REVIEWS OF TOPICAL PROBLEMS

Macroscopic and molecular shear viscosity

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<u>Abstract.</u> A brief review of the effect of Newton's macroscopic dynamic shear viscosity on the rotation of a cylinder and a ball in a viscous fluid is presented. The approximate nature of some of Stokes' formulae is discussed, and formulae from elementary viscosity theory are given. The concept of molecular viscosity is introduced, and it is shown that, among other information sources, spectra of depolarized molecular light scattering and electromagnetic wave dispersion in liquids of constant-dipolemoment molecules may, within a certain scheme, be used to derive the value and temperature dependence of the coefficient of shear dynamic molecular viscosity. As an example, the temperature behaviour of molecular viscosity in salol and *o*-terphenyl is presented and discussed qualitatively.

1. Introduction

The internal friction, or viscosity, of a liquid manifests itself in the motion of bodies through the liquid or in the motion of the liquid itself through pipes or channels. In the process of motion of a viscous fluid some its momentum is transferred, just as heat conduction is accompanied by energy transfer and diffusion is accompanied by mass transfer.

All three transfer phenomena constitute sizable parts of hydrodynamics, thermodynamics, and the kinetic theory of matter, respectively, and are described by the single-type equations like that of the Fourier equation.

All phenomena involving viscosity are irreversible.

To our knowledge, internal friction, or shear viscosity, was originally introduced by Sir Isaac Newton in his famous treatise *Mathematical Principles of Natural Philosophy*,

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Received 18 April 1997 Uspekhi Fizicheskikh Nauk 167 (7) 721 – 733 (1997) Translated by E Yankovsky; edited by A Radzig commonly known as *Principia* [1], with the first edition published in 1687. Newton, however, did not use the modern terminology, i.e. 'internal friction' or 'viscosity,' but it is this concept that he had in mind when he spoke of 'lack of slipperiness.'

In Book Second of the *Principia*, in section IX, titled 'On the Circular Motion of Liquids,' in the 'Assumption' Newton writes: 'Resistance occurs because of lack of the liquid slipperiness, which is assumed, all other things being equal, to be proportional to the speed with which the liquid particles move apart'. It is apparent that the 'lack of slipperiness' is what we today call viscosity. Clearly, Newton's supposition implies that the force of 'resistance'

$$F = A\eta V, \tag{1}$$

where A is a constant, η is the quantitative measure of 'lack of slipperiness,' or the dynamic viscosity coefficient, and V is the linear velocity.

Then in 'Assumption LI of Theorem XXXIX' Newton writes:

'If in a homogeneous and boundless liquid there is an infinitely long rigid cylinder that rotates uniformly around its constant axis and the liquid is set in motion solely by this impact, with each particle of the liquid retaining its uniform motion, then I assert that the times of revolution of the liquid particles are proportional to the particle's distances from the axis of the cylinder.'

Newton then argues as follows: 'Since the liquid is homogeneous, the action of its layers on each other (by assumption) is proportional to their displacements along each other and to the size of the surfaces involved in the interaction. If the force applied to the convex surface of a layer is larger or smaller than the force applied to the concave side, the larger force will prevail and the layer will accelerate or decelerate, since at each point the force is directed either in the same direction as the motion or in the opposite direction.

Since each layer retains its uniform motion, the forces are equal and point in opposite directions, but since these forces are proportional to the size of the surfaces in contact and to their relative velocities, the difference of these velocities must be inversely proportional to the distances between the respective layers and the axis.'

This is hard to believe, but the great Newton did allow for an inaccuracy (it would be difficult to call this a mistake) in the above assertion, which was pointed out later by Stokes [2], who corrected it.

The point is that by 'forces' Newton understood forces of friction, but actually these should be moments of the forces of friction. According to Newton, the time of revolution $\tau = \tau_0 a/L$, while in reality, as shown by Stokes [2], $\tau = \tau_0 a^2/L^2$, where τ_0 is the time of revolution of a rigid cylinder, *a* the cylinder's radius, and *L* the distance from the rotation axis of the rigid cylinder to a cylindrical layer of liquid.

Newton's arguments and the six corollaries he formulated [1] imply that if two layers of liquid that are at distances L and $L + \Delta L$ from the rotation axis of a rigid cylinder of radius a and surface area S move with different velocities, then in the stationary case the moment M of the tangent forces acting on the cylindrical surface of radius L per unit length of the surface is

$$M = 2\pi L^2 \eta \frac{\mathrm{d}V}{\mathrm{d}L} \,. \tag{2}$$

If we introduce the angular velocity $\omega = V/L$, we arrive at the following expression for *M*:

$$M = 2\pi L^2 \eta \frac{\mathrm{d}\omega}{\mathrm{d}L} L \,. \tag{3}$$

The liquid between two cylindrical surfaces carries an angular momentum, which in steady-state motion remains constant, so that the moment of force (3) must be independent of L. This implies that ω has the form

$$\omega = \frac{C_1}{L^2} + C_2 \,, \tag{4}$$

where C_1 and C_2 are the constants.

If the liquid occupies a boundless volume and is at rest at infinity while a rigid cylinder of radius *a* rotates with an angular velocity ω_0 , from formula (4) it follows that

$$\frac{\omega}{\omega_0} = \frac{a^2}{L^2} \,, \tag{5}$$

with the result that the moment of the friction force acting on a unit length of the surface layer is

$$M = 4\pi \eta a^2 \omega_0 \,. \tag{6}$$

The entire range of these problems was first examined by Stokes and Saint-Venant and the results are presented in detail in Lamb's book [3], which we follow in some respects (see also Refs [4, 5]).

If instead of a boundless liquid we take two coaxial cylinders, an inner rotating cylinder of radius a and an outer (fixed) cylinder of radius b, calculations yield the following result:

$$\omega = \frac{a^2}{L^2} \frac{b^2 - L^2}{b^2 - a^2} \,\omega_0 \,, \tag{7}$$

and for the moment of the friction force, instead of (6), we have

$$M = 4\pi\eta \, \frac{a^2 b^2}{b^2 - a^2} \, \omega_0 \,. \tag{8}$$

which becomes (6) if we proceed to the limit $b \to \infty$.

2. A ball rotating in a viscous medium

For ball of radius r to rotate in a viscous medium bounded by an immobile concentric sphere of radius b, we must apply a rotation moment N to the ball. This moment of force is given by the following expression

$$N = 8\pi\eta \, \frac{r^3 b^3}{b^3 - r^3} \, \omega_0 \,. \tag{9}$$

For the case where $b \rightarrow \infty$ formula (9) becomes

$$N = 8\pi \eta r^3 \omega_0 \,. \tag{10}$$

Here it should be noted that formula (9) is valid to within second-order terms in the ratio

$$\frac{\omega_0 r^2 \rho}{\eta} \,, \tag{11}$$

where ρ is the density of the fluid. This means that formula (9) is valid only if near the equator of the rotating ball the inequality $\omega_0 r \leq \eta / \rho r$ holds true.

