

3- or 4-symmetry). The problem then of crystallization is the conversion of a system in 5-symmetry to one in 6-symmetry. This is difficult since it demands the cooperative breaking of many bonds in liquid clusters and subsequent movement to preferred positions in 6-symmetry. However, events take place one at a time and unimers move so that the largest number of bonds are formed. The unimers cannot foresee that later they will be more stable in 6-symmetry. Hence spontaneous or homogeneous nucleation occurs rarely. On the other hand, heterogeneous nucleation is simple, rapid, and predictable. In heterogeneous nucleation a seed crystal, which is a small crystal of solid, is introduced. *The seed crystal is in 6-symmetry and is of a size that is stable.* This seed can grow by utilizing the 1-mers that are in equilibrium with the liquid clusters because the stability of the unimer in the solid cluster is greater than that in the liquid cluster. The solid cluster then grows at the expense of the liquid clusters surrounding it. As the liquid clusters become smaller, it becomes easier for them to go into the form of the *t*-structure (6-symmetry) and hence more nuclei are formed. Thus the process is an accelerating one and the liquid rapidly changes from an *a*-structure (5-symmetry) to a *t*-structure.

Methods of inducing nucleation and subsequent crystallization are known other than introducing a seed. One such method is violent, prolonged agitation followed by a period of rest. It seems likely that in this method the mechanical agitation physically breaks up the large liquid clusters into smaller ones. Since the external conditions (P , T) are such that solids are stable, the smaller liquid clusters have a chance to convert into *t*-clusters, these being the nuclei around which further growth and crystallization occur. Another method of inducing nucleation is to store the liquid sample at very low temperatures (dry ice temperatures) for a long period of time and subsequently warm them up to allow for subsequent growth. Here storing the liquid clusters at very low temperature increases the lifetime of all clusters. Some small *t*-clusters may form and if warmed up slightly will persist long enough to allow them to grow to a stable size. After the clusters are large enough and hence stable enough, considerable warming is possible and growth continues by the unimer addition process. Such forms of homogeneous nucleation are not predictably certain and are difficult to achieve.

Melting

The reverse of crystallization, melting, is by comparison a simple problem. As the solid cluster in 6-symmetry is warmed, the clusters get smaller because of kinetic motion, that is, α decreases in value. Also, because of the amplitude of the vibration of the unimers, the specific volume increases. The unimers can migrate to other positions and small aggregates can form with 5-symmetry, which are more stable than the small aggregates in 6-symmetry. Hence the substance melts. In observing the melting process in crystals one can see that the corners melt first, then the edges, and finally the bulk. This happens because the unimers at the corners and edges are the least bound and hence can more easily rearrange to the stable 5-symmetry. The melting point is not absolutely sharp, the melting of the

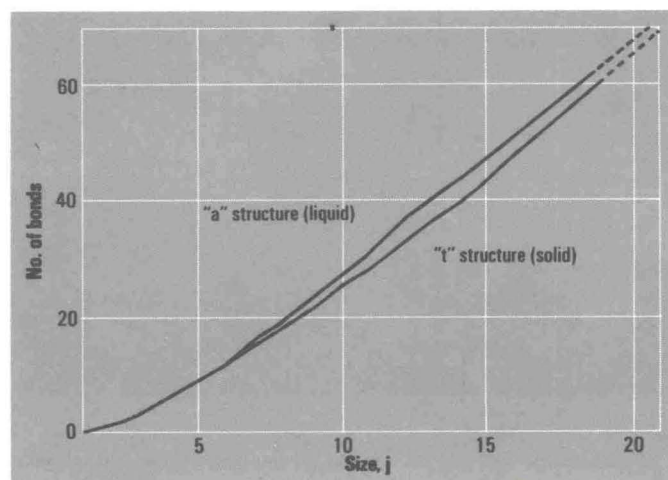


Figure 10. J vs. number of bonds

Contact points are considered bonds. Note that the 5-symmetry *a*-structure has more bonds than the 6-symmetry *t*-structure. The lines must cross at much larger sizes, the number of bonds in the *t*-structure then being more than in the *a*-structure

corners occurring at a slightly lower temperature. No nuclei are necessary in the process in contrast to crystallization.

The critical state and fluids (3)

An explanation of the curious phenomena which occur in this interesting state remains to be discussed. When an equilibrium system of a liquid and a vapor is heated, usually under pressures, the phase boundary is visible as the temperature increases. When, however, the critical temperature is reached it suddenly disappears. However, if the tube containing the mixture is not agitated during the process, density differences between the former liquid and former vapor regions persist for some time, if the temperature is kept close to the critical temperature. Gentle inversion of the tube does not destroy the density difference, although vigorous agitation and/or large temperature rises do. These phenomena are amenable to explanation by association theory.

At temperatures well below T_c , the liquid-vapor equilibrium system consists of a liquid phase containing 1-mers and large α -mers, where α is much greater than 5, and a vapor phase in equilibrium with the liquid phase containing 1-mers and 2-mers. The 1-mers of the liquid phase are in equilibrium with the 1-mers in the vapor phase. The gap consisting of species in zero concentration in the liquid phase is extremely large. The refractive index of the two phases is vastly different because differing species in the two phases and the phase boundary are distinct.

