



The Bakerian Lecture, 1962. The Structure of Liquids

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THE BAKERIAN LECTURE, 1962

The structure of liquids

By J. D. BERNAL, F.R.S.

(Delivered 14 June 1962—Received 25 February 1964)

[Plates 14 to 17]

A satisfactory picture of the structure of liquids has lagged far behind that of other states of matter. Ever since the time of Euler in the eighteenth century or, in a more precise form, since that of Maxwell in the nineteenth, we have had a convincing qualitative and quantitative picture of the chaos that is represented by the movements of the ideal gas molecules. The notion of a crystal or a solid in general as an arrangement of molecules 'in rank and file', as Newton put it, is, in fact, older than Newton yet its quantitative statement was made possible only through the work of Born and others in our own century. But it is admitted even by those who work most in the field that the study of the structure of liquids or any exposition of their properties in atomic terms is still largely to be sought. This is not for want of trying. A vast number of researches have been devoted to attempts to analyze the structure of liquids, either directly by the diffraction methods which have proved so successful in crystalline solids, or, indirectly, through the construction of models and their thermodynamic testing. But we still lack either an adequate picture of the arrangement of molecules in a liquid or the necessary quantitative theory to explain their thermal and other properties.

In this lecture I shall be developing in some detail a new approach to this problem. For completeness I ought to give a detailed account of the other theories that have been used in exploring in this field, but to do so in any degree of adequacy would, in itself, require a lecture longer than this one. All I can do here is to indicate their general character and leave it to further discussion to compare them among themselves and with that theory which I am about to expound.

My interest in the subject is of long standing. It came about in the first place through my biochemical interests, in that all living structures are mostly composed of water. This was to lead, thirty years ago now, to the paper on water and ionic solution which Professor R. H. Fowler and I brought out in the first number of the *Journal of chemical physics* (Bernal & Fowler 1933). My own approach to this problem was, frankly, one of crystal structure, trying to picture water structure as that of a mixture of the analogous four co-ordinated structures of silicon dioxide, quartz and tridymite.* This led to an evaluation, by model making, of the X-ray diffraction of water at various temperatures. From that I naturally passed to the study of other liquids, the close-packed so-called normal monatomic

* A form of silica, keatite (Shropshire, Keat & Vaughan 1959), would meet the relative densities of ice and water more closely but it was not known at the time of this original paper.

liquids which are actually rather rare—the liquid metals and the liquid rare gases. Most liquids, the typical organic liquids, are made of fairly complex molecules and are necessarily more complex in structure than the monatomic liquids.

I started on the basis which Zernicke & Prins (1927) had laid in their early analyses of the X-ray diffraction of liquids, pointing out the analogy between the scattering pattern of a liquid and that of a corresponding solid, the peaks of the first, second and third co-ordination spheres corresponding to the reflexions from planes of the same spacings in a crystal. This was ultimately to prove rather a delusive approach, postulating a greater degree of order, particularly long-range order, in the liquid than actually exists there. A liquid, in my present opinion, is not simply a blurred solid.

I attempted then in a paper to the Faraday Society (Bernal 1937), to express the structure of a liquid in terms of co-ordination and described a liquid structure by means of the number of atoms in $N_1 N_2 N_3 \dots$ and each co-ordination sphere of radii $R_1 R_2 R_3 \dots$ and their scatter widths $\lambda_1 \lambda_2 \lambda_3 \dots$ in each co-ordination sphere. I see now that this was a highly artificial description and, not surprisingly, it could not lead to any quantitative result because there were no means of calculating these different values although it was already evident to me that the characteristics of the higher co-ordination spheres were necessarily functions of those of the lower ones.

In the intervals of thirty years great efforts were made in the approach to the study of liquid structure with, however, disappointing results. They followed three, actually somewhat divergent, paths. The first and the most thorough was that of Born himself, associated with Green (1946) and was an extension of the theory of dense gases. This is a fundamental approach based on a study of the mutual potential between molecules in a liquid, treating the molecules first as pairs, then as triplets and so on. It led to extremely complex mathematical formulations but not, unfortunately, to any that could be readily handled by computation and consequently it was somewhat barren in practical results. A number of workers continued this approach which is essentially a virial one as used in the classical theory of imperfect gases.

The second approach was radically different, it treated the liquid as an imperfect solid, the simplest variation being the omission of certain of the atoms, the so-called hole theory of liquids, developed particularly by Kirkwood (1939, 1941, 1942, 1950) and his followers. As the density of a liquid does not vary very markedly, usually less than 15 %, from that of the corresponding crystal, this approach would necessarily give approximately the correct values of the energies, both potential and kinetic, of liquids. It failed, as indeed did the first, in an understanding of the entropy and of the properties depending on it, particularly those of pressure. This was, to a very large extent, remedied in the third approach, associated with the name of Eyring (1958) which was a kind of compromise between the first two, treating a liquid as a mass of submicroscopic crystals with order inside the crystals and dislocations or disorder of some kind or another between them.

It is evident that any approach to a theory of liquids which aims at producing a picture of their structure and properties, will have to use very considerable

approximations. The different theories I have mentioned effect their approximations in different ways and succeed very largely only in those properties in which the particular approximations have the least distorting effect. For instance, in the case of the theories based on crystalline structure, it is evident that the approximations may be very good for energy considerations but very bad for the scattering of X-rays which is particularly sensitive to any presence of long-range order. Here, both of these latter theories necessarily fail as this long-range order is effectively built into them.

However, even the prediction of the modified long-range order of the Prins variety, or what is now called the radial distribution function, the probability of finding two molecules at different distances apart is not a very good test for the adequacy of a theory of liquids. Even in crystals, with a very large number of independent reflexions of radiations such as X-rays or neutrons, it is always possible that the same kind of scattering can be explained by different structures. If the radial distribution function derived from a model does *not* agree with observations it is clearly wrong, but it is not equally clearly right if it does agree with the observations.

Throughout this period I found all these theories fundamentally unsatisfying to a crystallographer, however much they might appeal to a physical chemist or a mathematician. I wanted a more concrete picture of the structure and one making more use of Ockham's razor 'Not to multiply entities beyond necessity'. I wished to get some kind of theory of liquids that would be homologous to that of the crystalline solid as well as radically different in kind, and have a general quality of homogeneity without the assumption of any special groups, although, as will be seen later, such groups may arise spontaneously and out of necessity.

I had kept up an interest in liquids over the ensuing years, although distracted on the one hand scientifically by the study of proteins and viruses and on the other by compelling concerns such as the war. Four years ago I resumed an active interest in the subject when I was listening to a lecture by Professor F. C. Frank (1958) on the complex metal alloy systems, such as the sigma phases, in which he introduced the ideas of polyhedra with certain 'principal ligands' joining the atoms together and leading to many varieties of close packing, some containing fivefold arrangements. It occurred to me that some similar geometrical analysis might be possible for statistically disordered states of monatomic liquids. I started, therefore, with the most general hypothesis expounded in my first paper (Bernal 1959) in 1959. The essential feature is that it treats liquids as *homogeneous, coherent* and *essentially irregular* assemblages of molecules containing no crystalline regions nor, in their low temperature form, holes large enough to admit another molecule.

The rest of this lecture will be an attempt to construct on these minimal hypotheses a rational and verifiable image of liquid structures. I began, rather naively, by attempting to build models just to see what a structure satisfying these conditions would look like. I took a number of rubber balls and stuck them together with rods of a selection of different relative lengths ranging from 2·75 to 4 in. I tried to do this in the first place as casually as possible, working in my own office, being interrupted every five minutes or so and not remembering what I had

done before the interruption. However, I could not trust it: how did I know that some bias on my part had not led me to introduce more order than would be required by pure chance? Nevertheless, a first examination of this model (Bernal 1959) showed me clearly enough some of the properties which must follow from the absence of long-range order. One was the irrelevance to the structure theory of liquids of any of the more distant terms in the expansion of potential between molecules. In fact, the key word in the structure of liquids is the one which Humpty Dumpty used in *Alice through the looking glass*, 'impenetrability'. The actual structure must be determined largely by the form of the repulsive forces between close molecules.

This necessity is not peculiar to the structure of liquids. A careful examination of the structures of crystalline solids shows that for most structures it is the repulsive forces that determine the particular kind of structure. In fact this is the basis of the Goldschmidt and Pauling theory of crystals. Only where directed forces of the covalent or polarizing type dominate do factors other than repulsion effectively come in. The reason for this is simply expressed in realizing the high index to the variation of the potential of the repulsive forces with distance. Atoms cannot approach closer than the sum of their atomic radii without raising their mutual potential enormously. From twice the radius of a molecule outwards, the effects of the more distant molecules can be treated as a quasi homogeneous irregular assembly, which they cannot be in a crystalline lattice. This, in fact, enormously simplifies the problem and leads at once to a justification of the earliest method of approaching the problem experimentally, that is, the hard sphere hypothesis. This can be approached by models or by computations, as, for instance, in the so-called Monte Carlo method used particularly successfully by Alder *et al.* (1955). The weakness of this method, as indeed of all methods based on computation even with present machines, is that it is limited to a very small number of molecules, even though it is immensely superior to models such as I used in getting a realistic picture of the kinetic, though less so of the static, picture of the liquid structure.

I argued further, however, that in the first stages of analysis the static picture would be quite sufficient. Whatever kinetic properties the molecules of a liquid might have, its structure must satisfy the static requirement that two molecules do not occupy the same place. The first thing to examine was the nature of the static interaction of a number of hard spheres. In other words, a liquid could be treated simply as a *heap* of molecules in contradiction to the regular *pile* that characterized a crystal structure.

This notion, however, did not advance me very much because I found, when I had to consider it, that we did not know much about heaps and that to understand heaps we had to open a new subject, that of *statistical geometry*. I cannot claim that I have done this but I have at least drawn attention to the need to do so. It is clear that a complete description of any arrangement, regular or irregular, of points can be made simply by specifying the vectors between those points. This is equivalent to giving all the instructions necessary to construct a model starting from any point. But it is also evident that the totality of these vectors represent

much redundant information: that there must be a *minimum invariant* set of vectors which is sufficient to determine the structure *precisely*. Besides these there must be a number, an even more restricted number, of vector functions that characterize it as a statistical ensemble. The problem is to find out what these are.

