

continuously from the gas to the liquid. In particular, Equation 2a no longer holds and we must redefine certain quantities. In the liquid we make the following definitions:

$$\begin{aligned} C_1 &= C_1 \\ C_x &= 0; 2 \leq x < \alpha \\ &= C_x; \alpha \leq x \leq m \\ &= 0; m < x \end{aligned} \quad (7)$$

hence m is the largest species. Further

$$\begin{aligned} K_{1,x} &= \frac{C_{x+1}}{C_1 C_x}; x \geq \alpha \\ K_1 &= 1 \\ K_x &= 0; 2 \leq x < \alpha \\ K_\alpha &= \frac{C_\alpha}{C_1^\alpha}; \alpha > 2 \\ K_x &= K_\alpha \prod_{y=\alpha}^{x-1} K_{1,y}; \alpha < x \leq m \\ K_x &= 0; x > m \end{aligned} \quad (7b)$$

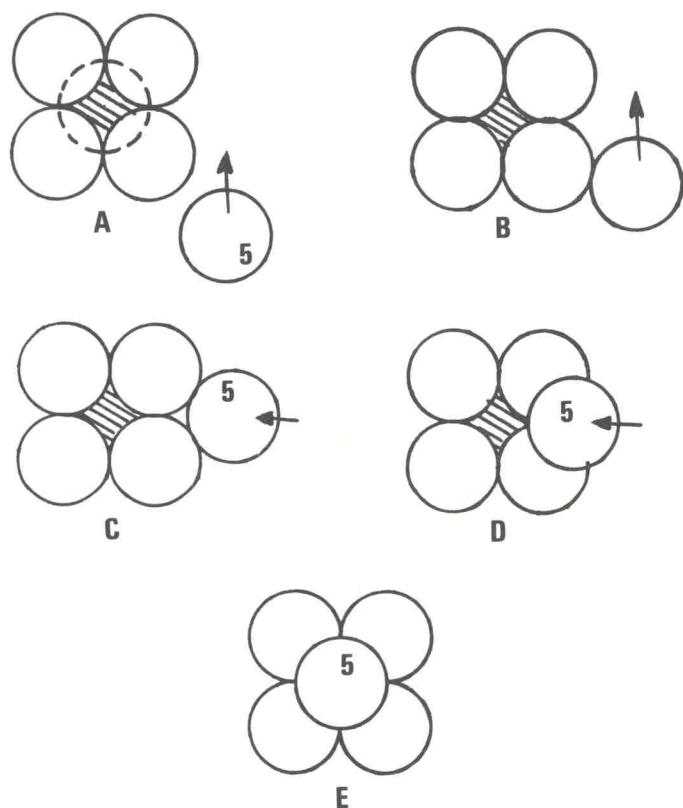


Figure 6. Formation of bonds in a 4-hole

A, Approach (the dotted atom is below the plane of the 4 atoms and fixes these 4 in position. It is only partially shown in the other views); B, First bond forms between atom #5 and one unimer of the 4-hole; C, Second bond forms between #5 and the adjoining unimer; D, Movement of unimer #5 on surface of plane of 4; E, Simultaneous formation of bonds 3 and 4 between unimer #5 and 4-hole. These two bonds must be formed simultaneously

Degradation of unimer #5 in a 4-hole: The first step is the reverse of step E; the simultaneous breaking of 2 bonds. The next two steps are the reverse of steps C and B

Equation 7b is the redefined Equation 2a. With these redefinitions, the equation of state, Equation 3, remains unchanged.

The solid and the liquid states (2)

The remaining questions propounded previously are still to be answered. To be able to do this we must first investigate some of the still larger clusters (larger than the 5-mer). We shall neglect the simply bonded clusters and only examine the closely packed (multiply-bonded) species since at this point we realize that the multiply-bonded clusters are those that comprise the liquid and solid.

