

## Association Theory. The Discontinuous Case and the Structure of Liquids and Solids

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The assumption of the continuous case of association which is that all species of particles are always present is discussed. It is shown that a more appropriate model of the liquid or solid is given by the discontinuous case which postulates that certain smaller species are completely absent. A discussion of the nature and cause of the gas-liquid transition is given. This transition coincides with the change from a treatment by the continuous case to the discontinuous case. Various modifications of the mathematical treatment are derived and discussed.

In previous work<sup>1,2</sup> a theory of association of matter was presented which led to an equation of state<sup>3</sup> and finally to a derivation of Tait's equation.<sup>4</sup> This theory was applied both to liquids<sup>5</sup> and solids<sup>6</sup> and showed success in enabling us to calculate the atomic radii<sup>7</sup> of the five alkali metals from a knowledge of their compressibility data and their crystal form. However, a further detailed examination of the equations in this theory showed that there were some difficulties both conceptually and mathematically. Among other things, the number of 1-mers in liquids and solids under high pressure calculated by this theory were found to be too great. Careful analysis of the equations traced the difficulties to one assumption in the original derivation; this is the assumption that all species from 1-mer to  $m$ -mers were always present. If in these derived equations the concentration of any species became zero, then the mathematical equations broke down giving a singular case. This paper then is devoted to an examination of this assumption and to the consequences of removing its restrictions.

*The Assumption of Continuous Distribution.* The origin of this assumption probably lies in the kinetic derivation of the distribution equations, which assumes that we start with a hypothetical matrix of single atoms and from this build an associated substance. This is equivalent to assuming that we start a mass of matter at

infinite volume where there are no collisions and suddenly compress it to some arbitrary volume where the molecules start colliding and associating. This is an unnecessary concept, although a convenient one, since the same equations can be obtained by considering the equilibrium situation.<sup>8</sup> The concept of this assumption was reinforced by the thought experiment<sup>1</sup> in which the individual frames of a hypothetical motion picture of a gas were examined one by one. In such examination, 1-mers, 2-mers, 3-mers, etc., were seen. From a dynamic point of view the 2-mers were static representations of binary collisions, the 3-mers, ternary collisions, etc. This picture is the one presented by the kinetic-molecular theory and is undoubtedly true of a gas. The extrapolation to liquids and solids came with

(1) For a review article see: R. Ginell, p 41-48, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," S. Gratch, Ed., American Society of Mechanical Engineers, New York, N. Y., 1965.

(2) R. Ginell, *Ann. N. Y. Acad. Sci.*, **60**, 521 (1955).

(3) R. Ginell, *J. Chem. Phys.*, **23**, 2395 (1955).

(4) R. Ginell, *ibid.*, **34**, 1249 (1961); **34**, 2174 (1961); **35**, 1135 (1961).

(5) R. Ginell, *ibid.*, **35**, 473 (1961).

(6) R. Ginell and T. J. Quigley, *J. Phys. Chem. Solids*, **26**, 1157 (1965).

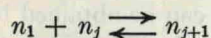
(7) R. Ginell and T. J. Quigley, *ibid.*, **27**, 1173 (1966).

(8) R. Ginell and J. Shurgan, *J. Chem. Phys.*, **23**, 964 (1955).



the derivation of Tait's law, and the successes and troubles started at this point.

*The Liquid and Solid State.* The correct approach is to extrapolate our thought experiment from the gas case described above to the liquid and solid cases. One must therefore look for an acceptable picture of a liquid and a solid. The subject of the nature of the liquid and solid state has been the subject of many papers and reviews, and an introduction to the current views can be found in a general text like Moelwyn-Hughes or Hirschfelder, *et al.*,<sup>9</sup> and need not be detailed here. However, the association approach to liquids and solids is not widely known. Part of this problem has been considered<sup>10,11a</sup> in connection with a discussion of close-packing in  $j$ -mers of large size, and the suggestion has been made that the essential difference between liquids and solids is one of symmetry. From this work it appears that higher  $j$ -mers that are packed in 4- or 6-symmetry give rise to particles of regular form which are recognizable as prototypes of crystals, while on the other hand higher  $j$ -mers that are packed in approximate 5-symmetry form particles of irregular shape, full of voids that seem to correspond to our current views of the structure of liquids. This work showed, moreover, that particles in 5-symmetry had more bonds and hence are more stable, at least in the smaller sizes, than particles in 6-symmetry. This symmetry difference leads to an explanation of the mechanism of nucleation. From our present work it seems that we must consider a liquid to consist of an array of such 5-symmetry particles separated by defects, all in equilibrium. The equilibrium is due to 1-mers breaking off one particle ( $j$ -mer), crossing the defect volume and joining another  $j$ -mer. The equation would be