These remarks are important since, as noted by Lamb [3]: 'If second-order terms are taken into account, then the stationary motion of this kind becomes impossible. The ball begins to act as a centrifugal fan, i.e. at a certain distance from the ball the motion is an outward flow from the equator and an inward flow to the poles, and this motion is superimposed on the rotational motion' (see also Ref. [6]).

3. Viscous flow around a ball

Another problem was that of the force F acting on an immobile ball of radius r from the flow of an incompressible viscous fluid moving with a velocity V. Omitting the cumbersome calculations involving the equations of motion of a viscous fluid, we give only the final result

$$F = 6\pi\eta r V. \tag{12}$$

Formulae (6), (9) and (12) are known as the Stokes formulae and have found numerous application in various fields of physics.

Various researchers have calculated many other types of flow around bodies of different shapes, but usually certain simplifying assumptions are introduced.

Detailed discussions of many examples can be found in Lord Rayleigh's book [7].

We would like to stress again that all these cases refer to motion in a viscous fluid of bodies of macroscopic sizes. This means that the equations of motion of a viscous fluid and the boundary conditions that correctly reflect a specific problem can be used.

4. Equation of motion of a viscous fluid

After Newton [1] many scholars studied the general equations of motion. Here we cite only the fundamental results contributed by Navier [8], Poisson [9], and Stokes [10].

The general equation of motion in a viscous compressible fluid is

$$\rho\left(\frac{\partial V_i}{\partial t} + V_k \frac{\partial V_i}{\partial x_k}\right) = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_k} \left[\eta\left(\frac{\partial V_i}{\partial x_k} + \frac{\partial V_k}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial V_e}{\partial x_e}\right)\right] + \frac{\partial}{\partial x_i} \left(\eta'\frac{\partial V_e}{\partial x_e}\right), \quad (13)$$

which is known as the Navier – Stokes equation. Here *P* is the pressure, and η' is the bulk viscosity which determines energy losses in the course of uniform compression and expansion (sound propagation).

If η and η' are position-independent, then (13) can be written in a vector form as follows:

$$\rho \left[\frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \nabla) \mathbf{V} \right] = -\operatorname{grad} P + \eta \Delta \mathbf{V} + \left(\eta' + \frac{1}{3} \eta \right) \operatorname{grad} \operatorname{div} \mathbf{V} \,. \tag{13a}$$

If we follow Rayleigh's arguments for U(x, t) [7, 11], we can write the equation of motion for a viscous compressible fluid, the Stokes equation [2] for the propagation of sound along the *x* axis, in the form

$$\frac{\partial^2 U}{\partial t^2} - v^2 \frac{\partial^2 U}{\partial x^2} - \Gamma \frac{\partial^3 U}{\partial x^2 \partial t} = 0, \qquad (13b)$$

where v is the phase velocity of sound, U the component of velocity of the fluid element, and

$$\Gamma = \frac{1}{\rho} \left[\frac{4}{3} \eta + \eta' + \frac{\kappa}{C_p} (\gamma - 1) \right]$$
(14)

with κ the thermal conductivity coefficient, and C_p the specific heat at constant pressure; Γ determines the sound absorption and the halfwidth of the Mandelshtam – Brillouin components [11, 12].

In Rayleigh's treatise, just as in the original Stokes paper, η' is dropped, but not because Stokes did not consider bulk viscosity an important quantity.

In their paper [13], Mandel'shtam and Leontovich built a relaxation theory of sound propagation through liquids and quoted Stokes [2]: 'We can, of course, set $\eta' = 0$ if we assume that in uniform expansion the pressure at each point in time depends solely on the density and temperature at that moment and not on the rate of expansion. In most cases of interest for the application of the theory of a viscous fluid, the density remains constant or may be assumed constant without a noticeable error or, finally, can slowly vary with the passage of time. In the first two cases the result is the same, and in the third it is almost the same irrespective of whether we assume that $\eta' = 0$ or not. Consequently, even if theory and experiment in these cases yield the same result, this cannot be taken as a proof of the validity of the assumption that $\eta' = 0$.'

Stokes, therefore, clearly understood the importance of η' in those phenomena where it clearly manifests itself.

Further development in this field of science unquestionably demonstrated that the absorption of sound in liquids caused by the bulk viscosity η' for such liquids as, say, carbon disulfide at sound frequencies in the 1–10 MHz range is higher by a factor of 1200 than the absorption caused by shear viscosity η . Correspondingly, for benzene the absorption caused by η' is 280 times higher than that related to η at 1– 165 MHz, for acetic acid this factor amounts to 5300 at 0.5 MHz, and so on.

Generally, we would not be far from the truth if we said that for many organic liquids η' plays a greater role in sound absorption in the ultrasonic region than η .

What is measured by a viscosimeter is the shear viscosity, while η' plays no part in such experiments if the viscosimeter

depends for its operation on the slow motion (fall) of a ball in the viscous fluid or the flow of viscous fluid through a capillary tube or if some other type of viscosimeter is used in which volume expansion plays no role.

In this paper we discuss the motion of macroscopic bodies or layers of liquids and anisotropic molecules in which bulk viscosity does not manifest itself.

Solving the equations of motion for different cases makes it possible to obtain relationships between measured and known quantities that can be in use when obtaining the viscosity coefficient η with the aid of viscosimeters whose diversity is astonishing [14].

It appears that a crucially simplest way to measure viscosity is to employ the Stokes method, which is based on measuring the velocity of stationary motion of a small ball falling in a viscous fluid.

In this method the viscous drag given by formula (12) and the force of gravity making a ball of radius *r* fall are equalized. In a steady-state motion

$$6\pi\eta r V = \frac{4}{3}\pi r^3(\rho - \rho')g,$$

where ρ , ρ' , and g are, respectively, the density of the material from which the ball was manufactured, the density of the viscous fluid, and the acceleration of free fall. The above equality yields

$$\eta = \frac{2}{9} r^2 (\rho - \rho') \frac{g}{V}.$$
 (15)

If we know both densities, finding η amounts to measuring the radius of the ball and the velocity of its upward or downward stationary motion, depending on the sign of the difference of densities. This is all true, however, if the following conditions are fulfilled:

(a) the velocity V of ball motion is so small that its square and higher powers can be ignored;

(b) there is no slip between the surface of the ball and the liquid;

(c) the liquid occupies an infinitely large volume. These conditions cannot be met in a real experiment, so that measuring the viscosity coefficient is not a simple problem: it requires corrections to the straightforward formula (15).

Rayleigh [6] examined the criterion of smallness of the velocity and found that V can be considered small if the Reynolds number Re obeys the following inequality

$$\operatorname{Re} = \frac{r\rho V}{\eta} < 1.$$
(16)

By setting $r\rho V/\eta = 1$ in (16), which means that the 'critical radius' is

$$r_{\rm c} = \frac{\eta}{\rho V} \,, \tag{17}$$

Arnold [15] experimentally established that for different ball materials and radii Stokes' law holds to within the experimental error ($\sim 1\%$) if

$$r < 0.6r_{\rm c}$$
 (18)

From (15)–(17) it follows that the Stokes law is obeyed for water at $V = 1 \text{ cm s}^{-1}$ if $r < 10^{-3} \text{ cm}$.

