

The Molecular Scattering of Light in Vapours and in Liquids and its Relation to the Opalescence observed in the Critical State.

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(Communicated by Dr. Gilbert T. Walker, F.R.S. Received June 19, 1922.)

1. *Introduction.*

It has long been known that in the immediate vicinity of the critical state, many substances exhibit a strong and characteristic opalescence. In recent years, the phenomenon has been studied by Travers and Usher* in the case of carefully purified CS₂, SO₂, and ether, by S. Young,† by F. B. Young‡ in the case of ether, and in a quantitative manner by Kammerlingh Onnes and Keesom§ in the case of ethylene. An explanation of the phenomenon on thermodynamic principles as due to the accidental deviations of density arising in the substance was put forward by Smoluchowski.|| He obtained an expression for the mean fluctuation of density in terms of the compressibility of the substance, and later, Einstein applied Maxwell's equations of the electromagnetic field to obtain an expression for the intensity of the light scattered in consequence of such deviations of density. He showed that the fraction α of the incident energy scattered in the substance per unit volume is

$$\frac{8\pi^3}{27} RT\beta \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{N\lambda^4} \quad (1)$$

In this, R and N are the gas constant and Avogadro's number per gram-molecule, β is the isothermal compressibility of the substance, μ is the refractive index and λ is the wave-length of the incident light. Keesom** tested this formula over a range of 2.35° above the critical point of ethylene and found good agreement except very close to the critical point.

Of an altogether different order of intensities is the phenomenon of light-scattering in gases and vapours under ordinary pressures observed experimentally by Cabannes†† and the present Lord Rayleigh.‡‡ The effect studied

* 'Roy. Soc. Proc.,' A, vol. 78, p. 247 (1908).

† *Ibid.*, p. 262.

‡ 'Phil. Mag.,' vol. 20, p. 793 (1910).

§ 'Roy. Soc. Proc. Amsterdam,' 1908.

|| 'Ann. der Physik,' vol. 25, p. 205 (1908).

¶ 'Ann. der Physik,' vol. 33, p. 1275 (1910).

** 'Ann. der Physik,' vol. 35, p. 591 (1911).

†† 'Comptes Rendus,' vol. 160, p. 62 (1915); and 'Ann. de Physique,' vol. 15 (1920).

‡‡ 'Roy. Soc. Proc.,' A, vol. 94, p. 453 (1918).

by these investigators is, in comparison with the phenomenon of critical opalescence, feeble, and requires powerful illumination and special arrangements to enable it to be observed in the laboratory. The measurements made by them show that the magnitude of the effect* is in substantial agreement with the theory of molecular scattering of light developed by the late Lord Rayleigh, according to which the extinction-coefficient α is given by

$$\frac{32\pi^3 (\mu - 1)^2}{3 n\lambda^4}, \quad (2)$$

where n is the number of molecules per unit volume. The scattering of light in passage through *dust-free liquids* has also been observed by the present Lord Rayleigh† and W. H. Martin,‡ and it was found by the former that the intensity of scattering in the liquid studied (ether) was considerably smaller than that given by the formula (2), though, owing to the greater density of the liquid, the absolute magnitude of the effect is many times larger than in the vapour.

It is important to notice that these three phenomena, namely, critical opalescence, scattering of light by gases and vapours, and scattering by liquids, which are of such different orders of magnitude, and apparently so distinct, stand in reality in the closest relationship to each other. It has been pointed out by Prof. C. V. Raman§ that the observed scattering power of liquids under ordinary conditions agrees with that calculated from the Einstein-Smoluchowski formula; and further, that this law which reduces to Rayleigh's formula in the special case of a gas obeying Boyle's law, is much more generally applicable than the latter and should be regarded as the fundamental relation determining the magnitude of light-scattering in all fluid media. It thus becomes a matter of great importance to make a thorough test of the Einstein-Smoluchowski formula over the widest possible range of experimental conditions. A series of investigations with this object has been undertaken at Calcutta.

