

The Liquid State, Part 1—General Theory

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This is the first of a series of publications that will describe an entirely new theory of the liquid state of matter: a theory which not only provides a full qualitative explanation of the physical properties of liquids but also furnishes the means whereby accurate numerical values of these properties applicable to different liquids can be calculated from the chemical composition, temperature, and pressure. The new theory is the result of an extension and elaboration of the consequences of two new postulates as to the nature of space and time which were formulated and discussed by the author in a recently published work.¹ As explained in that publication, it follows directly from the fundamental postulates that there exists a progression of space-time (of which the observed progression of time is merely one aspect) such that each location in space-time moves outward at a constant velocity from all other locations. It also follows from the postulates that the atoms of matter are rotating systems (the exact nature of which is immaterial for present purposes) and that this rotation is greater in magnitude than the space-time progression, and opposite in direction. Because of this directional requirement the atomic rotation is translationally effective; that is, a rolling motion. By virtue of the same motion which gives them their atomic status, therefore, the atoms of matter are reversing the pattern of free space-time and are moving inward toward each other: a phenomenon which we call gravitation.

In the absence of any other type of motion gravitation will cause the atoms to approach each other until they are separated by only one unit of space, beyond which point the characteristics of both the gravitational motion and the space-time progression undergo some changes which are discussed at length in the work previously published. If thermal motion is introduced into the system it acts in the outward direction and adds to the motion of the space-time progression. At some particular value of this thermal motion (that is, at some particular limiting temperature) the sum of the outward motions may exceed the gravitational motion in one dimension and at some higher temperature it may exceed the gravitational motion in all three dimensions simultaneously. When the direction of the net resultant motion is thus reversed either in one dimension or in all dimensions the characteristics of the motion, are substantially modified and the corresponding properties of the substance are altered to such a degree that we regard the substance as being in a different physical state. We will identify the condition below the lower temperature limit as the *solid* state and the condition above the upper limit as the *gaseous* state.

Between these two temperature limits, which we identify as the melting point and the critical temperature respectively, there are two possibilities. An extension of the gaseous structure into the intermediate zone results in the *vapor* state, whereas an extension of the solid structure into this zone produces the *liquid* state: the subject of the present discussion. As can be seen from this description the relation between the liquid and vapor states is quite different from the solid-liquid and liquid-gas relationships. So far as the latter are concerned, the physical state of a molecule is uniquely determined by its temperature, but in the intermediate zone the choice between the two possible states is purely a matter of relative probability.

It should be recognized that on the foregoing basis physical state is essentially a property of the individual molecule and not a “state of aggregation” as commonly assumed. In a complex substance the cohesive forces between the atoms—the atomic bonds, as they are usually called—are stronger for

¹ Larson D.B., *The Structure of the Physical Universe*, North Pacific Pub., Portland, Oregon, U.S.A., 1959

same combinations than others, but as soon as the weakest bond is broken the molecule enters the new state and acquires all of the properties appertaining thereto. The properties of an aggregate are determined by the state or states of its constituent molecules.

If all of the molecules of a liquid were at the same temperature (that is, if they all possessed the same amount of thermal energy) this distinction between the state of the molecule and that of the aggregate would have no particular significance in application to homogeneous liquids, but because of the distribution of molecular velocities due to the operation of the probability principles the temperatures of the individual molecules are distributed through a range of values of which the temperature of the aggregate is merely the average. A liquid in the vicinity of the melting point therefore contains a certain proportion of molecules with individual temperatures below the melting point and on the basis of the concept of physical state developed herein, these molecules are in the solid state. Similarly the solid aggregate just below the melting point contains a certain proportion of molecules which are individually at temperatures above the melting point and which are therefore in the liquid state.

Where a continuous property is involved the characteristics of a mixed solid and liquid aggregate are intermediate between those of a pure solid and those of a pure liquid. In the case of a discontinuous property such as the transition between physical states, the condition of the aggregate is basically determined by the condition of the majority of its constituent molecules. For the transition from solid to liquid nothing is required other than the necessary proportion of liquid molecules and the change of state therefore takes place automatically as soon as the melting temperature is reached. For this reason it is impossible to heat a solid above the melting point corresponding to the prevailing conditions. The reverse transition from liquid to solid is not automatic. Formation of a crystal lattice requires not only the presence of the required proportion of solid molecules but also the establishment of contact between these molecules and maintenance of this contact against the disruptive thermal forces for a long enough period to permit attachment of additional molecules and the formation of stable crystal nuclei. Under suitable conditions this process may be hindered to a considerable degree and with appropriate precautions liquids can be subcooled to temperatures well below the freezing points normally applicable.

