A VERIFICATION OF ANDRADE'S FORMULA OF VISCOSITY

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The well known formula of Andrade[1] for the viscosity η of a liquid at its freezing point is

$$\eta=\tfrac{3}{4}\,\nu m/\sigma, \tag{1}$$

where m is the molecular mass, σ the average intermolecular distance (center-to-center), and ν the frequency of molecular vibration of the liquid. Denoting molar volume by V, Avogadro number by N, freezing point by T, gas constant by R, molecular weight by M, and molecular radius by a, we may put

$$\sigma=(V/N)^{1/3}$$

and, as given by Lindemann's theory[2] of fusion,

$$\nu=CT^{1/2}M^{-1/2}V^{-1/3},$$

where

$$C=\frac{\sqrt{2}}{\pi\rho}\,R^{1/2}N^{1/3}, \tag{2}$$

ρ being a fraction defined by

$$2a=\sigma(1-\rho). \tag{3}$$

Equation (3) means that $\sigma\rho$ is the shortest face-to-face distance between the assumed spheres representing two neighboring molecules when they are at their mean positions.

In support to Andrade's theory, we have found a simple, though not very rigorous, way of verifying formula (1). The motion of each molecule may be treated as one in a discontinuous medium composed of all the rest molecules. The resistance offered by this medium to each molecule moving through it with velocity v is [3,4]

$$R=4\pi a\eta v/f, \tag{4}$$

where

$$f=1+\frac{l}{a}\left(0.864+0.29e^{-1.25a/l}\right), \tag{5}$$

l being the mean free path of the molecules. If we set l equal to $\sigma\rho$, i.e., twice the amplitude of vibration in Lindemann's theory of fusion, equation (3) gives

$$\frac{l}{a}=\frac{2\rho}{1-\rho}. \tag{6}$$

Adopting Gruneisen's value[5] 2.8×10^{12} for C, equation (2) yields $\rho=0.124$. By (6) and (5), we have $f=1.27$ for any liquid at its freezing point. The equation of motion for any chosen direction x is

$$m\frac{d^2x}{dt^2}=-\alpha\frac{dx}{dt}+X,$$

where X is the force causing motion and

$$\alpha=4\pi a\eta/f. \qquad (7)$$

As in Langevin's theory of Brownian movement, multiplying through by x changes this equation into

$$\tfrac{1}{2}m\frac{d^2(x^2)}{dt^2}-m\left(\frac{dx}{dt}\right)^2=$$

$$-\frac{\alpha}{2}\frac{d(x^2)}{dt}+Xx.$$

Taking the statistical average of this equation over all the molecules, we have

$$m\overline{\frac{d^2(x^2)}{dt^2}}-2kT=-\alpha\overline{\frac{d(x^2)}{dt}},$$

since $\overline{Xx}=0$ and, by the principle of energy equipartition, $\frac{1}{2}m\overline{\left(\frac{dx}{dt}\right)^2}=\frac{1}{2}kT$, k being the Boltzmann constant. The solution to this equation is

$$\frac{d(x^2)}{dt}=\frac{2kT}{\alpha}\left(1-e^{-\frac{\alpha}{m}t}\right).$$

If t is greater than 10^{-14} second, the exponential term in the bracket is negligible compared to unity for all molecules except hydrogen. In this case, neglect of this term gives

$$\int_0^x d(x^2)=\frac{2kT}{\alpha}\int_0^t dt,$$

or

$$\left(\frac{x}{t}\right)^2=\frac{2kT}{\alpha t}.$$

If t is the time between two successive collisions, i.e., equal to $1/2\nu$, then x/t is the average component speed, $\bar{v}$, of the molecules along the x-direction chosen. I.e.,

$$\left(\frac{x}{t}\right)^2=(\bar{v})^2=\left[\frac{\int_0^\infty ve^{-\frac{1}{2}\frac{mv^2}{kT}}dv}{\int_0^\infty e^{-\frac{1}{2}\frac{mv^2}{kT}}dv}\right]^2$$

$$=\frac{2kT}{\pi m}.$$

$$\therefore\quad \pi m=\alpha t=\frac{\alpha}{2\nu},$$

or

$$\alpha=2\pi m\nu.$$

Substituting this expression of α into (7), we have

$$\eta=\frac{m\nu f}{2a},$$

which, by (3), becomes

$$\eta=\frac{m\nu f}{\sigma(1-\rho)}.$$

Putting in the numerical values of f and ρ previously given, we have

$$\eta=1.45\frac{m\nu}{\sigma}. \qquad (8)$$

which is only 1.09 times that of Andrade's expression (1).

For diatomic liquids, the molecular shape is not spherical and therefore equation (8) is not expected to give accurate values. It however yields the correct tendency of change for different molecules as shown in the following table:

Molecule	Freezing point	calculated	observed
Cl_2	171°K	7.7 c.p.	10.3c.p.[6]
Br_2	265.7	9.8	13.8[6]
I_2	286	14.5	23.2[6]
O_2	54	3.1	8.1[7]
H_2	14	0.037	0.013[8]

We note that the discrepancy is largest in the case of hydrogen. This is in the present theory due to the fact that for hydrogen

$$e^{-\frac{at}{m}}=e^{-\frac{a}{2mv}}=e^{-0.79}=0.45,$$

which is certainly not negligible compared to unity so that the simple solution here used is not applicable.

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