Diffraction by molecular clusters and the quantum structure of light

The investigations on the molecular scattering of light now in progress under the writer's direction (regarding which previous communications have been published in *Nature*) have brought to light some very remarkable cases in which the observed facts are in sharp contradiction with the theories of light-scattering based upon Maxwell's electromagnetic equations. According to the Einstein-Smoluchowski formula for the scattering power of a fluid, viz

$$\frac{\pi^2 RT\beta}{18N\lambda^4}(\mu^2 - 1)^2(\mu^2 + 2)^2,$$

the intensity of the diffracted beam should be proportional to the compressibility β of the fluid and should thus be very large near the critical temperature as the compressibility there is great. Experiments by Keesom and Kammerlingh Onnes have confirmed this result in the case of ethylene vapour over a range of a few degrees above the critical temperature. The scattering powers of liquid carbon dioxide and vapour for a considerable range of temperatures below the critical point have been determined in the writer's laboratory by Mr K R Ramanathan, who has discovered that the formula is approximately valid only for a range of a few degrees below the critical temperature, and then falls off much more rapidly than according to the formula. These observations are significant in view of the observation by the present Lord Rayleigh that the scattering power of saturated carbon dioxide vapour at 21° C is only 102 times that of the gas at atmospheric pressure, whereas according to the Einstein–Smoluchowski formula, it should have been 855 times as great.

The failure of the formula indicated above is especially surprising in view of its successes in other directions, namely, in the case of gases obeying Boyle's law, in the case of liquids under ordinary conditions, and, with certain restrictions, even in the case of solids. In attempting to find an explanation of the failure, at first sight one naturally seeks to find some flaw in Einstein's theory, or in the application of it, but the very successes of the formula in other cases would tend to discourage such an attempt. The formula was deduced by Einstein by applying Boltzmann's principle of entropy-probability in order to find the magnitude of the fluctuations of density of the fluid arising from thermal agitation and deducing the light-scattering due to these fluctuations by application of Maxwell's electromagnetic equations. It is clear that density fluctuations due to

thermal agitation must occur; that their magnitude is proportional to the square root of the compressibility of the medium as contemplated in the theory may be confirmed independently by identifying the thermal energy of the molecules with the energy of sound waves of all possible wavelengths in an enclosed volume of the fluid and equating the energies. Further, the idea that the non-uniformity of the density of the medium is the factor determining light scattering, at least according to the wave theory, is confirmed by the very complete analysis of the problem given by the late Lord Rayleigh in one of his final papers (*Philos. Mag.*, Dec. 1918, p. 449). How, then, are we to escape the difficulty?

A very luminous suggestion made by Jeans in his "Dynamical Theory of Gases" (page 203) is here of great help. Jeans distinguishes between two kinds of clustering in fluid media, *mass-clustering* and *molecular-clustering*, and points out that they tend to become identical at the critical temperature. Einstein's theory is based on the idea that the fluctuations of density and the resulting scattering of light are both due to *mass-clustering*. If, however, we assume that it is *molecular-clustering* that is of importance and results in an increased scattering of light, it is easy to see that in the case of molecules such as carbon dioxide, which are ordinarily non-associated, the clustering of molecules would only be appreciable near the critical temperature, and that at lower temperatures the clusters would rapidly break up and resolve themselves into single molecules. A double molecule would scatter four times as strongly as a single molecule, a triple molecule nine times as strongly, and so on, and if we assume that the energy-effects of separate molecules or groups are additive, and calculate the number of associated molecules from thermodynamic principles, it is easy to give the theory quantitative expression and explain the increased scattering near the critical point, and the rapid fall at lower temperatures.

But the fundamental difficulty remains, why the *mass-clustering* considered by Einstein does not, as it should, according to the classical wave theory of light, give rise to an increased scattering of light?

To the present writer, at any rate, it appears that this contradiction of the electromagnetic theory by experience may have to be classed with its other known failures in the theory of photoelectricity and other modern fields of inquiry. We may, in fact, have to adopt the quantum theory of the structure of light as propagated in space (and not only when it is absorbed or emitted) in order to explain the facts of molecular diffraction. Fuller experimental data which are now being obtained in the writer's laboratory may pave the way towards the clearing up of this fundamental question.

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