The Scattering of Light by Liquid Boundaries and its Relation to Surface Tension.—Part II.

By C. V. RAMAN, M.A., D.Sc., F.R.S., Palit Professor of Physics, and L. A. RAMDAS, M.A., Palit Research Scholar, University of Calcutta.

(Received May 11, 1925.)

1. Introduction.

In the first paper, a description was given of the scattering of light by metallic liquid surfaces, particularly of the manner in which the intensity and state of polarisation of the scattered rays vary with the angle of incidence of the primary rays and the direction of observation. We now proceed to consider the phenomena observed when the clean and dust-free surface of a transparent liquid is strongly illuminated. Whereas in the case of metals we have a very few substances which are liquid at ordinary temperatures, an enormous variety of transparent liquids is available for the purpose of the present study. In fact, at the time the investigation was taken up, an extensive collection of pure organic chemicals had been obtained from Kahlbaum, and bulbs containing some 64 different liquids, rendered dust-free by repeated distillation in vacuo, were ready for a programme of quantitative studies of the internal lightscattering. This collection naturally proved very convenient also for the purpose of the comparative study of the surface-scattering, and the extended observations made possible by its aid served to bring out very clearly the influence on the phenomenon of the surface tension of the liquid, and thus to establish its molecular nature.

As already remarked in the first paper, in the case of transparent fluids, the surface-scattering is accompanied by the internal-scattering within the liquid when a pencil of light is concentrated upon the surface, but the two effects are distinguishable from each other in several particulars. By using a good achromatic lens to focus a well-defined image of the sun on the boundary, the surface opalescence appears as a sharply bounded circular or elliptic disc of light, whose aspect varies very much with the direction of observation while that of the internal-scattering does not. The colour of the surface opalescence is also much less blue than that of the internal-scattering, and, indeed, by contrast with it appears nearly white. Green, yellow and red filters held in front of the eye diminish the brightness of the volume effect much more (in increasing order) than they do that of the surface effect, and hence assist greatly

Scattering of Light by Liquid Boundaries. 151

in studying or photographing the latter phenomenon. The brightness of the surface-scattering also varies with the direction of observation, while that of the internal-scattering in dust-free liquids is practically invariable. In the case of oblique incidence of the primary beam, the surface-opalescence is conspicuously brighter when viewed in directions adjacent to those of the reflected or transmitted pencils than in other directions. In fact, it then stands out very clearly, and may be distinguished even with liquids such as carbon disulphide or nitrobenzene, in which the internal-scattering is so strong that it usually overpowers the surface effect.

2. Comparative Study of the Surface-Scattering with Different Liquids.

The following is a list of the substances studied :---

Paraffins and Hydrocarbons.--Normal pentane, iso-pentane, hexane, heptane, octane, and iso-amylene.

Bromides.-Ethyl, propyl, iso-butyl, allyl and ethylene bromides.

Chlorides.—Normal propyl, iso-propyl, iso-butyl, allyl, methylene and ethylene chlorides, chloroform, carbon and silicon tetra-chlorides.

Sulphides.--Carbon disulphide, methyl and ethyl sulphides.

Fatty Acids.—Formic, acetic, propionic and butyric acids.

Oxides and Anhydrides.—Acetic and propionic anhydrides, ethyl-ether and water.

Benzene Derivatives.—Benzene, toluene, ethyl-benzene, ortho-, meta- and para-xylenes, benzyl and benzal chlorides, chlorobenzene, bromo-benzene, nitro-benzene, ortho-nitro-toluene and meta-nitro-toluene.

Alcohols.—Methyl, ethyl, normal propyl, iso-propyl, normal butyl and isobutyl alcohols, trimethyl carbinol, amyl, allyl and benzyl alcohols.

Esters.-Methyl, ethyl and propyl formates, ethyl and propyl acetates.

Aldehyde and Ketones.—Acetaldehyde, di-methyl, methyl-ethyl, di-methyl and methyl-propyl ketones.

All these liquids show the phenomenon of surface-opalescence, but in varying degrees. In the entire list of substances studied, *water*, by reason of its high surface-tension and the ease with which it acquires a surface contamination, stands in a special position; the observations made on its surface-scattering will be described separately. The results obtained with the other liquids will now be summarized.

