 24D &= \frac{4\eta^*}{\eta} (\gamma - \zeta \dot{E} + 6D_1), \\ \frac{8A}{21} + \frac{B}{2} + 2C - 8D &= \frac{2\eta^*}{\eta} (\gamma - \zeta \dot{E} - 4D_1). \end{aligned} \right\} \quad (50)$$

It will be noticed that for $\dot{E} = 0$ equations (47), (49) and (50) are identical with (32)–(34), while both equations (48) become equivalent and can be used to calculate E . This represents one solution of the system of equations. It leads to the value (2) for η^* . Having thus determined η^* now find the influence of the elasticity of the spheres of radius a on the flow, i.e. one is now interested in solutions for which $\dot{E} \neq 0$. Now (47)–(50) is a system of eight inhomogeneous equations for the seven unknowns A, B, C, D, D_1, E and \dot{E} . As discussed above one of the equations (48) must be considered as a consequence of the other equations because the value of one further unknown F has been anticipated by writing the deformation of the elastic spheres in the special form (39) which requires only one constant. This leaves seven equations for seven unknowns. They have one solution expressing them in terms of the coefficients of the equations. This is the solution mentioned above in which $\dot{E} = 0$. Other solutions for which $\dot{E} \neq 0$ will express the six unknowns A, B, C, D, D_1, E not only in terms of the coefficients but also in terms of \dot{E} . They exist only if the coefficients fulfil a certain condition which will be used to determine ζ .

The actual solution can be found quickly if again, as in (35),

$$A = 0 \quad (51)$$

is anticipated. Inserting this into (47), then

$$D = \left(\frac{\dot{E}}{2} - C\right)a^5, \quad B = 10\left(\frac{\dot{E}}{2} - C\right)a^3, \quad (52)$$

which, introduced into the first equation (48), yields

$$10C - 3\dot{E} = \frac{2k}{\eta} E. \quad (53)$$

The second equation (48) is then fulfilled without leading to any inconsistency which means that (39) was anticipated correctly.

Inserting (51) and (52) into (49), then

$$C = \gamma(1 + a^3) - \frac{\dot{E}}{2}a^3, \quad D_1 = \gamma a^3 - \frac{\dot{E}}{2}a^3, \quad (54)$$

so that neglecting higher order terms in a , (52) and (53) become

$$D = \left(\frac{\dot{E}}{2} - \gamma\right)a^5, \quad B = 10\left(\frac{\dot{E}}{2} - \gamma\right)a^3, \quad E = \frac{\eta}{2k} [10\gamma(1 + a^3) - (3 + 5a^3)\dot{E}]. \quad (55)$$

Equations (51), (54) and (55) represent the six quantities A, B, C, D, D_1 and E in terms of γ and \dot{E} , as required. Inserting them into the first equation (50) and neglecting terms of a higher order than a^3 , then

$$\zeta = \frac{5}{4}a^3. \quad (56)$$

With (51), (54)–(56) the second equation (50) is fulfilled which shows that $A = 0$ was anticipated correctly. Thus all equations (47)–(50) have been satisfied and the solutions of the required type found.

Now insert the value (56) into the relation (43), i.e.

$$T = 2\eta^*(\gamma - \frac{5}{4}a^3\dot{E}). \quad (57)$$

To obtain the required connexion between stress and flow of the macroscopic substance it is necessary to eliminate \dot{E} from this relation. This can be done by introducing the time derivatives \dot{T} and $\dot{\gamma}$. Using E from equation (55), then, neglecting terms of a higher order in a than a^3 ,

$$T + \tau_1\dot{T} = 2\eta^*(\gamma + \tau_2\dot{\gamma}), \quad (58)$$

where
$$\tau_1 = \frac{3\eta}{2k}(1 + \frac{5}{3}a^3), \quad \tau_2 = \frac{3\eta}{2k}(1 - \frac{5}{2}a^3). \quad (59)$$

Equations (2), (58) and (59) represent the main result of the calculations.

