

## The nature of the liquid state

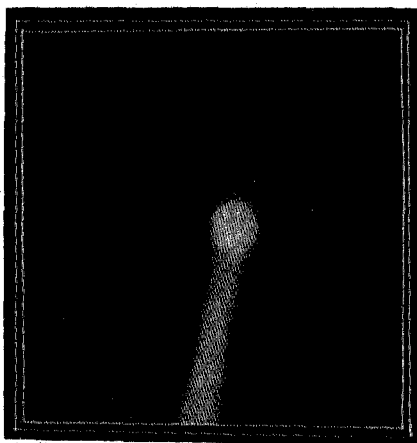
The characteristic properties of the liquid state may be grouped under various headings, the most familiar being the mechanical properties, *viz.*, the capacity to transmit hydrostatic pressure, the viscous resistance to flow and the tension exhibited by free surfaces. The elucidation of these and other physico-chemical properties of liquids in terms of their molecular structure is one of the major problems of physics to which a great deal of attention has been given. Laplace's theory of capillarity, and Van der Waal's equation of state are the classic examples of attempts to explain liquid behaviour. They are typical of the purely theoretical approaches to the subject in which hypothetical assumptions regarding the properties of molecules or the nature of the liquid state form the starting point, while the resemblance between the conclusions drawn from the theory and the experimental facts of observation is regarded as an indication of the truth of such assumptions.

That a wholly different approach to the problems of the liquid state is possible became apparent from the investigations undertaken by the present writer in 1921 in order to explain the dark blue colour of transparent oceanic waters. Observations made during sea voyages in that year suggested that this phenomenon had its origin in the molecular diffusion of light in great depths of clear water traversed by sunlight. This explanation was confirmed by laboratory observations which showed that dustfree water traversed by a beam of light exhibits a feeble blue opalescence. The intensity of this opalescence was found to be in fair accord with a formula originally developed by Einstein from the thermodynamic theory of density fluctuations to explain the enormously stronger effect observed in fluids at the critical temperature. It soon became clear, however, that Einstein's theory did not cover all the facts, and that the diffusion of light in liquids was in reality a molecular phenomenon, and that its detailed study could be expected greatly to enlarge our knowledge of the liquid state of molecular aggregation.

As is well known, a substance may exist in different physical states, e.g., a gas or a vapour, a liquid, an amorphous glass or a crystalline solid. One of the most important questions regarding the liquid state is that of its relation to the other possible states of molecular aggregation. The comparative study of the molecular diffusion of light in the different physical states of a substance is very helpful in enabling the nature of the differences between these states to be understood. The most readily observed changes are those of the *intensity* of the diffused light. This is a maximum in the gaseous state when considered in relation to its density, and a

minimum in the crystalline condition, while the liquid and the amorphous solid usually occupy the intermediate positions in the order stated. The scattering of light, though fairly intense and therefore easily observed in liquids, is usually much feebler than the scattering in the vapour if the far greater density of the liquid is taken into consideration. These facts stand explained when it is recalled that the molecules in a vapour are distributed in space at random and in a crystal with geometric regularity, while they indicate that the space-grouping in the liquid and in the amorphous solid is very far from being chaotic, though it does not possess the complete regularity characteristic of crystals. If we accept the thermodynamic theory of Einstein, the compressibility of the substance is, in each case, a measure of the spatial uniformity of distribution. The smaller the compressibility, the more nearly perfect would be the uniformity of the space-distribution of the molecules, and the more completely, therefore, would the secondary radiations from the molecules cancel each other out by interference.

We have next to consider the orientations of the molecules in a liquid. In the crystal, as we know, these orientations form a geometrically regular pattern and taken together with the optical anisotropy of the molecules determine the optical birefringence of the crystal. Since liquids are optically isotropic, it follows that there can be no regularity of molecular orientation when averaged over any volume of macroscopic dimensions. We are justified, however, in asking whether there is any tendency for neighbouring molecules to align themselves similarly or to form groups in which near neighbours stand in some definite relationship. Comparative studies of the intensity and the state of polarisation of the light scattered transversely in vapours and in the corresponding liquids furnish valuable evidence on this point. The optical anisotropy of the molecules in a fluid



