CHAPTER IV

Molecular scattering in liquids

32. As early as the year 1899, in his first paper on the scattering of light in the atmosphere,* the late Lord Rayleigh clearly emphasised the principle that his theory of molecular scattering is not applicable in the case of highly condensed media such as dense vapours, liquids and solids, for the simple reason that the molecules in them possess only a greatly restricted freedom of movement. The distribution of the molecules cannot in the circumstances be regarded as a simple random arrangement, and hence the phases of the scattered waves arising from the individual waves are not uncorrelated. The total energy scattered by a volume of a liquid or a solid cannot therefore by any means be equated to the sum of the energies scattered by the individual molecules in it. In the face of this clearest possible declaration of principles, some recent writers, notably Fowle, and Cabannes[†] have put forward the obviously incorrect suggestion that Rayleigh's theory is applicable also in the case of liquids. How far such an assumption must be from the truth can be realised easily in the light of the discussion of fundamental principles contained in our first chapter. As we have seen, it is the degree of approximation of the compressibility of the medium to that given by Boyle's law which is the measure of the degree of applicability of the principle of random phase on Rayleigh's theory. As is well-known, the compressibility of a liquid or a solid is usually only an extremely minute fraction of what it would be if Boyle's law were applicable. This itself is sufficient to show that we shall be greatly in error if we attempted to extend the principle of additivity of the energy effects of the individual molecules to the case of liquids. In fact, Strutt has already found that liquid ether scatters a great deal less light than the vapour in proportion to the relative density of the two media. We can easily see why this should be so. Owing to the near approach of the molecules to each other in the liquid state they occupy a large proportion of the total volume of the containing vessel. Hence the non-uniformity in their spatial distribution is far less striking than in the case of gases, and in consequence there is a partial correlation of the phases of the waves starting out from the individual molecules which entails as the result of

^{*}Philos. Mag., 47, pp. 375-384 (1899). Scientific Papers, 4, p. 397.

[†] Astrophys. J., 38, p. 392.

[‡]Ann. Phys., 15, pp. 1-150.

interference, a great falling off in the total energy scattered. A very interesting calculation* which was made by Rayleigh of the energy scattered by a cloud of particles having a restricted freedom of arrangement clearly illustrates this principle.

The Einstein-Smoluchowski theory

33. The complexities of the problem of molecular diffraction in liquids are so great that we have evidently to proceed by statistical methods. Fortunately, this has already been accomplished in great measure in the beautiful "theory of fluctuations" developed by Einstein[†] and Smoluchowski[‡] and used by the latter especially to explain the peculiar opalescence exhibited by fluids near the critical state. In this theory, scattering is considered not as due to individual particles but to small local variations of density arising from the heat movements of the molecules. These variations are quantitatively determined by Boltzmann's principle. Smoluchowski's statistical thermodynamical reasoning gives for the mean square of fluctuation of density in volume V of density ρ_0 an expression, which except in the immediate neighbourhood of the critical point is equal to[§]

$$(\triangle \rho)^2 = \frac{RT\beta_0 \rho_0^2}{N_1 V} \tag{1}$$

where R is the gas constant, N_1 is the number of molecules in a grammolecule, β_0 the compressibility corresponding to density ρ_0 equal to

$$-\frac{1}{v}\cdot\frac{\mathrm{d}v}{\mathrm{d}p}$$
.

At right angles to the incident light the intensity of scattered light is given by the expression

$$\frac{\pi^2 V^2(\Delta \varepsilon)^2}{2\lambda^4} \cdot \frac{1}{r^2},\tag{2}$$

 $(\triangle \varepsilon)$ being the variation of the dielectric constant.

Now as these individual local variations are irregularly distributed, the phases of the various scattered beams are also quite arbitrary, and hence for calculating

^{*} Philos. Mag., Dec. 1918, p. 449.

[†]Ann. Phys., 33 (1910), p. 1275.

[‡]Ann. Phys., 25 (1908), p. 205. Also, Epstein, Encycl. Math. Wiss, Band V. 3, p. 520.