The present paper describes the results of a study made of the scattering of light in ether, both in the liquid and in the saturated vapour phases at different temperatures from 30° up to the critical point 193.6°, and also in the gaseous phase above the critical temperature up to 217° C. Ether was chosen as the first substance to be investigated, because it possesses a high refractivity

* 'Roy. Soc. Proc.' A, vol. 95, p. 155 (1918).

† 'Roy. Soc. Proc.' A, vol. 95, p. 95 (1918).

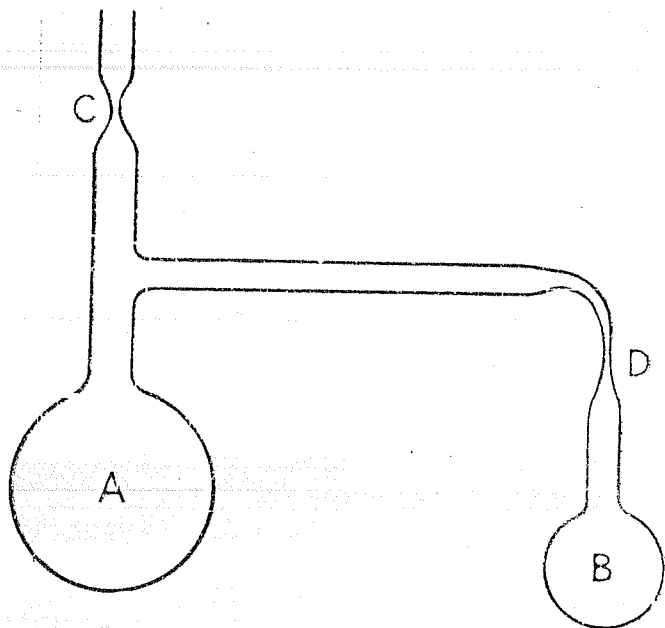
‡ 'Journal of Physical Chemistry,' 1919.

§ 'Nature,' November 10, 1921, and 'Roy. Soc. Proc.' A, April, 1922. See also "Molecular Diffraction of Light," by C. V. Raman, published by the Calcutta University Press, 1922, pp. 12 and 60.

and hence a large scattering power, is easily obtained pure, and can withstand the action of heat and moderately intense light without appreciable change. Moreover, the classical work of Ramsay and Young* on the pressure-volume relations of the substance over a wide range of temperature provides the necessary data for calculation.

2. Experimental Arrangements.

The ether used was Merck's pure ether, redistilled four or five times *in vacuo*. It was contained in a thick, uniform glass bulb of about 3 cm. external diameter. The necessary quantity of ether was introduced into it in the following manner. A glass apparatus of the form shown in the figure was made. The bulbs and connecting tube were well heated over a Bunsen flame and the air exhausted by means of a pump. Nearly four times the required quantity of ether was introduced into the bulbs, and in order to remove the dissolved air, the apparatus was exhausted until more than half



the ether had evaporated and it was then sealed off from the pump at C. All the ether was transferred to the bulb A, and a portion was distilled over into B by placing A in a vessel of warm water at 45–55° C. and B in a vessel of water at the room-temperature (about 30° C.). When B was nearly half filled, its inside was washed out with the distilled ether, which was then transferred back to A without allowing the undistilled ether to come into B. This process was repeated four or five times in order to get the ether perfectly dust-free, and finally, when the required quantity had collected in B, the bulb was sealed off at D.

* 'Phil. Trans.,' A, vol. 178, p. 57 (1887).

The outside of the bulb was painted dead black, leaving three windows, two at the sides to let in and let out light, and one at the base for the observation of the scattered light. It was then mounted in the centre of a thick iron cross-tube, blackened inside, similar to the one employed by Lord Rayleigh (*loc. cit.*). The cross-tube was nearly 1.5 inches external diameter, and each arm of the cross was 7 inches long. Its ends were closed with glass windows, and it could be heated to any temperature up to 250° C. by passing an electric current through a coil of Eureka wire wound uniformly over it. The temperature could be maintained steady within less than half a degree for hours. The distribution of temperature was very uniform in the middle of the tube. The tube was mounted horizontally and sunlight was concentrated at the centre of the bulb by means of a lens. Different apertures could be introduced in front of the lens to regulate the quantity of light. Suitable diaphragms were also introduced inside the cross-tube to prevent diffuse light from reaching the eye. With this arrangement the track of the light in the ether vapour was easily visible through the window at the base of the bulb at room temperature when an aperture of 1 inch diameter was in front of the lens.