The closely packed forms of the 6-mers are shown in Figure 7. There are two of these, both of which have the same number of bonds. While the 6a-mer can be formed directly from the closely packed 5-mer, the 6t-mer can only be formed from the closely packed 5-mer by first forming the 6a-mer and then going through an isomeric transition where one bond is broken and another formed. These forms are interesting only because of this isomeric transition and because they are a step toward the closely packed 7-mers, which are shown in Figure 8. With the closely packed 7-mers an important phenomenon appears, namely, the closely packed forms do not have the same number of bonds. One of the forms, the 7a-mer, differs from the other forms in that it has an extra bond. This extra bond is slightly weaker than the other bonds in the 7-mers. By weaker I mean that whereas all previous bonds are considered to be at places where the atoms touch, in the 7a-mer there is one stable position where, while the atoms do not touch, they are uniquely close together. This is shown in Figure 9. Further the 7a-mer is degenerate, since this weak bond can appear in 6 different positions (5 identical) by an isomeric shift that should require very little activation energy. The result of this extra bond and degeneracy is that this form has added stability. As we go from the 7-mers to the 8-mers, then the 9-mers and up, this a structure persists in having more bonds than the structures built up from the other forms (the t structure). A graph showing the results obtained by model building with spherical unimers is shown in Figure 10. Figure 11 is a photograph of models of the 19a-mer and the 19t-mer. The 19a-mer resembles our mental image of a liquid while the 19t-mer has a regular shape corresponding to our mental image of a crystal.

The models were built with beads of uniform size. Each successive bead was placed in the most highly bonded position possible with the results shown in Figure 11. In the 19t-mer each bead is firmly fixed into position, that is, it fitted exactly into a 3- or 4-hole. Within the 19a-mer, very often there were positions in which a bead could be placed in two closely spaced alternate spots, which were, however, not close enough to be called an extra weak bond, but close enough so that another bead would not fit. The bead could then move between these two positions with little activation energy. By this I mean that the center of gravity of the bead would not need

to be "raised very high" to go to the adjoining position. (A bead in a 3-hole has to be raised to a considerable height to move from one 3-hole to the adjoining 3-hole. One bond is broken and then one is formed in this process. A still more difficult process is the case of the 4-hole). The symmetry of the 19*a*-mer is approximate 5-symmetry, that is, it is built around the pentagon. A single bead lies in the center of five beads in a 5-hole, above and below the plane of the pentagon, while over this central bead is another pentagon. The planes of the pentagons are generally not parallel. This type of arrangement is not efficient in filling space and the 19*a*-mer is full of voids that are less in volume than a whole bead. On the other hand the 19*t*-mer is built around 6-symmetry and such a structure fills space efficiently. Bernal (5) has noticed the same phenomenon when he wrapped "Plasticene" spheres in film and dropped them into a large container in a random fashion. The impressions of the surrounding spheres on any sphere were in groups of 5. Apparently approximate-5-symmetry is the result of random packing. From this approximate-5-symmetry packing stem many of the characteristic properties of liquids; their fluidity and flow properties and their increased specific volume. This behavior is in contrast to that of the solid where rigid 6-symmetry (or 3- or 4-symmetry) is the rule. Unimers in this latter type of symmetry fill space efficiently. The unimers in the liquid can move from position to position with little or no activation energy and no elastic restoring force, while in the solid clusters, since the space is filled efficiently, movement is very difficult and there are large restoring forces.

Hence a liquid consists of large clusters in approximate 5-symmetry while a solid consists of still larger particles in 6-symmetry (or 3- or 4-symmetry). From Figure 10 we see that the 19*a*-mer has more bonds than the 19*t*-mer counting the weak bonds. At some size greater than 19 (the models were only built up to this size) these curves must cross, because as the sizes become larger two things happen: in the *t*-structures more positions consisting of 5- and 6-holes appear, while in the *a*-structure very few of such positions are apparent. However, the large clusters are formed systematically from small clusters in the natural process of condensation. Hence it is obvious why liquids usually form preferentially in condensation. The smaller clusters that form first are the more stable liquid clusters and they give rise to clusters that have the *a*-structure, which is the liquid structure. In the larger size clusters the most stable clusters (those having more bonds) are the solid clusters. The question now arises what is the process by which liquids change to solids. We know that this change is a difficult one, often very difficult.

Nucleation and the conversion of liquids to solids (2)

Experiment shows that conversion of liquids to solids is difficult: the formation of supercooled liquids is common. The postulation has been that nuclei are necessary for such a conversion process. The question is: what are these nuclei and how are they formed?

