ON THE RELATIONSHIP BETWEEN THE VISCOSITY OF LIQUIDS AND THEIR THERMAL PROPERTIES

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It is shown that in the coordinate system T; $-1/(1/v)(\partial v/\partial p)_T = K$ the lines of constant viscosity for liquids should be rectilinear.

According to the widely-accepted views of Frenkel' [1, 2], the microstructure of liquids a long way from the critical point is characterized by relatively infrequent jumps of the molecules from one set of temporary equilibrium positions to another, and thermal vibrations around these positions between the jumps. For the case of nonspherical molecules, rotations and rotational oscillations of the particles are added to this. In spite of its simple nature, this picture gives a clear representation of the true microstructure of liquids. The decisive quantity characterizing the microstate of liquids is the so-called "settled" life-time of the particles τ, i.e., according to Frenkel', the average time lag between jumps of the molecules.

If the time during which an external force acts on the liquid (or the time during which this force varies) is much shorter than τ, the behavior of the liquid follows the macroscopic laws of the theory of elasticity: elastic deformations (tension and compression) arise in the liquid, and also elastic shear strains, involving tangential stresses [3]. Furthermore, when the time of action of the force is very short and the force itself great, the strength of the liquid may be disrupted in a manner more typical of crystals, by way of breaks and cracks [4]. Only when the time of action of the force or the period of its variation become much greater than τ does the property of fluidity, normal for liquids, appear.

Long before Frenkel', Maxwell used the general principles of elastic theory to develop a theory of viscosity requiring no assumptions as to the microstructure and state of aggregation of the material [5]. For an ideal solid, the stress arising under the influence of external forces is expressed by the equation

$$F = G\gamma. \tag{1}$$

For an ideal liquid, this relationship takes the form

$$\frac{d\gamma}{dt} = \frac{1}{\mu} F. \tag{2}$$

Let us differentiate (1) with respect to t:

$$\frac{d\gamma}{dt} = \frac{1}{G} \cdot \frac{dF}{dt}. \tag{3}$$

Hence the total deformation of a viscoelastic substance is, according to Maxwell,

$$\frac{d\gamma}{dt} = \frac{1}{\mu} F + \frac{1}{G} \cdot \frac{dF}{dt}. \tag{4}$$

From the point of view of the foregoing considerations regarding the liquid state of matter, Eq. (4) reflects the behavior of liquids under the influence of external forces for cases in which the period of action of these forces (or the period during which they are varying) is short enough to reveal the elastic forces, and yet long enough for fluidity effects to appear. It follows from Eq. (4) that, in the case under consideration, when deformation ceases ($d\gamma/dt = 0$), the stress F does not vanish instantaneously, as in

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ideal liquid, nor does it become equal to a constant quantity, as in the case of an ideal solid; rather it varies with time in accordance with the equation

$$\frac{1}{G}\cdot\frac{dF}{dt}+\frac{1}{\mu}F=0. \tag{5}$$

The solution of this equation is

$$F=F_0e^{-\frac{Gt}{\mu}}. \tag{6}$$

The exponential reduction in stress (relaxation) for a viscoelastic body is characterized by the time τ_M during which the stress falls by a factor of e:

$$\tau_M=\frac{\mu}{G}. \tag{7}$$

No experimental determination of the coefficient of dynamic viscosity from Eq. (7) can as yet be made, in particular, because of the small value of the time τ_M. Frenkel' and Predvoditelev used the Maxwell equation to construct theories of the viscosity of a liquid [5, 6]. The Frenkel' equation gives a reasonable qualitative representation of the temperature dependence of the viscosity of liquids, but fails to provide quantitative agreement with experiment. This is possibly because Frenkel' directly identifies the settled life-time of the particles τ with the Maxwell relaxation time τ_M. Justifying the identification of τ with τ_M, Frenkel' writes:

