Bernal and the structure of water

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Abstract. Bernal recognised early on the importance of water in biological systems and processes, and hence the need to understand the structure of the liquid if he was to understand its biological functionality. Although the structure of crystalline ice had been solved only a few years earlier, and little was understood about the structures of liquids in general, in 1933 he published what is still regarded as a seminal paper which treated not only the structure of liquid water itself, but also addressed an impressively wide range of problems of ice and ionic solutions. Imaginatively exploiting ideas that were developing at the time, he proposed a model for water that reproduced the main features of its x-ray diffraction pattern. Despite the success of this model, however, he subsequently found it unsatisfactory – "a delusive approach, postulating a greater degree of order in the liquid than actually exists there". Building on the very successful "random packing" model of simple liquids that he developed in the 1950s and 60s, he was ultimately led to a "random network" model that was consistent with the known properties of the individual water molecules, and that again could reproduce a range of experimental data – but this time without the model being too ordered. Todays state of the art experiments essentially verify the underlying validity of his ideal model. And even his 1933 model of the water molecule itself is mimicked in some of the more successful molecular models used in todays computer simulations of aqueous systems.

1. Introduction

Figure 1, which is reproduced on page 371 of Andrew Brown's biography of Bernal, shows Bernal at work in his office. It illustrates him experimenting in a way that many scientists would consider rather odd. He said himself that he began very naively to try and build models just to see what a structure satisfying certain conditions would look like. He took a number of rubber balls, and stuck them together with rods of different lengths taken at random from a particular distribution of lengths. He tried to do this as casually as possible, being interrupted every five minutes or so in his office and therefore forgetting what he had just done. Despite – or perhaps at least partly because of – these interruptions, the resulting model showed him some critical aspects of the complex system he was trying to understand. What he was trying to do was perhaps the earliest attempt to model the structure of a simple liquid. A liquid in which you consider the atoms to be more or less spherical and pack together in a particular way.

What has this got to do with the structure of water? In contrast to the spherical atoms he was considering in the experiment shown in figure 1, the water molecule is rather more complex. It's not just a sphere. Rather it's a sphere with two 'legs' on it which attract other water molecules in a particular way. In trying to understand the structure of liquid water, these attractive legs influence fundamentally the way in which the water molecules arrange themselves in the liquid. It is the nature of this influence that Bernal explored in two bouts of activity separated by some
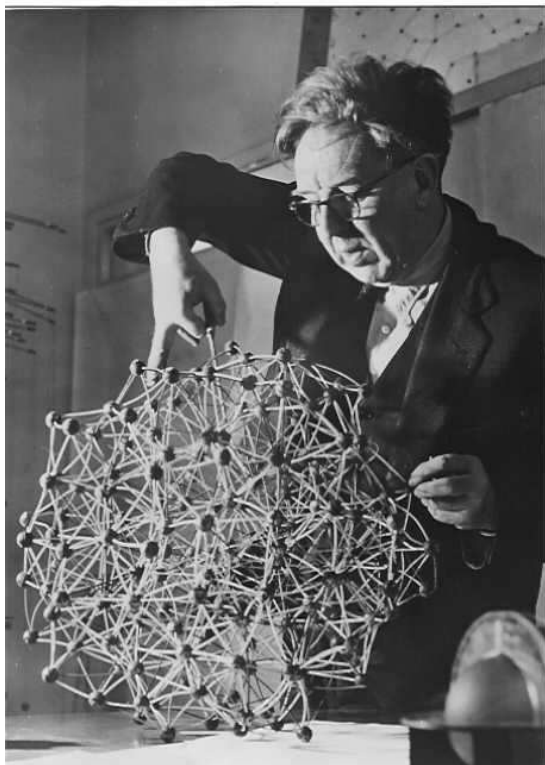
Figure 1. Bernal building a simple liquid model in his office (J L Finney private collection).

SMALL SUMMARY

ON the basis of the model of the water molecule derived from spectral and x-ray data and a proposed internal structure for water, the following properties of water and ionic solutions have been deduced quantitatively in good agreement with experiment.