The lighter paraffins have a low surface-tension (15 to 20 dynes/cm.) and are found to show the surface-opalescence conspicuously. Not only is the effect intrinsically bright, but it is also seen well in contrast with the internal-scattering,

C. V. Raman and L. A. Ramdas.

which is of very moderate intensity in these substances (about five times the internal-scattering in dust-free water). Ethyl bromide shows the effect moderately strongly. Some of the other bromides are liable to decomposition by the action of light and hence are not very suitable. The surface-scattering is found to be rather inconspicuous in ethylene bromide, which has a high surface tension (37 dynes/cm.), and also a large internal-scattering. All the chlorides studied show the surface-scattering conspicuously, carbon tetrachloride being specially strong. Carbon di-sulphide has an enormous internal-scattering (about 50 times that of pure water), and the surface-scattering can hardly be distinguished except for certain favourable directions of incidence and observation. Methyl and ethyl sulphides, on the other hand, show the effect quite strongly, their internal-scattering being relatively small.

The fatty acids afford a very interesting study. Formic acid has practically the same internal-scattering as acetic, propionic and butyric acids, but shows the surface-scattering much less conspicuously than those other acids. As the surface-tension of formic acid is notably higher than that of its three homologues, this furnishes a striking illustration of the relation between surfacetension and surface-opalescence. Ethyl-ether has a low surface-tension, about 15 dynes/cm., and the fact that it exhibits a strong surface-opalescence is another illustration of the general principle. The benzene derivatives all have a very strong internal-scattering, which tends to make their surface-opalescence somewhat inconspicuous. The alcohols (except benzyl alcohol) show the effect tolerably well, though not so strongly as ethyl-ether for instance. Acetaldehyde shows a conspicuous effect, while the esters show an effect of the same order of magnitude as the alcohols. The ketones are liable to decomposition, but such of them as can be obtained clear and dust-free (*e.g.*, acetone) show a conspicuous surface-scattering.

The comparative study of the effects shown by so many liquids, and the regularities and differences amongst them, afford the strongest possible demonstration of the molecular origin of the phenomenon and of its relation to surface-tension.

3. Intensity and Polarisation of the Scattered Light.

The intensity and the state of polarisation of the scattered light depends in a very interesting way upon the angle of incidence of the primary beam and the direction of observation. In order to save time and space, we shall give only a description of the phenomena noticed with a single liquid, ethyl-ether, which shows the surface-scattering strongly, and content ourselves with the general remark that other liquids show very similar effects. It is possible, of course, that further quantitative and detailed studies may reveal features depending in a special way on the nature of the liquid and not merely on its physical constants, namely the surface-tension and refractive-index, which determine the general features of the phenomenon.

(a) Light Incident Normally from Above.—When unpolarised light is incident vertically on the horizontal surface of a liquid half-filling a spherical bulb, the surface-opalescence is barely visible from above, but is much more conspicuously seen from below the surface of the liquid. In the latter case, when viewed in a nearly vertical direction, the opalescent patch is quite distinct; as the eye is moved away to one side so as to view it more obliquely, there is no marked change in its intensity until the direction of observation is inclined to the vertical at an angle equal to the critical angle $(\sin^{-1} 1/\mu)$ of the liquid, at which stage it suddenly brightens up. With further increase in the angle of observation there is a steady diminution in intensity until, for observation parallel to the liquid surface, the patch ceases to be visible.

The scattered light in nearly vertical directions is unpolarised. With the sudden increase in intensity which occurs at the critical angle, there appears also a remarkably complete polarisation of the scattered light with the electric vector parallel to the liquid surface. In more oblique directions this polarisation becomes partial.

(b) Light Incident from Above at the Polarising Angle.—When the primary beam, instead of falling normally, is incident obliquely on the liquid surface, the scattered light exhibits a notable asymmetry in its distribution of intensity, becoming much more marked in directions adjacent to the plane of incidence and lying between the transmitted and reflected rays than in others more remote. It continues, however, to be appreciably more distinct below than above the liquid surface. The light scattered *upwards* exhibits a polarisation which, for small angles of incidence, is partial, but becomes complete with the electric vector parallel to the surface, when the incidence is at the Brewsterian angle, practically for all angles of observation. The light scattered *downwards*, on the other hand, exhibits quite distinct phenomena; it shows little or no polarisation in the plane of incidence, but in a perpendicular plane shows strong polarisation with the electric vector *inclined* to the liquid surface and practically transverse to the track of the primary beam within the liquid.