Boltzmann, Wien. Ber., 63, p. 397. A Einstein, Ann. Phys., 19, p. 373.

the total intensity of scattered light we have merely to sum up the above expression over the total volume ϕ . The expression contains a factor

$$\sum (\triangle \varepsilon)^2 V^2$$

which may be evaluated by use of the Mosotti-Lorentz law

$$\frac{\varepsilon-1}{\varepsilon+2} = \text{const. } \rho.$$

Differentiating we obtain

$$(\Delta \varepsilon)^2 = \frac{(\varepsilon - 1)^2 (\varepsilon + 2)^2}{9} \cdot \left(\frac{\Delta \rho}{\rho_0}\right)^2. \tag{3}$$

Substituting in this the value given above for fluctuation of density we obtain

$$\frac{(\varepsilon-1)^2(\varepsilon+2)^2}{9} \cdot \frac{RT\beta_0}{N_1} \cdot \sum V = \frac{RT\beta_0}{N_1} \cdot \frac{(\varepsilon-1)^2(\varepsilon+2)^2}{9} \cdot \phi. \tag{4}$$

Thus the intensity of light scattered by a cubic centimetre of fluid at right angles to the incident rays is

$$\frac{\pi^2}{18} \cdot \frac{RT\beta_0}{N_1} \cdot \frac{(\varepsilon - 1)^2 (\varepsilon + 2)^2}{\lambda^4} = \frac{\pi^2}{18} \cdot \frac{RT\beta_0}{N_1} \cdot \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{\lambda^4}.$$
 (5)

In the case of gases

$$\beta_0 = \frac{1}{p}$$
 and $\mu^2 + 2 = 3$, nearly

and μ differs only slightly from unity. The formula then reduces to Rayleigh's result. Equation (5) may be applied with confidence to find the intensity of light scattered in liquids, for the work of Perrin and others on the Brownian movement in liquids has furnished a strong confirmation of Einstein's fundamental work on the subject and has shown that the energy of translation of molecules in a liquid is the same as in the gaseous state of matter. The formula thus expresses in a perfectly general manner the scattering power of a fluid associated with its ordinary refractivity taken together with the non-uniformity of optical density resulting from molecular movements. It is a point worthy of notice that according to the formula the scattering power of liquids is proportional to the absolute temperature, if we leave out of account the changes which would result from variation in compressibility and refractive index with temperature. The constant N_1 is a pure number independent of the particular state of molecular aggregation of the substance or its density.

34. It must be remembered of course, that the whole theory depends for its validity on Maxwell's electromagnetic equations for the propagation of light, and the assumption of a continuous interaction between the molecules and the

Experimental study

35. To determine whether the absolute scattering power of liquids for light is correctly given by equation (5), some preliminary observations have been made by the writer and by Mr K Seshagiri Rao working in his laboratory at Calcutta. As is quite obvious, it is of the highest importance to get very pure liquids. Water as is well known is difficult to get free from motes. On examination the ordinary tap water showed a very strong scattering when a beam of light was sent through it. The track was practically white and showed innumerable motes floating about in the water. Repeated filtration through several thicknesses of Swedish filter paper made an improvement, the track being now of a bluish colour, and a still better result was obtained when an earthenware filter was used. Suspended matter was however still in evidence, and the track was also much brighter when viewed nearly in the direction of the source than when seen transversely or in the opposite direction. A somewhat casual attempt was then made to clear the water by adding alkali and alum and thus throwing out a gelatinous precipitate of aluminium hydroxide. This made a further improvement, but small particles of the precipitate remained floating about, apparently because the depth of the water was insufficient and the appearance of the track of the beam was not very prepossessing. The next attempt was made with ordinary distilled water which had been prepared without any special precautions and stored for some time in the chemical laboratory. This gave immediately a much smaller intensity of lightscattering than the tap water had done after several attempts at filtration. For purpose of observation, the distilled water was put into a stoppered glass bottle with square sides and allowed to stand. Test observations from day to day of the scattered beam with a double image prism and a set of Wratten colour filters showed a progressive improvement. After about a fortnight's standing, the track of the light was hardly conspicuous unless a dark background was provided for it to be viewed against, and the defect of polarisation at the violet end of the spectrum was much less striking than it was when the observations were begun. Small motes were still to be seen, particularly when viewed in the direction of the source, but the track was of a blue colour and it was judged that the greater part of the observed luminosity was probably due to the water itself. A sample of water which had been distilled at the Calcutta Mint and stored for 3 months also showed the blue track very well. Allowing it to stand for some time improved matters appreciably.

