

Measurement of the anisotropy relaxation time in liquids with a broad range of viscosities

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Experiments show that the expression which describes the anisotropy relaxation time in low-viscosity liquids as being proportional to the shear viscosity and inversely proportional to the absolute temperature is not valid at high viscosities. The discrepancy can reach several orders of magnitude.

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1. In the first quantitative relaxation theory for the spectrum of depolarized light scattered in a liquid¹ and also in later theories (see a review²), the anisotropy relaxation time τ is used as a parameter.

If we adopt the Debye model, as Leontovich¹ did, the relaxation time for the dipole moment, $\tau_D = 4\pi r^3 \eta / KT$, is three times the anisotropy relaxation time τ :

$$\tau = 4\pi r^3 \eta / 3KT, \quad (1)$$

where r is the radius of the ball,¹⁾ η is the shear viscosity of the medium, and T is the absolute temperature. The origin of Eq. (1) is the same as that of the rotational-diffusional coefficient $D_r = KT/8\pi\eta r^3$, so we have $\tau = 1/6D_r$. Strictly speaking, the expressions for the anisotropy relaxation time τ are valid for only a macroscopic ball, but Einstein³ accepted the following argument: If one assumes that the solute molecules are approximately spherical and are large in comparison with the solvent molecules, then the equation $R = 6\pi\eta r$ can be applied to the individual solute molecules. In other words, one can determine the size of the molecule, r , from D_r .

The expressions written above have been applied successfully to individual molecules not only for solutions but also for individual liquids at low viscosities.⁴

Expression (1) contains an important physical quantity: the shear viscosity η . The viscosity η is measured by viscometers; it is the same quantity which appears in expression (1). It depends strongly on the temperature, but nothing has been said about its role in expression (1) in papers on Brownian motion.⁵ A direct proportionality between the anisotropy relaxation time and the shear viscosity follows from the relaxation theory at small values of η , from the kinetic theory, in terms of the diffusion coefficient D , and from Maxwell's picture of viscosity ($\eta = \tau\mu$, where μ is the shear modulus). Does this relationship remain in force at arbitrary values of the viscosity?

An experimental study of the spectrum of depolarized light scattered in various liquids is described by a least two anisotropy relaxation times, τ_1 and τ_2 , where $\tau_1 > \tau_2$ (Refs. 2, 6, and 7). An experimental determination of τ_D and τ_1 has shown that these quantities are described well by the expressions for τ_D and τ_1 at low viscosities.^{4,2,7}

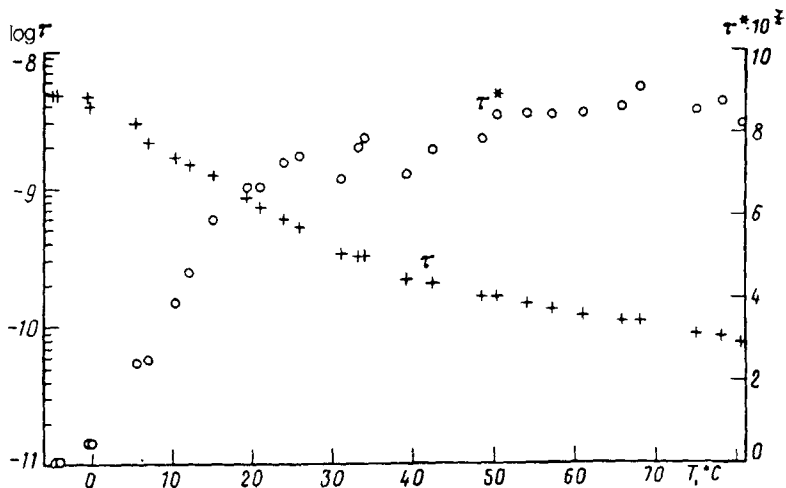


FIG. 1. Temperature dependence of the anisotropy relaxation time τ and of the reduced time τ^* . The experimental data shown here demonstrate that the deviations from expressions (1) and (2) amount to four orders of magnitude. As the viscosity is raised, the discrepancies increase substantially.