"The relaxation time. . . may naturally be identified with the time during which the liquid particles remain settled in one particular equilibrium position. . . . The vanishing of the elastic stresses in the material when the macroscopic deformation suddenly stops at some constant value should clearly be attributed to redistribution of the particles, by passing from certain positions into neighboring positions, which requires a times of the order of their settled life" [5, p. 347]. This hypothesis is not supported closely enough by experiment. Thus, for example, Panchenkov indicates that "all the formulas proposed by Frenkel' for the temperature dependence of the viscosity of a liquid only give the right order of magnitude for the viscosity, not its true numerical value" [6, p. 53]. Panchenkov also points out [6] that there are clear indications "as to the inapplicability of the Stokes' formula for defining the coefficient of friction experienced by one particular particle of the liquid by virtue of the surrounding particles in terms of the coefficient of macroscopic viscosity of the liquid" [6, p. 50]. The Stokes' formula was, in fact, derived for the conditions of motion of a macroscopic particle in a continuous medium, i.e., strictly speaking, the dimensions of the particle experiencing the friction should be much greater than those of the particles in the surrounding medium. Hence the formula derived by Frenkel' for the viscosity on the basis of the identification of the coefficients of macroscopic and microscopic viscosity, cannot – and indeed does not – give adequately accurate results. Thus the Frenkel' equations cannot be used for the direct calculation of viscosities, nor for the analysis of experimental data.

Panchenkov suggests that the inaccuracy of the Frenkel' equations is related to the lack of experimental confirmation of the Maxwell equation; in his opinion this equation is quite inapplicable to a liquid. The direct verification of this equation would require a logarithmic relationship between F and t to be obtained over a period of time very short for low-viscosity liquids, which would present extreme experimental difficulties. However, relaxation phenomena in liquids over short periods of time have been fairly extensively studied, both theoretically and experimentally, in connection with the electromagnetic constants of the molecules. Thus, for example, Debye [7] made a theoretical study of the problem as to the time required by dipolar molecules to return from the oriented to the disordered state after the removal of an electric field. The electric field F_e acts on a dipolar molecule, tending to rotate it into the direction of the field; the rotational moment thus arising is

$$M=-\mu_0F_e\sin\theta. \tag{8}$$

Under the influence of this moment, the molecule will rotate with a constant angular velocity, experiencing a resistance due to its interaction with surrounding molecules. The moment of the resistive forces, also equal to M, will be given by the equation

$$M=\zeta\frac{d\theta}{dt}, \tag{9}$$

where ζ is the constant of internal friction.

Using the Maxwell–Boltzman distribution, and equating the moments created by the electric field and by the forces of internal friction, Debye then obtains an expression for the distribution function of the orientations of the molecules, the variable part of which takes the form

$$\varphi(t) = e^{-\frac{2kT}{\zeta}}. \tag{10}$$

After the removal of the field F_e, the molecules start returning to their original disordered state, and the function $\varphi(t)$ falls by a factor of e in a time $\zeta/2kT$. In contrast to τ_M we call this the Debye relaxation time:

$$\tau_D = \frac{\zeta}{2kT}, \tag{11}$$

where T is the absolute temperature.

The Maxwell relaxation time (the fall in the mechanical stress after the removal of the external force) and the Debye relaxation time (the return of the molecules to the disordered state after the removal of an external electric field) reflect differing relaxation processes which are nevertheless similar in their physical nature. We may therefore expect that these quantities will be, even if not equal, at least proportional to one another, i.e.,

$$\tau_M = c_1 \tau_D.$$

The coefficient of internal friction in (11) was regarded as constant by Debye, constituting an averaged characteristic of interactions at the microscopic level. The macroscopic viscosity in the Maxwell equation constitutes the total result of the microscopic interactions. There are thus good grounds for considering that the coefficient of dynamic viscosity is uniquely determined by the microscopic coefficient of internal friction ζ (and conversely):

$$\mu = f(\zeta) \text{ and } \zeta = f_0(\mu).$$

Thus Eq. (7) may be written as follows

$$\frac{\mu}{G} = c_1 \frac{\zeta}{2kT} = c_1 \frac{f_0(\mu)}{2kT} \tag{12}$$

or

$$\frac{\mu}{f_0(\mu)} = c_1 \frac{G}{2kT}.$$

The shear modulus G in Eq. (12) is, according to elasticity theory,

$$G = \frac{E}{2(1+\mu_p)}. \tag{13}$$

Since the Poisson coefficient μ_p remains constant with the limits of applicability of Hooke's law, we have

$$G = c_2 E. \tag{14}$$

The Young's modulus may be expressed in the following manner

$$E = 3(1 - 2\mu_p)K = c_3 K, \tag{15}$$

and in turn [8]

$$K = -\frac{1}{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T}. \tag{16}$$