36. For a quantitative estimate, the brightness of the beam in the water was compared directly with that of its track in saturated ether vapour. The latter was contained in a pear-shaped bulb with a long neck which was covered over with black paint and formed the "black cave" against which the light scattered by the vapour was observed. The bottle and the bulb were set side by side and a parallel beam of light passed through both. An Abney rotating sector was placed in front

be of equal intensity in both vessels as judged visually. The opening of the sector gives the ratio of intensities, a correction being made for the loss of light by reflection in the passage of the direct and scattered pencils through the glass walls. The determinations made in this way were not anything more than approximate estimates. The scattering of light in saturated ether vapour has been measured by comparison with air by Rayleigh and shown to be accurately proportional to the square of its refractivity. Using this result, the observation showed the scattering power of the sample of water used was 175 times that of dust-free air at N.T.P. From theory we find taking for air

$$\beta = 0.987 \times 10^{-6} \text{ cm}^2 \text{ dyne}^{-1}$$
, $T = 273^\circ$, $\mu = 1.000293$ and for water at 30° C,
 $\beta = 43.5 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$, $T = 303$, $\mu = 1.337$.

that volume for volume, water should scatter 140 times as strongly as air at N.T.P. This, though not agreeing exactly with the observed value is only slightly smaller and the difference may be explained as due to the effect of residual suspended particles in the water used in the experimental work.

37. More accurate measurements were made a month later by Mr K Seshagiri Rao when the sample of water had still further improved. The method used was the comparison of intensities by a double image prism and a nicol. Sunlight was used as the source of light and a long-focus lens was used to give an intense and nearly parallel beam. The two bottles were placed on either side of the focus and the track viewed through two parallel slits. The double image prism was placed so that the four images seen were in a line with the planes of vibration horizontal and vertical. The weaker image from the water was adjusted so as to appear just in contact with the stronger image from the ether vapour. By the nicol, these two were reduced to equality. The ratio was then given by $I_1/I_2 = \tan^2 \theta$, where θ is the angle through which the nicol is rotated from the zero position. Measurements by this method gave the ratio of scattering of water at 25° to air at N.T.P. as 158. The ratio was still higher than that given by theory. Possibly it might be due to the motes not having been completely eliminated. But it seems more probable that the higher ratio may be due to the anisotropy of the molecules of water which is evidenced by imperfectness of polarisation. According to the theory of Einstein and Smoluchowski, the light scattered in a direction perpendicular to the incident rays should be completely polarised. As already mentioned in a previous chapter, the work of Cabannes and Strutt shows that most gases depart from this ideal sphericity of molecules. Cabannes has amplified Rayleigh's theory by considering the anisotropy of the molecule and shown that the expression for the intensity of scattered light should be multiplied by

$$\frac{6(1+\rho)}{6-7\rho}$$

where ρ is the ratio of the weak component of polarisation to the strong one. It is

from sphericity, the greater is the intensity of scattered light. It is clear that a similar correction must also be made in the case of liquids. The value of ρ for the specimens of water used is 12% and for air 4%. When this correction is applied the theoretical ratio comes out at 160 and is in fair agreement with that actually observed.

Determination of the Avogadro constant

38. More accurate comparisons of intensities by photographic methods are in progress. It is also intended to measure the coefficient of scattering absolutely using liquids completely freed from motes by repeated slow distillation in a vacuum. From a knowledge of the absolute scattering power, the values of R, T, β and μ being known, it should be possible to calculate the Avogadro constant N_1 from experiments on liquids in much the same way as Cabannes has done with gases. The method by which it is proposed to measure the coefficient of scattering is as follows. The intensity of the scattered light will be of the order of 10^{-7} of that of the incident beam. To make comparisons we have to reduce the intensity of the incident beam considerably and it is proposed to effect it in the following manner. A very short focus lens will be used to condense the light. The light coming to its focus will diverge very rapidly. The radius of the solar image at the focus will be of the order of a millimetre while at a distance of about 2 metres, owing to great divergence the intensity will have been reduced in the ratio of about 10^{-4} or 10^{-5} . Further reduction will be made by a rotating disc with a small radial slit at the edge. The width of the slit will be varied till the light incident on a fixed aperture placed behind it is reduced to the same intensity as the image of the track in the water, as determined by photography. Incidentally the λ^{-4} law will also be tested.