Arnold's experiments [15] revealed that conditions (a) and (b) appear natural if the liquid wets the ball.

As for condition (c) which requires that the volume occupied by the liquid be infinitely large, it cannot be met. The first experiments showed that the Stokes formula (12) does not hold for an arbitrarily shaped vessel with liquid.

The wall effects can be exactly accounted for a cylindrical vessel in which the ball falls along the axis. Ladenburg [16] took account of these effects and found that for the case of an infinitely long cylinder the denominator in (15) acquires a factor equal to $(1 + 2.4r/R_1)$, with R_1 being the cylinder's radius.

In the experiments that followed, Ladenburg established that the finite size of the cylinder also introduces a correcting factor in the denominator of (15) and that this factor is (1 + 3.1r/l), where *l* is the cylinder's length.

Thus, instead of (15), the final formula takes the form

$$\eta = \frac{2r^2(\rho - \rho')g}{9V(1 + 2.4r/R_1)(1 + 3.1r/l)}.$$
(19)

Ladenburg [16] verified formula (19) for a viscous medium, and Arnold [15] showed later that the formula can be used for less viscous media, provided that $r/R_1 < 0.1$.

Notice that the above reasoning and relationships hold only if the ball remains undeformed. The motion of air bubbles and other deformable balls has been examined in the scientific literature, but we do not consider these cases here.

The above example points to the fact that the procedure of measuring the shear dynamic viscosity η is not so simple as might be expected from glancing at formulae (12) and (15).

As we have said earlier, there are many devices for measuring viscosity coefficient [14]. The theory of such devices has been developed, and it permits inferring of the values required from measurements with η ranging from infinitesimal values in gases to enormous values in supercooled liquids and in the region close to the vitrification point of various composites.

It should be noted that in all cases of viscosimetric determination of the coefficient η we are actually dealing with a characteristic of friction between macroscopic layers of the liquid or the liquid and macroscopic bodies — the walls of the pipes or the balls or other bodies to which the liquid has stuck. The shear viscosity η deduced from viscosimetric experiments is the quantity that enters into the Navier – Stokes equation and characterizes the motion of bodies or the propagation of a perturbation through a viscous medium, with these phenomena being described by the Stokes formulae (13).

The equations of motion in a viscous fluid or of the motion of a viscous fluid itself are described by the Navier – Stokes equation, which is approximate in the sense that it is valid only for certain viscosities and losses in the motion of the bodies or in sound propagation [17].

If a perturbation with a wavelength Λ propagates through a viscous medium with an amplitude absorption coefficient α , the Stokes equation can be used as long as $\alpha \Lambda \ll 1$. This is the criterion of applicability of the Stokes equation (13). For cases accessible to the experimenter the results are always approximate, and the above examples are a clear indication of this situation.

Shear viscosity for various substances being in different states can vary within very broad limits.

For instance, for vitrifying substances, both organic and inorganic, the viscosity coefficient η can vary by 20 orders of

magnitude from several fractions of a centipoise to 10^{16} – 10^{18} P when the temperature changes within the range pertinent to the substance found in the liquid state and in the vitreous state, respectively.

So far we have been dealing with static viscosity, which can be measured by viscosimeters of disparate design. Such viscosity manifests itself only in extremely slow processes. From the standpoint of their mechanical properties, substances with such viscosities are described by the well-known Maxwell equation, which links the Hooke elasticity of the solid and the Newtonian flow of the liquid:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{1}{G}\frac{\mathrm{d}S_{\mathrm{sh}}}{\mathrm{d}t} + \frac{S_{\mathrm{sh}}}{\eta} \quad \text{or} \quad \frac{\mathrm{d}S_{\mathrm{sh}}}{\mathrm{d}t} = \left(\frac{\mathrm{d}\theta}{\mathrm{d}t} - \frac{S_{\mathrm{sh}}}{\eta}\right)G, \quad (20)$$

where θ is the strain, $S_{\rm sh}$ the shearing stress, and G the shear modulus.

If the strain remains constant ($\theta = \text{const}$), the Maxwell equation (20) implies

$$S_{\rm sh} = S_{\rm sh}^0 \exp\left(-\frac{t}{\tau_{\rm M}}\right),$$

where the Maxwellian relaxation time τ_M is related to the viscosity coefficient η and the shear modulus *G* as follows:

 $\eta = \tau_{\mathrm{M}} G$.

Here the relaxation time $\tau_{\rm M}$ is the time it takes $S_{\rm sh}^0$ to decrease *e*-fold (*e* = 2.7).

The coefficient of static viscosity measured by a viscosimeter used with media characterized by enormous values of shear viscosity has practically no effect on the phenomena most common not only in science but also in ordinary life.

By way of an example we take the absorption of sound in the ordinary window glass.

For ordinary liquids and glass, the amplitude absorption coefficient α multiplied by the wavelength Λ is given at low frequencies, i.e. as $\Omega \tau \rightarrow 0$, by the following formula

$$\alpha \Lambda = \frac{\pi \Omega}{\rho V^2} \left(\frac{4}{3} \eta + \eta' \right). \tag{21}$$

Taking into consideration that the main audio frequencies of the male voice lie in the range $f \approx 100-150$ Hz [18], and setting $\Omega = 2\pi f$, $V = 3 \times 10^5$ cm s⁻¹, and $\rho \approx 1.22$ g cm⁻³, we get

$$\alpha \Lambda \approx 2.5 \times 10^{-8} \left(\frac{4}{3} \eta + \eta' \right). \tag{22}$$

Even if we ignore the bulk viscosity η' , which is most likely to be of the same order of magnitude as the shear viscosity, and take $\eta \approx 10^{16}$ P for glass, we get $\alpha \Lambda \approx 10^8$, and since even at $\alpha \Lambda = 2\pi$ there can be no propagation of waves, the value of $\alpha \Lambda \cong 10^8$, if we could actually reach it, would mean that glass is an ideal sound-proofing material.

All this is untrue, of course, in relation to window glass, since glass is a good conductor of sound, it reverberates and can even break if high-intensity sonic waves are applied to it, which would not be the case if a shear viscosity of 10^{16} P actually manifested itself in glass.

The explanation lies in the viscosity relaxation process. The point is that the viscosity coefficient ceases to be a constant quantity and becomes frequency-dependent; in our case it becomes dependent on the frequency of sound. As noted earlier, the relaxation theory was developed by Mandel'shtam and Leontovich [13] for the case of combined effect of bulk viscosity and was later generalized by Isakovich [19] to the case of the combined effect of bulk and shear viscosity.

