

On the Viscosity of Liquid.

By Kunihiro KIGOSHI.

(Received October 1, 1948.)

Introduction. Up to this time, a number of theories on the viscosity of simple liquid were proposed by several authors,⁽¹⁾ each from a different point of view. Among these, H. Eyring's theory seems to be the most clear and general. But not in any of them was the shearing force caused by liquid viscosity made clear by the molecular kinetic theory. According to the idea of H. Eyring, the work done by shearing force on a molecule in the process of transition may be transferred to the potential energy barrier of transition of this molecule. However this approximation leaves something to be explained and it must be justified theoretically or experimentally.

The present author intends to give a theory of viscosity based on the similar idea of liquid structure used by Eyring and others. Thus the number of jumps of a molecule from one equilibrium position to the next is given by the simple formula $\nu \exp(-\omega/kT)$, where ν is the vibrational frequency of a liquid molecule, ω is a potential barrier formed by the nearest neighbour molecules, and kT , the product of Boltzmann's constant and the absolute temperature of the liquid. However, in a non-uniform flow a difference in a number of jumps between different directions may be caused not by a difference of ω , as has been usually considered, but by the directional difference of T . In this case T is not a temperature but a mean mutual kinetic energy of two molecules which effectively exerts to overcome the potential barrier. A gradient of flow and shearing force are calculated from this standpoint.

Shearing Force in a Non-Uniform Flow. Molecular arrangement in a liquid may be considered as follows. Around one molecule, Z_0 nearest neighbour sites are located on a spherical shell with a radius R . Among these sites Z_m are occupied by the nearest neighbour molecules. We may neglect molecular interaction except the force f between the nearest neighbours. This force is determined by the distance between two molecules, which varies from R by the thermal motion of molecules. There exists such a force between each molecular pair, and f is the mean value of these forces. Therefore we can consider f as a function of R and θ , where θ is a variable expressing the mutual thermal motion of two molecules and we may give it the same dimension as tem-

(1) H. Eyring, *J. Chem. Phys.*, 4 (1936), 238; S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", 480 (1941); J. Frenkel, *Trans. Faraday Soc.*, 33 (1936), 58; S. Kaneko, *This Bulletin*, 15 (1940), 276.

perature. In general, especially in a non-uniform flow θ is a function of θ, φ which are respectively the polar coordinates of one molecule taking the other as an origin. The directional difference of θ may be small in comparison with the magnitude of θ and when we put the mean value of θ as equal to T , we may get:

$$\theta = T + \Delta\theta(\theta, \varphi) \quad \langle \Delta\theta(\theta, \varphi) \rangle_{AV} = 0 \quad (1)$$

where $\Delta\theta$ is a function of θ, φ and the average is taken over all possible directions. In this case f can be expressed as follows:

$$f(R, \theta) = f(R, T) + \Delta\theta \partial f / \partial T \quad (2)$$

When the non-uniformity of a flow is expressed by a single flow gradient du/dz , where u is a flow velocity on x -direction, and the other flow gradients are zero, the consideration on the space symmetry deduces that at $\theta = 0$, $\Delta\theta = 0$, and variation of the directional variation of $\Delta\theta$ is a periodic function of θ and φ having periods π and 2π respectively. Then we may write $\Delta\theta$ in the following simple expression;

$$\Delta\theta = \alpha \sin 2\theta \sin(\varphi + \delta) \quad (3)$$

where α is a constant depending on du/dz and δ is a constant which will be determined in the next section.

Only the forces f between the nearest neighbours are taken into consideration, so we can easily obtain the shearing force in a liquid. If we denote by F_x the x -component of a shearing force per unit area of x, y -plane at the origin of coordinates, we may obtain F_x as a sum of x -component of the forces which act between the molecules on one side of x, y -plane (e.g. $z > 0$) and the molecules on the other side ($z \leq 0$). Then we may write:

$$F_x = \int_0^R \int_0^{2\pi} \int_0^{\cos^{-1}(z/R)} f(R, \theta) \sin \theta \cos \varphi (Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz \quad (4)$$

where ρ is the particle density of molecules in a liquid. $f(R, \theta) \sin \theta \cos \varphi$ is x -component of a force f between a molecular pair having the distance R and direction θ, φ . $(Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz$ is the number of molecular pairs which have one of pair having a coordinate z between z and $z+dz$ and the other one having the direction θ, φ respectively in the small region $(\theta, \theta+d\theta)$ and $(\varphi, \varphi+d\varphi)$. The value of θ is restricted within $0 \leq \theta < \cos^{-1}(z/R)$ by the condition that one has a coordinate $z \leq 0$ and the other $z > 0$.