39. According to formula (5), the scattering power is proportional to the absolute temperature of the liquid apart from any variations in μ and β due to the same cause. This effect should be particularly noticeable in the case of liquids such as ether whose compressibility increases rapidly with temperature. In the case of water, we should not expect much change as both the compressibility and the refractive index diminish with rise of temperature. These points are also under investigation.

Molecular scattering and transparency of liquids

40. Since the energy of the light laterally scattered is derived from the primary beam, there must result a certain attenuation in the intensity of the latter in its passage through the liquid, the magnitude of which may be readily calculated from the coefficient of scattering. The multiplying factor necessary is $16\pi/3$ which

of volume of the scattering fluid. The transmitted light is given by the formula $I = I_0 \exp(-\alpha l)$ where l is the length of the path traversed through the liquid and

$$\alpha = \frac{8\pi^3}{27} \cdot RT\beta_0 \frac{(\mu^2 - 1)^2 (\mu^2 + 2)^2}{N_1 \lambda^4}.$$

As in the case of atmospheric scattering we may expect that the coefficient of attenuation α will exactly indicate the observable transparency of the medium in those parts of the spectrum for which it does not exercise any selective absorption. From the data already given and the known values of R, T and N_1 , α may be readily determined for any value of the wavelength.

41. From the observations of various experimenters* it is known that water exercises a selective absorption on the longer wavelength side in the visible spectrum and also in the ultraviolet region. Measurements of the coefficient of absorption in water have been made by various investigators, but the values obtained by each are hopelessly different from those of others. Calculations on the basis of Evans's and Aschkinass' values show that water is actually six to ten times less transparent than it should be. It is not evident from their papers whether they had taken care to get the water mote-free. The most reliable measurements of any hitherto made appear to be those of Count Aufsess. This experimenter used double-distilled water and convinced himself that it was free from suspended matter. It was found by him that the selective absorption in the visual region ceased for wavelengths less than 558 $\mu\mu$. For the two wavelengths $522 \mu\mu$ and $494 \mu\mu$ Aufsess gives as the coefficient of absorption 0.00002. For these two wavelengths the coefficient of attenuation β calculated from the formula given above is respectively 0.000022 and 0.000029. The agreement of observation and theory is significant. It is desirable that further accurate measurements for different wavelengths for carefully purified water up to the extreme violet end of the spectrum were available so that the increase of the coefficient of attenuation inversely as the fourth power of the wavelength could be tested. It would be interesting to determine by careful experiment whether the intensity of the light scattered by water follows the fourth power law exactly. It would be also interesting to investigate scattering at or near an absorption band and to investigate what becomes of the energy absorbed, whether it appears as selective scattering or is merely stored up in the liquid. If there is any selective scattering we might expect deviations from the fourth power law in that region of the spectrum.

^{*}Evans, Proc. R. Soc. London (1894), 57.

Observations of polarisation

42. Reference has already been made to the imperfect polarisation of the light transversely scattered by liquids. The detailed results on this point will now be described. The determinations of polarisation for water have been made by visual methods. Sunlight was used as the source of light and the track was viewed through a small rectangular aperture. The double image prism was so set that the two images were in line and just touching each other, and the directions of vibrations were horizontal and vertical. The two images were brought to equality by a nicol on either side of the zero position. Half this angle gave the angle θ through which the nicol was rotated from the zero position and the ratio of the two intensities was of course given by $\tan^2 \theta$. Measurements were made in different regions of the spectrum by using Wratten colour screens.

The results are given below

	V-11	Green	Blue	Violet
Red 13·2	Yellow 10·3	11.5	15.3	21.7

Inspection of the values shows an increase of polarisation in the red and violet regions with a minimum value at the yellow. It is well known that water has an absorption band in the red and another in the ultra-violet. The experiments thus indicate that near the absorption bands the imperfectness of polarisation increases. It will be noticed that the figures show a rapid increase near the violet end of the spectrum. This may be partly due to the small particles still remaining suspended in the liquid whose influence will only be greatly evident in the region of shorter wavelengths. But that the phenomenon is real, is shown by the fact that at the red end where the influence of the particles is small there is a slight perceptible increase of polarisation. It would be interesting to make observations at and near the absorption bands, using carefully purified liquids. Another point worthy of investigation would be to observe what influence the temperature has on the polarisation. It is well known that water in liquid form exists as molecular aggregates and that temperature has a great effect on them. We might expect therefore a change of polarisation with temperature.