If we are dealing with shear viscosity at a certain frequency Ω , then we can write [11]

$$\eta_{\Omega} = \frac{\eta_0}{1 + \Omega^2 \tau_s^2} \,, \tag{23}$$

where $\eta_0 = G\tau_s$, and τ_s is the relaxation time. The quantity η_Ω remains equal to the static viscosity coefficient when $\Omega \tau_s \ll 1$, and then we can ignore $\Omega^2 \tau_s^2$ in (23) in comparison to unity. But if $\Omega \tau_s \gg 1$, the 'one' can be neglected and η_Ω becomes smaller than η_0 or even infinitesimal. Then the acoustic properties of viscoelastic media, as well as those of organic or inorganic glass, become clear. Notice that here we examined only shear viscosity, characterized by the shear viscosity relaxation time τ_s .

Obviously, when calculating η_{Ω} by formula (23) we must include a term, similar to (23) in structure, that allows for the relaxation of the bulk viscosity with a characteristic time τ_v , the bulk viscosity relaxation time.

Amorphous substances, such as highly viscous liquids and glass, are not adequately described by formula (23) or even contradict it. To overcome this difficulty, a set of relaxations times or, more precisely, a continuous arbitrary function of relaxation times, is introduced [20]. Such a set of relaxation times has no physical content, which means that kinetic equations with local derivatives do not describe phenomena taking place in amorphous media and nonlocal theories like the Isakovich–Chaban theory [21] are needed in these cases.

5. Brownian motion of small solid balls in a viscous fluid

In Section 4 we examined the motion of bodies in viscous fluids and motion of fluid (flow) in a medium containing solids in conditions where the motion of the fluid is fairly slow, $\text{Re} \ll 1$, and the bodies are sufficiently large that the liquid, which consists of individual molecules, can be interpreted as a continuous medium. Such motion is exactly Brownian motion.

In 1827, the British botanist Robert Brown discovered that small particles suspended in a liquid are in perpetual random motion. The particles moved, it seemed, without any regard for external action, since neighbouring particles were observed to be independent of each other in their motion. Isolating the suspension from vibrations and light had no effect on the particles' movements. But as the particles grow larger and the viscosity of the medium in which they are suspended increases, their displacements decrease.

The first to put forward the idea that small particles move because of collisions with the molecules of the liquid, which are in random motion, was Wiener [22], thirty-six years after Brown's observations.

A quantitative theory of Brownian motion was developed by Einstein [23] and Smoluchowski [24]. It does not seem logical to present the full line of reasoning that led to the derivation of relationships for the longitudinal (D_L) and rotational (D_r) diffusion coefficients defining motion of small balls in the viscous fluid, since all of this can be found in numerous textbooks and monographs. Here we give only the calculation results: Einstein's formula for the longitudinal diffusion coefficient reads as follows

$$D_L = \frac{kT}{6\pi r\eta} \,, \tag{24}$$

where k is the Boltzmann constant, while the formula for the rotational diffusion coefficient is

$$D_r = \frac{kT}{8\pi r^3 \eta} \,. \tag{25}$$

In the very idea of their derivation, the two formulae contain the shear viscosity coefficient, which can be measured by a viscosimeter. Notice that Einstein [23] derived the above formulae for the case where the number of macroscopic solid balls is so great that their distribution over the coordinate and time can be expressed by a function f(x, t) for motion along the x-axis (more precisely, the projection on the x-axis of random particle motion):

$$f(x,t) dx = n (4\pi Dt)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right) dx$$
 (26)

with *n* being the total number of particles.

The square root of the arithmetic mean of the squares of displacements along the *x*-axis takes the form

$$\lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{2D_L t} \,, \tag{27}$$

so the average displacement of a small ball along the *x*-axis is proportional to the square root of time.

For the rotational movements we have an expression similar to (27):

$$\lambda_r = \sqrt{\langle \Delta_r^2 \rangle} = \sqrt{2D_r t} \,, \tag{28}$$

where D_L and D_r are defined in (24) and (25), respectively.

The basic relationships of kinetic theory were subjected to experimental verification in great detail and with the highestpossible accuracy by Perrin [25] and other researchers, and it was found that the theory is in full agreement with the experimental facts.

In his doctoral thesis, 'A new determination of molecular dimensions', Einstein [26] took a bold new step by using the formulae of Brownian movement in determining the size of molecules.

The boldness consisted in that he interpreted a solution of sugar in water as a suspension of small balls in a continuous medium. Of course, there was the possibility that such a model and Einstein's assumption would disagree radically with experimental results for those reason alone that the motion of an individual molecule has little in common with the motion of a microscopic particle, and Einstein fully understood the risk. Nevertheless, he proceeded with his assumption.

Einstein [23, 26] derived a formula for the viscosity coefficients of the solvent, η , and the solution, η^* . By ignoring the higher-order terms he arrived at the following expression linking above viscosities:

$$\eta^* = \eta (1 + 2.5\varphi) \,, \tag{29}$$

here the φ is the fraction of the volume occupied by the balls, $\varphi = (4/3)\pi r^3 n$, with *n* being the number of balls per unit volume, so that

$$\eta^* = \eta \left(1 + \frac{10}{3} \pi r^3 n \right), \tag{30}$$

and, hence,

$$\Delta \eta = \eta^* - \eta = \eta \frac{10}{3} \pi r^3 n \,. \tag{30a}$$

Using formulae (29)-(30a), Einstein [26] found that for a 1% sugar solution in water the densities of both substances are additive, while the viscosity coefficients are not (for a 1% sugar solution in water the viscosity is greater than that from addition by a factor of 1.5).

In this connection Einstein wrote [26]: "...It appears to me that this result can hardly be explained in the light of molecular theory, in any other manner than by assuming that the sugar molecules present in solution limit the mobility of the water immediately adjacent, so that a quantity of water, whose volume is approximately one half ... the volume of the sugar-molecule, is bound on to the sugar-molecule.'[†]

Allowing for the fact that $n/N = \rho/M$, where N is the number of molecules in one grammolecule, ρ is the mass of the dissolved substance per unit volume, and M is the molecular weight, we conclude from formulae (24) and (30) that

$$Nr^{3} = \frac{3}{10\pi} \frac{M}{\rho} \left(\frac{\eta^{*}}{\eta} - 1 \right), \quad Nr = \frac{RT}{6\pi\eta} \frac{1}{D_{L}}.$$
 (31)

In his example of a sugar solution Einstein found that $Nr^3 = 80$ and $Nr = 2.08 \times 10^{16}$, which implies that

$$r = 6.2 \times 10^{-8} \text{ cm}, \quad N = 3.3 \times 10^{23} \text{ mol}^{-1}.$$
 (32)

The modern value of $N = 6.02 \times 10^{23} \text{ mol}^{-1}$ is in good agreement with Einstein's result, and for r the agreement is within order of magnitude. So we can see that Einstein made a bold and decisive step by using the phenomenological formulae (30) and (31) in calculating the molecular radius and Avogadro's number $N = N_A$. It is remarkable that calculations using the above formulae yield correct orders of magnitude for the molecular size and number of molecules $N_{\rm A}$. What is really astonishing is that the value of the phenomenological viscosity η measured by a viscosimeter proves to be close to the value of molecular viscosity, which should have been incorporated in the respective formulae. The 'viscosity' formulae for a molecule and its characteristics should be different, but before a microscopic theory of liquids or its equivalent is developed there is no way we can know the real form of such formulae.