(1) The crystal structure of ice.
(2) The x-ray diffraction curve for water.
(3) The total energy of water and ice.
(4) The degree of hydration of positive and negative ions in water.
(5) The heats of solutions of ions.
(6) The mobility of hydrogen and hydroxyl ions in water.

And the following inferred in a qualitative way.

(7) The density and density changes of water.
(8) The explanation of the unique position of water among molecular liquids.
(9) The dielectric properties of water and ice.
(10) The viscosities of dilute ionic solutions.
(11) The viscosities of concentrated acids.

Figure 2. The short summary of the 1933 paper.

twenty years.

2. The 1933 Bernal and Fowler paper

The first bout of water structure activity was a seminal water paper published in 1933 [1] which is still regarded as a major contribution to our understanding of the structure of water.

Figure 2 reproduces the short summary of the 1933 paper. As you can see, the paper claims to explain a remarkable range of phenomena related to water and aqueous solutions, to say nothing of the several references also to ice. Today's scientists would be tempted to write several different papers to cover this wide range – we are after all partly assessed on the number of papers we publish, and we have to consider the next Research Assessment Exercise – but characteristic of the man, Bernal saw how this broad range of topics could be integrated into a unified story on the basis of a few relatively simple fundamental concepts. And in 1933, considering the conceptual environment at the time (for example the structure of ice had been solved only three years earlier), this was a tremendous list of things to try to understand.

Of all the items in the summary in figure 1, I will focus only on item 2: the x-ray diffraction curve for liquid water. This is quite simply because this was the only experimental information that was available to Bernal that related directly to the liquid structure he wanted to understand.

As a crystallographer, Bernal knew that scattering x-rays from an assembly of molecules gave information that related to the structure of the molecular assembly. The diffraction pattern measured reports back, in a particular convoluted way, the structure of that system. In the context of the time, however, most of what was known about x-ray diffraction from condensed matter systems related to understanding the structures of crystals. And even in that field,

understanding of the structure solution process was still relatively rudimentary. It was, after all, barely twenty years since Paul Ewald as a young theorist Ph.D. student went to see Max von Laue to suggest that x-rays might be able to give information on the structures of crystals, stimulating the first x-ray diffraction pattern of a crystal by Friedrich and Knipping in 1912.

Getting a diffraction pattern is, however, only the first step. We have then to work back from this pattern to deduce the arrangement of the molecules in the regular crystal, and this was not then a trivial operation. Historically, the Braggs had a major influence on the early interpretation of diffraction patterns. As a crystal is a regular arrangement of molecules – in Bernal's words, a regular 'pile' of molecules – sets of parallel planes of atoms can be identified in the crystal. The spacings between these planes can then be related via a simple equation – Bragg's law – to the separation between the lines observed in a particular kind of diffraction pattern, a so-called powder pattern.
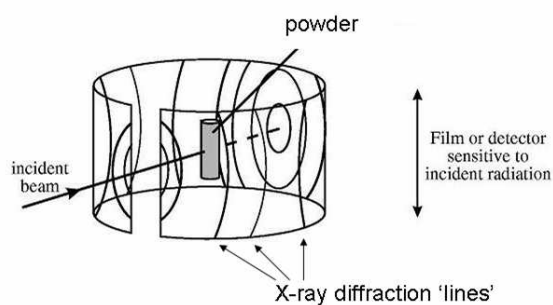

Figure 3. A schematic of an x-ray powder diffraction experiment using film to detect the x-rays scattered from the sample.
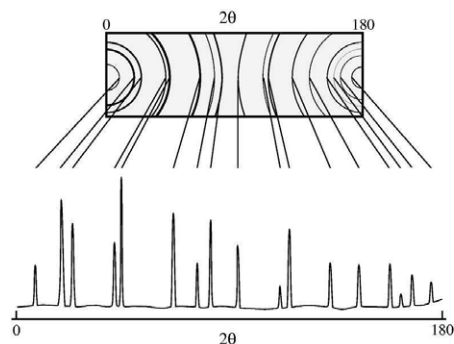

Figure 4. The x-ray film in figure 3 opened out flat; (bottom) the kind of intensity plot obtained by scanning across the x-ray film. Each 'line' relates to different planes of atoms in the crystal, and Bragg's equation tells us what the actual spacings between these planes are. The horizontal axis refers to the angle 2θ through which the x-rays are scattered.