**Figure 1.** Volume and surface scattering of light in liquid methyl alcohol (Photograph by P S Hariharan).

or amorphous solid gives rise to an "orientation" scattering which is depolarised to the extent of  $6/7$ , and is therefore readily distinguished from the fully polarised "density" scattering associated with the isotropic part of the polarisability of the molecules. It is readily shown that if groups of neighbouring molecules in a liquid were similarly orientated, the orientation scattering would be enormously enhanced in its intensity as compared with its intensity for a state of completely random orientation. Actually, we find that the depolarisation exhibited by the light diffused within a liquid is usually much more striking than the depolarisation of the light scattered by the vapour. This cannot, however, be regarded as indicating that the orientation scattering is larger in the liquid than in the vapour when considered in relation to the density. Indeed, in most cases, the reverse is true; the larger depolarisation of the total scattering in liquids is due to the fact that the reduction of the intensity per molecule of depolarised orientation scattering is not so great as that of the polarised density scattering in passing from vapour to liquid.

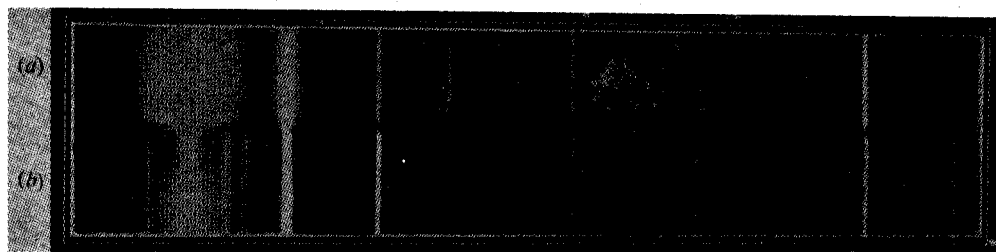


Figure 2. Spectrum of light scattered in (a) molten and (b) solid naphthalene (Photograph by R Norris).

Thus, the phenomena of light scattering give no support to the idea often expressed that liquids have a micro-crystalline structure. Neither is such a supposition true for the amorphous solid state. On the other hand, there is good reason for the belief that the liquid and the amorphous solid states stand in the closest relation to each other. The well-known fact that liquids may sometimes be super-cooled without crystallisation occurring and made to pass over into the glassy condition is a *prima facie* indication of that such a relationship exists.

The study of light scattering enables us to obtain a much deeper insight into the nature of the liquid and solid states of aggregation when, as was done by the present writer early in 1928, the monochromatic radiations of the mercury arc lamp are employed and the aid of the spectroscopist is enlisted for such studies. The changes of frequency then observed in the scattered radiations are of two different kinds in the case of liquids. Firstly, we have new lines appearing in the spectrum with fairly large and discrete frequency shifts; secondly, a continuous spectrum of radiations with altered frequency is also noticed. The latter effect is most

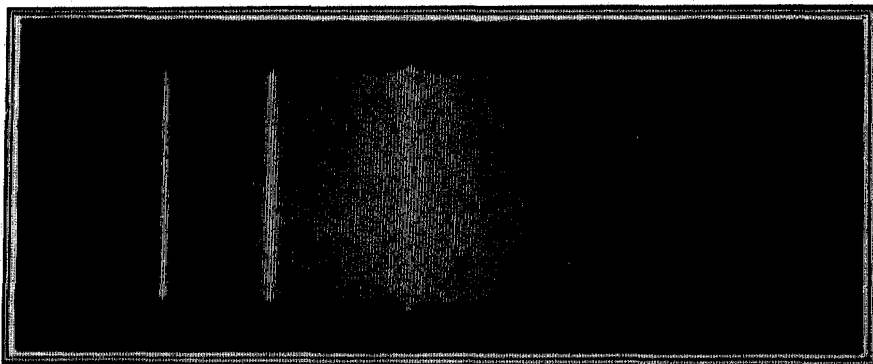


Figure 3. Rotation "wings" in the spectrum of light scattered in benzene liquid (Photograph by C S Venkateswaran).

conspicuous in the vicinity of the original lines of the mercury arc, taking the form of "wings" stretching out in the spectrum somewhat unsymmetrically on either side of these lines. To describe this phenomenon as a broadening of the spectral lines, as has been done by some writers, would be incorrect. Figure 3 represents the group of four lines in the vicinity of 4358 A.U. in the light of the mercury arc scattered by benzene liquid and photographed with a Hilger 3-meter spectrograph. It is seen that the "wing" has its maximum intensity at the wave-length of the incident radiations; its presence, however, does not influence the spectral width of these radiations. As is evident from the figure, these radiations when not overexposed continue to be seen as lines of extreme sharpness in the spectra.