Einstein's attempt to replace molecular viscosity with macroscopic viscosity and the success that followed was remarkable and, naturally, had many critics. Here we do not even attempt to discuss everything that has been written on the topic. We touch only on Vavilov's paper [27], which contains not only critical remarks concerning Einstein's method of determining the size of molecules but also an attempt to develop a method for finding the size of molecules that is more realistic and for determining molecular viscosity differing from the macroscopic viscosity. In particular, Vavilov writes: 'By its very definition the viscosity coefficient is a macroscopic factor that has meaning only for internal friction between layers of liquid. However, Sutherland [28] and Einstein [23, 26] generalized the idea of viscosity to the case of individual molecules moving in a liquid, when one is forced to speak about the immobile liquid film that moves together with a molecule in a very ambiguous and even indefinite sense.

Only practical success, at least in making correct order-ofmagnitude estimates, might justify such an extrapolation. The physical reasons for the coincidence lie, of course, solely in the statistical averaging of an enormous number of individual deviations, which is automatically present in any real experiment.'

Formulae (24), (25), and (29) obtained by using the statistical hydrodynamic approach cannot give a molecular size r equal to the gas-kinetic size a. To be able to use the hydrodynamic model, Vavilov [27] employs an approximate scheme (Fig. 1) that illustrates how a molecule of the solute (sugar) is surrounded by molecules (of radius σ) of the solvent. Figure 1 depicts a temporary monomolecular layer of thickness 2σ . After that Vavilov suggests that

$$a + 2\sigma > r > a \,, \tag{33}$$

and writes that '... for a plausible value used in approximate calculations we can take

$$r \approx a + \sigma$$
. (34)

Generally, this correction is not equivalent to allowing for all the solvent shells constantly bound to a solute molecule and must be taken into account for all solutions. To our knowledge, correction (34) was never taken into consideration.'

In discussing the internal friction coefficient, Vavilov [27] further writes: 'The formulae (24), (45), and (35) contain the viscosity η ; this quantity should not be identified, for particles of a molecular size, with the macroscopic viscosity, which has meaning only when large surfaces are involved in friction.'

Below we shall see how Vavilov introduces the notion of molecular viscosity η_m , and here is Vavilov's opinion about



Figure 1. The minimum thickness (- - -) of the liquid layer surrounding a dissolved molecule is equal to the diameter of the solvent molecule [27].

the problem as whole: 'As we go over to very minute particles (e.g., neutrons), the hydrodynamic formulas lose all meaning. Despite the theoretical vagueness and even the arbitrary nature of formulae (24), (45), and [the formula for the dipole-moment relaxation time τ_D ; see below] when applied to molecules, they still form the only basis for understanding and calculating the kinetics of processes proceeding in liquids.'

As far as is known, these assertions are entirely true even today, 60 years later.

To introduce a quantitative expression for the molecular viscosity η_m , Vavilov [27] uses Einstein's formula (30) for a solution, derived in [23, 26], with *r* being a quantity of linear molecular dimensions, and n = 1. Then

$$\Delta \eta = \eta^* - \eta = \eta_{\rm m} \times \frac{10}{3} \pi r^3$$
, $\eta_{\rm m} = \frac{3}{10} \frac{1}{\pi r^3} \Delta \eta$. (35)

This is how Vavilov [27] determines the molecular viscosity $\eta_{\rm m}$ (35), which is defined, via (24) and (25), in terms of measurable quantities.

Notice that in the above-discussed [27] paper, the ratio of the macroscopic viscosity η to the microscopic viscosity η_m is assumed constant, $\eta/\eta_m = \text{const}$, with a concrete value chosen in such a way that it varies for real substances from 1.5 to 2.

However, it must also be noted that in [27] in all cases the solutions had values of η lying within the interval 1.25×10^{-2} P to 6.2×10^{-3} P, which means that these were media with low macroscopic viscosity.

6. The elements of viscosity theory

More than 200 years have passed since Newton introduced the notion of 'lack of slipperiness,' or viscosity, and before Jager [29] made the first attempt, albeit unsuccessful, to express η in terms of molecular and other physical parameters. The first formulae for η yielded a temperature dependence that was reciprocal of that observed in experiments.

Although there exists still no molecular theory of liquids, many different microscopic theories of viscosity in fluids were developed. Panchenkov [30] mentioned as many as 15 theories, including his own. The list certainly did not exhaust all the researchers who have contributed to the theory of liquids in one way or another (see also [14]).

There is an extremely large number of studies devoted to inorganic substances capable of vitrification. Monographs on the amorphous state have been written (e.g., see the monographs by Kobeko [31] and Feltz [32]) that expound the theories of various researchers. In the final analysis, however, everything boils down to three or even four arbitrary constants remaining in the formulae, and these constants must be adjusted in such a way that these formulae provide a good description of the experimental findings.

Sometimes the formulae are obtained not from theory but are written empirically so that they describe the experimental results in the best possible manner and contain the smallest possible number of arbitrary constants.

Perhaps the most widely known formula of this kind is the Vogel-Fulcher-Tammann formula [33-35], which can be written as follows:

$$\ln \eta = A + \frac{B}{T - T^*} , \qquad (36)$$

where η is the macroscopic viscosity coefficient (as before), and *A*, *B*, and *T*^{*} are the adjustable parameters.

Formula (36) has been used with equal success for organic and inorganic liquid viscous media over a broad temperature interval, up to the vitrifying point $T_{\rm g}$.

It must be noted, however, that (36) is not the soul formula used to describe the temperature dependence of the shear viscosity in viscid media. The constants A, B, and T^* in (36) are determined from the temperature dependence of viscosity measured in experiments, usually not the highest viscosities. After the constants have been found, formula (36) becomes valid at viscosities so high that measuring them becomes difficult or even impossible without using special types of viscosimeters. What is important, the parameters determined in this way are not universal, thus meaning that for each substance they have to be determined anew.

A microscopic theory governing high values of macroscopic shear viscosity η has yet to be developed.

For low shear viscosities the theory situation is not really any better.

Vast experimental data on the temperature dependence of shear viscosity made it possible for Batschinski [36] to establish a relation between the flowing quality of a liquid, $\varphi = \eta^{-1}$, and the liquid's specific volume v, namely

$$v = b + c\varphi, \tag{37}$$

where b and c are the constants. Here b may be interpreted as the volume occupied by the molecules of the liquid proper and, to within a numerical factor, assumed equal to the constant b entering the van der Waals equation, so that formula (37) can be written as

$$\eta = \frac{c}{v-b} \,. \tag{38}$$

This is the Batschinski formula, with v - b being the free volume. As noted earlier, there is no theory of liquids and no molecular theory of viscosity, but basing our reasoning on pure intuition it is possible to draw a microscopic picture of the phenomenon.