The introduction of \dot{T} requires a further condition because at certain times, e.g. on application or removal of stress, T will be allowed to be a discontinuous function of time. In this case an additional condition is required for the solution of the differential equation (58). To obtain it (57) is used to eliminate γ from equation (55) and yields, with the use of (2) and (3),

$$2kE + 3\eta\dot{E}(1 - \frac{5}{2}a^3) = 5T(1 - \frac{3}{2}a^3).$$

The solution of this equation can be written in the form

$$E = \beta e^{-\alpha t} \int_0^t e^{\alpha t} T(t) dt,$$

where α and β are constants easily derived from the preceding equation. This shows that E remains continuous when T has a discontinuity. Thus, using again (55) and (57)–(59), it is found that

$$-\frac{5}{2}a^3\eta E = \tau_1 T - 2\eta^*\tau_2\dot{\gamma} = \text{continuous}. \quad (60)$$

This is the condition which T and γ have to fulfil when T is discontinuous.

4. RESULTS AND DISCUSSION

From the discussion in § 2 it was seen that the main task was to calculate the quantity γ expressing the flow by equation (10) in terms of the stress. This has now been done (equations (58)–(60)). Hence it may be concluded that the connexion between the stress system (9) and the components of flow u_i is given by

$$S_{ii} + \tau_1\dot{S}_{ii} = 2\eta^* \frac{\partial}{\partial x_i} (u_i + \tau_2\dot{u}_i), \quad (i = 1, 2, 3). \quad (61)$$

This equation can easily be generalized to comprise an arbitrary stress system. First by a suitable rotation of the co-ordinate system, the system of tensile stresses can be transformed into a system of shear stresses, while the corresponding transformation of the components of flow follows from the isotropy of our substance.

Secondly, in view of the incompressibility of our substance the addition of a hydrostatic pressure p cannot have any influence on its flow. Thus equations (61) which refer to $p = 0$ can be extended to the case $p \neq 0$ by adding the term $-(p + \tau_1 \dot{p})$ to the right-hand side of the three equations (61), which in view of (7) just cancels the hydrostatic terms at the left-hand sides. The generalized equations (61) can thus be written as

$$\Theta_{ik} = -\pi \delta_{ik} + \eta^* \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right), \quad (62)$$

if one introduces the three quantities

$$\Theta_{ik} = S_{ik} + \tau_1 \dot{S}_{ik}, \quad \pi = p + \tau_1 \dot{p}, \quad v_i = u_i + \tau_2 \dot{u}_i, \quad (63)$$

derived from stress S_{ik} , pressure $p = -\frac{1}{3}(S_{11} + S_{22} + S_{33})$ and flow u_i . These equations have to be supplemented by condition (60) which, after being treated in a similar way as (58), leads to

$$\tau_1 (S_{ik} + p \delta_{ik}) - \tau_2 \eta^* \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) = \text{continuous}. \quad (64)$$

In general the stresses may now be allowed to depend on the co-ordinates x_i if only they can be considered as approximately constant within a region which contains many of our elastic spheres. The equilibrium of forces then demands

$$\sum_i \frac{\partial S_{ik}}{\partial x_i} = 0 \quad (k = 1, 2, 3),$$

if acceleration terms and external volume force (e.g. gravitation) are neglected. Differentiating these equations with respect to time, and making use of (62) and (63) then

$$\eta^* \Delta v_i - \frac{\partial \pi}{\partial x_i} = 0. \quad (65)$$

The condition of incompressibility requires $\text{div } \mathbf{u} = 0$ and hence

$$\text{div } \mathbf{v} = 0, \quad (66)$$

while (64) leads to

$$\tau_2 \eta^* \Delta u_i - \tau_1 \frac{\partial p}{\partial x_i} = \text{continuous on application or release of stress}. \quad (67)$$

Equations (62)–(67) together with (2) and (59) represent the results of the theory. They can be divided into two parts, (i) a macroscopic theory of flow which contains the three parameters τ_1 , τ_2 , and η^* , (ii) the calculation of these parameters from the properties and the concentration of the two components.

From the mathematical point of view the equations of flow have a great similarity to the hydrodynamic equations. In fact, the fundamental hydrodynamic equations (5), (6) and (8) are identical with equations (66), (62) and (65) if the three quantities Θ_{ik} , π and \mathbf{v} are replaced by S_{ik} , p and \mathbf{u} respectively. This means that to each hydrodynamical problem there exists a problem for our substances whose solution is

obtained from the hydrodynamic solutions by making the substitutions just mentioned. To obtain then the velocity of flow and the stresses, equations (63) have to be solved (in which Θ_{ik} , π , and v_i are now known) using the conditions (64) or (67). This mathematical similarity leads to a similar physical behaviour only if S_{ik} and u_i are independent of time, because only then are they equal to Θ_{ik} and v_i . Otherwise, the physical behaviour of our substance may be very different from that of a viscous fluid.

