The scattering of X-rays in liquids

In various notes published last year I dealt with the scattering of light in transparent media, and showed that its study initiated by the late Lord Rayleigh in his theory of the colour of the sky has other fascinating applications in the explanation of the colour of the sea and other transparent waters, and of the colour of ice on glaciers. The thermodynamic theory of "fluctuations" developed by Smoluchowski and Einstein formed the starting-point in the discussions, but I was careful to emphasise the important complications arising from the anisotropy of the molecules in fluid media and showed how the necessary corrections in Einstein's theory may be made. A considerable measure of success was attained in attempting to correlate the behaviour of substances in the liquid and gaseous states in this respect, and in predicting the effects due to alterations of temperature and pressure. The study of the changes in the intensity and states of polarisation of the scattered light in passing from the liquid to the solid crystalline state and their explanation forms another important line of inquiry in which some progress has also been made.

The purpose of the present note is to point out the relation between the optical effects referred to above and the very interesting recent work of Keesom and Smedt, who have obtained Laue photographs of various liquids traversed by a *homogeneous* pencil of X-rays (*Proc. Roy. Soc.* Amsterdam, 1922, page 119), and the similar work by Hewlett (*Physical Review*, December 1922, page 702), who used the ionisation method. Keesom and Smedt found that many of the liquids studied gave a well-marked diffraction ring at a considerable angle with the direct pencil. With liquid oxygen and argon, the first ring was formed at an angle of 27°. A weak second ring was also observed at 46° with oxygen and at 49° with argon. With water, on the other hand, the second ring was very broad and diffuse and practically abutted on the first.

Keesom and Smedt have attempted to explain their results by various special assumptions regarding the relative positions of the neighbouring molecules, while Hewlett suggests that liquids possess something of a crystal structure. To the present writer it appears that the experimental results may be explained without any such special assumptions. As in the optical case, the liquid molecules may be regarded as the diffracting centres which are arbitrarily oriented and distributed uniformly in space subject only to such variations as give rise to density fluctuations in accordance with the Einstein–Smoluchowski formula,

$$\overline{(\Delta\rho)^2} = \frac{RT\beta}{V}\cdot\rho_0^2$$

where ρ_0 is the mean density, $\overline{(\Delta\rho)^2}$ the mean square of its fluctuations, R the gas constant, T the absolute temperature, β the compressibility of the liquid, and V the elementary volume under consideration. When traversed by a homogeneous pencil of X-rays the wavelength of which is smaller than the average molecular distance, such a structure must give rise to diffraction rings which are more or less well defined according as the fluctuations of density are small or large. If in the expression for the density fluctuation, we take V to be a small cube with a molecule at each of its corners, the average fluctuation in its size and the resulting weakening of the diffraction pattern can be calculated somewhat on the same lines as in Debye's theory of thermal effect in X-ray reflection by crystals. In Keesom and Smedt's experiments, the low temperature in the case of liquid oxygen and argon, and the consequently diminished fluctuations of density must have helped in improving the definition of the diffraction ring of the second order.

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