For instance, it is obvious that the presence of viscosity is a direct consequence of the intermolecular interactions. The stronger the interaction, the smaller the free volume v - b and the higher the viscosity η . Similarly, the weaker the interaction between molecules, the larger the free volume v - b and the smaller the viscosity. Batschinski's formula (38) corresponds very well to this qualitative pattern: the shear viscosity of a liquid is inversely proportional to the free volume.

In exactly the same way, the higher the temperature, the larger the free volume and the lower the viscosity. The qualitative pattern discussed here agrees with experimental results. Many researchers have devoted their efforts to providing a physical interpretation for the Batschinski formula and the constants entering it [14, 30].

The difficulty in developing a theory that would govern the viscosity of liquids is that liquids differ from gases and solid crystalline bodies. In gases at ordinary pressures the mean free path of a molecule is much greater than the size of the molecules, and there occurs total randomness in the directions of molecular motions. In solid crystalline bodies the molecules or atoms occupy definite equilibrium positions (sites on the crystal lattice) and this order is repeated in all directions over all distances.

Liquids lack these distinctive characteristics of gases and crystals. Hence it is common practice to consider liquids as I L Fabelinskiĭ

being compressed real gases. It is possible that such an approach can be justified at temperatures close to the vaporization temperature.

Apparently, Frenkel [37-39] was the first to examine the case where a liquid can be interpreted as a solid at temperatures close to its melting point.

If we assume that the molecules of the liquid occupy their positions of equilibrium, where, because of thermal motion, they oscillate with a period τ_0 , then such a model contradicts reality since it strips the liquid of its essential property, i.e. fluidity. Frenkel [37–39] pointed to this fact and resolved the contradiction by noting that in a liquid the equilibrium positions, where the particles oscillate, are not retained for an indefinitely long time, as they are in a crystal, but remain such only for a limited time. A molecule that has oscillated about a position of equilibrium for a time τ (Frenkel called this the 'temporary settled time') goes over or hops into a neighbouring temporary settled position and so on. Fluidity proves to be a natural property of such a model describing the thermal motion of molecules in a fluid.

The temporary equilibrium positions are arranged in a completely random way, in contrast to the sites of a crystal lattice, which do not change their positions with the passage of time.

The duration of a particle stay at an equilibrium position is short, but still is much longer than the period τ_0 of particle oscillation.

According to Frenkel's model [39]

$$\tau = \tau_0 \exp \frac{U}{kT} \,, \tag{39}$$

where U is the activation energy of a molecule in the environment of its neighbours, and the frequency of molecular vibrations is $\omega_0 = \tau_0^{-1}$.

The viscosity of gases varies differently from that of liquids for variations of temperature. While in gases the viscosity increases in proportion to the square root of the absolute temperature, in liquids it always decreases with increasing temperature and its variation depends on the properties of the liquid substance and the temperature interval [e.g., see formula (36)].

A good illustration of the temperature dependence of gas and liquid viscosities can be found in Kobeko's book [31] and is reproduced here in Fig. 2.

Frenkel's theory [39] implies that the viscosity of a simple liquid depends on its temperature as follows:

$$\eta_{\rm m} = A \exp \frac{U}{kT} \,, \tag{40}$$

where $A = kT\tau_0/\pi r\sigma^2$, with *r* being the molecular radius, and σ the particle separation. All these quantities characterize an individual molecule or even an atom of a simple liquid. Hence, in terms of the adopted notation scheme, (40) is the formula for the molecular viscosity.

According to Frenkel [39], formula (40) can be used when describing not only simple liquids, but in this case the value of A obtained in experiments differs from that predicted by the theory if comparison is made with macroscopic viscosity data.

After Frenkel's work [37-39], several attempts were made in order for the viscosity theory of simple liquids to be developed.

Here we will mention only the research done by Born and Green [40, 41] (see also Ref. [42]), which led to the following



Figure 2. The universal curve representing the dependence of $\log \eta$ on *T* for liquids (curve *I*) and gases (curve 2). The dashed section represents the region where the two states 'meet.' In the vicinity of this meeting point the molecular mobility mechanism, corresponding to the gaseous (curve 2) and liquid (curve *I*) states, undergoes a drastic change [31].

expression for the shear viscosity:

$$\eta_{\rm m} = 0.48 \frac{r}{v} \left[m \varphi_a(r) \right]^{1/2} \exp \frac{\varphi(r)}{kT} , \qquad (41)$$

where *m* is the molecular mass, *v* the volume of one molecule, $\varphi_a(r)$ the component of the molecular pair potential corresponding to attraction (Cr^{-6}), which can be found from the London formula for dispersive forces [43], and *r* the distance between the centres of two neighbouring molecules.

At approximately the same time Eyring [44, 45] (see also Ref. [46]) built a theory of 'absolute reactions rates,' which made it possible to derive a general expression for the shear viscosity of a non-Newtonian liquid, i.e. a liquid whose shear viscosity depends on an external force or a velocity gradient:

$$\eta = \frac{F\delta}{2ak'_0\sinh(aF/2\delta n\,kT)}\,,\tag{42}$$

where *F* is the external field acting on a unit area of the molecular layer, δ the distance between the molecular layers, *a* the distance between the positions of equilibrium of molecules in the liquid, *n* the number of molecules per unit volume (the molecular number density), and k'_0 the Eyring reaction rate constant [45] equal to

$$k'_0 = \chi\left(\frac{kT}{h}\right) \exp\left(-\frac{\Delta G}{kT}\right)$$

with $\chi \sim 1$, *h* the Planck constant, and ΔG the free activation energy.

Eyring's formula (42) remains the only known molecular representation of non-Newtonian shear viscosity.

For ordinary liquids and weak external forces F, the quantity $aF/2\delta nkT$ in (42) (bearing in mind that $\delta/a \cong 1$) is small compared to unity, so that $\sinh(aF/2\delta nkT)$ can be replaced by the first term of its expansion in a Taylor series, i.e. $aF/2\delta nkT$, with the result that instead of (42) we have

$$\eta = \left(\frac{\delta}{a}\right)^2 \frac{nkT}{k'_0} = \left(\frac{\delta}{a}\right)^2 nh \exp\left(-\frac{\Delta G}{kT}\right). \tag{43}$$

All the formulae for η obtained from molecular-theory calculations are similar to Frenkel's formula [39]; the similarity even covers the quantities entering the formulae. Actually, in all cases the index of a power of the exponential function contains the ratio of activation energy to kT. All the differences are in the pre-exponential factors, which play no important role in the problem.

All the quantitative expressions for shear viscosity are valid for a molecule, but we are forced to use them when obtaining macroscopic results.

We can hope to achieve good agreement between theory and experiment for simple liquids like argon and methane, and such accord has indeed been achieved, at least for η [47, 48]. In an extremely narrow temperature interval the above formula provides a satisfactory description of the experimental results.