The intensity of the scattered light was measured by comparing it with the intensity of a similar track in distilled ether kept outside in a rectangular glass bottle. A lens of the same focal length as the one mentioned before was used to produce the track, and suitable apertures were introduced here also to regulate the brightness. The image of the second track was brought into the same field of view by means of two totally reflecting prisms. The prisms exercised very little absorption and the colour-match of the two tracks was practically perfect. The photometry was done with an Abney rotating sector disc. In order to minimise the heating effect of sunlight, the apertures were made of the smallest size consistent with the visibility of the track, and the light was kept on for as short a time as possible. Temperatures were maintained steady for nearly half an hour before readings were taken.

A correction has to be made for the loss of light on reflection at the glass windows and at the walls of the bulb. It will be noticed that there are six glass-air surfaces and two glass-vapour or glass-liquid surfaces to be taken into account in the case of the bulb, and six glass-air surfaces and two glass-liquid surfaces in the case of the other bottle used as standard. There would thus be an approximate compensation. To test if it is so, and to allow for any absorption which the right-angled prisms might exercise, a comparison was made of the light scattered by the ether in the bulb at room temperature and that scattered by the standard. The two were found to be equal within 2 per cent.

3. Results.

The observed data for the intensity of the scattering by the saturated vapour in terms of liquid ether as a standard are shown in Table I. The theoretical results indicated by the Einstein-Smoluchowski formula are shown in the third column after applying the correction for imperfect polarisation of the scattered light, as explained below in Art. 5. In order to calculate the theoretical value, it is necessary to know the compressibility, β or $-(1/v dv/dp)_t$, and the refractive index, μ , of the saturated vapour at the respective temperatures of observation, and similar data for the liquid used as a standard at 35° C. The compressibilities, $-(1/v dv/dp)_t$, of the vapour at different temperatures were determined by plotting Ramsay and Young's pressure-volume data on graph-paper and drawing tangents at the points of saturation. The values of μ were obtained by the application of Lorentz's refraction formula $(\mu^2 - 1/\mu^2 + 2) = k\rho$, where k has the value 1/3·317 for ether.

It will be seen that throughout there is a good agreement of the observed and calculated results. In column 4 of Table I, the ratio of the scattering power of the vapour saturated at t° to the scattering power of the vapour saturated at 35°, and in column 5 the ratio of the vapour densities under the same conditions, taken from Ramsay and Young's data, are shown. If Rayleigh's law of scattering had been valid throughout this range, the figures in columns 4 and 5 should have agreed. Actually there is an

Table I.—Scattering by Saturated Ether Vapour.

| Temperature (t° C.). | Scattering at t° C. | | Ratio of scattering at t° C to scattering at 35° C. | Ratio of density of vapour at t° C. to density at 35° C. |
|---------------------------------|----------------------------|--|--|--|
| | Observed. | Calculated from Einstein-Smoluchowski formula. | | |
| 33 | 0·038 | 0·036 | 1·00 | 0·92 |
| 54 | 0·075 | 0·074 | 1·97 | 1·81 |
| 75 | 0·150 | 0·140 | 3·95 | 3·22 |
| 91 | 0·22 | 0·23 | 5·79 | 4·79 |
| 108 | 0·45 | 0·45 | 11·8 | 7·1 |
| 123·5 | 0·71 | 0·71 | 18·7 | 10·0 |
| 144·5 | 1·31 | 1·29 | 34·5 | 15·7 |
| 164 | 2·7 | 3·0 | 71·0 | 24·0 |
| 170·5 | 3·9 | 4·0 | 103 | 28·0 |
| 179·2 | 9·1 | 7·9 | 239 | 35·3 |
| 183·5 | 13·0 | 12·2 | 342 | 39·8 |
| 186·5 | 21 | 19 | 553 | 44·2 |
| 190 | 42 | 39 | 1105 | 51·9 |
| 191 | 63 | 55 | 1658 | 53·3 |