Figure 3 shows schematically a simple powder diffraction setup. In the instruments of the time, a photographic film was wrapped in the form of a cylinder around the powdered sample placed on the cylinder axis. An incident x-ray beam gives rise to a series of lines on the developed x-ray film. If we open out this film, we get something like the top of figure 4. As each of the lines on this film can be related via Bragg's law to the spacings of particular lattice planes in the crystal, we can now begin to obtain some basic information on the structure of the crystal. Taking the argument further, if we measure the relative intensities of the lines, we can plot the kind of pattern shown in the lower part of figure 4. These relative intensities give further information on the details of the crystal structure, although the techniques for extracting this information were poorly developed at the time.

When Bernal published the 1933 paper, it was only about ten years since the ideas of the Braggs had been developed. Understanding crystalline diffraction patterns was therefore still a relatively new and challenging problem. How then could these kinds of arguments be applied to understanding x-ray diffraction from liquids? After all, a liquid is not a crystal, and there are therefore no lattice planes. And as the interpretive techniques developed for crystals rely on the

existence of such planes, we obviously have a problem in trying to understand the diffraction pattern from a liquid.

An attempt to make progress was made six years earlier by Zernike and Prins [2]. Despite the absence of lattice planes, they decided to try to apply a similar sort of approach to Bragg's law to try to extract information on characteristic distances in the liquid.

Figure 5 shows an x-ray diffraction pattern for liquid water taken from Bernal's 1933 paper. It is a typical liquid pattern in that, unlike the crystalline powder pattern of figure 4, it is a continuous distribution of intensity bereft of the sharp peaks that relate to separations between lattice planes in the crystal. Looked at closely, however, the liquid pattern does show three features that look like smeared-out peaks (see the arrows in the figure). Zernike and Prins argued that the distances to which these peaks can be related by Bragg's law might be referable to three dominant atomic spacings in the liquid. In trying to understand the x-ray diffraction pattern of water, Bernal used a similar approach.

In order to understand the structure, however, Bernal realised he needed additional information to that in the x-ray pattern. The 1933 paper sets out how he made use of this additional information in developing his ideas on the liquid structure.
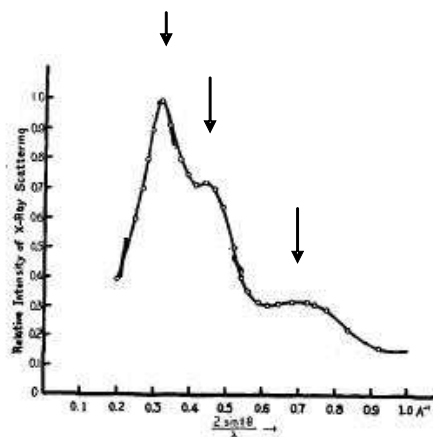
Figure 5. An early x-ray diffraction pattern of liquid water that Bernal used for fitting his early liquid water model. The arrows indicate the approximate positions of the maxima of the broad peaks. The data is thought to be that of Amaldi (Phys. Zeits. 1931 **32** 914).
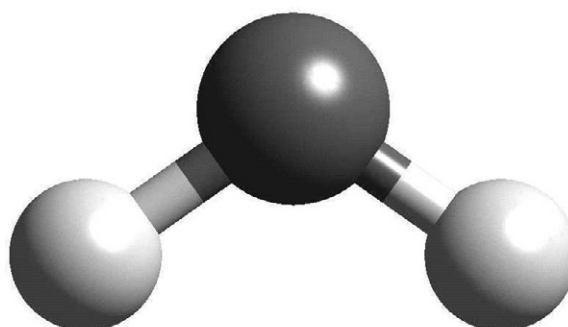
Figure 6. The water molecule.