The pressure P in a liquid may be considered as a z -component of a force per unit area of x, y -plane acting on one side of the plane by molecules in the other side of the plane. Then in the same manner as

above we may obtain the formula for P , but this time we have to take into consideration the kinetic pressure NkT/V .

$$P = NkT/V + \int_0^R \int_0^{2\pi} \int_0^{\cos^{-1}(z/R)} f_z(R, \theta) \cos \theta (Z_m/4\pi) \sin \theta d\theta d\varphi \rho dz$$

Where V is molar volume; N , Avogadro's number, and $f \cos \theta$ is z -component of a force f . The same result may be obtained by the use of the virial theorem. This integral is easily performed with the aid of equations (2) and (3). It is obvious that the result obtained is independent of u , i. e. of gradient of flow.

$$P = NkT/V + (1/6) Z_m \rho R f(R, T) \quad (5)$$

In the actual case, distance R and number Z_m of the nearest neighbour depend on V and T in a complicated manner, but the approximation that R and Z_m explicitly depend only on V may be allowed in a simple liquid model. By this assumption we can obtain $\partial f/\partial T$ in equation (2) by differentiation (5) with respect to T .

$$\partial f/\partial T = (6/Z_m \rho R) [(\partial P/\partial T)_v - Nk/V] \quad (6)$$

The integration of equation (4) is performed by equations (2) and (3), and referring to equation (6) the next result is obtained:

$$F_x = (2\alpha/5) [(\partial P/\partial T)_v - Nk/V] \quad (7)$$

where a constant δ is substituted by $\pi/2$ as we shall see in the next section.

The Gradient of the Flow Velocity. The molecular motion in a liquid may be considered as jumps of a molecule from one equilibrium point to another. The simplest assumption we can make is that the distance of a jump is equal to R , since a molecule jumps to any one of its nearest neighbour sites. When one molecule changes its site, it is naturally expected that some of its neighbouring molecules may change their sites at almost the same time, therefore we cannot make clear the idea of the equilibrium site of a molecule. On the contrary, the change in direction θ , φ or distance R of two molecules is the evidence of a jump of a molecule.

We suppose that a molecule A is situated at the origin and the polar coordinates of molecule B are at first R , θ , φ respectively. Now we consider a jump of molecule B which changes θ , φ to θ' , φ' but keeps R constant. Molecules which hinder this kind of transition are A and some of the other nearest neighbours of B molecule. These other molecules besides A, might jump in the process of transition of B molecule. A detailed discussion about the motion of these molecules is very dif-

ficult. But we can say that the potential barrier formed by these molecules is fixed to the molecule A, i. e. to the origin of the coordinates. The probability that the molecule B passes over this potential barrier will be given by $\lambda \exp(-\omega/k\theta)$ where ω is the height of this barrier and θ is a quantity having a dimension of temperature which represents the thermal motion of B with respect to A as mentioned in the preceding section. A constant λ may be determined as follows. The consideration on the uniform state i. e. $\theta = T$, may be allowed now. In this case the probability of jumps of a molecule may be proportional to the number of available sites around this molecule. Therefore the probability of jumps of a molecule in any direction may be proportional to the number of the nearest neighbour sites Z_g , but the probability of jumps mentioned above i. e. the jumps of B to the nearest neighbour sites of A may be proportional to the number of the nearest neighbour sites common to A and B. If we denote by Z_c this number of sites, we may write these proportional relations in the following manner.

$$\nu \exp(-\omega/kT) / \lambda \exp(-\omega/kT) = Z_g/Z_c$$

Therefore $\lambda = \nu Z_c/Z_g$

The numerator of the left side of the above equation implies a probability of jumps in any direction as given by Simha.⁽²⁾ Now we can obtain a number of jumps of B per unit time which changes θ, φ to θ', φ' but keeps R , the distance from A, constant.

$$(\nu Z_c/Z_g) \exp(-\omega/k\theta) \quad (8)$$

Suppose there is a spherical shell with a radius R around one molecule in a liquid. We consider the conservation of the number of molecules on the small area $R^2 dw$ on this sphere, which is intercepted by the small solid angle dw drawn at the center and directed to θ_1, φ_1 . The molecules on the area $R^2 dw$ jump away from this area by two processes, one changing only the coordinates θ_1, φ_1 and keeping R constant, the other changing R . At first we consider the latter process and its reverse i. e. jumping-in-process. These processes are the change in position of the molecules taking place on and outside of the sphere, therefore the net rate of increase of molecules on the area $R^2 dw$ in these processes may be written as follows:

$$\rho(du/dz) R \cos \theta_1 \sin \theta_1 \cos \varphi_1 R^2 dw \quad (9)$$

where $(du/dz) R \cos \theta_1$ is a flow velocity in the x -direction in the small area $R^2 dw$, and $\sin \theta_1 \cos \varphi_1 R^2 dw$ is an area projected to the y, z -plane. On the other hand jumps of the former case and its reverse process are