At this stage the problem of the structure of liquids resolves itself into two. First, there is the merely geometrical one—*what is the structure of a liquid?*: that is, what are the mutual positions of atoms and molecules?: and, secondly, *why* has it got this structure? In what sense is this structure an expression of an arrangement of minimum energy? The first is a question of statistical geometry, the second of statistical mechanics. My contribution is only to the first. If liquids consist of heaps of molecules, we must ask what a heap is. This is very much a going back to the beginning.

We are told that *science is measurement* but the first *measure* was the measure of a heap—the measure of a heap of corn—by filling it into baskets. Thus the measurement of volume preceded in this way the measurement both of length and of weight. But in all the millennia that have passed in between, the real study of the nature of heaps has had to wait. It seemed too simple, in one respect, and too complicated in another.

A *regular pile* of objects could be measured. That was the proper subject for *geometry*, such things as the pyramid calculations which are the first examples of Egyptian mathematics. For *irregular heaps*, people were practically contented with ‘good measure pressed down and running over’. Curiously enough, although measures of corn are reproducible, the method of filling the measure has to be very particularly stipulated, for the method of pressing down and that of piling up and knocking off, give results which differ by some 5%, though among themselves the difference is less than $\frac{1}{2}\%$. The only scientist, to my knowledge, who went into this in any detail was Osborne Reynolds (1886). He used this concept of measure to produce a highly paradoxical dilatency theory of gravitation. He imagined gravitation to be the interaction between the solid bodies which are holes in an even more solid ethereal sand.

What is the difference between a *heap* and a *pile*? I have tried to illustrate it with marbles; when I pour some of these into a specially prepared octahedral box, they arrange themselves in a pyramidal *pile* in very neat, rigid, geometrical order. The others I pour onto an even more carefully prepared irregular board, which produces a much lower and completely casual and unstable *heap*. I did this first at a lecture at the Royal Institution in 1958 (Bernal 1959) and in the lecture itself I noticed the clue that set me on to the track of how to analyze the nature of the heap and what is its geometrical origin. It was apparent that whereas in the regular pile the arrangement was always one in layers of sixfold symmetry; in the heap it was quite as often fivefold as sixfold.

Here I was back at a very classical problem which occupied mathematicians from the seventeenth century onwards, that of the filling of space by polyhedra. The regular solutions were provided by nature by the bee and its honeycomb with its hexagonal arrangement. But the corresponding irregular arrangement was what the botanists found in the pith of plants. One almost childish but very

instructive approach was the piling together of a number of chalk-covered Plasticine balls in a football bladder, removing the air to avoid bubbles and then squeezing them together until they adopted shapes which could actually be measured. I found afterwards that this was not by any means an original experiment. It has been carried out first, as far as we know, by the Reverend Stephen Hales in his *Vegetable staticks*, 1727, not with the idea of studying cells, which were then virtually unknown, but trying to see the swelling properties of peas which he enclosed in a heavy iron pot with a weighted lid:

'I compressed several fresh parcels of Pease in the same Pot with a force equal to 1600, 800 and 400 pounds; in which Experiments, tho' the Pease dilated, yet they did not raise the lever, because what they increased in bulk was, by the great incumbent weight, pressed into the interstices of the Pease, which they adequately filled up, being thereby formed into pretty regular Dodecahedrons.'

TABLE 1. DISTRIBUTION OF POLYGON TYPES FROM POLYHEDRA MADE
FROM A RANDOM ASSEMBLY OF SPHERES

Number of each polygon combination type arranged in the order of the number of pentagonal faces. The numbers for each polyhedron are put in the order of the polygonal faces. For example, 13451 stands for a polyhedron with 1 triangular, 3 quadrangular, 4 pentagonal, 5 hexagonal and 1 heptagonal face. The number in brackets gives the number in each category.

no. of pentagonal faces																						
12				10				9				8				7						
0	12	0	(2)	1	10	2	(4)	1	0	9	3	2	8	1	(2)	3	7	2	1	(3)		
0	12	2		1	10	4	(2)	2	9	5	1	2	8	2	(3)	3	7	3	1			
												2	8	3	(3)							
												2	8	4	(4)							
												2	8	6								
3				6				2				13				4						
no. of pentagonal faces																						
6				5				4				3				1						
3	6	2		1	2	5	3	1	3	4	3	1	5	3	3	1	1	4	1	5		
3	6	3	(5)	4	5	3	1	1	3	4	4	1	(2)									
3	6	4	(5)	4	5	4	1	(2)	1	3	4	5	1	(3)								
3	6	5	(3)						1	3	4	6	1									
3	6	6	(5)						4	4	2											
4	6	4	2						4	4	4											
									4	4	5											
									4	4	6											
20				4				11				1				1						

The dodecahedra—which were not quite as regular as Hales thought—were really the clue to the whole geometry of irregular or liquid structures. In preparing my first note on the subject, I had asked Dr Levison to count very precisely the number of edges of the faces of such little bits of Plasticine. The results of this tedious task are shown in table 1. The predominance of the pentagonal type of face is only too evident but the wide range is actually more important. The number

of faces of polyhedra filling three-dimensional space arranged in a regular manner was discussed by Kelvin and others and they came to the reasonable conclusion that this number was fourteen. What the actual number should be in the irregular case has been a great problem for pure mathematicians. The best solution available at the moment is that given by Coxeter (1958), obtained very indirectly through the study of five-dimensional polytopes. He obtains the number 13·56 as a solution to a quadratic equation. Such an expression seems to me intrinsically improbable for a statistical theory. Indeed, it cannot be the general solution for exceptions to it can easily be constructed, but it may very well be the correct solution for an arrangement occupying an overall minimum volume, that is, the closest packed arrangement for a certain number of spheres irregularly arranged. The various methods which I have used, as has Professor Scott of Toronto (1962) give a figure of 13·6 as against 13·56, an agreement which is much too good but does help to show that the various mechanical methods used for producing irregular arrangements have succeeded in their purpose of imitating a random distribution.

The obvious requirement of a good model to study such irregular arrangements are that it should have enough points so as not to be limited by the surface effects and that it should be free from any human interference. For this purpose, either computation or models with actual spheres seem to be indicated.

The first approach was still limited in numbers. I was able to produce, thanks to the assistance of my son, Dr M. J. M. Bernal, and the use of the computer in London University, a model with spheres derived from the simple process of choosing the co-ordinates of a succession of points strictly at random and keeping all of them that were not less than a certain distance from points already chosen. This method became more and more tedious and wasteful towards the end of the process and often as many as a thousand points had to be chosen for one to be accepted. Furthermore, although this was undoubtedly a random model, it was far from being a random close-packed model, as is shown by the radial distribution curves it gave (figure 1).

In the end I fell back on the study of a model of a large number of ball-bearings. Precautions had to be taken particularly to prevent any plane surfaces around the block even if it consisted of more than a thousand balls because, as will be shown later, any regular two-dimensional array produces an effect of regular packing which goes far into the mass, figure 16, plate 17. The problem of fixing such an arrangement so that it could be measured was achieved very simply by adding black paint and letting it harden. This provided, as figure 11, plate 14 shows, marks indicating contacts and near contacts. The counting of these contacts and near contacts for a large number of balls, of the order of several hundred, was carried out by Mr J. Mason (Bernal & Mason 1960). It provided one further clue of great importance, namely, that the numbers of contacts were arranged in some definite statistical order, that is, the number of balls having five, six, seven, etc., up to eleven contacts formed a determinate curve and was absolutely distinct from the regular arrangement, where every ball must have twelve contacts. It was evident that this *variation of contact numbers* or *co-ordination* was one of the most significant features, possibly the most significant feature of the irregular liquid

arrangement. But it was also clearly necessary to extend this a little further than the closest contacts, which are all that the ball model can show directly. This is necessary first to check the validity of the model by its diffraction effects and, secondly, to see how far the more distant distances were related to the closer ones.

Indeed, a study of the computer-built model already brought out some basic characteristic features of any rigid sphere, or for that matter, non-rigid sphere packing. I have alluded already to the co-ordination; in some ways more characteristic is the arrangement of the holes in such a model. In an ideally close-packed

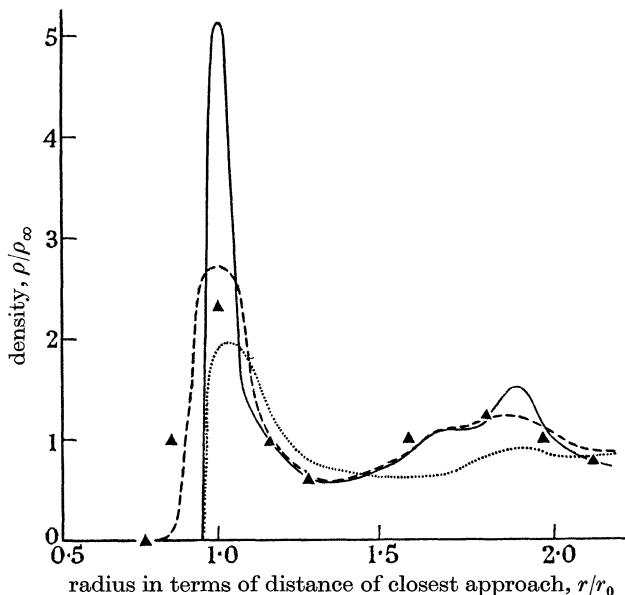


FIGURE 1. Radial distribution functions: variation of mean particle density as a function of r/r_0 .
....., Derived from calculated random model; —, derived from squeezed random model;
—, —, calculated for liquid lead by Furukawa (1960) with X-rays calculated for liquid argon by Henshaw, D. G. (*Phys. Rev.* **105**, 976; 1957) with neutron diffraction.

arrangement, any point which is not actually at the centre of one of the points of the system must lie in a polyhedral hole characterized by the lengths of its edges representing contacts between spheres, having in consequence the same, or approximately the same, length. The degree of approximation is itself a statistical consequence of the geometry of the system. Here, it is not possible, as in regular arrangements, to make all the distances precisely equal or even in the case of the balls which are marked by paint, equal within 5 %. However, within a permissible variation of 15 % the pattern emerges quite clearly as is shown in the large model to be described later.

As I noted in my paper of 1960, there are five and only five polyhedra, which may be called, following Cundy (1952) deltahedra, that is, with triangular faces, small enough not to admit another sphere of approximately the same size into their interior. Two of these are the tetrahedron and the octahedron, which also occur in regular crystals. They are followed by a low symmetry polyhedron,

consequently left unnamed by the Greeks, which may, nevertheless, be called the dodecadeltahedron—a very common co-ordination for the calcium ion in crystallography—and then by the trigonal prism and the Archimedean anti-prism. The holes represented by these polyhedra are of progressively increasing size. Another regular hole would be that of a regular icosahedron, but the icosahedron and the cube itself are excluded by the fact that they can be decomposed into smaller tetrahedra by placing another sphere at their centres.