The number of such 1-mers in the liquid is very small, the main bulk consisting of 5-symmetry  $j$ -mers. The equilibrium mechanism postulated here is very similar to the mechanism for the growth of crystals after heterogeneous nucleation.<sup>11b</sup>

If one lowers the pressure on the liquid, one ultimately reaches the vapor pressure of the liquid. This is the pressure which these 1-mers exert in the liquid at this temperature. In solids, the process is the same except that the particles are now in 4- or 6-symmetry. Thus the liquid and solid both consist of large particles in 5- or 6- (or 4-) symmetry, respectively, in equilibrium with 1-mers. The question of whether 2-mers exist in the liquid depends in part on the abundance of 1-mers. The quantity of 3-mers is still smaller and there undoubtedly is a gap between these small particles and the large  $j$ -mers which form the bulk of the liquid or solid. In many ways this concept resembles Eyring's significant structures theory.<sup>12</sup> This theory postulates that liquids are composed of a mixture of gas-like particles and solid-like particles. This is equiv-

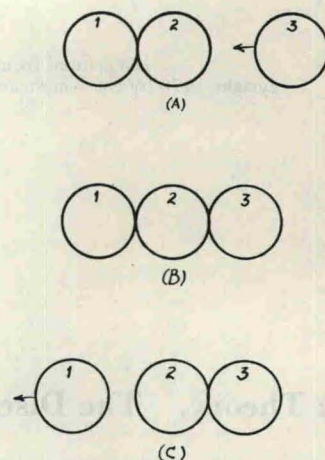


Figure 1. Straight line collision. The transfer of kinetic momentum is complete: (A) approach (origin of coordinates is on the 2-mer); (B) collision (the shapes of the molecules are distorted from spherical symmetry during the collision although this is not shown. During the lifetime of the 3-mer, the energy of the collision is stored as potential energy of distortion); (C) departure (molecule at opposite end departs taking all the kinetic energy. This is only true for a strictly straight line molecule).

alent to our 1-mers and  $j$ -mers. The difference in the theories is that we specify that the  $j$ -mers are 5-symmetric in liquids and 6- (or 4-) symmetric in solids, while Eyring's theory considers the solid-like particles to have the properties of solids and contains some arbitrary parameters. Our theory enables one to explain nucleation and the conversion of liquids to solids. This is impossible in Eyring's theory.

*Liquid-Gas Transition.* The concept of a discontinuous distribution raises several questions. The first: how and why does this distribution arise, and why is it more applicable to liquids and solids. Qualitatively this can be approached by a picture of this sort which turns out to give us a clearer understanding of the nature of the gas-liquid transition.<sup>13</sup> Let us imagine that we have a gas at some elevated temperature. The particles present will probably be linear forms of the 1-mer, 2-mer, 3-mer, 4-mer, and perhaps 5-mer. (Occasionally a linear form of a higher  $j$ -mer may form.) The lifetime of such particles is very short. Let us reduce the temperature of the gas. The effect would be to decrease the energy and hence the velocity and momen-

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(10) R. Ginell, *J. Chem. Phys.*, **34**, 992 (1961).

(11) (a) J. D. Bernal, *Nature*, **185**, 68 (1960); *Sci. Amer.*, **203**, 124 (1960); (b) S. E. Brown and R. Ginell, pp 109-118, "Symp. Nucleation and Crystallization in Glasses and Melts," M. K. Reser, C. Smith, and C. H. Insley, Ed., American Ceramic Society 1962.

(12) H. Eyring, T. Ree, and N. Hirai, *Proc. Natl. Acad. Sci. U. S.*, **44**, 683 (1958), and subsequent papers.

(13) R. Ginell, Proceeding of the 1st International Conference on Thermodynamics and Calorimetry, Sept 1-5, 1969, Warsaw, Poland, in press.