

The nature of the liquid state

In his recent lecture to the Chemical Society on "The Significance of Crystal Structure," Sir William Bragg has described and discussed the extremely important results obtained in his laboratory by the X-ray analysis of various carbon compounds, notably those belonging to the aromatic series. The special feature brought to light by the investigations is that the ultimate unit of crystal structure or elementary parallelepiped is not the chemical molecule, but, generally speaking, is a complex formed by the union of two, three or four molecules. Further, the symmetry of the crystal tends to increase with the number of molecules in the unit and also with the symmetry of the molecule itself. In fact, there are simple quantitative rules, first stated by Shearer, connecting these quantities.

The question naturally arises whether when a crystal is melted and passes into the liquid state, the units in the latter condition are the same as in the crystal, or whether these break up further into the individual molecules. A method of investigating this very fundamental point is furnished by studies on the molecular scattering of light. If the units in the liquid state are the chemical molecules, that is, the same as in the condition of vapour, there should be a simple quantitative relation between the amount of *unpolarised light* (due to optical anisotropy) scattered by equal volumes of liquid and vapour and the densities in the two states of aggregation. This relation was indicated in my letter in *Nature* of July 1, 1922, but the method of calculation there given has to be amended to make allowance for the fact that the electric polarisation within a fluid is, according to the Lorentz-Mosotti formula, greater than in free space. When this correction is made, it is found that the amount of *unpolarised light* actually scattered is considerably smaller than that indicated by the calculation. The conclusion thus appears to be forced upon us that the ultimate unit in the liquid state is not the same as in the state of vapour. On the other hand, if we adopt the view that the ultimate unit is the same in the liquid state as in the crystalline state, a way is opened for a satisfactory explanation of the observed result. For, according to Shearer's rule, the symmetry of the unit is always greater than that of the molecule, and hence the amount of unpolarised light scattered by it should be diminished, as is actually observed.

A further consideration which suggests that the ultimate unit in the liquid state is the same as in the crystalline solid is the existence of those remarkable substances, known as liquid crystals, studied by Lehmann and others. If a liquid be conceived of as a collection of elementary crystal parallelepipeds which are

ordinarily prevented from thermal agitation from forming regular arrays, it is easier to understand how in favourable circumstances, such arrays come into existence temporarily and as quickly disappear. This conception appears to fit in very well with the mathematical framework of the kinetic theory of liquid crystals recently developed by Oseen (Stockholm Academy, Handlingar, 1921).

The same conception also appears to furnish a satisfactory explanation of the tendency shown by many liquids to refuse crystallisation and to pass into a highly viscous or glassy condition when supercooled. We have only to suppose that the units gradually join up, but in an irregular way, and form an optically heterogeneous structure. This conception of the constitution of vitreous solids is supported by the results of an extensive series of observations on the scattering of light in optical glasses and in supercooled organic liquids carried out under the writer's direction.

Finally, it may be remarked that the conception suggested does not, so far as the writer can see, appear to be inconsistent with any other known facts regarding the physical properties of liquids.

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