AN EFFECT OF NORMAL STRESSES

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A curvilinear equilibrium shape of a thin stream of elastoviscous liquid is discussed. It is shown that one can estimate the elastic stresses, and consequently the elastic characteristics of the liquid, from the shape of the stream. The role of elastic forces in the stability of liquid filaments is analyzed qualitatively.

§1. If one directs a stream of elastoviscous liquid, for example a polymer solution, vertically downward from a capillary into a beaker, and then slowly displaces the beaker to the side, the stream will deviate from the vertical and follow the beaker. If the beaker is not moved too far, motion of the liquid in the curved stream is stable and stationary (in principle, for an unlimited time). The existence of a curved stationary stream is easily demonstrated. A typical photograph of an experiment is shown in Fig. 1.

§2. From the fact that a stationary stream in a gravitational field takes on a curved shape resembling a catenary, it follows that a marked longitudinal tension exists in the stream.

We consider a portion of the stream sufficiently removed from the beginning (exit from capillary) and end. Motion of the liquid can be considered one-dimensional in this portion. Let x(s), y(s) be the parametric equation of the stream axis; the coordinate s is measured along the axis and $\varphi(s)$ is the angle made with the horizontal by the stream axis.

Projecting the momentum equation on the tangent and normal to the stream axis and using the continuity equation, we have

$$\rho g f \sin\varphi\, ds + dT = \rho\, d(u^2 f), \tag{1}$$

$$\rho g f \cos\varphi\, ds - T d\varphi + \rho u^2 f\, d\varphi = 0, \tag{2}$$

$$\rho u f = \rho Q = M. \tag{3}$$

We obtain from Eqs. (2) and (3)

$$T = \rho Q^2/f + \rho g f \cos\varphi\, (d\varphi/ds).^{-1} \tag{4}$$

Equation (4) is of interest because easily measured quantities are on its right side; in order to find T by means of Eq. (4) it is sufficient to determine the flow rate (by a volumetric method, for example) and to determine f(s) and $\varphi(s)$ after having photographed the stream.

§3. An experiment (Fig. 1) was performed with a polyacrilamide solution having a concentration of about 1.5% at a flow rate Q = 0.30 cm^3/sec from a capillary with a radius a = 0.1 cm. The variation of the quantities φ and f along the stream is shown in Fig. 2. The measured results are approximated by the expressions

$$\varphi = 1.01 + 0.195\, s - 0.0289\, s^2,\; f = 0.01\,(0.53 + 0.183\, s)\ \text{cm}^2,\ s,\ \text{cm}. \tag{5}$$

(the coordinate s is measured from the point O shown in the photograph). Substitution of numerical values in Eq. (4) yields a value of ~30 dyn for T in the central position of the stream. [The curve for T(s), also shown in Fig. 2, was calculated using the approximations (5).]

§4. We now turn to an interpretation of the results. Longitudinal tension of the stream is made up of the tension T_c resulting from the effect of surface tension, the tension T_v created by the effect of viscosity, and the term T_e produced by elastic deformations:

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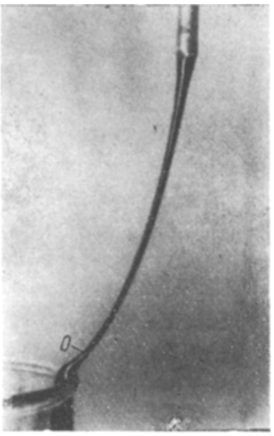

Fig. 1

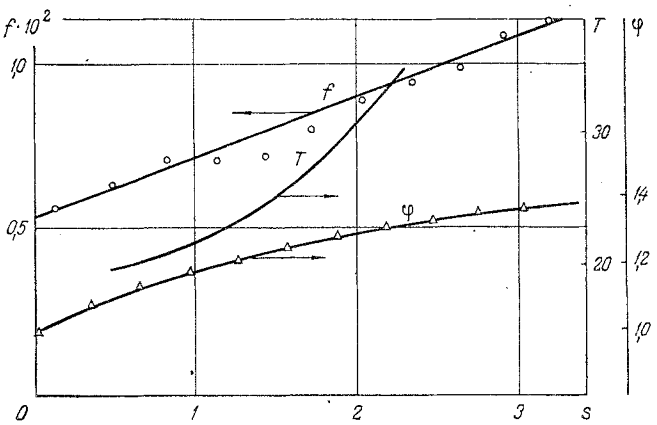

Fig. 2

Fig. 1. Curved stream of polyacrilamide solution: c = 1.5%, η_0 = 6 p, a_0 = 0.1 cm, Q = 0.3 cm³/sec.