(2) R. Simha, *J. Chem. Phys.*, 7 (1939), 202.

changes of molecules on the same sphere. The number of molecules jumping away from the area $R^2 dw$ per unit time by the change of θ_1 , φ_1 is expressed in a product of $\nu(Z_c/Z_g) \exp(-\omega/k\theta_1)$ and $(Z_m/4\pi) dw$, which is equal to the number of molecules in this area, where θ_1 means $\theta(\theta_1, \varphi_1)$. The reverse processes bring molecules to the area $R^2 dw$ from the small circle k on the spherical shell around A. The center and the radius of this circle are respectively the small area $R^2 dw$ and R . The number of molecules brought in by this process per unit time may be given by the product of the averaged value of (8) around the circle k and $(Z_m/4\pi) dw$. Therefore the net rate of increase per unit time in these two processes are

$$\nu(Z_c/Z_g) [\langle \exp(-\omega/k\theta) \rangle_{AV} - \exp(-\omega/k\theta_1)] (Z_m/4\pi) dw \quad (10)$$

The sum of the expressions (9) and (10) is the total increase of molecules in the small area $R^2 dw$ by any sort of jumps, therefore this must be zero and we obtain

$$\begin{aligned} \cos \theta_1 \sin \theta_1 \cos \varphi_1 (du/dz) &= (\nu Z_m Z_c / 4\pi \rho R Z_g) (\exp(-\omega/k\theta_1) \\ &\quad - \langle \exp(-\omega/k\theta) \rangle_{AV}) \end{aligned} \quad (11)$$

Then, using equations (1) and (3) we can write

$$\begin{aligned} \exp(-\omega/k\theta_1) - \langle \exp(-\omega/k\theta) \rangle_{AV} &= (a\omega/kT^2) [\sin 2\theta_1 \sin(\varphi_1 + \delta) \\ &\quad - \langle \sin 2\theta \sin(\varphi + \delta) \rangle_{AV}] \exp(-\omega/kT) \end{aligned} \quad (12)$$

When θ, φ are the coordinates of a point on the circle k and φ' is a parameter illustrated by Fig. 1. The calculation of the last term is performed by spherical trigonometry and we can obtain the following result.

$$\begin{aligned} &\langle \sin 2\theta \sin(\varphi + \delta) \rangle_{AV} \\ &= \frac{1}{2\pi} \int_0^{2\pi} \sin 2\theta \sin \\ &\quad (\varphi + \delta) d\varphi' = \frac{1}{8} \sin \\ &\quad 2\theta_1 \sin(\varphi_1 + \delta) \end{aligned} \quad (13)$$

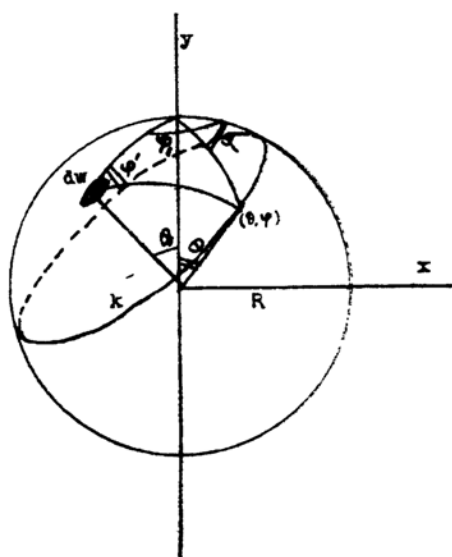


Fig. 1

Referring to equations (12) and (13), equation (11) i. e. the condition for a number of molecules in the small area $R^2 dw$ is constant, leads to the relation between α and du/dz , and at the same time, value of the constant δ is obtained.

$$\begin{aligned} du/dz &= (9u Z_m Z_c \nu \omega / 16\pi \rho R^3 Z_g kT^2) \exp(-\omega/kT) \\ \delta &= \pi/2 \end{aligned} \quad (14)$$