7. Relaxation times for a constant dipole moment and anisotropy

Here are two more examples where the formulae are derived for individual molecules but the phenomenological viscosity is used to determine the characteristic quantities.

We begin by studying the behaviour of molecules with constant electric moments in an external static electric field *E*.

Naturally, in the absence of an external electric field the molecules move at random, which also means they can be in rotational motion. Of course, the resistance to rotational motion is determined by the interaction between the selected molecule and the environment. What is unknown is the law governing this interaction, so it is usually assumed that the moment of the friction force is the same as for a ball and is given by formula (10).

Debye [49], following Einstein's reasoning, found the distribution function for dipole molecules comprising a liquid when a constant electric field E is applied to the liquid:

$$f(T,\eta,\vartheta,E) = A\left[1 + \frac{\mu E}{kT} \exp\left(\frac{kT}{4\pi r^3 \eta} t\right)\right] \cos\vartheta, \qquad (44)$$

where μ , *t*, and ϑ are, respectively, the constant dipole moment, the time variable, and the angle between the directions of the electric field and the constant moment.

Formula (44) implies that when the external field is instantaneously taken away, the distribution function will approximate to the random distribution e times closer for the time

$$\tau_{\rm D} = \frac{4\pi r^3 \eta}{kT} \,. \tag{45}$$

Here r is the molecular radius, and η is the macroscopic viscosity coefficient, although by the very essence of the physical problem this should be the molecular viscosity coefficient.

For low viscosities η the Debye formula (45) agrees with the experimental findings for the case where η is measured by a viscosimeter.

The relaxation time for a molecular dipole moment is expressed by formula (45). This formula incorporates the quantities r and η , which are characteristics of the behaviour of a single molecule, its size and its losses (friction resistance) during motion. An important parameter used in both experimental and theoretical studies on the spectra of molecular light scattering, caused by temporal variations in the anisotropy fluctuations, is the anisotropy relaxation time.

While the dipole-moment relaxation time τ_D is the time it takes the distribution of molecules that have been partially oriented by an external field to become entirely random after taking away the external field, the anisotropy relaxation time τ_a represents the time during which an emerging fluctuation in the anisotropy (e.g., the preferred orientation of the highestpolarizability axis) disperses as a result of the molecular random motion and the distribution of molecules becomes random. Based on pure intuition we suggest that these times (τ_D and τ_a) do not differ too much.

In the initial theory of the spectra of molecular light scattering caused by anisotropy fluctuations, Leontovich [50] derived an expression for the distribution of the scattered light intensity as a function of the frequency ω reckoned from the exciting light frequency:

$$I^{-1}(\omega) = C^{-1} + C^{-1}\omega^2 \tau_{\rm a}^2, \tag{46}$$

where C is a constant, and τ_a the anisotropy relaxation time. This yields

$$\tau_{\rm a} = \left[C \frac{\mathrm{d}I^{-1}(\omega)}{\mathrm{d}\omega^2} \right]^{1/2}.$$
(47)

For the time of anisotropy fluctuation relaxation Leontovich [50] obtained the following expression:

$$\tau_{\rm a} = \frac{4\pi r^3 \eta}{3kT} = \frac{1}{3} \tau_{\rm D} \,. \tag{48}$$

Quantities defined by (46)-(48) have been measured in experiments [11, 12] and thoroughly discussed [51, 12].

Actually, it was found that the intensity distribution in the spectrum of depolarized light scattering, or in other words, on the wing of the Rayleigh line, is not described by a single relaxation time τ_a , meaning that the theory must incorporate at least two relaxation times, τ_1 and τ_2 , and for various substances τ_1 and τ_2 belong to different intervals of variation. For instance, for carbon disulfide $\tau_1 = 2.4 \times 10^{-12}$ s and $\tau_2 = 2 \times 10^{-13}$ s, and for a liquid such as salol (phenyl salicylate) τ_1 is longer than τ_2 by a factor of 100. What is also important is that τ_1 and τ_2 exhibit different temperature dependences, where τ_1 follows the variations of η/T at low values of η , while τ_2 varies much more slowly.

A theory that describes the entire spectrum of molecular light scattering and allows for any number of parameters was developed by Rytov [52, 53], and Romanov and Solov'ev [54].

Here we do not intend to discuss the entire spectrum of molecular scattered light. We only note that experiments make it possible to measure $\tau_1 = \tau_a$ and its temperature dependence.

The Lorentzian (46) implies that the half-width of the Rayleigh line wing at half-height in intensity, $\delta\omega$, is the reciprocal of τ_a , so that $\tau_a = \delta\omega^{-1}$ can be examined experimentally.

We notice again that the quantity r, which enters into (48) and is determined by the molecular size, refers to a single molecule. This statement is based on experimental findings. Indeed, if the light was scattered by a conglomerate of spherically shaped molecules of radius 2r, then $\delta\omega$ would be

greater than experimental value by a factor of almost 10, which means that the *r* in (48) is the radius of one spherical molecule and $(4/3)\pi r^3$ is the volume of such a molecule.

As noted earlier, in all the formulae that refer to a molecule we used the macroscopic values of the viscosity coefficient, which are measured by viscosimeters. Almost always the calculation result was satisfactory, at least in the order of magnitude, and in all cases the viscosity was low, amounting to several centipoises. But one would like to know the highest value of the macroscopic viscosity at which formulae (45), (48) and those akin to them yield results that are in satisfactory agreement with experimental data. If we turn to formula (48), we can set up a quantity τ^* such that

$$\tau^* = \tau_a \frac{kT}{\eta} = \frac{4}{3} \pi r^3 \equiv \text{const} \,. \tag{49}$$

Hence, τ^* must be independent of the temperature and the viscosity if (49) is true, and τ^* would not be a constant if for some values of η and T formula (49) is invalid. An experimental verification of the validity of formula (49) for salol was carried out by Kovalenko et al. [48]. Phenyl salicylate is convenient for experimental tests because it admits of supercooling and its viscosity can be changed, by varying the temperature, from small fractions of a centipoise to the viscosity of a vitreous state amounting to $\eta \approx 10^{16} - 10^{18}$ P. A distinctive feature of phenyl salicylate is that its molecules display a large optical anisotropy, which produces a well-resolved doublet and triplet in the spectrum of depolarized molecular scattering [12].

In Figure 3 the logarithm of the anisotropy relaxation time τ_a and the reduced relaxation time τ^* are plotted against the temperature on the Celsius scale over the interval -5 to 80 °C. Figure 3 demonstrates that even in this small temperature interval the deviations from the results predicted by formula (49) amount to four orders of magnitude. Clearly, for higher viscosities the deviations are larger still.