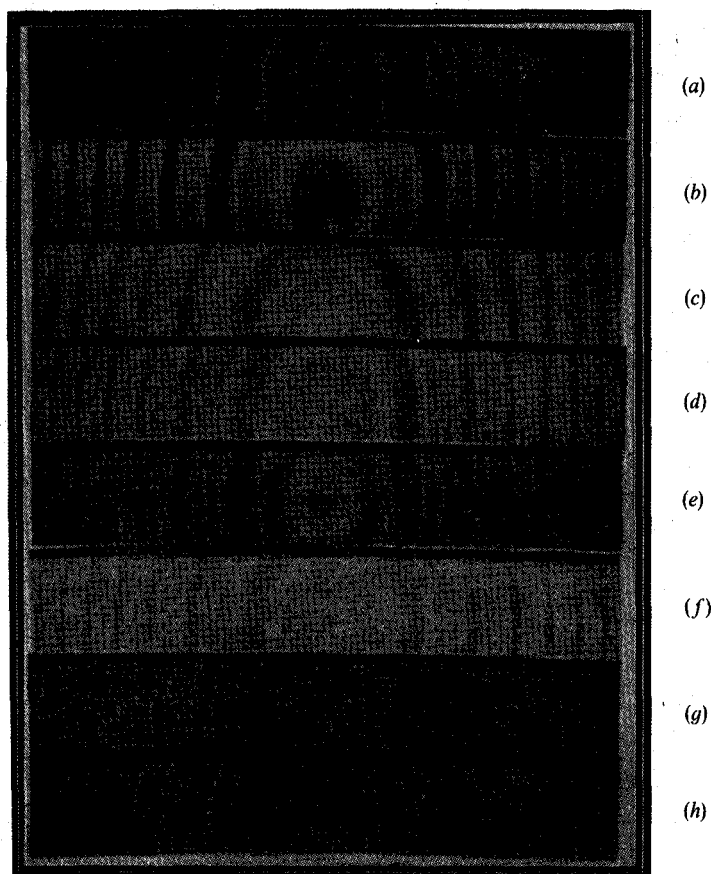
The origin of these "wings" has been the subject of much discussion. The experimental evidence which has accumulated, however, clearly supports the explanation of the same suggested in 1928 by the present writer and K S Krishnan. In the first place, the wings are fully depolarised to the extent of  $6/7$  in all the cases so far studied. Secondly, they appear in the same region of moderately small frequency shifts as that in which the rotation of the molecules in compressed gases and vapours and in liquid hydrogen records itself in light scattering. Thirdly, the "wings" are most intense in liquids containing ions or molecules which have a high degree of optical anisotropy, *e.g.*, fused inorganic nitrates and aromatic compounds. Fourthly, when the substance is in the crystalline state, the wing disappears, and is replaced by discrete lines exhibiting a wholly different distribution of intensity (see figure 2). Fifthly, when the liquid is cooled down into the amorphous solid state, the wings become very weak and practically disappear. These observations clearly indicate that the "wings" are principally in the nature of "orientation" scattering and arise from the rotation of the molecules or molecular groups within the liquid. Here, again, the facts give no support whatever to the hypothesis of a micro-crystalline structure for liquids.

We now proceed to consider the character and origin of the scattered

radiations which are recorded by the spectroscope in the same position as the radiations of the mercury arc. As stated above, the "wings" accompanying these lines represent depolarised orientation scattering. The question naturally arises, do the undisplaced lines consist only of polarised density scattering or do they include also any depolarised orientation scattering? This question is obviously of great importance and has been exhaustively investigated at Bangalore by Mr B D Saxena and more recently also by Mrs K Sunanda Bai. These authors used a Littrow prismatic spectrograph by Hilger with a high resolving power to analyse the transversely scattered radiations and determine their state of polarisation. With the spectrograph slit opened very wide, the depolarisation of the total scattering by the liquid could be determined and came out practically the same as that observed without spectroscopic analysis. The slit was then made very fine to give the full resolving power of the instrument, and thus enable the depolarisation of the "undisplaced" scattering to be measured. It was found that in every case this was partially polarised and that the difference between the "wide slit" and "narrow slit" values of the depolarisation ratio depended greatly on the viscosity of the liquid and its temperature. The difference was found to be quite small for highly viscous liquids, *e.g.*, formic acid, benzophenone and glycerine, and much more marked in mobile liquids as also in viscous liquids at high temperatures. It was clear from the observations that the "undisplaced" scattering included a notable amount of depolarised orientation scattering, the proportion of this to the polarised scattering increasing with the viscosity of the liquid as well as with the optical anisotropy of the molecules contained in it.