The orientation of the molecules

43. It is important here to notice that imperfect polarisation of the transversely scattered light is noticed not only when the primary beam is unpolarised, but also when the latter is itself completely polarised. To test this point a nicol was placed so that the incident light passed through it. It was found that when the plane of

minimum respectively. In the latter case, that is, when the scattered light was a minimum, it was viewed through a second nicol and its intensity was found to be independent of the plane of polarisation of the latter. It could however be extinguished by two nicols or a double image prism and a nicol, thus showing that it was unpolarised light. A similar phenomenon is also observed in the case of molecular scattering in gases and is a consequence of the fact that the *orientation* of the molecules in fluid media is arbitrary. The observed intensity of scattering is the resultant effect of molecules in all possible positions and orientations, so that the weaker component of polarisation stands in no definite relation of phase to the stronger component, in other words, the scattered light consists partly of common light. The intensity of the Tyndall cone as observed by a nicol when the primary beam is unpolarised is given by the relation $J = C_1 + C_2 \cos^2 \delta$ where δ defines the orientation of the plane of polarisation of the observing nicol.

Relative scattering power of different liquids

44. The observations of Strutt with liquid ether, and of the present writer with Mr Seshagiri Rao on water have clearly shown that the absolute scattering power of liquids is much smaller than that of the corresponding vapours making allowance for the difference of density. This diminution is clearly explained on the Einstein-Smoluchowski formula as the result of the extreme smallness of the compressibility of the liquid which more than sets off the result of the increased refractivity. Naturally, therefore, we should also expect the Einstein-Smoluchowski formula to give the relative scattering power of different liquids correctly. The opportunity for testing this point is furnished by some recent observations of W H Martin on light scattering by dust-free liquids.* Martin found a strong defect in the polarisation of the light scattered by all the liquids observed by him, the defect increasing with the light-scattering power. The Cabannes factor $(6(1+\rho))/$ $(6-7\rho)$ in the intensity is thus very important. The necessary data for compressibility and refractive index are not forthcoming for all the liquids experimented upon by Martin. So far as the available data permit, the results for the liquids listed in column I of the table below have been compiled and the relative scattering powers shown in column II without applying the Cabannes correction, and in column III after applying the Cabannes correction. It will be seen that the computed ratios in column III and those given by Martin's observations shown in column IV agree tolerably. It is to be noted that the Cabannes correction cannot be applied when ρ is more than 50%, and this maximum value must be used in the formula when the observed defect of polarisation exceeds 50%.

Table 2. Water is taken as the standard

Liquid	Calculated from Einstein-Smolu- chowski formula without correction	Calculated from formula with Cabannes's correction	Experimental results
Water	1.00	1.00	1.00
Ether	4.53	4.78	3.94
Methyl Alcohol	2.03	2.04	2.67
Ethyl Alcohol	2.86	2.87	3.00
Benzene	6.38	19-5	15·17
Toluene	5.60	17-1	16.6

Transition from the liquid to the gaseous state

45. As we have seen, the Einstein-Smoluchowski formula, when corrected for the effect of molecular anisotropy gives results in fair agreement with observations in non-fluorescent liquids, and it also automatically reduces to the Rayleigh formula in the case of gaseous media. Further, the formula which was originally developed in order to explain the observed enormous light-scattering power of gases at temperatures slightly above the critical point has been quantitatively confirmed for this region by the very fine measurements of Keesom* on the opalescence of ethylene. In view of these striking successes of the formula, we may, primá facie, feel confident that it would correctly represent the sequence of phenomena throughout the entire range of transition between the liquid and the gaseous states. But, surprisingly enough, the law seems to break down in the case of gases under high pressure. Strutt has shown experimentally that the scattering by saturated carbon dioxide at 21°C at a pressure estimated at 60 atmospheres and a density 114.7 times the density at atmospheric pressure is 102 times the scattering at the latter pressure. This agrees fairly satisfactorily with the Rayleigh formula. But when we calculate the scattering according to the Einstein-Smoluchowski formula, the value of the ratio is given by

$$\frac{\beta_1(\mu_1^2-1)^2(\mu_1^2+2)^2}{\beta(\mu^2-1)^2(\mu^2+2)^2}$$

where β_1 and μ_1 refer to carbon dioxide under pressure and β and μ refer to the gas at ordinary pressure.