First of all he wanted an idea of the shape of the water molecule itself. The previous year, in 1932, Mecke and Baumann [3] had proposed, on the basis of spectroscopic measurements, that the water molecule was essentially V-shaped. A popular present-day representation of the molecule is shown in figure 6, where the oxygen is connected to two hydrogens to form the molecule of H_2O. Bernal then argued what this shape might mean for the way electrical charge was distributed around the molecule, an important question to answer if he wanted to understand how water molecules were likely to interact with each other. Using his understanding of quantum mechanics (another relatively new scientific concept at the time), he argued that there were likely to be positive charges on the hydrogen atoms and negative charges 'behind' the oxygens in the regions shown in figure 7 (again taken from the 1933 paper itself).

This deduced charge distribution was a key factor in his next suggestion. With this kind of near-tetrahedral arrangement of (two positive and two negative) charges, he argued that, since
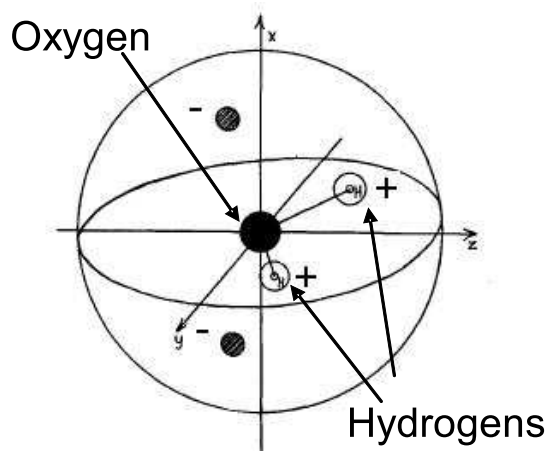
Figure 7. Bernal's conclusions about the distribution of charge in the water molecule.
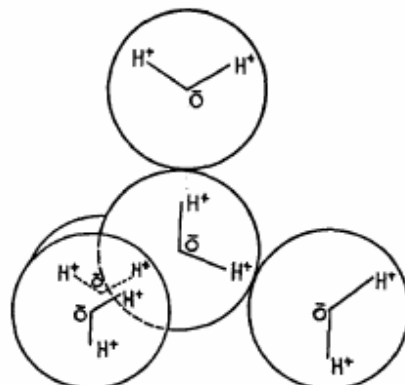

Figure 8. Bernal's idea of the local tetrahedral coordination of water molecules that results from the charge distribution shown in figure 7.

unlike charges attract, a single water molecule would tend to interact with four neighbours to form the kind of tetrahedral motif of figure 8. This four-coordinated local arrangement was to be a central concept in his models of the liquid water structure.

One can imagine this tetrahedral local structure setting a bell ringing – for a similar motif is found in the structures of silicates. Perhaps, therefore, something can be learned about the structure of water from the known structures of silicates? Two silicate structures that were of particular interest to him in this context were quartz and tridymite. These two structures are different from each other and have different densities. But, like other silicates, they both have the same underlying tetrahedral motif of a silicon connected to four neighbours via intervening oxygens that is similar to the way one water molecule is linked to four neighbours through intervening hydrogens. With this similarity in mind, he then appealed to the approach of Zernike and Prins to try to interpret the x-ray diffraction pattern of water.

Figure 9 is a copy of his original sketch of one of the figures in the 1933 paper which gives a good idea of the arguments he was using. He puts lines at positions corresponding to the maxima of the broad peaks of the experimental curve, calculates the equivalent distances using Bragg's law, and proceeds to identify those distances with – suitably scaled – characteristic distances in the silicate structures. Because the peaks are broad rather than narrow, he recognised that the liquid is obviously a disordered structure, but using the silica analogy he argued that he could reproduce the main features of the experimental x-ray pattern by constructing an appropriately disordered quartz-like structural model.

