

The Maxwell effect in liquids

Clerk Maxwell many years ago surmised that viscous liquids in a state of flow should exhibit birefringence, and devised methods of observing the phenomenon. Vorländer and Walter (*Z. Phys. Chem.*, 118, 1; 1925) have recently investigated no fewer than 172 liquids of known chemical composition by Maxwell's method, and their work has demonstrated conclusively that a great many pure liquids which cannot by any stretch of language be classed as colloids, exhibit birefringence when subjected to viscous flow. The Maxwell effect, as it may be called, is thus a characteristic property of pure liquids just as much as the power of exhibiting birefringence in strong electrostatic or magnetic fields. We wish briefly in this note to indicate a molecular theory of the Maxwell effect we have worked out which has provided itself very successful in explaining the observed phenomena.

It is easily seen that the stresses in flowing liquid can be considered as equivalent to a set of tensions and a set of pressures acting perpendicularly to each other, and at angles of 45° to the plane of sliding. When the liquid consists of molecules which are highly asymmetric in shape, there would be a tendency for the molecules to orientate under the influence of this system of stresses in such manner that the longest dimension of a molecule tends to lie along the axis of tensions and the shortest one along that of pressures; because such orientation would evidently result in the fluid, regarded as a densely packed assemblage of molecules, expanding along the direction of tensions and contracting along the direction of pressures, thus allowing the system of stresses to do work. By considering the work done during such deformation by the acting stresses as equivalent to the change of energy of the molecules resulting from orientation under a system of couples acting upon them, we can determine the latter in terms of the viscous forces and the asymmetry of shape of the molecules; it being remembered that the orientation is opposed by the thermal agitation of the fluid and that the resulting equilibrium is to be determined statistically in accordance with the Boltzmann principle.

The birefringence of the fluid resulting from the orientation of the molecules under the viscous stresses and their known optical anisotropy, is then readily worked out on lines analogous to those used by Langevin in his theory of electric and magnetic double refraction. The final expression obtained in this way for the difference between the refractive indices n_r and n_p for the vibrations along the axes

of tensions and pressures respectively, is:

$$n_i - n_p = \frac{(n^2 - 1)(n^2 + 2)}{5n\nu kT} \times \frac{(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)}{(a_1 + a_2 + a_3)(b_1 + b_2 + b_3)} \cdot \eta \frac{v}{c},$$

where n is the mean refractive index of the fluid, ν is the number of molecules per unit volume, k is the Boltzmann constant, T is the absolute temperature, a_1, a_2, a_3 are the linear dimensions of the molecule along the three principal axes, b_1, b_2, b_3 are the optical moments induced in the molecule along these axes by unit field acting on it successively along the same three directions, η is the coefficient of viscosity and v/c is the velocity gradient.

The birefringence calculated from our formula, utilising the optical anisotropy ascertained from observations on light scattering and the geometrical dimensions derived from X-ray data, comes out in excellent agreement with the determinations of Vorländer and Walter.

The extension of the theory of the case of colloidal solutions and gels is at present engaging our attention.

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