A further study of the geometry of these structures reveals various arrangements which may have physical significance. One is the fact that there must be a minimum volume for any such arrangement but as long as irregularity is preserved this minimum will be greater than the regular close-packed arrangement by some 15 %. It is evident that except in crystal structures which only contain tetrahedra and octahedra, there must be some holes of the trigonal prism, of the Archimedean anti-prism or of the dodecadeltahedron shapes in such structures. These lack the symmetry which enables them to form regular structures by themselves, although in regular combination with others they can even occur in crystal structures.

From the five types of hole it is possible to see that an indefinite number of structures can be constructed which have equal or quasi-equal shortest distances between their points. This was realized practically by making, from extensible plastic foam, a number of small polyhedra of each of these five types which could be fitted together. The extensibility of the foam allowed for the small differences of the order of 5 % which are permissible in the edge lengths in a random, close-packed, aggregate. The work of Miss J. Wilkinson (1961) established that it was possible to fit these together in at least 197 different ways around a given point. Further, it established a more important theorem that every point on such an aggregate could itself be the centre of further aggregates. In other words, that it was possible to construct such a system indefinitely in space.

Not all such systems are equivalent. It is clear that those which contain a larger proportion of the larger holes, that is, the Archimedean anti-prisms, would have a larger volume, that is, a lower co-ordination, than those which contained the largest proportion, for instance, of tetrahedra. There must, however, be some limits and some law connecting the relative numbers of each kind of hole. Such a structure is essentially a compact one to be relatively easy to allow for empty spaces, in other words, larger holes different from the strictly condensed hole system.

It would be very well worth while to examine the purely geometrical properties of random close-packed aggregates without holes, particularly in relation to kinds of lines that can be drawn through neighbouring points. This should be one of the first tasks of the proposed *statistical geometry*.

Further, the holes are not absolutely discrete, they merge into each other and if we concentrate on the smallest holes of all, the tetrahedral kind, they may be considered as an aggregate of tetrahedra packed together sharing triangular faces. These arrangements I have called (1960) *pseudonuclei*, the ‘pseudo’ aspect being that, unlike true crystal nuclei, they cannot be continued indefinitely, except in

one dimension leading to a triple helix, as shown in figure 12, plate 14, but must gradually merge into irregularity and therefore can continually replace each other. Study of the large model shows that the pseudonuclei are not necessarily discrete structures. They are so, indeed, only if links < 1.1 of the minimum are counted. With a greater tolerance of distances from 1.1 to 1.4 they tend to join up to build the whole structure, wrapping themselves so to speak around the larger holes. A pseudonuclear aggregate will, in fact, have even higher density than can be found in the regular arrangements which contain almost the proportion of two tetrahedra to one octahedron. Those containing tetrahedra only would have an ideal density which is some 15% higher.

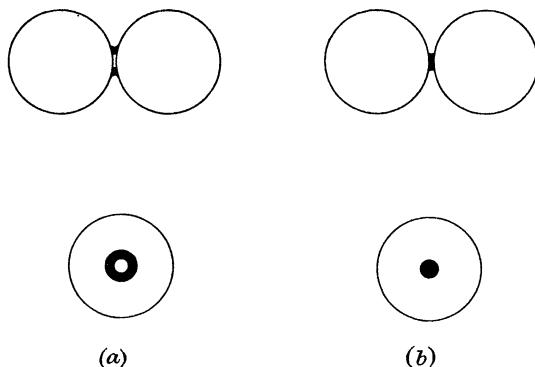


FIGURE 2. Diagram of method of marking (a) close, and (b) near contacts between spheres.

It is by considering such pseudonuclei that we can relate this picture of a liquid to that of Eyring *et al.* (1958) with his small crystals. In fact, his theory does not require that the small particles out of which a liquid is built should be crystalline, only that they should be extremely dense and, therefore, the whole of the rest of his theory can be adapted to this model and may, indeed, be the most convenient way of translating it into thermodynamic terms.

To study the arrangement of close-packed spheres adequately, it is clearly necessary to work on a fairly large scale and to be able to see through the whole structure. This was done in an extremely direct, if crude, way in my laboratory through the ingenuity of Mr Mason. Taking one of the paint-fixed masses of ball-bearings he had prepared, he rigged up a milling machine as a triaxial measuring device and measured directly the co-ordinates of about 1000 balls in the mass to an accuracy of 1%. The measurement was used as a basis for calculating the distances between these balls, carried out by Mr K. Knight on the University computer and from this, using both the co-ordinates and the distances, constructing a scale model which is shown in figure 13, plate 15.

Much has been learned already by a preliminary study of this model. It illustrates the presence of the five minimal holes already found in the smaller models, as well as pseudonuclei. The extremely tedious task of counting the actual number of holes of each category has been carried out by Miss Shirley King.

The results are shown in table 2. This shows that in the close-packed assembly the number of tetrahedral holes absolutely predominate by number and also by volume, though less so. An adequate theory of random distributions should enable these proportions to be calculated but pending that these empirical ratios may be of use.

TABLE 2. PERCENTAGES OF THE FIVE POLYHEDRA OCCURRING IN
THE LARGE BALL-AND-SPOKE MODEL

type of polyhedra	symbol	no. %	vol. %
tetrahedra	A	73.0	48.4
half octahedra	$\frac{1}{2}B$	20.3	26.9
trigonal prisms	C	3.2	7.8
Archimedean anti-prisms	D	0.4	2.1
tetragonal dodecahedra	E	3.1	14.8

The model is sufficiently extensive to bring out other features such as collineations and holes. The former consist of long strings of molecules in more or less straight lines. This is a consequence of the symmetry of the fairly high co-ordinations around each point. If, around any of these, for every vector there is another vector approximately equal and in the opposite direction, a continuation of this will give rise to straight lines of molecules, ranging up to eight in number but apparently averaging at four. Some of these are marked on the big model (figure 13).

When the model was first made it was noticed that there were inevitably a few mistakes, balls which had been wrongly numbered and which could not be properly put into the picture. In some cases the correct co-ordinates could be found but in at least six they could not. However, when the structure was looked at it was found to contain a larger number—ten—of fairly large holes. Only six of these could have been filled by the wrongly numbered balls and the others must have been genuine holes. The occurrence of these holes can be considered as the kind of accident which might occur in the structure of a real liquid, especially at higher temperatures, that is a mutual arrangement which is sufficiently symmetrical to be stable, a kind of dome of atoms. Hill (1958) has shown that the probability of the occurrence of these holes can be calculated from statistical arguments and that information on holes and cells in real liquids can be derived from their experimental radial distribution curves.

Calculations from our big model showed that the results obtained by the smaller ones could be further refined and were essentially correct, namely, the range of co-ordination numbers. Some of these are shown on the three separate models (figure 3) which give the two extremes and the mean co-ordination, one which has five close neighbours, one—the commonest form—which has eight and one with the highest, which has actually ten. The relative numbers of these are fixed for the particular closest packing arrangement but must clearly be a function of the degree of packing.

When this model was being made, we learned that Professor Scott (1962) had carried out an essentially identical measurement with ball-bearings with technical differences of using wax instead of paint and measuring by an optical rather than a mechanical method. His measurements and ours have been interchanged and it

is at least shown that within the limits of the method the results are identical. Both radial distribution functions correspond within the limits of experiment, with that found for ideal liquids by X-ray scattering methods, as shown (figure 4).*

We may therefore say that the first question of what is a structure of liquid, at least of a simple liquid, has effectively been solved. The hypothesis of homogeneous

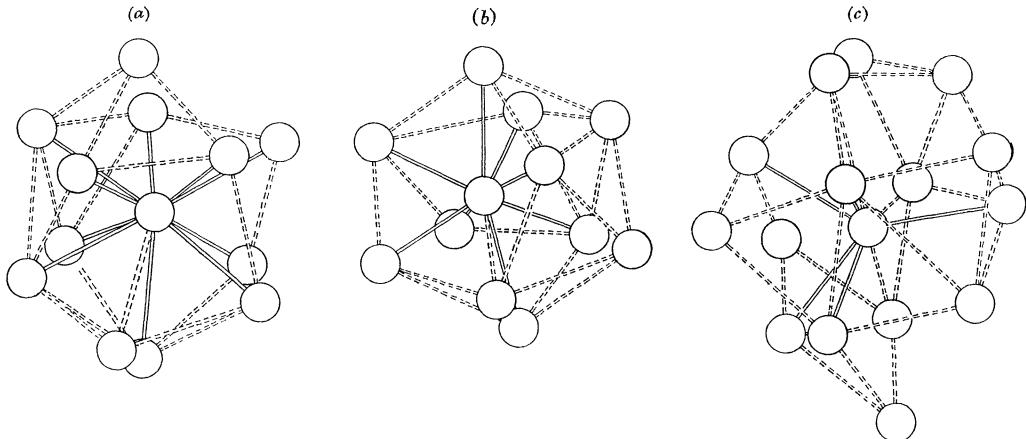


FIGURE 3. Some different co-ordinations occurring in the model. (a) ten close neighbours, (b) eight close neighbours, (c) five close neighbours.

— close neighbours. ······· more distant neighbours.

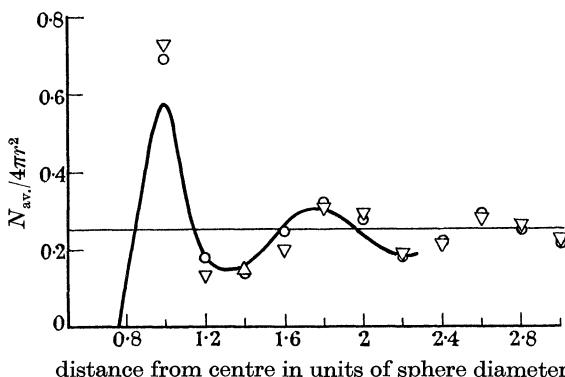


FIGURE 4. Radial distribution of random close packing of equal spheres. $N_{av.}$ is the average number of spheres in intervals of 2 sphere diameters. —, Calculated for liquid argon from neutron diffraction; ∇ , calculated from Scott's random model; \circ , calculated from Bernal's random model.