As a simple example consider the case of a homogeneous flow. Suppose a tensile stress S_{11} acts parallel to the axis of a prism which is assumed to be the x_1 -axis. This will lead to a homogeneous flow and its x_1 -component u_1 will be calculated. Let σ_{11} be the tensile strain in the l -direction. Then clearly

$$u_1 = \dot{\sigma}_{11} x_1. \quad (68)$$

Suppose that the stress is applied at the time $t = 0$, having the magnitude κ , and that it is removed at $t = t'$. Thus since $S_{22} = S_{33} = 0$,

$$S_{11} = \begin{cases} 0, \\ \kappa, \\ 0, \end{cases} \quad p = \begin{cases} 0, \\ -\frac{\kappa}{3}, \\ 0, \end{cases} \quad \text{at } \begin{cases} t < 0, \\ 0 < t < t', \\ t > t'. \end{cases} \quad (69)$$

Inserting these expressions for u_i and p into (62) one finds, making use of (63),

$$\frac{2}{3}(S_{11} + \tau_1 \dot{\sigma}_{11}) = 2\eta^*(\dot{\sigma}_{11} + \tau_2 \ddot{\sigma}_{11}), \quad (70)$$

i.e. a differential equation for σ_{11} .

Assuming $k = 0$, (70) with the use of (69) becomes

$$2\eta^*(\dot{\sigma}_{11} + \tau_2 \ddot{\sigma}_{11}) = \begin{cases} 0 & t < 0 \text{ and } t > t', \\ \frac{2}{3}\kappa & 0 < t < t'. \end{cases} \quad (71)$$

Since S_{11} is discontinuous, use must be made of condition (64) at $t = 0$ and $t = t'$.

Inserting (68) and (69) this condition becomes

$$\frac{2}{3}\tau_1 S_{11} - 2\tau_2 \eta^* \dot{\sigma}_{11} = \text{continuous}. \quad (72)$$

Since $\dot{\sigma}_{11} = 0$ for $t < 0$, then, making use of (69),

$$\dot{\sigma}_{11} = \frac{\kappa}{3\eta^*} \frac{\tau_1}{\tau_2} \quad \text{at } t = 0$$

$$\dot{\sigma}_{11}(t' + 0) - \dot{\sigma}_{11}(t' - 0) = -\frac{\kappa}{3\eta^*} \frac{\tau_1}{\tau_2} \quad \text{at } t = t',$$

where $\dot{\sigma}_{11}(t' \pm 0)$ refers to the value of $\dot{\sigma}_{11}$ just before ($t' - 0$) or after ($t' + 0$) the time $t = t'$.

With these conditions and with $\sigma_{11} = 0$ at $t = 0$ the solution of (71) becomes

$$\sigma_{11} = \sigma_{el.} + \sigma_{vis.}, \quad (73)$$

where

$$\sigma_{vis.} = \frac{\kappa}{3\eta^*} \begin{cases} t & 0 < t < t', \\ t' & t > t', \end{cases} \quad (74)$$

$$\text{and} \quad \sigma_{\text{el.}} = \frac{\kappa}{3\eta^*} (\tau_1 - \tau_2) \begin{cases} (1 - e^{-t/\tau_2}) & 0 < t < t', \\ (1 - e^{-t'/\tau_2}) e^{-(t-t')/\tau_2} & t > t'. \end{cases} \quad (75)$$

It is seen that the total deformation can be split into (i) a viscous part $\sigma_{\text{vis.}}$ which increases proportional to t during the application of stress and remains constant when the stress is removed, and (ii) an elastic part $\sigma_{\text{el.}}$ which on application of stress becomes time independent if $t \gg \tau_2$, and on removal of stress is recovered following an exponential law.