The comparison between the x-ray pattern predicted by his 'quartz-like' model of liquid water and the experimental data is shown in figure 9. The broad peaks are all in the right places. Their average intensities are not quite right, but for a first try the agreement is very impressive. In fact, the agreement is as good as some of those obtained by much more sophisticated computer simulation models of water produced in the 60s, 70s and 80s. The agreement is far from perfect, but is extremely good considering the state of the field at the time. Using the intellectual tools that were available, he drew conclusions about the structure and properties of water that have influenced fundamentally the field ever since.

The 1933 paper established the electronic structure of the water molecule as being near tetrahedral, a local structure that determined the essential local structure in both the crystal and the liquid. Moreover, the final model of the water molecule that he came up with (figure
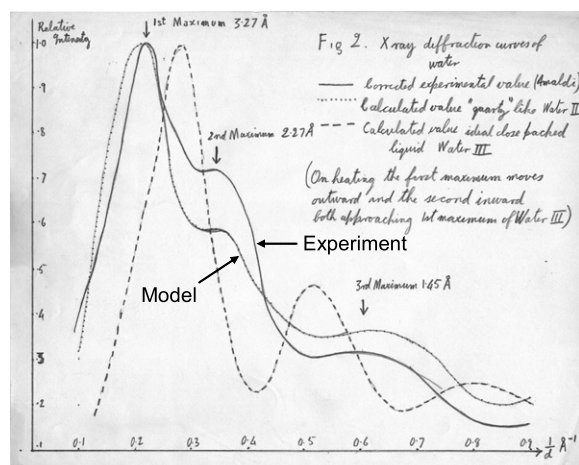
Figure 9. A copy of the original figure showing Bernal's original attempts to fit his distorted quartz model of water to the experimental data.
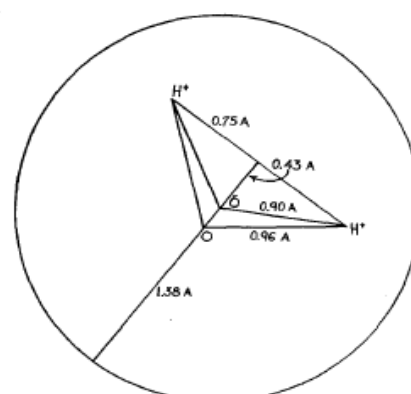

Figure 10. Bernal's quantitative model of the water molecule from the 1933 paper. The position of the negative charge shows remarkable insight that later workers found to be essentially correct.

10) is in essence both conceptually and semi-quantitatively what is used today in some major simulations of water in a whole range of aqueous systems. Based on this model of the way water molecules could interact with each other, he argued that the liquid water structure at normal temperatures could be thought of as a sort of variation of a quartz-like structure. To explain water's odd behaviour at low temperatures – it begins to expand on cooling below 4C – he proposed a mixture of quartz-like and tridymite-like structures, while to explain the change in structure at higher temperatures he proposed that the structure approached that of an ideal simple liquid, though it is not clear what he understood to be the structure of such an ideal liquid. Those ideas must have been at least partly developed in his mind at the time, even though they do not seem then to have been put into published form. They were to be developed more fully later, and would eventually feed back into his later ideas of the structure of liquid water itself.

3. The random tetrahedral network model

Then there was a long gap in his work on water and on liquids generally. During that gap, other researchers beavered away trying to understand the structure of simple liquids. It is interesting to look at the concepts which underlay the ideas being developed in that period.

One idea of liquid structure was based on that of compressed gases. As a gas is compressed, the atoms or molecules are pushed closer together, and consequently increasingly interact more strongly. Further compression results in further increase in intermolecular interactions until a point comes at which the molecules begin to cohere and the liquid condenses out. Theoretical approaches were developed, notably by Yvon, Born and Green, based on theories of dense gases. Unfortunately, as the gas becomes denser, the approximations that have to be made to the theory become increasingly problematical, so although these theories can help us understand some aspects of liquid structure, they are not really satisfactory.