Substituting (15) and (16) into (14), we obtain

$$G = -c_2 c_3 \frac{1}{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = -c_4 \frac{1}{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T}. \tag{17}$$

If we then put (17) into (12) we obtain

$$\frac{\mu}{f_0(\mu)} = c_5 \frac{K}{T}. \tag{18}$$

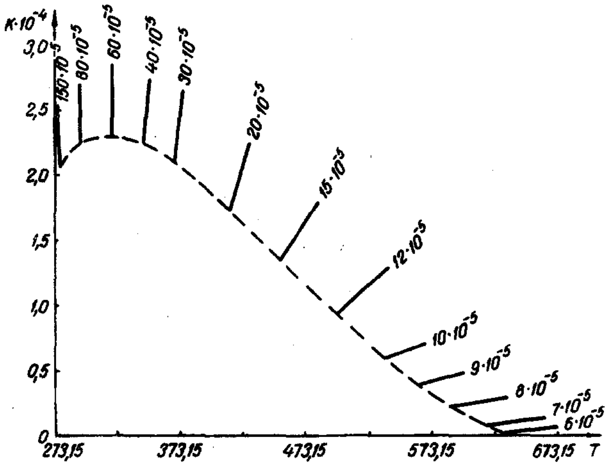

Fig. 1. Lines of μ = const from the experimental data of [9, 10], plotted in coordinates of T (°K) and K (bar) (the broken curve is the saturation line; the figures on the lines give values of μ, N · sec /m^2).

Equation (18) leads to a conclusion which is important in the analysis of experimental data, namely, that in the coordinate system K, T the lines of constant viscosity should be straight lines.

We attempted to verify the foregoing conclusion for water, the viscosity of which has been studied over a number of years in the Physical Laboratory of the All-Union Thermotechnical Institute. To this end we took reliable experimental data relating to the viscosity of water [9, 10] and plotted lines of constant viscosity (μ = const) in the p, T diagram for pressures up to 1000 bar; for various values of p and T along these lines we made a computer calculation of the quantity $-1/(1/v)(\partial v/\partial p)_T = K$, using the international system of equations of state for water [11].

Using these values, we plotted the dependence of K on T for various values of μ = const. As seen in Fig. 1, these relationships may to a fairly high degree of accuracy be approximated by straight lines, thus confirming the foregoing conclusions, at all events as regards water. The scatter of the points relative to the smoothing straight lines never exceeds 1% (with respect to viscosity), and this lies within the limits of experimental error.

On the basis of the foregoing theoretical considerations we have thus established a fairly simple relationship between the coefficient of dynamic viscosity and the thermal properties of liquids. This relationship may, in particular, be used for correlating data relating to the viscosity of liquids over a wide range of parameters of state. Our analysis has shown that along the lines μ = const the quantity K is proportional to the pressure. It follows that the lines μ = const will also be straight lines in coordinates (p, T), giving a comparatively simple equation convenient for practical calculations between the viscosity coefficient and the experimentally measured parameters of state (p and T).

This equation was proposed in a similar form in [11]. It should be noted that the equation describes the viscosity of water not only in the liquid phase but also over a considerable range of supercritical parameters.

NOTATION

τ	is the relaxation time;
G	is the shear modulus;
μ	is the dynamic viscosity;
μ_0	is the dipole moment;
θ	is the angle between the direction of the dipole moment and the field direction;
ξ	is the microscopic viscosity;
k	is the Boltzmann's constant;
T	is the temperature;
c_1, c_2, c_3, c_4, c_5	are the constants;

E is Young's modulus;
K is the bulk modulus;
v is the specific volume;
p is the pressure.

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