* Professor Scott has (1964a) subsequently analyzed his model for the average angular distribution function, the co-ordination of first, second and third neighbours in random close-packing. The results are shown in the accompanying figure 5 (Scott 1964a). This shows some approximation to the angular co-ordination distribution of regular structures; in particular it helps to explain the occurrences of the collinearities noticed in our model. If in a co-ordination arrangement there is a perceptible probability of finding a point within a cone of say 15° from the opposite pole of any other, then these three points will be approximately collinear. This arrangement continued will give a line at which no angle of more than 15° will occur. The number of such collinearities is correspondingly arbitrary. Our observations have shown them to be approximately four or five. This fits in with Professor Scott's computations.

coherent and essentially irregular assemblages has been justified. We cannot consider this an absolute proof, but at any rate it cannot be disproved on the basis of the scattering results alone. As will be seen, it fits very well with other results of the properties of liquids.

It should be evident from a study of the models alone that a characteristic of irregular close-packed aggregate, or, indeed, irregular aggregates of all kinds, is that the *co-ordination is itself a variable*. This I believe to be an *essential* distinguishing feature of the liquid state.

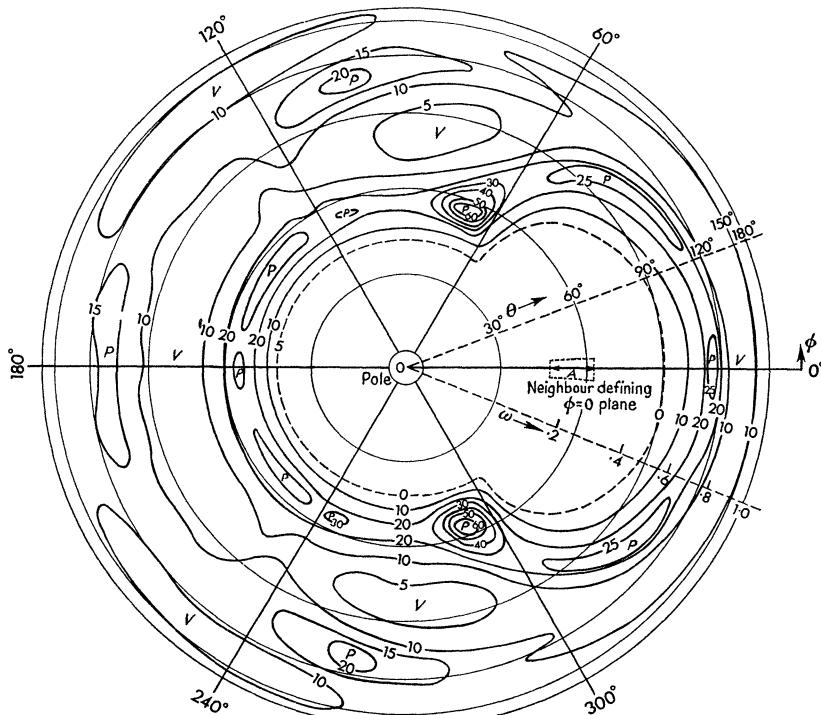


FIGURE 5. Contours showing the complete average angular distribution of the first shell neighbours. θ is polar angle, ϕ azimuth; P is a peak, V a valley (Scott 1964).

From it there follows another corollary, that whereas in the regular packing of crystals, the characteristic depends on the quasi-equality of the types of atom that compose them, in a liquid this is no longer the case. Everything that has been said so far about the packing of *equal* spheres could be applied without substantial difference to the packing of *unequal* spheres except when the degree of inequality is such that the smaller spheres have a free play among the larger ones, so that they would constitute, so to speak, a gas enclosed in a liquid. In fact, the degree of close-packing of models with unequal spheres is necessarily greater than that with equal spheres. If we imagine any arrangement with a different co-ordination, then it would be clearly possible to replace those of larger co-ordination with larger spheres without changing the general arrangement and therefore to include more mass in the same volume. The concept of *purity* has consequently far less

relevance for liquids than it has for crystals. The process of crystallization itself shows the necessity for atoms or molecules of approximately the same kind, but in liquids a wide variety is possible. In fact, there are probably two—or at the most three—kinds of simple liquids which can be absolutely separated from each other all over their phase field, metallic liquids, ionic liquids and, to a certain extent, homopolar liquids. All others, even if immiscible, taken in pairs can be shown to be parts of extended phase fields. As Furukawa (1959, 1960) has shown, for instance, nearly all the metallic liquids have essentially the same structure.

How can variety of co-ordination in a liquid be understood mathematically? A theory such as I have put forward so far would not appeal to the mathematical physicists or even to the physical chemists. It lacks the essential quantitative character, it is really only a geometrical picture of what a liquid structure might be like. There is always a conflict between the mathematical physicist who must work with manageable mathematical expressions to arrive at numerical results and those favouring geometrical or mechanical methods which are probably closer to the real state of affairs but are mathematically difficult to reduce to any computable values. Nevertheless, I feel that it is better to start with a geometrical model and find out how to express its behaviour by approximations based on the model than to try to use the model by the postulation of mathematically manageable functions. Certainly in the case where the model arrived at in this way can be demonstrated by physical methods to deviate from the facts. I feel that the solution to the problem of liquid structures really falls into two parts, a geometrical part and a physical and thermodynamic part. So far I have only considered the former, and further limited it to considerations of the highest density state or random close-packing. As such it takes no account of the temperature movement of molecules (see p. 315). The latter, at least in principle, has been attacked—successfully, I believe—by Dr R. Fürth whose paper is being published elsewhere (1964). He bases the statistical mechanics of such a system on a mathematical model with a number s of locations and a number v of elements, molecules or atoms, which can fill these locations, and tries to derive a ‘next-neighbour distribution function’ $f(n)$ for the number n of nearest neighbours to a specified particle, a way in which the geometry is specified only statistically and the variation of the co-ordination is made the central feature.

In some sense his theory is a hole theory but holes are not now stipulated to be holes in any regular kind of lattice. They can be holes in the kind of random lattice which I have suggested. If we imagine the close-packed crystalline state to have a value s of 12 and a co-ordination number n of 12 also, then there are only two ways of arranging it, cubic and hexagonal, and in each every molecule has 12 co-ordinations. If, however, s increases up to, let us say, 20 there is a wider and wider range of co-ordination running from 4 to 12. The statistical weight $\omega(n)$ of all nearest neighbour arrangements belonging to the same co-ordination number n can be calculated according to the combination formula

$$\omega(n) = \frac{[v!(s-v)!]^2}{n!s![v-n]!^2(n+s-2v)!} \quad (n \leq s),$$

which is plotted, for various values of s , in figure 6(a). The quantity s is closely related to the free volume of the structure.

The theory cannot, by itself, go farther than this at present in determining the structure of the irregular aggregate. To do so it would require to be supported by pure statistical geometry, to enable us to find the actual volumes that provide the apparent number of alternative positions. However, it is possible to match the

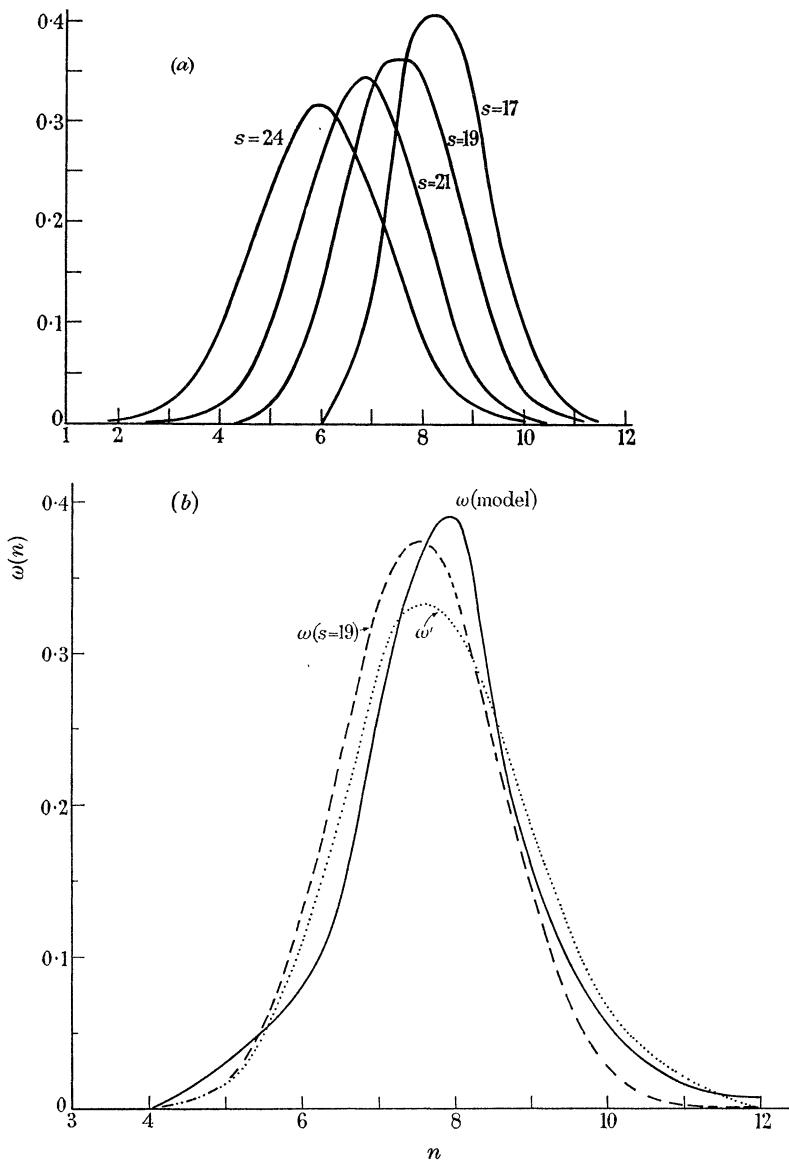


FIGURE 6. (a) Exact geometrical distribution function $\omega(n)$ for $\nu = 12$ and various values of s .
 (b) Comparison of the empirical distribution function ω (model) of close-packed spheres according to Bernal & Mason with the exact theoretical distribution function $\omega(n)$ for $s = 19$ and the approximate distribution function $\omega'(n)$ having the same values of \bar{n} and σ^2 as ω (model).

curves for the co-ordination distribution $\omega(n)$ with those taken from the model. It would seem (figure 6(b)) that $s = 19$ gives the best approximation to the random close-packed arrangement of atoms.