enormous difference, showing that, at least in the case of ether, Rayleigh's law breaks down completely, and that the "principle of random phase," on which he founded his theory of molecular scattering, is inapplicable except at very low pressures, where the deviation from Boyle's law is negligible. The scattering power of the vapour is greater, and at the higher temperatures enormously greater, than if the molecules of the gas scattered secondary waves in arbitrary phase-relationships with each other.

The experimental results of the scattering power of ether in the gaseous phase above the critical point are shown in the second column of Table II. In this case, in order to calculate the compressibilities and refractive indices, it is necessary to know the actual mass of ether used, and the volume of the bulb in which it is contained, and these were separately determined at the completion of the experiment, and were found to be 3.164 gm. and 13.98 c.c. respectively. The theoretical value of the scattering power as given by the Einstein-Smoluchowski formula is shown in column 3.

Table II.—Scattering by Ether above Critical Temperature.

| Temperature (° C.). | Scattering at t° C. | | Ratio of scattering at t° C. to scattering at 35° C. | Ratio of density of vapour at t° C. to density at 35° C. |
|------------------------|------------------------------|--|---|--|
| | Observed. | Calculated from Einstein-Smoluchowski formula. | | |
| 194 | 378 | 290 at 195° | 9950 | 71.6 |
| 196 | 172 | 200 at 197° | 4530 | 71.6 |
| 198 | 126 | | | |
| 200 | 84 | 87 | 3316 | 71.6 |
| 202 | 64 | 65 | 1680 | 71.6 |
| 212.5 | 27 | 30 | 710 | 71.6 |
| 217 | 21 | 26 | 553 | 71.6 |

Considering the unavoidable experimental uncertainties such as a slight fluctuation of temperature, which has an enormous influence in the neighbourhood of the critical point, the presence of a trace of dissolved air or other impurity in the ether, and the difficulty of determining the value of the compressibility accurately, the agreement should be considered good. The figures in columns 4 and 5 further illustrate the fact that the scattering power of the gas throughout the range of temperature is far greater than would be the case if the "principle of random phase" were valid.

Finally, Table III shows the observed scattering power of liquid ether.

The density data for liquid ether have been taken from Ramsay and Young's paper; the compressibilities below 100° from Amagat's determina-

Table III.—Scattering by Liquid Ether.

| Temperature (° C.) | Scattering at t° C. Scattering at 35° C. | |
|-----------------------|--|--|
| | Observed. | Calculated from Einstein-Smoluchowski formula. |
| 33 | 1.00 | 1.00 |
| 61 | 1.23 | 1.34 |
| 80 | 1.85 | 1.65 |
| 91 | 1.90 | 1.83 |
| 104 | 2.3 | 2.13 at 100° |
| 125 | 3.0 | |
| 139 | 3.8 | |
| 145 | 4.9 | 8.2 at 150° |
| 153 | 6.3 | |
| 170 | 12.0 | 14.1 at 175° |
| 179 | 22 | |
| 185 | 38 | 27.2 |
| 190.5 | 82 | 73 at 190° |

tions, and those above 100° from Ramsay and Young's work. There seems to be an inaccuracy in Ramsay and Young's compressibility data for liquid ether at 150°; the values of the pressure and volume do not plot into a smooth curve, and in the curve accompanying Ramsay and Young's paper one can notice an unusually rapid change of curvature in the close proximity of the vapourisation point. Making allowance for this, a satisfactory agreement appears between the theoretical and observed values of the scattering power.