From this simple example it is seen that for a homogeneous stress the theory leads to a strain-time dependence of the same type as that found experimentally on certain bitumens (figure 1). In particular, it shows an elastic recovery described by a time of relaxation τ_2 . Suppose that a substance has been found which obeys the equations given. Then in an experiment of this type (figure 1) all the three parameters τ_1 , τ_2 and η^* can be determined. η^* is obtained from the slope of the strain-time curve for a time $t \gg \tau_2$ (i.e. the dotted curve in figure 1), because according to (73)–(75)

$$\dot{\sigma}_{11} = \frac{\kappa}{3\eta^*} \quad \text{if } t' > t \gg \tau_2.$$

τ_2 is obtained as the time of relaxation of the elastic recovery, while $(\tau_1 - \tau_2)/\eta^*$ and hence τ_1 can be determined from the total strain recovery, since according to (73)–(75)

$$\Delta\sigma = \sigma_{11}(t') - \sigma_{11}(\infty) = \frac{\kappa}{3\eta^*} (\tau_1 - \tau_2) \quad \text{if } t' \gg \tau_2. \quad (76)$$

Having thus determined the three parameters it is possible to check the results by an independent experiment. Supposing that at the time t' , instead of removing the stress, the strain is kept constant so that $\dot{\sigma}_{11} = \ddot{\sigma}_{11} = 0$. It then follows from equations (68) and (72) that S_{11} decays exponentially

$$S_{11} = \frac{\tau_1 - \tau_2}{\tau_1} \kappa e^{-(t-t')/\tau_1},$$

with the relaxation time τ_1 .

So far equations (62)–(67) have been discussed as macroscopic equations containing three parameters, τ_1 , τ_2 and η^* . According to the present theory these quantities are connected by equations (2) and (59) with the three microscopic quantities a^3 , k and η , i.e. with the relative volume of the elastic spheres, their modulus of rigidity, and the viscosity of the fluid in which they are dispersed. It should be possible to check these formulae by varying a^3 , and by using various materials whose k and η values are known. A variation of a^3 , for instance, changes all three quantities η^* , τ_1 and τ_2 . It is connected in a very direct way with the total elastic recovery which can be easily measured and which according to (76), using (2), (59) and (3), is given by

$$\Delta\sigma = \frac{25}{6} a^3 \frac{\kappa}{k}, \quad \dots \quad (a^3 \ll 1).$$

There are, at present, no experiments available which allow a quantitative check of our theory. Such experiments would require sols or dispersions of a known structure. We have tried to compare our results with experiments on bitumens, some of which, according to Pfeiffer & Saal (1940), form sols. We compared the elastic recovery curve of a bitumen measured by Lethersich (1942) with our results, according to which it should be an exponential function of time. Figure 3 shows that this is the case for most of the recovery curve, but for (relatively) short times there is an additional recovery. It seems evident that the structure of bitumens is more complicated than was assumed in our model, and there are a number of suggestions one can make to account for the additional recovery (e.g. an interaction between the elastic spheres, or an elasticity of the fluid in which they are dispersed). It is not the object of this paper to study bitumens, but it seems interesting to notice that such a simple analysis in the light of our theory leads at once to suggestions concerning their structure.

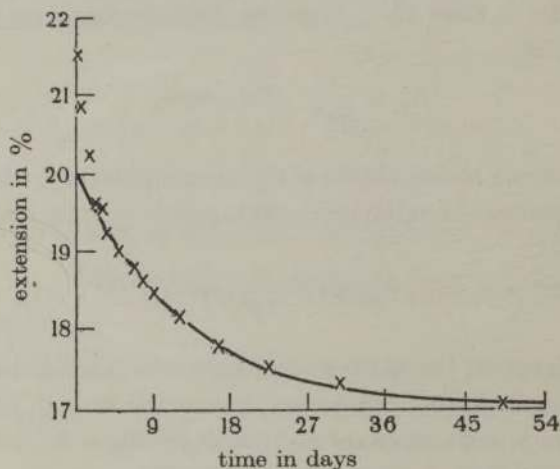


FIGURE 3. Experimental values of the elastic recovery of a bitumen according to Lethersich (1942) compared with an exponential function.

Before going into a detailed study of such complicated substances it seems desirable to have experiments on materials which agree as closely as possible with our model. We do not doubt, however, that it will be possible to generalize our theory so as to comprise more complicated structures.

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