Fig. 2. Variation of stream area f, cm², angle φ, and tension T, dyn, along the stream s, cm.

$$T = T_c + T_v + T_e. \tag{6}$$

Of course, complete separation of the last two terms is only possible in the region of linear behavior of the material.

The tension which is the result of capillary forces is the difference between "film surface tension" and the oppositely directed forces from capillary pressure, so that

$$T_c = 2\pi r\alpha - \pi r^2(\alpha/r) = \pi r\alpha. \tag{7}$$

Even if we keep the same value as that for water for the surface tension of the solution (actually, the value should be lower), we obtain for a stream of radius r ~ 0.05 cm

$$T_c = 3.14 \cdot 0.05 \cdot 70 = 11 \text{ dyn}.$$

Thus, in this experiment, surface tension is clearly responsible for no more than a third of the observed tension.

The contribution of viscosity to the tension is given by the well-known formula

$$T_v = 3\eta f \frac{du}{ds} = -\frac{3\eta Q}{f}\frac{df}{ds}. \tag{8}$$

The flow curve for the solution with which the experiment was performed is shown in Fig. 3. In the required range of shear rates (hundreds of inverse seconds), the effective viscosity varies little and is close to 1 p. Substituting numerical values into Eq. (8), we obtain $T_V \simeq 0.22$ dyn. Thus, the contribution of viscosity (assuming that it is of the same order of magnitude as in shear flow) is negligibly small.

If, in estimating the contribution of viscosity, one assumes that under tension it maintains a constant value equal to the viscosity η_0 for infinitely slow flow and takes the value 5.4 p for η_0, (see Fig. 3), the contribution from viscosity is small (~1.2 dyn). Thus, only the forces of surface tension and of the elasticity of the liquid are important for the flow under consideration. The "elastic" component of the longitudinal force at the point s = 1 is T_e = 19 dyn, as is easily calculated. When f = $7 \cdot 10^{-3}$ cm², this yields the elastic stress

$$\sigma = T_e/f = 2.7 \cdot 10^3 \text{ dyn/cm}^2.$$

Based on this value, we estimate the modulus G for an elasticoviscous liquid. Assuming that an element of the liquid in the stream is deformed so rapidly that it fails to relax, we assume its deformation after emergence from the capillary as a uniform expansion by a factor λ,

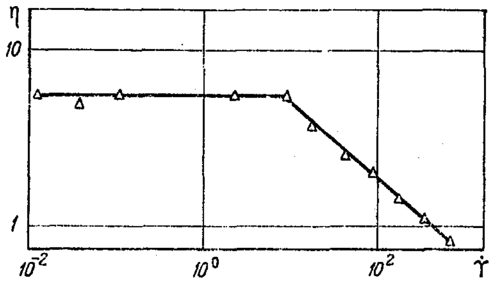

Fig. 3. Flow curve for polyacrilamide solution used in experiments. η, p; $\dot{\gamma}$, $\sec^{-1}$.

$$\lambda = f/f_0, \tag{9}$$

where f_0 is the cross section of the capillary. Assuming that the elastic behavior of the material is roughly described by the theory of rubber-like elasticity, we have for sufficiently large λ

$$\sigma = 2G\lambda^2, \; G = 1/2\sigma\lambda^{-2}. \tag{10}$$

Substituting numerical values corresponding to the point $s = 1$, we find $\lambda = 4.5$ and $G = 68$ dyn/cm^2. We then have for the relaxation time of the liquid

$$\theta = \eta/G = 0.08 \text{ sec.} \tag{11}$$

The relaxation time can also be estimated from the flow curve for the liquid (Fig. 3) by comparing it with the flow curves for some model of a elasticoviscous liquid. In the Spriggs model ([1], Eq.(3.82)), such a match yields $\alpha = 1.5$ and $\theta_s = 0.09$. When $c \simeq 0.8$, we have $\theta = 0.11$ sec. Thus both estimates yield similar values for the relaxation time ($\theta \sim 0.1$ sec). Note that this time is of the same order of magnitude as the time for motion of an element of liquid in the stream.