At high viscosities the Debye expression for τ_D fails to describe experimental results.⁸

Our purposes in the present study were to experimentally determine $\tau = \tau_1$ over a broad range of η values in phenyl salicylate and to determine whether the experimental results conform to a relation which follows from (1), specifically,

$$\tau^* = \tau_1 \frac{T}{\eta} = \text{const.} \quad (2)$$

Here τ_1 , T , and η are found in independent measurements.

2. Spectra of the depolarized light scattered in phenyl salicylate were measured over a broad range of the viscosity on an apparatus with a five-pass Fabry-Perot interferometer with dispersion regions (the free region of the spectrum) of 15, 7.5, and 6 GHz, as described in Ref. 9. The half-width of the instrumental function was $\delta\nu = 65$ MHz. The spectrum was recorded by a Burleigh DAS-1 electronic system. The signals were fed to a computer, where they were processed by a special program to extract the actual intensity distribution in the spectrum. This distribution was then used to find the half-width $\delta\nu$. The experimental conditions were otherwise the same as in Ref. 9. The viscosities were taken from Ref. 10 over the entire temperature range.

3. Figure 1 shows the experimental results along with calculated results. The quantities measured directly are the temperature T , the viscosity η , and the half-width ($\delta\nu$) of the central component in the spectrum of the depolarized light scattered in phenyl salicylate with various viscosities. The relaxation time τ_1 was calculated as the reciprocal² of the half-width $\delta\nu$. The reduced relaxation time τ^* was calculated from expression (2), in which the quantities mentioned above appear.

Figure 1 shows the temperature dependence of τ_1 and τ^* . At high viscosities, $\delta\nu$ becomes smaller than the instrumental half-width $\delta\nu_a$, so a determination of $\delta\nu = \tau_1^{-1}$ is afflicted with a large error. The quantity τ^* is afflicted with the same error.

4. A calculation of the relaxation time described by expression (1) is a formal procedure which shows that the values of τ_1 lie between 10^{-10} and 10^{-7} s over the entire range of viscosities studied. These values are slightly larger than the values of τ_1 found for less-viscous liquids. For nitrobenzene with $\eta = 2 \times 10^{-2}$ P, for example, we have¹¹ $\tau_1 = 5 \times 10^{-11}$ s.

It follows from Fig. 1 that at low viscosities the time τ^* differs only slightly from a constant value, but at high viscosities or at temperatures below 20°C the deviation from expression (2) is simply catastrophic. Down to -50°C, the time τ^* deviates from a level $\tau^* = \text{const}$ by four orders of magnitude. At even lower temperatures, where η exceeds 10^{10} P, the deviation is far greater.

By virtue of this behavior of τ^* , we can conclude that (2) does not hold even in a qualitative sense at high viscosities. This conclusion means that Rytov's theory and other such theories, which also lead to the prediction $\delta\nu = \tau_1^{-1}$, give a good description of the doublet structure of the spectrum at low viscosities, but they are totally inapplicable for the spectra of depolarized scattered light in high-viscosity media,^{13,14} just as the relaxation theories with local derivatives fail to describe the acoustic properties of viscous media and glasses.^{2,13,15}

It follows from the set of experimental data that the existing theories are successful in the case of low-viscosity media but fail to describe high-viscosity media.

We should also point out that the assumption that it is legitimate to represent a molecule as a macroscopic ball is apparently unjustified at high viscosities. There is a need for some appropriate models and theories of the amorphous state which would make it possible to construct theories describing the optical and acoustic properties of such media.

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¹⁰This expression was derived for the rotational Brownian motion of a spherical particle, but it must have an optical anisotropy, for otherwise there would be no depolarized light in the scattered light.

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