Taking the results contained in the three Tables together, it will be seen that the scattering rises rapidly as the critical point is approached, and the values for the saturated vapour, liquid and gaseous phases approach each other and converge to a very large value at this point. The intensity of the scattering under critical conditions is enormous, being about 750 times that of liquid ether at ordinary temperature.

4. Critical Opalescence.

The Einstein-Smoluchowski formula (1), as it stands, gives an infinite value for the scattering power at the critical point. This is physically impossible, and both Smoluchowski and Einstein have pointed out that, in the immediate neighbourhood of the critical point, terms involving $(d^3p/dv^3)_t$ and higher order terms should be taken into account. It is, however, doubtful if even the inclusion of these terms would be sufficient, for the scattered light is markedly less blue in this region, which Einstein's

theory does not contemplate. Ornstein and Zernike* have pointed out that the independence of density-fluctuations in different elements of volume assumed by Einstein is inadmissible in this region, and, taking these mutual influences into account, they have deduced a modified equation for the opalescence in which the term $-(dp/dv)_t$ is replaced by

$$-\left(\frac{dp}{dv}\right)_t + \frac{4\pi RT}{v^2} \frac{\epsilon^2}{\mu^2 \lambda^2} \quad (3)$$

where v is the molecular volume and ϵ is a measure of the radius of action of a molecule, beyond which its influence is negligible. Using this, the total fraction of light scattered per unit-volume, instead of being infinity at the critical point, has a finite value

$$\frac{2\pi}{27} \frac{\mu^2 (\mu^2 - 1)^2 (\mu^2 + 2)^2}{N \lambda^3 \epsilon^2}, \quad v. \quad (4)$$

Also the proportionality of the scattering light with λ^{-4} gives place to one of proportionality with λ^{-2} .

The change of colour of the opalescent light in the neighbourhood of the critical point, is easily observable when the opalescent beam is reduced in intensity by means of the rotating disc photometer to equality with the scattered light from liquid ether. If we assume that the maximum value of the scattering coefficient is given by (4), we can easily obtain an estimate of ϵ . Observations of the maximum intensity of the scattered light were made by heating the ether about 10° above the critical temperature, and then *very slowly* cooling it. With the particular quantity of ether used (3.164 gm. in 13.98 c.c.) the maximum scattering was found to be 750 times that of liquid ether at 35° C. Putting in the numerical values, and taking λ equal to be 5000 Å.U., the scattering coefficient works out to be 8.6×10^{-3} , and ϵ to be 4.6×10^{-7} cm.

However, this correction to the Einstein-Smoluchowski formula is of secondary importance, and does not affect the broad aspects of the question.

5. Polarisation of the Scattered Light.

It has been shown by Lord Rayleigh, that the light scattered by dust-free gases and vapours in a direction at right angles to the incident beam is, in most cases, imperfectly polarised. In the case of ether vapour, he found that the ratio of the weak component to the strong in the scattered light was 1.7 per cent. It was interesting to study how the imperfection of polarisation changes as the condition of the substance changes from liquid to vapour. At ordinary temperatures, the light scattered by liquid ether showed an

* 'Roy. Soc. Proc. Amsterdam,' vol. 17 (1914), and 'Phys. Zeitschrift,' vol. 18 (1917).

imperfection of polarisation amounting to 8 per cent. As the temperature was raised, it remained constant until a temperature of about 125° was reached and then fell off, rapidly at first, and then more slowly to the value corresponding to that of the vapour at the critical point. Table IV gives the results of the polarisation measurements on liquid ether at different temperatures.

Table IV.—Polarisation of Light Scattered by Liquid Ether.

| Temperature. | Weak component compared with strong. |
|--------------|--------------------------------------|
| 33° C. | 8 per cent. |
| 60 | 8 .. |
| 80 | 7 .. |
| 100 | 7·5 .. |
| 120 | 7·5 .. |
| 135 | 5 .. |
| 145 | 3 .. |
| 165 | 1·7 .. |
| 189 | 1·3 .. |

In the case of the vapour, measurements of polarisation were made from 160° to about 200° C. The values of the ratio of the weak component to the strong ranged from 1·3 to 1·0 per cent. There was no change in the value of the ratio on passing through the critical point.