The Expression for the Viscosity Coefficient. If we denote by η the viscosity coefficient of a liquid, the shearing force F_x in equation (5) is equal to $\eta du/dz$. Then equations (7) and (14) lead the expression for η .

$$\eta = (32\pi \rho R^3 Z_g kT^2 / 45 Z_m Z_c \nu \omega) [(\partial P / \partial T)_r - Nk/V] \exp(\omega/kT) \quad (15)$$

We may consider Z_m/Z_g as the ratio of the number of occupied sites to that of total sites. In the case of approximation for the face-centered cubic lattice,

$$Z_g = 12, \quad Z_c = 4 \quad (16)$$

and the value for Z_m may be put at 10 without great error. When we use the density of lattice point $2^{1/2}/R^3$ for the density of total sites, then the density of molecules is given as follows:

$$\rho = 2^{1/2} Z_m / R^3 Z_g \quad (17)$$

By these relations expression (15) may be reduced to the following more or less simple form,

$$\eta = 0.787 (kT^2 / \nu \omega) [(\partial P / \partial T)_r - Nk/V] \exp(\omega/kT) \quad (18)$$

From this expression we can lead a formula which is quite alike that given by Eyring. We may neglect Nk/V when compared with $(\partial P / \partial T)_r$, since the latter is at least ten times larger than the former at an ordinary pressure. Furthermore we adopt the next well-known formulas concerning the molecular vibration ν and free volume v_f .⁽³⁾

$$\nu^{-1} = (2\pi m / kT)^{1/2} v_f^{-1/3}, \quad v_f = N^{-1} V^{-2} [2R / (\partial P / \partial T)_r]^3 \quad (19)$$

Then equation (18) becomes

$$\eta = KT^{-3/2} M^{1/3} Q^{-1} V^{-2/3} \exp(Q/RT) \quad (20)$$

where $K = 8.4 \times 10^{-4}$ R = gas constant, cal/mol. deg.

(3) H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41** (1937), 249.

M = molecular weight, V = molar volume, cm^3 .

Q = activation energy for jumps, cal/mol.

Expression (20) obtained by the author differs somewhat from that of Eyring', namely, the latter has the term of heat of vaporization L_v instead of Q in the denominator of (20), i. e. it has a factor $(Q/L_v)K$ instead of K in equation (20). This difference has resulted from the different views on the relation between the flow and transition probability of a molecule. We may discuss the relative value of K of different liquids with a considerable degree of accuracy in spite of rough approximation as equation (19). The constancy of the value K for different liquids, especially in metallic liquids, each having a different and proper value of L_v/Q , is shown in Table 1. In this table the values of

Table 1.

	$\eta_m \times 10^3$	Q	L_v	L_v/Q	$K \times 10^4$
Na	7.9	0.96	25	26	5.4
K	5.5	1.15	21	18	3.8
Ag	4.4	4.87	59.5	12	3.1
Zn	33.4	2.92	24	8.2	3.7
Cd	25.3	1.59	26	16	4.0
Hg	20.1	0.598	14	23	3.9
Sn	20.3	1.608	78	49	3.5
Pb	28.5	2.32	46	20	3.2
Sb	14.6	2.92	45	16	2.0
Bi	18.6	1.715	46	27	2.7
A	2.83	0.524	1.50	2.9	1.2
N_2	3.11	0.468	1.34	2.9	1.3
O_2	8.09	0.406	1.67	4.1	3.0
CH_4	2.25	0.740	2.20	3.0	1.1
C_2H_4	7.24	0.739			3.2
CO	3.21	0.463	1.41	3.1	1.6

The values of viscosity coefficients η_m at the melting points and that of Q and L_v have been taken from Ward's table.⁽⁵⁾ Q and L_v are given in kilocalories per gram atom or gram molecule.

Q are obtained by the simple formula of Andrade's⁽⁴⁾ $A \exp(Q/RT)$, since we may neglect the temperature dependence of the term $T^{\frac{3}{2}} M^{\frac{1}{3}} Q^{-1} V^{-\frac{2}{3}}$ in expression (20) when compared with the rough approximation used in the course of derivation of this expression.

It may be said that Table 1 offers the experimental verification of the idea used in this paper.

(4) E. N. Da C. Andrade, *Phil. Mag.*, 17 (1924), 698.

(5) A. G. Ward, *Trans. Faraday Soc.*, 32 (1936), 88.

In conclusion the author would like to express his thanks to Dr. Y. Miyake and members of his laboratory for valuable discussions.

*Meteorological Institute, Central Meteorological
Observatory of Japan.*