(c) Light Incident from Above nearly Grazing the Surface.—In this case, again, it becomes somewhat difficult to see the opalescent area except from below the surface. The light scattered downwards into the liquid by the surface shows

polarisation effects very similar to those mentioned in the last sentence of (b) above.

(d) Light Incident from Below nearly Grazing the Surface.—In this case, of course, the beam of light is totally reflected. No surface-opalescence can be observed except in directions very close to that of total reflection; it is then found to be completely unpolarised.

(e) Light Incident from Below at the Critical Angle.—The surface-opalescence is found to be much more conspicuous than in case (d), and can, in fact, be easily seen in all azimuths from below the surface, being most intense, however, in the plane of incidence and in directions adjacent to the reflected rays. From above it is not so distinct, and is best seen in directions nearly parallel to the liquid surface in the plane of incidence. The polarisation of the scattered light is most conspicuous in a plane at right angles to the plane of incidence, and when viewed nearly parallel to the liquid surface ; the principal component of the electric vector is then nearly vertical. In the plane of incidence, and in directions intermediate between the horizontal and the reflected rays, the scattered light is unpolarised. It is, however, partially polarised (with the electric vector horizontal) in directions intermediate between the vertical and the reflected rays.

(f) Light Incident from Below at the Polarising Angle.—As the angle of incidence is gradually altered from the critical to the Brewsterian angle for internal reflection, there is at first a remarkable increase, and then an equally remarkable diminution in the brightness of the opalescence as seen from above. At the polarising angle of incidence, the scattering is brightest seen from below; the changes in its state of polarisation with the angle of observation are then extremely striking. Viewed in the plane of incidence from vertically below, it is strongly but not completely polarised; as the direction of observation approaches that of the reflected rays, the intensity increases and at the same time the polarisation improves and becomes sensibly complete. On further increasing the angle of observation the scattered light brightens up rapidly further, but the polarisation becomes less perfect, and at the critical angle it nearly disappears. For directions of observation still more nearly horizontal, the scattered light is sensibly unpolarised. Viewed at right angles to the plane of incidence, the scattered light appears partially polarised, with the principal component of the electric vector inclined to the liquid surface, and practically perpendicular to the track of the primary beam within the liquid.

(g) Light Incident from Below Normally.—The phenomena noticed in this case are practically the same as for normal incidence from above.

154

Observations have also been made in the several cases noted above with the incident light *polarised* in or at right angles to the plane of incidence. A detailed description of them seems hardly necessary, as, except for directions of observation very remote from the plane of incidence, the character of the results is such as might reasonably be inferred from those noted above for the cases in which the incident light is unpolarised. The further consideration of the effect of polarising the incident light may, therefore, be deferred for the present.

4. Measurement of the Intensity of the Surface-Opalescence.

The scattering power of transparent liquid surfaces was compared with that of white plaster of Paris by the aid of suitable apertures and a revolving sector to reduce the illumination of the latter, in much the same way as was done in the case of metallic mercury. (Paper I.) In order to avoid errors due to the superposition of the internal-scattering, a case had to be chosen in which the surface-scattering was as intense as possible. For this purpose, the case in which the light was incident on the surface from below at the critical angle, was found to be the most suitable. The opalescence was most intense when viewed nearly in the direction of the reflected rays, and was brought into the field of view for comparison with the plaster of Paris with the help of a small silvered mirror suitably held. Two sets of measurements were made; the first was with methyl alcohol, to illustrate the manner in which the intensity of the opalescence varies with the azimuth of observation, the scattered light being always observed in a direction inclined to the vertical at nearly the critical angle (Table I). In the second set of measurements, the scattering powers of different liquids were determined in terms of plaster of Paris, to illustrate the order of magnitude of the effect and its dependence on the surface-tension and the refractive index of the fluid used (Table II).

Azimuth measured from plane of incidence.	0°	10°	20°	- 3 0°	4 0°	50°	60°	75°	90°
Intensity in terms of plaster of Paris $\times 10^6$	18.8	14.1	6·3	5.6	5.1	4.1	3.5	2.1	1•4

Table I.—Methyl Alcohol, Intensity in various Azimuths.

Scattering of Light by Liquid Boundaries.