The situation is qualitatively the same for the dipolemoment relaxation time. This was established by measurements [55] of the temperature-dependent dielectric constant and the loss tangent that used glycerin and electromagnetic waves in the centimetre range. It was found that according to measurements of the loss tangent tan $\varphi = \Omega \tau_D$ (with Ω being



Figure 3. Dependence of the anisotropy relaxation time τ_a (+) and the reduced time τ^* (\circ) of phenyl salicylate on the temperature measured in Celsius. Experimental data show that the deviations from the values predicted by formula (49) amount to four orders of magnitude. As the viscosity grows, the deviations increase considerably.

the frequency of the electromagnetic waves) the value of $\tau_D = 5 \times 10^{-12}$ s, while calculations that use (48) yield $\tau_D = 1.3 \times 10^{-8}$ s. These aspects were also discussed in [56].

The constant on the right-hand side of (49) represents actually the volume of the molecule of the liquid being studied. Such a volume is an effective quantity, meaning that, depending on the external conditions, it can vary somewhat, but the variations cannot be too large — in any case they cannot amount to orders of magnitude.

In Figure 3 one can clearly see that at small values of the shear viscosity the quantity τ^* is indeed a constant. This does not mean that the shear viscosity η measured by a viscosimeter coincides with the molecular viscosity in the same conditions, but it does mean that the temperature dependences of η and η_m remain roughly the same up to a certain value of η . When η becomes high, the proportionality between η and η_m vanishes and the two quantities begin to depend on the temperature differently. That had been intuitively obvious was finally verified by experiments.

What do such large deviations of τ^* from a constant, clearly visible in Fig. 3, mean?

Firstly, as has repeatedly been noted, the macroscopic viscosity measured by a viscosimeter of the Stokes or Ostwald type [14] must not be confused with molecular viscosity. Obviously, the energy losses or transfer of momentum by a macroscopic body differ from that of a molecule, and most likely the temperature dependences are different, too.

Secondly, the formulae (45) and (48) and some of the other formulae above were obtained from equations containing local derivatives. But as we have seen, many properties of viscid and vitreous media cannot be described by theories based on equations with local derivatives [12, 21, 57].

8. Finding the molecular viscosity from experiments

The first theoretical investigations, based on a nonlocal model that could not be fully substantiated, were made by Isakovich and Chaban [21]. These investigations provided a satisfactory description of sound propagation through highly viscous media. However, the researchers were unable to generalize their model so it could describe the molecular light scattering in viscous and vitreous media.

Here it must be noted that the physics of the amorphous state is still underdeveloped, and although some attempts to describe the spectra of scattered light in viscous media have been made, it is difficult to use their results. There is hope, however, that the theory will eventually be developed to a state in which it can be used for describing the spectra.

But since a theory that adequately reflects the properties of the object of investigation has yet to be developed, we are forced to rely on the model employed by Einstein [23], Debye [49], Leontovich [50], and Rytov [52], which remains valid up to a certain values of shear viscosity. The fact that the quantity τ^* expressed by formula (49) remains constant (temperature-independent) can serve as the criterion of validity of the adopted model.

Within the framework of this model, all the above formulae that involve the molecular viscosity coefficient η_m can be used in determining the experimental values of η_m , since

$$\tau_{\rm a} = \frac{1}{3} \, \tau_{\rm D} = \frac{1}{6} \, D_r^{-1} = \delta \omega^{-1} \,. \tag{50}$$

The choice of the proper formula for obtaining η_m is dictated only by the quantity in (50) that can be measured more easily and with higher accuracy. The present author and his collaborators prefer to determine η_m by using (48) together with the spectrum of molecular scattered light.

Earlier we discussed a method that uses the intensity distribution in the wing of the Rayleigh line for finding $\tau_1 = \tau_a = \delta \omega^{-1}$.

Using formula (48), we arrive at the following expression for the molecular viscosity η_m :

$$\eta_{\rm m} = 3.3 \times 10^{-17} \frac{T}{\delta \omega \, r^3} \,, \tag{51}$$

where the numerical factor and the power of the linear dimension r of a molecule are obtained on the assumption that a molecule is a ball of radius r.

Of course, in reality, a molecule is shaped differently, but we assume that this fact will manifest itself only in the insignificant change in the magnitude of the numerical factor.

Formula (51) implies that the molecular viscosity η_m is determined by T, $\delta\omega$, and r, which can be found from independent experiments. The errors in measuring these quantities have a direct effect on the absolute value of η_m and a much weaker effect on the temperature dependence of molecular viscosity.

Figures 4 and 5 show the temperature dependences of η_m in salol [48] and o-therphenyl [58]. Here we have plotted the molecular viscosity η_m calculated using formula (51) on the basis of spectral measurements of $\delta\omega$ and simple temperature measurements, assuming that r^3 is a constant quantity.

In the experiment somewhat unexpected was the appearance of two exponential functions instead of one in the temperature range being studied.

Following the line of reasoning of Frenkel [formula (40)] and of Born and Green [formulae (41) and (43)], we arrive at the following formula

$$\eta_{\rm m} = \eta_{\rm mo} \exp \frac{U(T)}{kT} \,, \tag{52}$$



Figure 4. Temperature dependence of the molecular viscosity $\eta_{\rm m}$ in salol calculated using formula (51).



Figure 5. Temperature dependence of the molecular viscosity $\eta_{\rm m}$ in *o*-therphenyl calculated using formula (51).

where U(T) is the depth of the potential well occupied by a molecule, which is surrounded by its 'neighbours'. But why even within a limited temperature range do there appear two exponents for the description of η_m instead of the one predicted by the theory? There must be an explanation for this, but more importantly, we should establish how η_m behaves at extremely high viscosities. This leads in turn to difficulties in determining $\delta\omega$ by spectral measurements.

In this case it is impossible to rely on interferometric spectral measurements, since the instrument 'linewidth' proves to be much broader than the true linewidth, which is determined by η_m . This means employing spectral correlation techniques.

However, we need an unambiguous relation that would link the spectral line halfwidths obtained from interference and correlation spectra. We believe that such a link can be established, but this has not yet been done, and is possibly not so easy when numerical results are needed.

A solution to this problem has yet to be found, but we also have to explain the presence of two exponents in the description of η_m .

Our preliminary explanation of this fact looks as follows. At low values of η_m , where $U/kT \ll 1$, the molecule can freely change its position or freely rotate within its potential well. But if η_m is high, which means that the molecule finds itself in a 'deep' potential well, or $U/kT \gg 1$, we must also require that there occurs an interaction between the molecule and the environment, since otherwise the molecule would never be able to hop to another such well or rotate, thus meaning that the liquid lost its main property of fluidity.

Closer inspection of the observed behaviour will have to be left to the future, and possibly a more rigorous description of the experimental data will differ from that presented in this paper. From Figs 4 and 5 it follows that experiments make it possible to find U_1 and U_2 , the quantities similar to the activation energy. We can find this energy from the following equation:

$$k \frac{d \ln(\eta_{\rm m}/\eta_{\rm 0m})}{dT^{-1}} = U(T), \qquad (53)$$

as was done in [57].

In conclusion we note that although there exists no microscopic theory of viscosity, it is quite possible to derive the molecular viscosity coefficient η_m from spectral measurements by remaining within the Einstein–Debye–Frenkel model, and this paper tried to show how it can be done.

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