In order to develop a thermodynamic theory of the liquid state the interaction forces between the particles have to be taken into account. It can be shown that the next-neighbour distribution function $f(n)$ can be broken up into two terms: $f(n) = \omega(n) w(n)$. We have already discussed the term $\omega(n)$ which gives the static co-ordination distribution; the other term has the form of a Boltzmann factor $w(n) = e^{\epsilon_n/kT}$ (where ϵ_n is a molecular interaction energy) which contains the

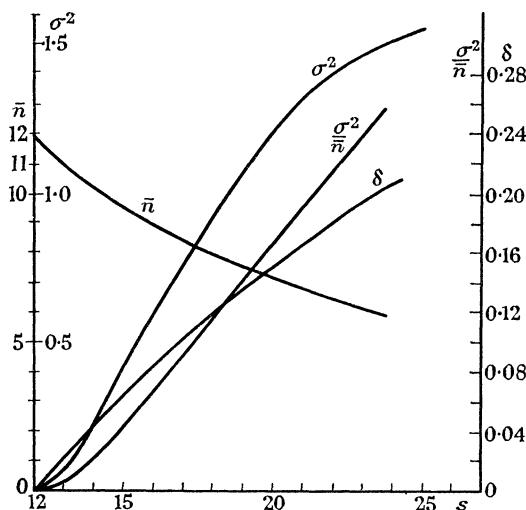


FIGURE 7. Dependence of the mean value \bar{n} of n its variance σ^2 , σ^2/\bar{n} and the width $\delta = \sigma/\bar{n}$ on s according to the geometrical distribution function $\omega(n)$ for $\nu = 12$.

variation of n due to temperature. The partition function Z of a system of N particles is now obtained from

$$Z = [\sum_n f(n)]^N Z_0 = [\sum_n \omega(n) e^{\epsilon_n/kT}]^N Z_0 \quad (Z = Z_0 \text{ for } \epsilon_n = 0).$$

In order to get the relevant formulae in analytical form, Fürth replaces the function $\omega(n)$ by an approximate function $\omega'(n) = C e^{-an} n^b$ which closely resembles $\omega(n)$ if the two constants a and b are related to the mean \bar{n} of n and its variance σ^2 by the relations $a = \pi/\sigma^2$, $b = (\bar{n})^2/\sigma^2 - 1$. \bar{n} and σ^2 in turn can be calculated from $\omega(n)$ as functions of s and are shown in figure 7. From Z one can derive all the thermodynamic properties of the system over the whole range of its stability.

Fürth's theory, though not an absolute one, is far from being merely empirical. The data with which it works are not derived from measurements on any liquid but contain only measurements from the model of random close-packed spheres. It does not, moreover, involve expressions for the mutual potential of two molecules and is therefore only a formal statistical theory of random close-packing.

Pending the formulation of a full thermodynamic theory we can, however, see what makes a liquid what it is, that it is really a particular kind of disordered arrangement of objects of the same or different sizes which are subject to heat motion. The nature of this heat motion is itself another question because we now have a certain amount of experimental evidence to add to theory as to the character of liquids. What has impressed people from the dawn of time about liquids and, in fact, gives rise to their name of fluids and all their mechanical properties—is their ability to flow or, in more scientific terms, inability to stand any kind of shearing stress, but to yield instead steadily under shear at a rate which is an expression of the fluidity = $1/\text{viscosity}$ of a liquid. Now it is evident that this does not and cannot affect any of the pictures already given of the structure of liquids because the transport phenomenon, the yield and shear of a liquid, is a phenomenon several orders of magnitude slower than the mainly vibrational thermal motions of the atoms in the liquid. This is a situation quite unlike that of a gas in which the velocity of sound and the velocity of the molecules are of the same order of magnitude*.

The study of inelastic neutron collisions with liquids by Henshaw & Woods (1961) and Egelstaff *et al.* (1957, 1961), show that for sufficiently high frequencies a liquid behaves like a solid; in other words, it has a whole range of phonon spectra very similar to those of a solid though without the abrupt changes which characterize the Debye spectrum in a crystal. It is, so to speak, a smeared out Debye spectrum due to the absence of long-range order which gradually fades as the liquid is heated and reaches the critical point. At the same time there appear, at low values of the energy loss, diffracted neutrons indicating the presence of virtually free molecules or groups of molecules and indeed even under the extreme conditions of compression, there are probably a small number of free molecules in every liquid.

It is not too difficult to see qualitatively what the actual geometrical structure will be at higher temperatures. At temperatures far from the critical point where the maximum density is exceeded only by a few parts per cent, expansion would take place, not primarily by an increase of distance between molecules but by the expansion of the holes between them. A greater proportion of larger, trigonal prism or Archimedean anti-prism, holes in itself would give an expansion up to about 17 %. At higher volumes still the five canonical holes would be supplemented by icosohedral and larger holes still while preserving the same minimal distance between molecules. This is in accord with the analysis of X-ray diffraction from liquids at higher temperatures which show about the same mean distance between molecules but a smaller number in the first co-ordination sphere. These larger holes can be expected to be filled by individual or small groups of free molecules behaving

* Professor Scott (1964b), has used, to elucidate the viscous properties of simple liquids, an experiment in which some 16000 ball-bearings were placed at random in a box, the parallel sides of which could be sheared. The randomly arranged ball-bearings showed very low resistance to shearing. This rapidly grew and he has demonstrated that this was due to regular arrangements occurring in the mass leading to the formation of mono-crystals. I have subsequently studied this phenomenon more closely and shown that the nuclei of these crystals are formed on the bottom and sides of the box but they are caused to grow by each shearing motion adding more balls in regular positions (see figure 14, plate 16).

like a gas in a very restricted room. This picture, however, is purely qualitative. It might be approximated to by removing molecules at random from the close-packed model. However, adequate thermodynamic theory would have to consider the energy and the entropy of all such arrangements.

All through, the mean co-ordination will be a function of the temperature and the range of co-ordination will gradually shift to lower values. When a co-ordination value of three or four is passed, then all intrinsic coherence is lost. This is the equivalent to the critical point where all liquids seem to have a volume approximately $3\frac{1}{2}$ times their volume at lowest temperatures.

The nature of the coherence of a liquid seems to be much more dependent on its volume than on the temperature. Some early measurements by Stewart (1933) on

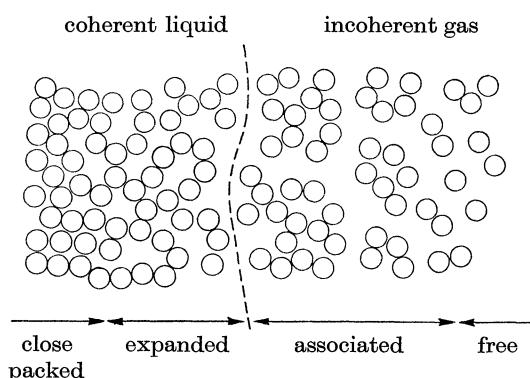


FIGURE 8. Diagram of transition of molecular arrangements passing from close packed liquid to gas through hypercritical line.

the X-ray diffraction of liquid ether show practically no alteration over temperatures on varying through the critical point, as long as the volume has remained constant, but showed wide variations at the same temperature with change in volume. There is a sharp distinction between the steady fall off of scattering with angle characteristic of a gas and the appearance of the first maximum indicating a probable near neighbour distance in the liquid. The kind of transition one might expect between the liquid and the gas around the critical point is shown in figure 8. It is now known, from the work of Jones & Walker (1956), that the critical point is only one point on a line, which may be called the *hypercritical line* (figure 9), which indicates that there is this sharp distinction between liquid and gas at temperatures at least up to three times the critical point, and probably more as shown on some of the steam tables. The difference in the critical point is essentially due to the coherence at the surface which provides the physical distinction between the volume occupied by the liquid and the volume occupied by the gas.

A clue to critical-point phenomena may indeed have been furnished from the ball-bearing models previously mentioned. It is very difficult to make these fully irregular in any kind of vessel or container with smooth sides. Even a balloon which we used produced on its surface regular crystalline patches (figure 15,

plate 17). An attempt to make such surfaces by introducing into the balloon an actual regular circular plate of brass, showed effective nucleation of crystals several layers thick (figure 16, plate 17).

Now the interesting observations of Scott (1960) have shown that the apparent density of a sphere filled with ball-bearings decreases with the size of the sphere. In other words, the effect of the surface is to increase the mean density because the more surface the more densely packed material of solid density and the less irregular material. A detailed study of a ball-bearing specimen, examined in this way, showed that beyond the eight or nine layers of regularly packed molecules, and before the structure reaches the average density of a completely disordered

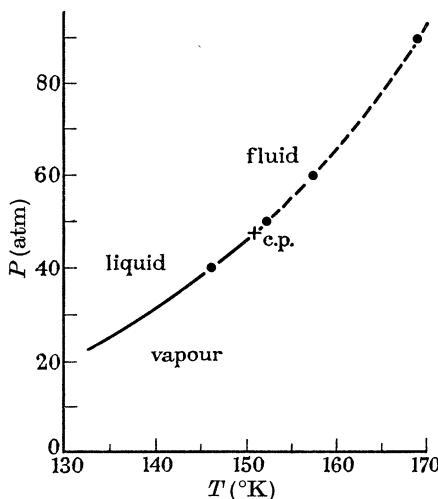


FIGURE 9. Variation of pressure with temperature for argon; position of the anomalous points showing a hypercritical line extending the boiling point line (Jones & Walker 1956).

array, there is a misfit region of particularly low density. This may or may not actually exist in liquids. We cannot be sure because heat motion even at low temperatures can destroy this regularity. If the regularity exists, however, it would explain a certain possibility of concentration of foreign atoms in the region just below the surface through their pushing out by the most stable arrangement of the surface atoms.

The concept of the free surface of a liquid being normally covered by a crystalline layer is new and possibly far reaching. How true it is depends on whether such a crystalline layer could be maintained against a heat motion. If it were so, it would explain in a rather simple way the phenomena of the critical point where there is a difference, a sharp difference, in the appearance or the disappearance of a free surface without a correspondingly large difference in the change in state above and below the critical point, as has already been mentioned. It would indeed be surprising if any valid molecular theory of liquids did not have a great deal to say about surface tension as well.