Substance.				Surface-tension in dynes/cm.	Refractive index.	Intensity as fraction of plaster of Paris.		
Methyl alcohol				23	1.328	$18\cdot8 \times 10^{-6}$		
Ethyl alcohol				22	1.360	$21\cdot3 \times 10^{-6}$		
i-Propyl alcohol				$21 \cdot 3$	1.376	$21\cdot3$ $ imes$ 10^{-6}		
n-Butyl alcohol				$24 \cdot 4$	$1 \cdot 400$	$25 \cdot 8 \times 10^{-6}$		
<i>i</i> -Butyl alcohol]	$22 \cdot 8$	1.395	$33\cdot4~ imes~10^{-6}$		
Tri-methyl-carbine	ol					$51 \cdot 2 \times 10^{-6}$		
Amyl alcohol	••••			$23 \cdot 7$	$1 \cdot 406$	$51 \cdot 2 \times 10^{-6}$		
Allyl alcohol]	$25 \cdot 9$		54.5×10^{-6}		
Benzyl alcohol]		1.536	38.0×10^{-6}		
Ethyl-ether				$15 \cdot 3$	$1 \cdot 352$	$43 \cdot 4 \times 10^{-6}$		
Pentane (normal)		•••••		15.0	$1 \cdot 359$	$39 \cdot 3 \times 10^{-5}$		

Table II.—Intensity measured with Red Light.

In Paper I the scattering power of mercury under approximately comparable conditions was given as $5 \cdot 7 \times 10^{-7}$ times that of plaster of Paris. The scattering power of methyl alcohol is thus about 33 times that of a metallic mercury surface. The surface-tension of mercury is some 547 dynes, and is thus about 23 times greater than that of methyl alcohol. Allowing for the fact that mercury reflects only about 70 per cent. of incident light, and taking into account its vastly higher surface-tension, its smaller surface-opalescence is readily understood. The greater the surface-tension, the more perfectly would the surface under thermal agitation approximate to a perfect optical plane, and the smaller would be the proportion of the incident light scattered by it in all directions.

5. Summary.

The paper describes observations and measurements made on the scattering of light by the surface of transparent liquids. Some 64 different substances were studied. The main results of the work may be stated as follows :---

(a) Surface-scattering is most conveniently observed with liquids that show a small internal-scattering; the lighter paraffins, ether, and the alcohols may be cited as examples.

(b) Other things being the same, a liquid having a higher surface-tension shows a smaller surface-opalescence and *vice versa*. Transparent liquids show an effect some 30 to 50 times more intense than that observed with metallic mercury.

(c) The variation of the intensity and state of polarisation of the scattered light with the angles of incidence and direction of observation shows some very remarkable features which are fully set out in the paper.

(d) Studies of the scattering of light by pure and contaminated surfaces of water, by liquid carbon dioxide at and near its critical temperature, and by the interfaces between different liquids under various conditions will be described in a further instalment of the work.

> The Capture and Loss of Electrons by a-Particles. By G. H. HENDERSON, Ph.D.

(Communicated by Prof. Sir E. Rutherford, F.R.S.-Received June 6, 1925.)

Introduction.

In a recent paper the writer* presented evidence of α -particles bearing a single positive charge and of α -particles which were neutral. These were found by deflecting α -particles by a magnetic field in a good vacuum and registering them photographically on Schumann plates. A band appeared on the plate deflected only half the amount of the regular α -particle band. This was ascribed to α -particles, which had captured electrons in passing through an absorbing screen and thus were singly-charged. The behaviour of these particles was described qualitatively. The proportion of singly- to doublycharged particles increased rapidly as their velocity decreased. From the effects of air in the path of the α -particles it was suggested that each particle must capture and lose electrons many times.

Sir E. Rutherford[†] has recently published the results of a very interesting quantitative study of these particles by the scintillation method. By electrostatic deflection of the beam he showed that the particles undergoing only half the normal deflection must be singly-charged α -particles and nothing else. By counting methods he found values for the mean free paths for capture and for loss of an electron by the α -particle, and found the way in which these mean free paths varied with the velocity.

The mechanism involved in the capture and loss of electrons, particularly in the former, is difficult to understand. It is a matter of considerable interest to find out how these captures and losses occur in materials of widely different kinds, whose atoms contain different numbers of electrons with different degrees

- * Henderson, 'Roy. Soc. Proc.,' A, vol. 102, p. 496 (1922).
- † Rutherford, ' Phil. Mag.,' vol. 47, p. 277 (1924).