As the temperature is increased the gap becomes smaller, that is, α decreases in value and the number of 1-mers in the liquid increases. At the same time in the vapor, the number of 1-mers increases because they are in equilibrium with the 1-mers in the liquid phase. Because of the temperature rise and the increase in the number of 1-mers in the vapor phase, the number of collisions in the vapor phase increases. This means that as the temperature increases the number of 2-mers, 3-mers and 4-mers and linear 5-mers in the vapor increases. The phase boundary becomes more indistinct although still visible. At the

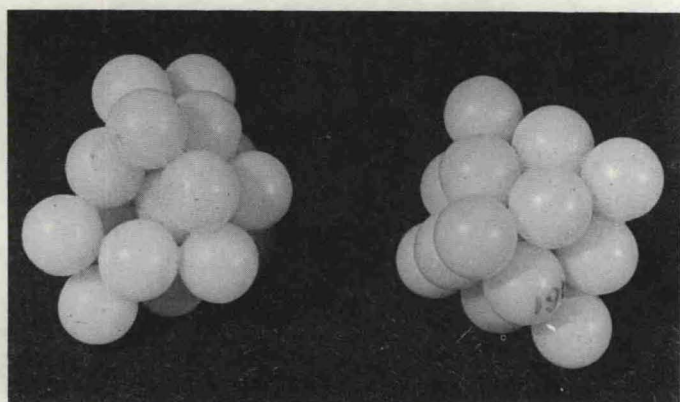


Figure 11. The 19-mers

The 19 α -mer on the left and the 19 β -mer on the right. Notice the compact regular array of the 19 β -mer. This is typical of crystalline solids. On the other hand the 19 α -mer looks random and has a number of small gaps in the structure. Some are shown. This is typically the liquid structure

critical point, α in the liquid phase becomes five. This means that the smallest species in the liquid is the 5-mer, while the largest species in the vapor is also the 5-mer. Hence at this point the distribution in species becomes continuous between the two phases. Since the composition is continuous, the refractive index is the same and the phase boundary disappears. In this same process the densities of the two phases have been approaching one another (Law of rectilinear diameters). However, in an undisturbed tube the densities do not become equal at this point. At the temperature, T_c , where the refractive index disappears, the former vapor phase region consists of species of sizes from 1 to linear 5, while the former liquid

phase region consists of clusters from 5 up. Hence there is a density difference. This difference disappears on mixing by violent agitation, although gentle inversion of the tube does not destroy it. Thermal currents owing to temperature differences will also destroy the density gradient as will kinetic motion owing to a temperature rise.

Above the critical temperature, the distribution of species is continuous, no gap is present. This fluid state resembles a gas in that a continuous distribution of species is present and a liquid in that large multiply-bonded species exist. The high temperature ensures that no gap forms in the fluid state that exists above the critical temperature.

Quantitative experimental tests

The argument thus far has been theoretical and descriptive, and, we feel, plausible. The test of a theory is however its quantitative agreement with experiments. In this section we will set forth the points where we can contact numbers.

First: If we calculate α for the substances (δ), argon, oxygen, nitrogen, and water from the triple point to the critical point from the known values of the vapor pressure P the liquid volume V and T , we obtain Table 1. As can be seen from the table the value of α at the critical point is approximately 5 for all these substances, even for one as complex as water. The theory does not predict that α will be exactly 5 at the critical point but approximately so. While the values of α , the smallest size of liquid cluster in the various liquids, varies enormously at the triple point, they approximate 5 at the critical point. The principal

Table 1. Average degree of association of the α -mer from the triple point (T_{tp}) to the critical point (T_c)

T(°K)	$P_{\text{sat}}(\text{exp})$ (atm)	$P_{\text{sat}}(\text{calc})^d$ (atm)	α^c	T(°K)	$P_{\text{sat}}(\text{exp})$ (atm)	$P_{\text{sat}}(\text{calc})^d$ (atm)	α^c
Argon^a				Nitrogen^a			
83.8(T_{tp})	0.6798	0.6813	4000	63.15(T_{tp})	0.1230	0.1268	14000
90	1.321	1.314	1700	70	0.3800	0.3774	3600
100	3.210	3.194	550	80	1.349	1.323	820
110	6.591	6.606	220	90	3.551	3.527	250
120	12.00	12.10	97	100	7.676	7.710	96
130	20.00	20.20	47	110	14.48	14.62	40
140	31.30	51.34	23	120	24.80	24.92	17
150.86(T_c)	48.34	47.28	5.3	126.26(T_c)	33.56	33.34	5.2
	$\sigma = 0.85\%$ ^e				$\sigma = 1.26\%$ ^e		
Oxygen^a				Water^b			
54.35(T_{tp})	0.001500	0.001693	1,200,000	0°C(t_{tp})	0.006027	0.007519	2,000,000
70	0.06140	0.05932	24,000	50	0.1217	0.1202	100,000
85	0.5610	0.5249	2,300	100	1.000	.9138	11,000
100	2.509	2.415	460	150	4.698	4.303	2,100
115	7.454	7.459	130	200	15.35	14.60	540
130	17.25	17.76	48	250	39.26	39.23	170
145	34.02	35.35	18	300	84.79	88.70	61
154.77(T_c)	50.14	51.51	4.8	350	163.2	176.0	21
	$\sigma = 4.75\%$ ^e			374.15(t_c)	218.0	235.8	6.1
					$\sigma = 7.84\%$ ^e		

^a Data from H. M. Roder, R. D. McCarty, and V. J. Johnson, *Nat. Bur. Stand. Tech. Note 361* (1968).

^b Data from N. E. Dorsey, *Properties of Ordinary Water-Substance*, Reinhold, New York, 1940.

^c These numbers are rounded off from an 8-digit calculation.

^d From a least-squares fit of experimental data (rounded off).

^e $\sigma = \left(\frac{1}{n} \sum [P - P_{\text{calc}}/P]^2 \right)^{1/2}$; measure of goodness of fit of experimental data in P to least-squares equation.