In order to further elucidate the nature and origin of the "undisplaced" radiations observed in light scattering, C S Venkateswaran and more recently also K Sunanda Bai have carried out elaborate studies, using a Fabry-Perot etalon for a spectral analysis of these radiations and a Lummer-Gehrcke plate to determine their state of polarisation. Investigations of this kind are not easy, and only by a careful choice of suitable interferometers and of the light sources and the most exacting care in experimental technique is it possible to obtain reliable results. It is not surprising, therefore, that these new investigations fall to confirm many of the conclusions stated by earlier workers in this field and in fact throw a completely new light on the subject.

A few remarks may appropriately be made here regarding the thermodynamic theory of light-scattering. Einstein considered the density fluctuations to be static and isothermal, while in the theory of Brillouin they are considered as dynamic stratifications or sound-waves and therefore presumably adiabatic in character. The assumption that the fluctuations of refractive index arising from the density fluctuations are connected with them by the well-known Lorentz formula is neither necessary nor justifiable. The adiabatic piezo-optic coefficient of several common liquids has been recently determined at Bangalore by the present writer and K Venkataraman. Using these coefficients and assuming the density fluctuations to be adiabatic in character, Sunanda Bai has recalculated the



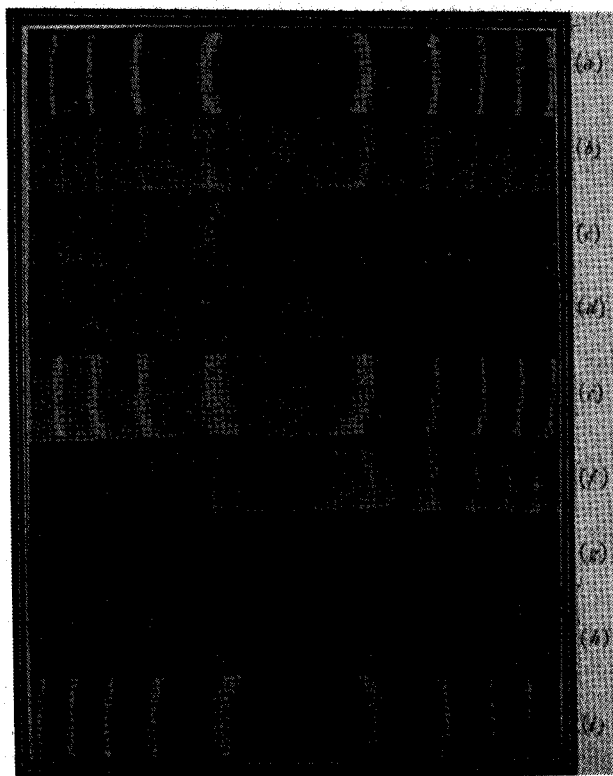
**Figure 4.** Fabry-Perot patterns of light scattering in the alcohols (4678 A.U. Hg arc) (a) methyl, (b) ethyl, (c) *n*-propyl, (d) *iso* propyl, (e) *n*-butyl, (f) *iso*-butyl, (g) *iso*-amyl, (h) allyl alcohol (Photographs by K Sunanda Bai).

intensity of light scattering given by the thermodynamic theory and compared it with her own observations. When the presence of the depolarised orientation scattering is taken into account, the observed intensities are found to support the adiabatic hypothesis rather than the isothermal one.

It must not, however, be concluded from this approximate agreement of the observed and calculated total intensities that the thermodynamic theory of light-scattering is either correct or complete. The Fabry-Perot patterns of mobile liquids obtained by Venkateswaran exhibit a continuous band overlying the central or undisplaced component and the outer or Doppler-shifted components indicated by the Brillouin theory and suggest that these are imperfectly resolved.