The ability of a liquid aggregate to incorporate solid or gaseous molecules into its structure is not confined to molecules of the same chemical composition. If the non-liquid molecules are of a different kind the aggregate is a *solution*. Such a solution is structurally identical with a liquid which contains solid or gas molecules of its own composition but the different physical properties of the solute introduce some additional variability. Where the solute has a high melting point, for example, the solid-liquid solution may persist through most or all of the liquid temperature range of the aggregate. An interesting point in this connection is that the properties of solutions furnish a positive verification of the existence of distinct solid and liquid molecules in the liquid aggregate. It has long been recognized that these properties are quite sensitive to the melting point of the solute; that is, the properties of a liquid-liquid solution often differ materially from those of the corresponding solid-liquid solution. Some of the less soluble substances, particularly, show a very marked change at the solute melting point, separating into the two-layer structures characteristic of many of the liquid-liquid solutions.² In preparing a liquid-liquid solution of this kind it makes no difference whether we put the solid into the liquid and then raise the temperature of the solution beyond the solute melting point or whether we liquefy the solid independently and add the liquid solute to the solvent. In either case there is a very decided change in properties at a specific temperature and in both processes this is the same

² For a discussion of this point see Hildebrand and Scott, *The Solubility of Non-Electrolytes*, 3rd Edn., Reinhold, New York, 1950.

temperature: the solute melting point. The logical conclusion is that the solute is in the solid state below its melting point regardless of its environment and it makes the transition to the liquid state at its normal melting temperature in solution as well as out of solution.

The significance of these points in relation to the present subject lies in the fact that the solute is known to exist in units of molecular or ionic size. If the solute is in the solid state below its melting temperature and in the liquid state above this point, this means that it exists in the form of *solid molecules* (or ions, which will be included in the term “molecules” in this discussion of solutions) and *liquid molecules* respectively. Obviously the existence of distinct solid and liquid molecules under *any* conditions precludes the possibility that the liquid and solid states are “states of aggregation” and establishes the fact that physical state is essentially a property of the individual molecule, as required by the principles developed in this work.

Each increment of thermal energy added to a molecule alters the behavior of the molecule to some extent; that is, it modifies the physical properties. Normally the incremental change is minor and a matter only of degree, but at the points where the unit levels are exceeded as previously described some properties undergo drastic modification and it is this transition to a new general type of behavior which we recognize as a change of state. The most distinctive feature of the solid state is that in this state the average positions of the molecules under any specific set of conditions maintain a constant relationship. In the crystalline form of the solid state the centers of thermal motion are fixed and maintain the same relative positions indefinitely. In the glassy or vitreous form the instantaneous positions of the centers of motion are variable but the average positions of these centers over any appreciable period of time are fixed.³ A solid aggregate of either kind therefore has a definite size and shape.

When the melting point is reached and the thermal motion becomes free in one dimension (that is, the inward-directed force is no longer able to reverse the direction of motion in this dimension), the fixed molecular positions are eliminated. Each molecule must still maintain the solid-state relationships in two dimensions but it has complete freedom in the third dimension, and since there is no requirement that this always has to be the same dimension any liquid molecule has the ability to move about at random through the aggregate. A liquid thus has no permanent shape and is able to accommodate itself to any external forces which may be impressed upon it. In practice this normally means that it assumes the shape of the container.

The distinctive properties of liquids arise from this dual character of the dimensional relations. The property of *fluidity* and its reciprocal, *viscosity*, are obviously direct results of the freedom of motion in one dimension and the fluidity increases in magnitude as the temperature rises, since the energy in the free dimension then constitutes a larger proportion of the total thermal energy. *Surface tension*, on the other hand, is due to the solid-state forces exerted in the dimensions in which the outward forces are below the unit level and it decreases in magnitude as the temperature rises. *Vapor pressure*, another characteristic liquid property, is a result of the distribution of molecular velocities which brings a certain proportion of the liquid molecules up to the critical temperature and causes them to enter the gaseous state even though the average temperature of the aggregate is still within the liquid range. These properties, together with the liquid aspects of the more general physical properties such as density, specific heat, etc., will be covered in detail in the subsequent papers in this series.

In some instances the theoretical development in these papers is complete and specific numerical values are obtained directly from theory. In other cases the theory in its present state leads to several possible values rather than to one unique result and for the present the selection from among these

³ Larson D.B., *The Structure of the Physical Universe*, op. cit., p. 40

possibilities is dependent on a study of series relationships or some similar expedient. It should be pointed out, however, that no arbitrary numerical constants are introduced anywhere in this development. Aside from the conversion constants required for expressing the results in conventional systems of units, all numerical constants which enter into the relationships are structural constants: integral or half-integral values which represent the actual numbers of the various types of physical units entering into the particular phenomenon under consideration.

No satisfactory theoretical system for the calculation of the numerical values of these liquid properties has ever been developed heretofore, although a vast amount of effort has been devoted to the task. Many ingenious and useful mathematical expressions have been developed to facilitate interpolation and extrapolation of the experimental data but in most cases it has been impossible to attach any theoretical significance to these expressions. As one observer puts it, referring specifically to the property of volume, "The quantitative representation of the volumetric behavior of fluids over both gas and liquid regions has proven to be an unusually difficult problem."⁴ The nature of the obstacle which has stood in the way of a solution to this problem is revealed by the discussion in the foregoing paragraphs.

It has been taken for granted that a liquid is a complex structure requiring complex mathematical expressions for accurate representation of its properties. According to the theory developed herein this concept is erroneous; the liquid aggregate is *not* a complex structure but a composite in which relatively simple structures coexist in definite proportions. This theory eliminates the need for any complex mathematical treatment and the subsequent papers in this series will show that in each case accurate results can be obtained by very simple mathematics.

4 Pitzer K,S., *J. American Chemical Soc.*, 77-3427