§5. The analysis made permits certain qualitative conclusions about the role of elastic effects in the "spinability" phenomenon [2], i.e., the capability of the liquid to form elongated filaments. Note that the question is not what forces ensure filament equilibrium (it is easy to see that the force of surface tension can be such a force for a sufficiently thin filament) but why the filament is stable, i.e., why local thinning does not develop. Local thinning in a long filament will not continue to develop if the reduction in filament diameter leads to an increase of the longitudinal force acting on the filament. If the deformation occurs sufficiently rapidly (deformation time small in comparison with relaxation time), the total force in a cross section is given by

$$T = \pi\alpha r + 2G\lambda^2 f. \tag{12}$$

Here λ is the elastic elongation of an element of the liquid (reversible portion of the deformation). If $\lambda = \lambda_0$ corresponds to the unperturbed cross section f_0, $\lambda = \lambda_0 f_0/f$, and

$$T = \pi\alpha r + 2G\lambda_0^2 f_0^2/f = \pi\alpha r + \pi\sigma_0 r_0^4/r^2. \tag{13}$$

The function $T(r)$ has a minimum at $r = r_* = (2\sigma_0 r_0/\alpha)^{1/3} r_0$. Therefore, if $2\sigma_0 > \alpha/r_0$, the longitudinal tension is a decreasing function of filament radius and the filament is stable; if $2\sigma_0 < \alpha/r_0$, local compression develops in the filament to a radius r_1, which is determined by the equation $T(r_1) = T(r_0)$ so that

$$r_1 = 1/2\sigma_0 r_0^2 [1 + (1 + 4\alpha/r_0\sigma_0)^{1/2}]/\alpha, \tag{14}$$

and subsequent extension of the filament takes place stably. Of course, the analysis, which does not consider viscosity, is an approximate one but it clearly shows the stabilizing role of elastic stresses in thin filaments. It is also clear that the decay time for an extended filament cannot be significantly less than the relaxation time of the elastic stress. The qualitative considerations advanced can be confirmed by study of the hydrodynamic stability of a capillary stream of elastoviscous liquid.

The authors thank A. N. Prokunin for help in measuring the viscosity of the test solution at low deformation rates.

NOTATION

s	is the longitudinal coordinate;
φ	is the angle between stream axis and horizontal;
ρ	is the density;
η	is the viscosity;
G	is the shear modulus;
θ	is the relaxation time;
α	is the surface tension of liquid;
a	is the stream radius;
$f = \pi a^2$	is the stream area;
$\Pi = 2\pi a$	is the perimeter of stream cross section;
u	is the liquid velocity in stream;
$Q = uf$, $M = \rho uF$	are the volumetric and mass flow rates;
T	is the longitudinal tension in stream;
c	is the solution concentration;
$\dot{\gamma}$	is the shear rate;
λ	is the degree of elongation of element of liquid;
g	is the acceleration of gravity.

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THEORY OF EQUATION OF STATE FOR REAL GASES

1.

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UDC 536.711

An equation of state for real gases is derived by using correlation relations between the components of the thermal velocity.

§1. Correlation of Velocities and Multiple Collisions in Phase Space

The principles of mechanics were extensively used for molecular-kinetic interpretation of the properties of gases in the works of Professor Clausius at Bonn. He succeeded in setting up the famous equation known as the virial equation. In modern molecular physics, it is written in the form

$$pv = \frac{2}{3}K - \frac{1}{3}\sum_i \mathbf{r}_i \cdot \frac{\partial \Phi(\mathbf{r}_i)}{\partial r_i} . \tag{1}$$

We recall that the product pv is interpreted here as the virial of the external forces acting on a gas enclosed in a given volume. The quantity K expresses the kinetic energy resulting from motion of the particles in the gaseous system. The second term on the right side of Eq. (1) expresses the virial for the internal forces.

Two phase spaces are introduced for the derivation of an equation of state from Eq. (1). The first is a velocity phase space, the coordinates of which are the three components ξ, η, and ζ of the thermal velocity vector. The quantities $(\partial\Phi/\partial r)n_x$, $(\partial\Phi/\partial r)n_y$, and $(\partial\Phi/\partial r)n_z$ are taken as the coordinates of the second phase space.

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