In less mobile liquids, the components are more clearly separated. A central component is observed in all cases and is found to exhibit a clearly noticeable defect of polarisation, while the outer components appear to be polarised, though whether such polarisation is complete is open to doubt. The relative intensities of the central and outer components appear to be controlled by two distinct factors, one being the viscosity of the liquid and the other the optical anisotropy of the molecules. The more viscous the liquid, the stronger the central component relatively to the outer ones. A greater optical anisotropy of the molecules appears to have a similar effect.

The outer or Brillouin components clearly owe their origin to the thermal agitation of the liquid. How does the central component arise? The most natural supposition is that it is due to the fundamental structure of the liquid which is akin to that of a glass or amorphous solid. This hypothesis is supported by the observation that its intensity relatively to the outer components increases with



**Figure 5.** Fabry-Perot patterns of highly viscous liquids (a) Glycerine ( $0^{\circ}\text{C}$ ), (b) Glycerine ( $26^{\circ}\text{C}$ ), (c) Glycerine ( $42^{\circ}\text{C}$ ), (d) Glycerine ( $110^{\circ}\text{C}$ ), (e) Castor oil, (f) Cyclohexanol, (g) Glycol, (h) Phenol, (i) Styrol glass (Photographs by C S Venkateswaran).

the viscosity of the liquid, in other words, with the approach of the fluid to the amorphous solid state. Since the molecules would occupy fixed but random orientations in the amorphous solid, the presence of both polarised and depolarised components in the light diffused by it without any change of frequency is readily understood.

Further striking confirmation of these ideas is furnished by Venkateswaran's measurements of the hypersonic velocities in viscous liquids from the spectral displacements in the Fabry-Perot patterns. For ordinary or mobile liquids, the hypersonic velocity comes out practically the same as the ordinary ultrasonic velocity observed at much lower frequencies. But in the highly viscous liquids glycerine and castor oil, there is a marked difference between the two velocities and it is noticed that this difference falls off with rising temperature. A very satisfactory explanation of these facts is furnished by the consideration that for sufficiently high frequencies of vibration, a viscous liquid may to all intents and purposes be regarded as an amorphous solid, and the hypersonic velocity should therefore depend both on its compressibility and the rigidity coefficient.

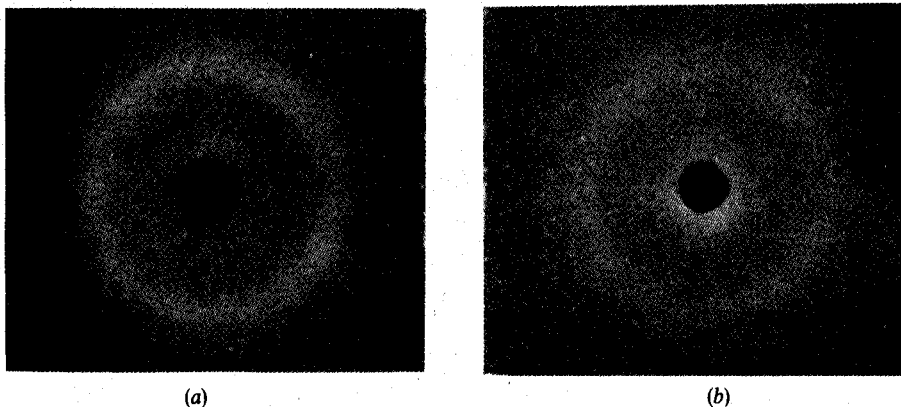


Figure 6. X-ray halo of glycerine, (a) glass and (b) liquid (Photographs by T M K Nedungadi).

The experimental facts of light-scattering may thus be summarised in the statement that the basic structure of a liquid is the same as that of the corresponding amorphous solid, though disturbed and enlarged by thermal agitation. Precisely the same conclusion is indicated by the study of the X-ray diffraction haloes (see figure 6) in liquid and glass. Indeed, the fundamental relationship between the phenomena of light-scattering and the X-ray effects was pointed out as long ago as 1923 in a paper by the present writer with K R Ramanathan. It is the same orderliness of molecular spacing which explains the diminished light-scattering which is also responsible for the diminished intensity of diffraction at small angles as compared with the vapour which is the most characteristic feature of the X-ray haloes of both liquids and amorphous solids.