What happens at the lower temperatures is also one of the new ideas introduced from this model. In Dr Fürth's theory, the thermal term indicates that as the

temperature falls, the ultra dense pseudonuclei will increase in volume relative to the more disordered and emptier regions separating them. Further, Fürth's theory indicates that for every liquid there will be a new temperature instability, this time at low temperatures beyond which the density of the solid parts reaches its limit and the liquid would become unstable and break up into a mass of crystals separated by quite large empty spaces.

This has never been precisely observed, but the recent very careful studies by Mason (1961) indicate that for a well-studied liquid, namely water, it is intrinsically impossible to maintain it in the liquid form below a fairly precise temperature of -41°C . This figure is achieved by extrapolating the spontaneous crystallizing temperature of water as a function of the size of drops. For very small drops at any temperature below -41°C , complete crystallization would take place. It is evident that if any kind of stability can be reached in a drop containing only a hundred or so atoms, it is more likely to be pseudocrystalline than crystalline.

Such extreme precautions are necessary—on a small scale—to maintain liquids in this state of suspended crystallization, although not at all on a large scale for we have all seen the clouds floating overhead and not realized that they are practically water super-cooled down to very near its super-cooling limit. It may, however, happen that the viscosity of a liquid gets so large long before the super-cooling limit is reached, that the liquid never reaches its basic equilibrium but already turns into a glass at a higher temperature.

This is probably the explanation of a phenomenon, well known in practice, of the induction or destruction of crystals by use of additives. We can call them mineralizing agents, such as fluorine or borates, which lower the viscosity when we are trying to make something crystallize. There are also agents with the opposite effect which raise the viscosity. These are the inhibitors, such as sugar, which are used when we want to produce effectively a glassy state.

The general properties of liquids can be accommodated very well with the picture I have given for their structure, making the appropriate alterations for different types of liquids. Eyring's theory (1936) of viscosity as a chemical reaction process fits very well with the substitution of the pseudonuclei to the true crystal nuclei which he postulated, but without making use of their crystalline properties. Similarly, the electrical properties of liquids would follow from the crystal analogy, such things as Brillouin zones being smeared out, so that every crystalline property has its analogous property in the liquid.

If, from the strictly structural point of view there are no major differences between kinds of liquids, this is clearly not true from the physical and physico-chemical points of view. The major difference observable is between that of the molecular liquids on the one hand, together with some of the ionic liquids, and the metallic liquids on the other. In the latter case the properties of the liquids, apart from their mechanical properties, are far more like that of the solid than in the other cases. This is because, essentially, a liquid metal is a mass of free electrons in which the rare-gas-like positive ions are suspended and where the particular volume or domain occupied by the ions is a relatively small part of the structure. As a consequence, the volume changes on melting are very much less. To put it in

another way, the distance apart of atoms in a metallic crystal is fixed by the electron wave functions controlled by the fermi surfaces. When it is melted the cores can approach each other to smaller distances than they would in the crystalline case. The sodium ion, for instance, has a radius of approximately 1 Å, whereas sodium atoms in the crystalline state of metallic sodium are separated by distances of 2 Å. In the liquid it would obviously approach much closer so that the mean distance as shown by the neutron diffraction is only 1.5 Å.

The structure of some ionic liquids also have been studied. It would appear here that the basic character is determined by the packing of the large negative ions which behave essentially like gaseous ions, the small, positive, metallic ions fitting in general into smaller tetrahedral interstices according to Goldschmidt's principles.

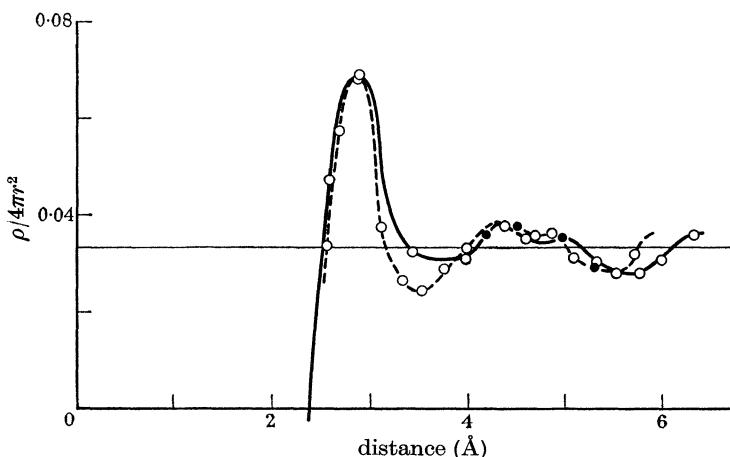


FIGURE 10. Radial distribution function for water calculated from ball and spoke model (---) compared with observed (—).

In organic or truly molecular liquids, differences may occur as a result of the capacity of complex molecules to pack fairly closely together in the solid state, where there is little rotation, and to change their volume very much on melting as the effective volume becomes on rotation that of the circumscribing sphere. For instance, the expansion on melting of sulphur hexafluoride is 36%—the difference between neatly fitted fluorine atoms in the one case and the completely rotating sulphur hexatetrafluoride molecules on the other.

In the case of very complex molecules, the tendency of the rotating molecules themselves to pack in parallel will be accentuated, leading into the formation of liquid crystals. There may even be certain more or less fixed pseudonuclei which operate as larger molecules. In general it might be said for very complicated molecules that it is likely that the mutual potential of two such molecules forming a pseudonucleus will be greater than if they were arranged in larger numbers in a crystalline order. That is, melting, itself, may be a multistage process, which would explain some of its anomalies.

Curiously enough, the most typical liquid, water, the one which is the basis of all our ideas of liquidity, belongs to a particular group of molecular structures

where the forces between the molecules are directed, in this case, by hydrogen bonds. As I was able to show many years ago (Bernal & Fowler 1933), this results, not in a close-packed co-ordination, but in a loose tetrahedral co-ordination. Here, the irregularity is not in the co-ordination itself, but in the rings that are formed by co-ordinated molecules. Mostly on account of the internal structure of the molecule, these rings usually contain five members. This is a justification for Pauling's dodecahedral model for water, but, in my opinion, his model is too regular and would correspond rather to a crystal than to a liquid. My picture of water now is that of a network of linked four-co-ordinated molecules forming rings of four, five, six, seven or even more molecules arranged in various sets of random order and, consequently, complexly responsive to temperature and pressure changes, leading to anomalous expansion at low temperatures.* This seems also to be true in general for glasses, where the bonding at high temperatures may be through metal-oxygen rather than hydrogen bonding.

The problems of transport in liquids can be treated in a number of ways, some of which have already been mentioned. One, which emerges from the study of the large model that has just been completed, indicates that it may be profitable to seek a solution along new lines. This has shown the presence, on the one hand, of holes, and on the other, of collineations of molecules. Now, the hole theory of viscosity was first explicitly expounded by Fürth (1941) twenty years ago; however, he then considered the holes to be essentially hydrodynamic entities. If they are also structural entities then the possibility of the movement of holes is very much enhanced. If there is a collineation which ends at a hole, as in many cases it will, then a whole group of atoms may move together along their common line to fill that hole and create another hole at the other end of the collineation. This will give rise to a very rapid virtual movement of the holes and to an effectively long mean free path, at least of four or five atomic diameters.

It is clear that the picture that I have just given of a liquid is one which could be followed up, to study many of their properties both experimentally and theoretically.

In drawing this lecture to a close, I would like to summarize the essential features that have emerged from this study. The original concept of liquid being essentially a *heap* of molecules, that is, being *homogeneous* and *continuous* without containing hypothetical regular inner structures, has been well substantiated for, at least, monatomic liquids. This is compatible with, and in my opinion really implies, the absence of long-range order. There is no reason, other than convenience, for mathematical treatment of long-range order as being the only kind of

* I have gone farther with this picture, basing myself in particular on a new analogy between the structure of water and the four-co-ordinated structure of forms of silica. Previously (Bernal & Fowler 1933) I had taken water as intermediate in structure between quartz and tridymite, taking the structure of ice as that of tridymite; at density 0.92 quartz would appear to be density 1.08. Recently a new form of silica has been discovered, keatite, also with a density of 2.50 g/cm³ intermediate between that of quartz and that of tridymite; it would come out on the same scale as that used above as 1.01 g/cm³. In models of disordered keatite we have been able to show that to a first approximation they give the same distribution function as that of liquid water (figure 10).

order. It is clearly very much less probable than short-range order and long-range disorder.

This, in turn, implies the irrelevance of the more distant part of the interaction curve between atoms in considering the property of a liquid. The structure of a liquid, in this view, depends primarily on the repulsive elements of the potential and only secondarily on the attractive effects and on the external pressure which can be added together.

The picture of liquid structure arrived at here can be made more than a qualitative one by the addition of the free volume considerations introduced by Fürth, which could clearly be much further developed, leading possibly to a complete theory in which it was not necessary to arrive empirically or purely geometrically at the mutual random arrangements but rather to deduce them directly from the interaction potentials and external pressure.

For instance, it should be possible to use the random positions arrived at by packing experiments to start an order-type Monte Carlo approach with a much larger number of initial points if the machine capacity was sufficient to cope with a significant number.

The chief value I would attach to the present approach is that it links a way of treating liquids with that of crystalline solids. It has already been so far advanced and gives a picture which is not really formal but a material representation in space of the instantaneous positions of the molecules in a liquid.

I wish to record my grateful thanks to the D.S.I.R. for financial support which enabled the research to be undertaken on which this paper is based. My thanks are due also to the following members of my research team for contributions to the elucidation of the problems which often involved long and tedious calculations on the one hand, and much ingenuity in respect of materials and design of apparatus on the other: Mr J. Mason, Miss J. Wilkinson, Miss S. King, Mr I. Cherry, Mr K. R. Knight and Mr G. Atkinson.