The structure of the liquid is based on 5-symmetry while the structure of the solid is based on 6-symmetry (or

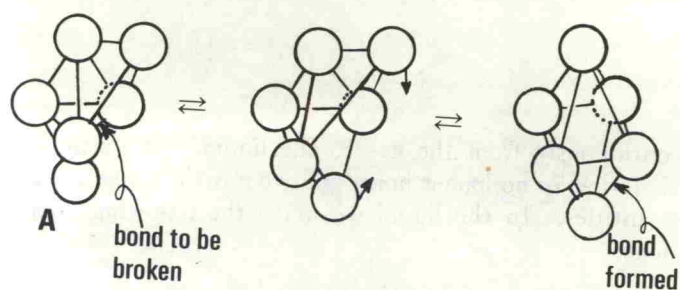


Figure 7. The 6-mer transition
A, the 6*a*-mer formed from a nine-bonded 5-mer and a 1-mer (12 bonds); B, the transition form: one bond broken; C, the 6*t*-mer (12 bonds); bond remade

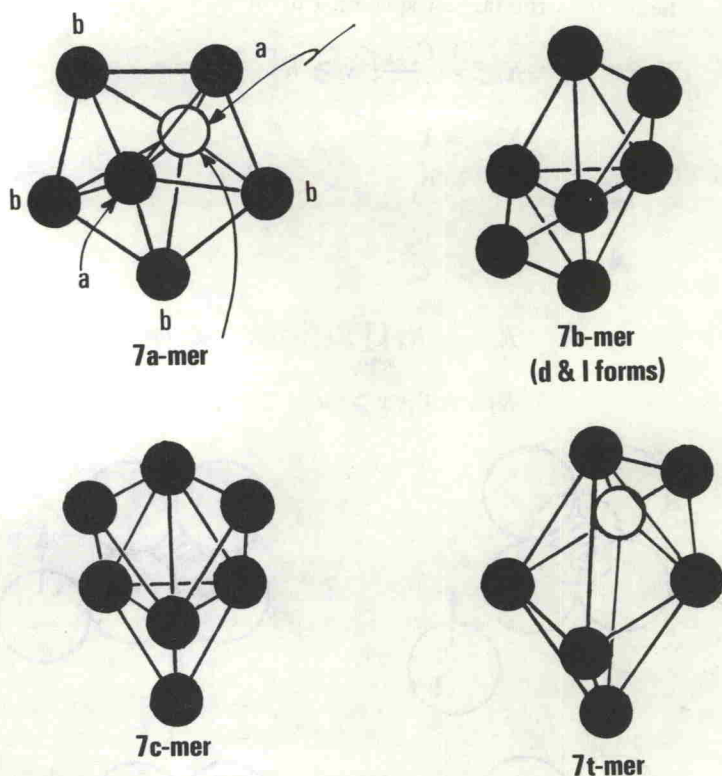


Figure 8. Closely packed forms of the 7-mers
The weak bond in the 7*a*-mer appears either as a b-b bond or an a-a bond. Probably the whole structure adjusts so that all the bonds are equivalent. The 7*a*, 7*b*, and 7*c* are formed from the 6*a*-mer while the 7*t*-mer comes from the 6*t*-mer

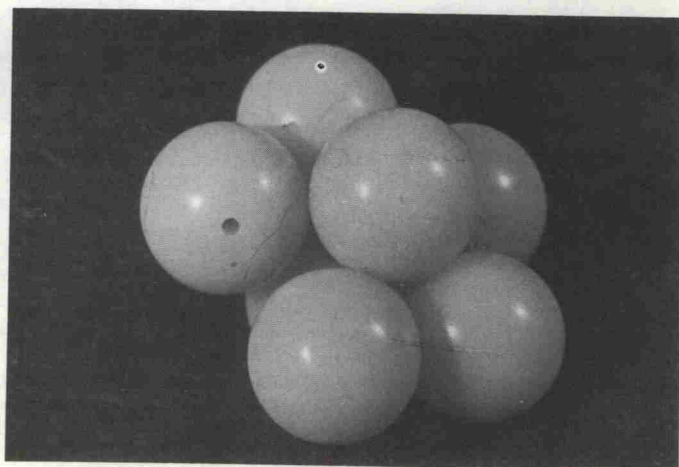


Figure 9. Photo of bead model of the 7*a*-mer
The weak bond is shown. All the beads touch at the other bonds