46. In the following calculation, the unit of pressure is taken to be 1 atmosphere.

Now $\beta = 1$ and $\mu - 1$ at 21° C = $4.50 \times 10^{-4} \times (273/294)$. We may put $(\mu^2 - 1) = 2(\mu - 1)$ and $\mu^2 + 2 = 3$

$$\beta(\mu^2 - 1)^2(\mu^2 + 2)^2 = 6.29 \times 10^{-6}.$$

The compressibility of the condensed vapour may be obtained in either of two ways; one, by making use of the experimental isothermal of CO_2 for 21° C and the other by calculation on the assumption of a suitable equation of state.* The value of β obtained from Andrews' isothermal curve[†] 23.5° is 1/17. On assuming Clausius' equation of state

$$\left(p + \frac{a^1}{T(v+c)^2}\right)(v-b) = RT$$

(which is found to represent the isothermals of CO₂ at high pressures with great accuracy[‡]), we get for the coefficient of compressibility

$$\beta = -\frac{1}{v} \frac{dv}{dp} = \frac{v-b}{v} p + \frac{a^1}{T(v+c)^2} - \frac{2a^1(v-b)}{T(v+c)^3}.$$

Taking p = 60 atmos.

 $v = \frac{1}{115}$ of the volume at the atmospheric pressure at 21° C

$$= \frac{1}{115} \cdot \frac{294}{273}$$
 of the volume at 0° C

and the constants

$$a = 2.092$$

 $b = 0.000866$ and
 $c = 0.000949$.

We get $\beta_1 = 1/18.1$.

We may take the mean of these results 1/17.5 as the compressibility of the vapour at 21° C.

The value of μ_1^2 is easily calculated from the data given by Dr Phillips.§ It comes out to be 1.099 and the value of

$$\beta_1(\mu_1^2-1)^2(\mu_1^2+2)^2$$
 to be 5.38×10^{-3} .

^{*}Kaye and Laby's tables.

Hence

$$\frac{\beta_1(\mu_1^2 - 1)^2(\mu_1^2 + 2)^2}{\beta(\mu^2 - 1)^2(\mu^2 + 2)^2} = \frac{5.38 \times 10^{-3}}{6.29 \times 10^{-6}} = 855.$$

Whereas the actual scattering observed by Strutt was only 102. It seems very remarkable that a law which holds good for such widely different conditions as (1) a gas at ordinary pressures, (2) in the immediate neighbourhood of the critical point and (3) for liquids, should not also hold good for saturated vapours below the critical temperature. The reason why the law apparently fails is not clear. The question is one of very great importance and its solution may be expected to throw light on the mechanism of scattering. What is urgently wanted is a careful determination of the scattering coefficient over a wide range of pressures and temperatures, from the state of vapour through the critical point to the liquid. If it is indeed found that Strutt's results are confirmed for the whole region of temperatures and pressures below the critical point, it might mean that the arrangement of the molecules in space is of far less importance in determining the phase of the scattered waves than is assumed in the treatments so far given, and that the attempt to explain the molecular scattering of light on the basis of the classical theories of electromagnetic wave-propagation and the continuous interaction between light and the electrons is really a failure. We may then be forced to adopt explanations based on a discontinuous type of action, exactly as in the theories of photoelectricity, ionization and so on.

- 47. A related question is the imperfect polarisation of the scattered light. In all the cases investigated by the authors and by Martin, the scattered light from the vapour is found to be more perfectly polarised than that from the liquid. Why this should be so is not clear. There are no observations available regarding the polarisation of the light scattered by vapours under pressure. The changes in the polarisation of the scattered light in the transition from the gaseous to the liquid state should be investigated side by side with its intensity.
- 48. The discussion given here has perhaps raised more difficulties than it has solved. But this only demonstrates the importance of the subject and the need for an extended study of the phenomena both from an experimental and a theoretical standpoint.