The difference between the liquid and the vapour at the lower temperatures is striking. In the case of gases, the late Lord Rayleigh has shown that imperfection of polarisation can be explained on the assumption of asymmetry of the molecules. The increased value for the imperfect polarisation in liquids, and its rapid decrease with temperature, are results of great interest which await explanation.* Further studies on this point, with a number of other vapours and liquids, are being made by the writer

This imperfection of polarisation has to be taken account of in calculating the intensity of the scattered light. In the case of gases, Cabannes has shown that the scattering is greater in the ratio $6(1+r)/(6-7r)$, where r is the ratio of the weak component to the strong in the light scattered in a perpendicular direction. The question can be viewed in yet another way. The imperfectly

* Since the above was written, a theory based on the conception of molecular anisotropy has been developed by Prof. C. V. Raman, which not only explains these phenomena, but predicts also that the imperfectness of polarisation, both in the case of liquids and vapours, should decrease and tend to a minimum at the critical point. Observations by the writer on benzene confirm this result.

polarised light can be looked upon as being caused by an admixture of a certain quantity of unpolarised light with the polarised light. If to a beam of polarised light of intensity A , there be added a beam of unpolarised light of intensity $2B$, the resultant light will be imperfectly polarised and the ratio of the weak component to the strong would be given by $r = B/(A + B)$ and the intensity of the resultant light will be $A(1 + 2B/A) = A \left(1 + \frac{2r}{1-r}\right)$.

When r is small this reduces to $A(1 + 2r)$. An expression of this form is found to agree with the intensity of the scattered light in gases and liquids, when A is taken to be the scattering calculated from the Einstein-Smoluchowski formula. The factor $1 + 2r/(1-r)$ becomes of great importance when r is large. It will be noticed that when r is not very large, this expression becomes practically equal to the correction factor $6(1+r)/(6-7r)$ introduced by Cabannes. In the Tables I, II and III given above such a correction has been introduced. The imperfection of polarisation for ether vapour has been throughout taken to be 1.2 per cent. and that of liquid has been taken as given in Table IV.

6. Summary.

1. Three instances of light scattering by homogeneous media are known; opalescence of a substance near the critical point, scattering of light by gases, and scattering of light by liquids. The present investigation was undertaken to test the view put forward by Prof. C. V. Raman that these phenomena are fundamentally related to each other, and that the intensity of scattering in all these cases should be represented by the Einstein-Smoluchowski formula, which is more general than the Rayleigh law of scattering and supersedes it except in the special case of gases obeying Boyle's law.

2. Experiments on the scattering of light by ether, in the vapour and liquid phases at different temperatures from 33°C . up to the critical temperature 193.6° , and in the gaseous phase from 193.6° to 217° , are described.

3. The results are in accord with the Einstein-Smoluchowski formula and not with the Rayleigh law of scattering.

4. The Einstein-Smoluchowski formula is inapplicable in the *immediate neighbourhood* of the critical point. The scattered light is markedly less blue here. Following the theoretical work of Ornstein and Zernike, from the maximum value of the intensity of the scattered light, the value of ϵ the radius of action of an ether molecule is deduced to be 4.6×10^{-7} cm.

5. The light scattered at right angles to the incident beam is imperfectly polarised; the ratio of the weak component to the strong is throughout nearly 1.2 per cent. in the case of vapour, while, in the case of liquids, the

ratio is 8 per cent. at ordinary temperatures which remains constant till about 120° , and then falls off, rapidly at first and then slowly to about 1.2 per cent at the critical point. There is no change of imperfection of polarisation on passing through the critical point. The correction due to this in the expression for the intensity of the scattered light is given.

In conclusion, I have great pleasure in recording my indebtedness to Prof. C. V. Raman who suggested the research, and who continued to take an inspiring interest in its progress. The experimental work was carried out in the Physical Laboratory of the Indian Association for the Cultivation of Science, Calcutta.