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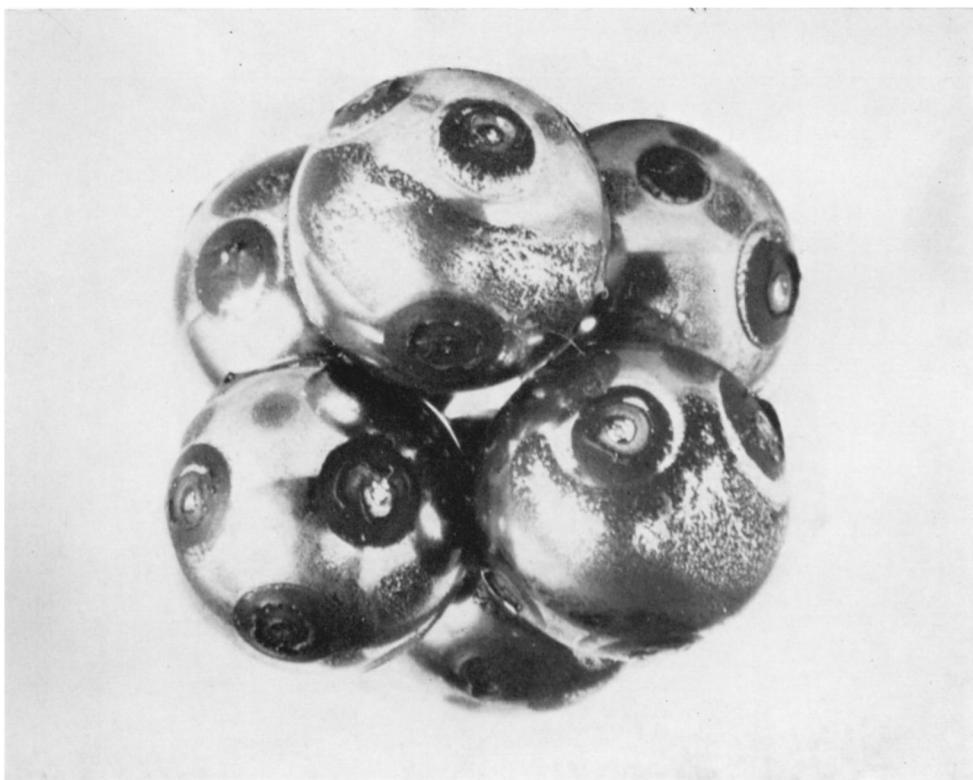


FIGURE 11. Portion of random close-packed ball assembly showing marks of further contacts.

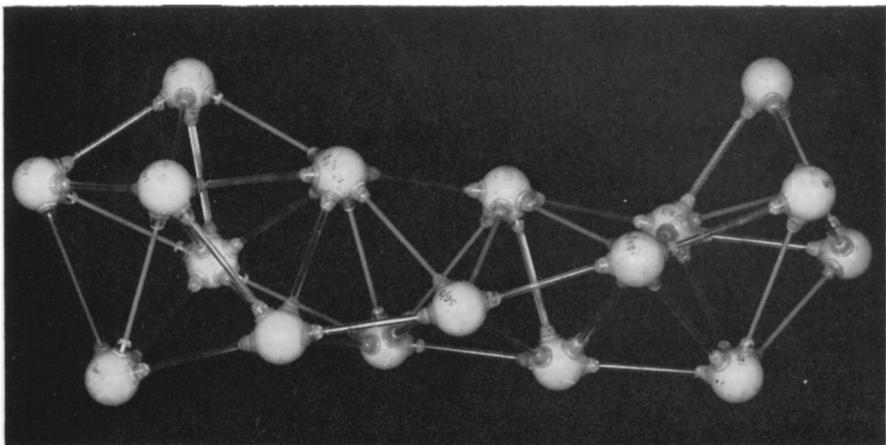
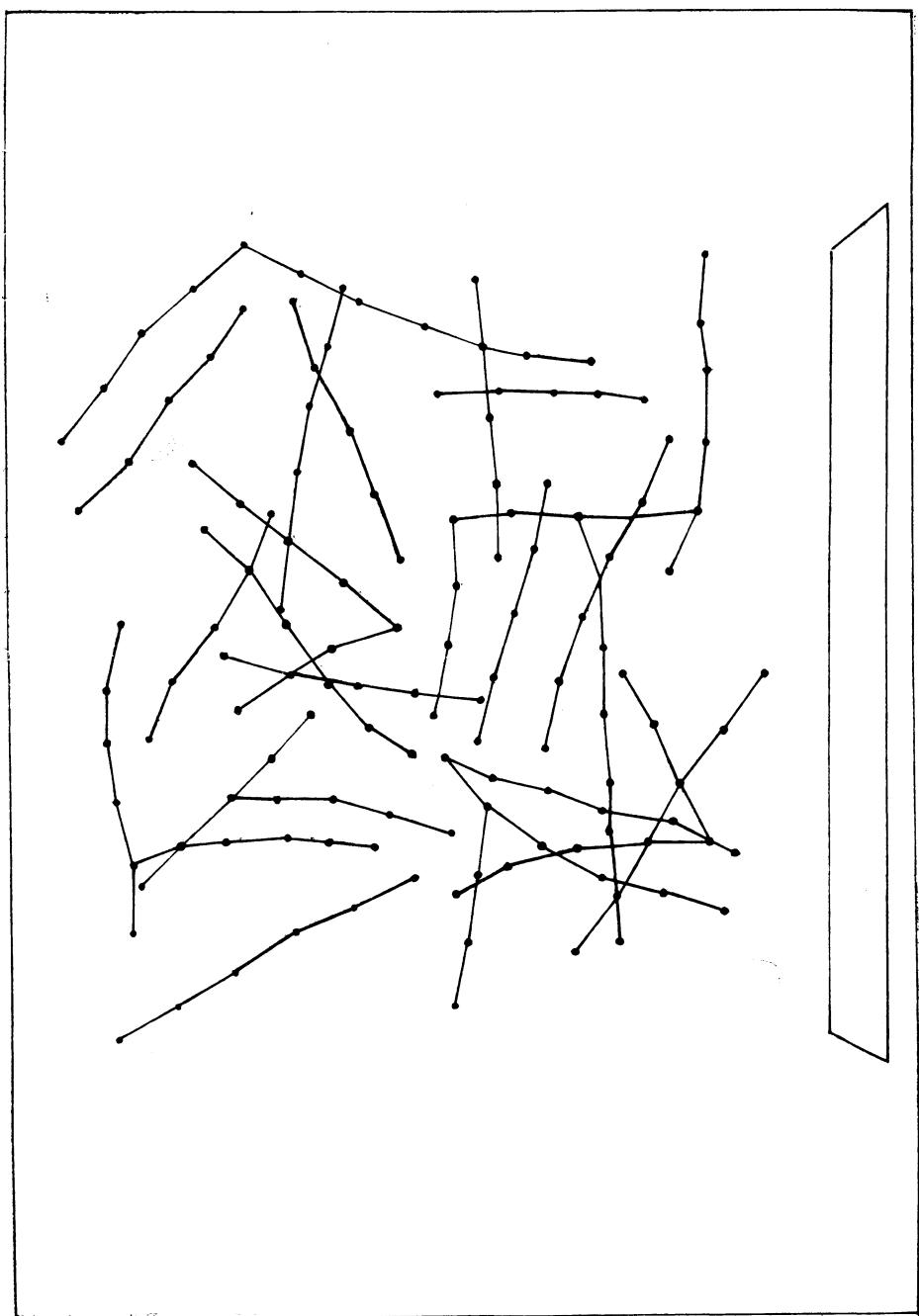


FIGURE 12. Triple helix of tetrahedra showing pseudonucleus from random rigid sphere assembly model.

(Facing p. 322)



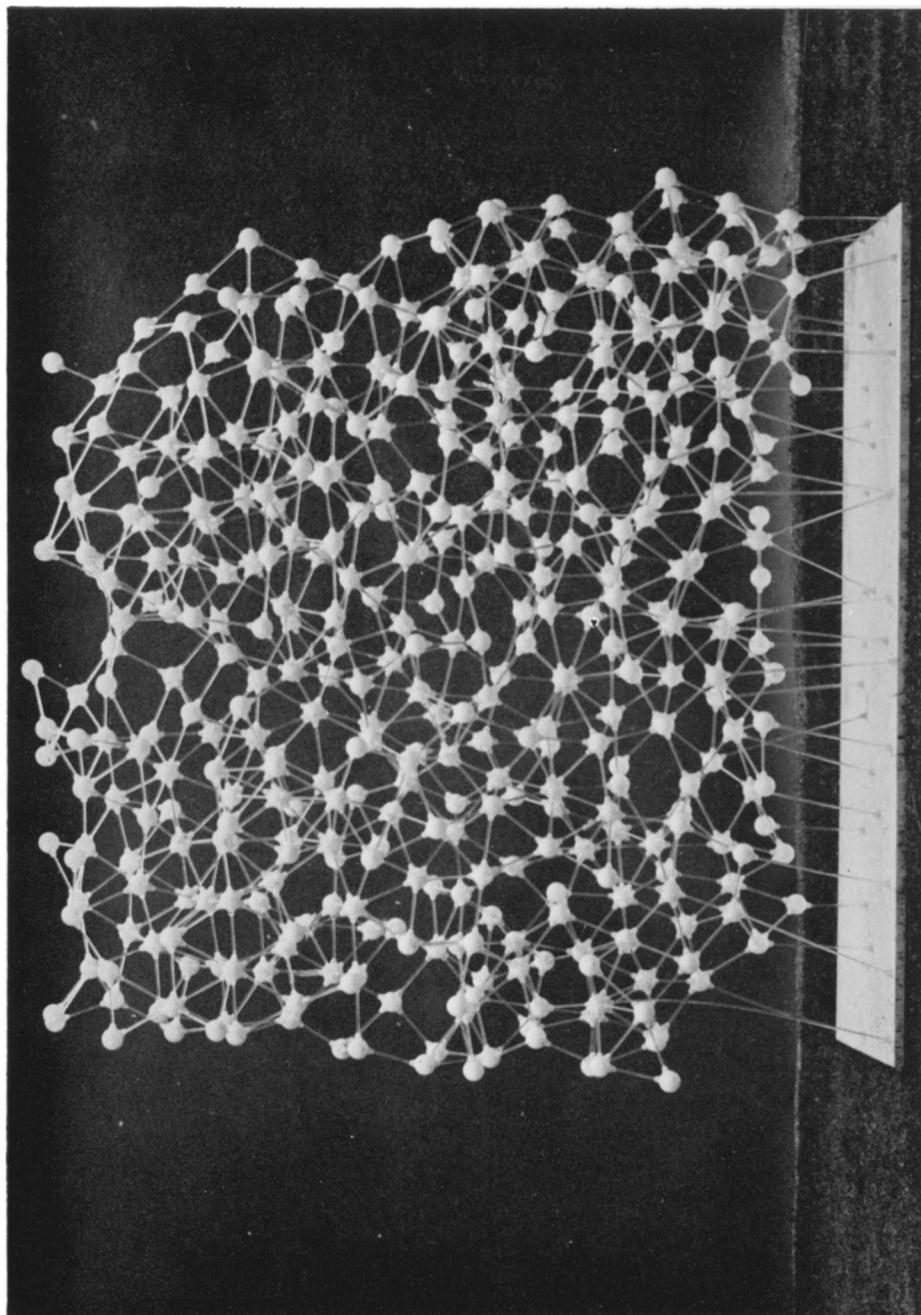


FIGURE 13. Ball and spoke model of random rigid sphere assembly. The transparency shows some of the collinearities which occur in it.

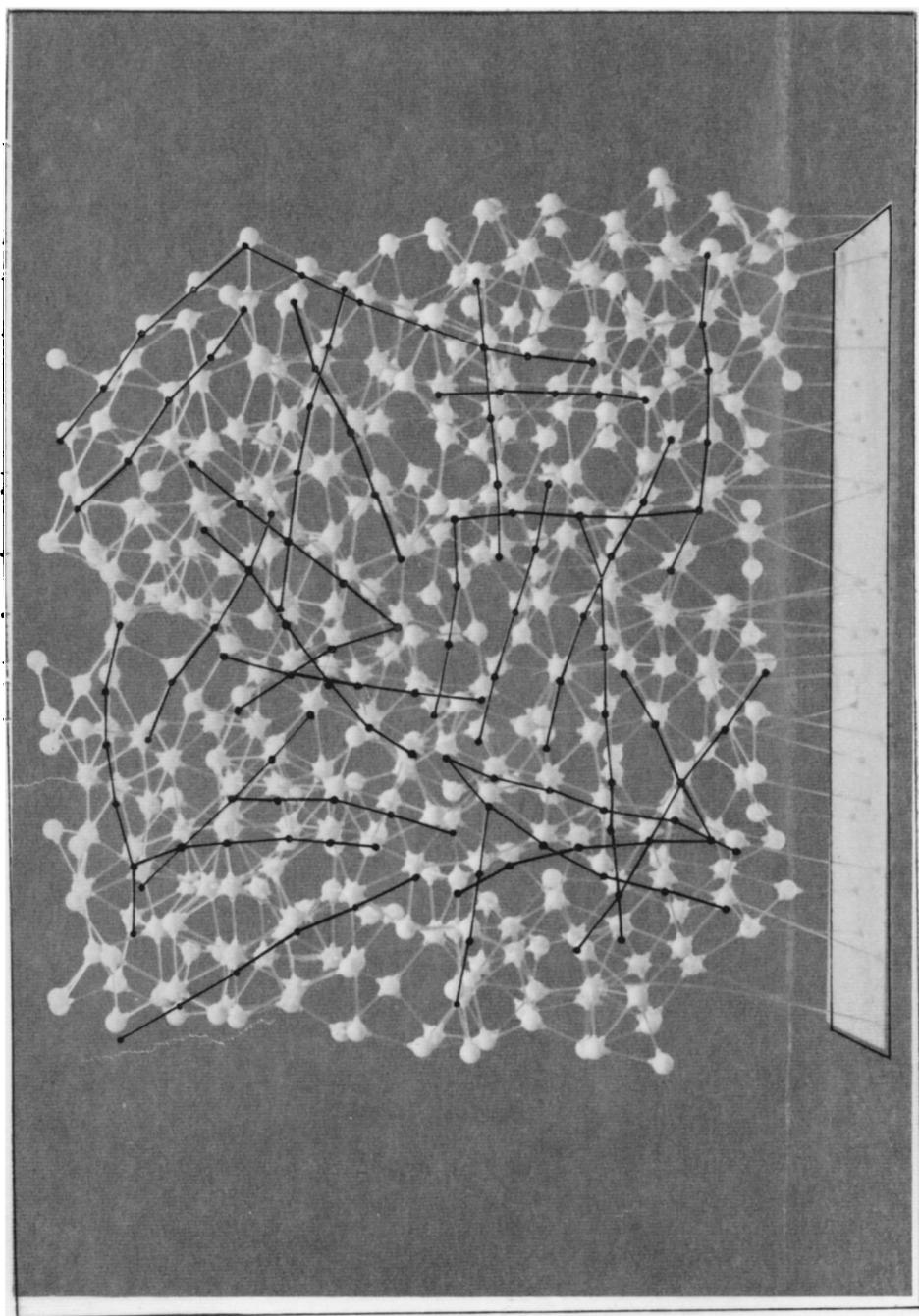


FIGURE 13. Ball and spoke model of random rigid sphere assembly. The transparency shows some of the collinearities which occur in it.

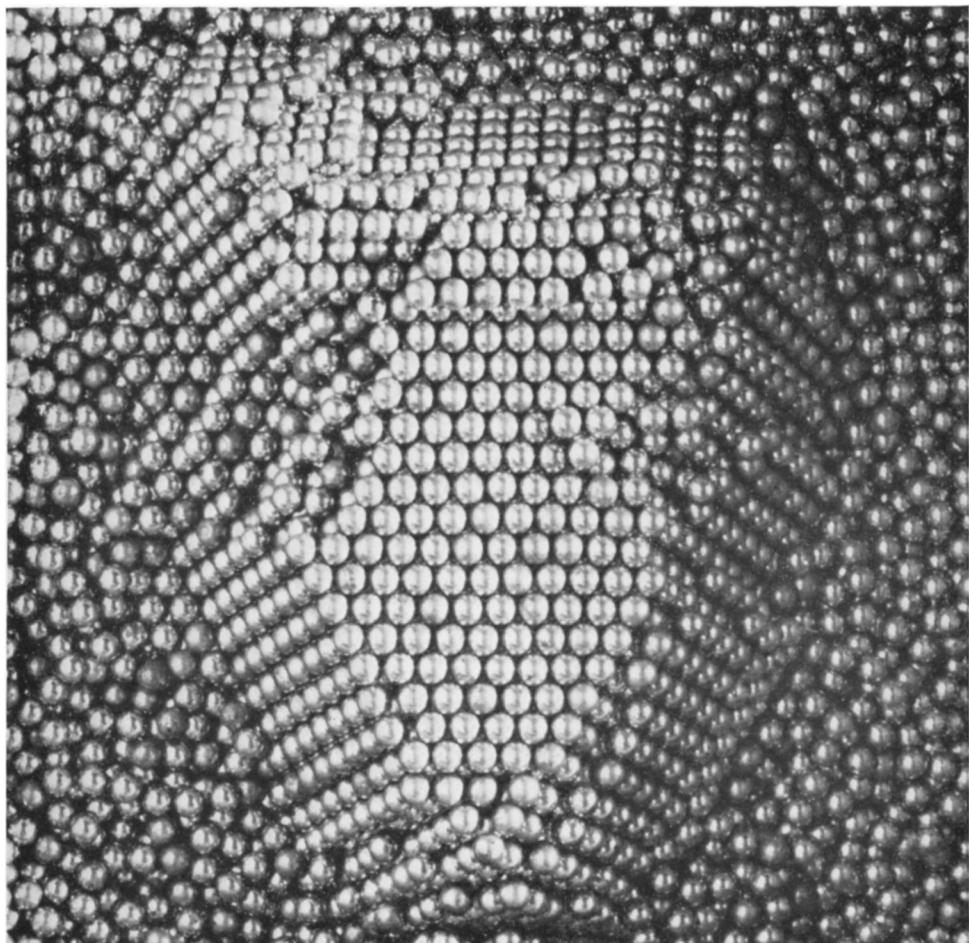


FIGURE 14. Face-centred cubic 'crystal' surrounded by 'liquid' caused by shearing ball-bearing mass. 111 face is shown at the top surface.

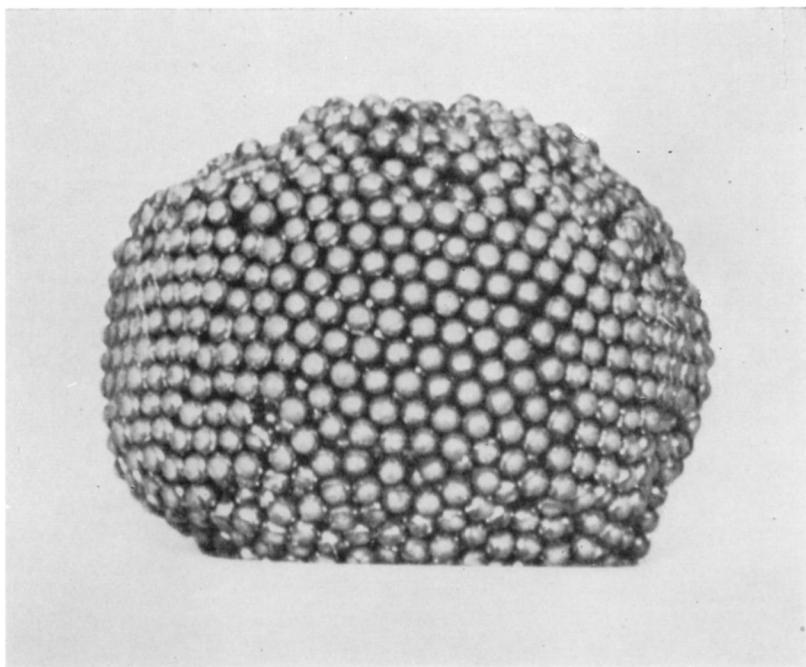


FIGURE 15. Regular crystalline patches induced on the sides of ball-bearing mass due to smoothness of balloon surface.

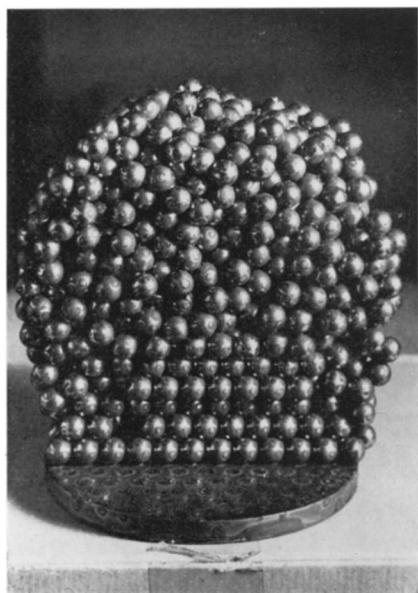


FIGURE 16. Ball-bearing assembly showing transition from random close-packing to regular crystalline array induced by inserting a flat plate.