In contrast to approaching liquid structure from the gas side, other attempts were made to liken the liquid to a disordered crystal. One particular crystal-like theory was developed in the mid 20th century by Kirkwood. In this model, the crystal was disordered by putting holes in it by removing atoms. In a way this was the kind of approach Bernal was taking himself in

the 30s: the water model developed in the 1933 paper is essentially one based on disordered crystals, although it would appear that the limited disordering he introduced was not one of creating holes. Another model proposed by Eyring and developed by a number of other workers conceived a liquid as a mass of sub microscopic crystals with disordered material between them.

Bernal found all these approaches fundamentally unsatisfying. As he said in his Royal Society Bakerian Lecture in the early 1960s, in which he put forward the ideas he was then developing on liquid structure, he wanted a more concrete picture of the structure of a liquid than these theories provided. He recognised that he needed to understand simple liquids – those whose intermolecular interactions are isotropic, as between atoms envisaged as attractive soft spheres – before he could understand more complex ones such as water. For a simple liquid, he wanted a simple model which wasn't too complicated. He wanted a more concrete picture of the structure and one making use of Ockham's razor: *"Not to multiply entities beyond necessity"*. As a crystallographer, he also wanted *"some kind of theory of liquids that would be homologous to that of the crystalline solid as well as being radically different in kind, and have a general quality of homogeneity"*. Unlike a crystal, a liquid doesn't contain lines or planes of molecules or atoms. So a satisfactory model must not assume structural entities such as these as they are just not there in the liquid.

He also commented in the lecture that he found his earlier 1933 approach unsatisfactory. It was, he said, *"frankly, one of crystal structure, trying to picture water structure as that of a mixture of the analogous four co-ordinated structures of . . . quartz and tridymite"*. That model was too ordered: *"This was ultimately to prove rather a delusive approach, postulating a greater degree of order . . . in the liquid than actually exists there"*. So in the 1950s he went back to the problem of simple liquid structure. Which brings us back to the beginning of this talk and to figure 1.

Perhaps largely because we cannot make the simplifying assumptions that allow us to deal very successfully with crystalline solids, liquids appear to be difficult and complex to understand. Bernal simplified the conceptual picture of liquids with a very visual and inherently simple idea.

You will recognise the left hand picture in figure 11 as a 'crystal' of steel balls. The 'atoms' are arranged in a regular, repeating arrangement, and lines and planes of 'atoms' are obvious. This is a regular pile of 'atoms'. The right hand picture of figure 11 is in contrast an irregular heap. It represents a snapshot of the structure of a liquid of spherical atoms – here of a 'liquid' of steel balls. As Bernal put it simply and succinctly, the structural difference between the crystal and the liquid is essentially the same as that between a pile and a heap of atoms. Because of the simplifying order found in them, we have highly sophisticated theories of piles. But at the time there were no theories of heaps. Interestingly, this situation has changed significantly in the last ten years or so. Theoreticians have put their minds to the problem and we are now beginning to get some good theories of heaps. Not specifically for understanding liquids however. There isn't a lot of money to be made from heaps of molecules, but there is a lot to be made from heaps of other things.

Figure 12 contrasts the liquid structure of the upper part of the model with the regular crystalline structure at the bottom. In putting forward this inherently simple but very effective concept, Bernal did recognise that an apology to the theoreticians, who had put in a lot of work on liquid structure theories in the preceding two decades, was perhaps needed. So he apologised to *"the modern theoretical physicist for introducing such a simple way of looking at things, but I believe on the whole that it is better to start with a model that has some resemblance to reality"*.

As it stands, however – and in the absence of any theory of heaps – this model, although conceptually appealing, was still only a concept. Not only did it need quantitative development to test its validity, but it also needed some kind of 'realisation' to try to understand how it could explain liquid properties and behaviour. The model building shown in figure 1 was one early way to explore the properties of the model. Another is shown in figure 13, which was an early
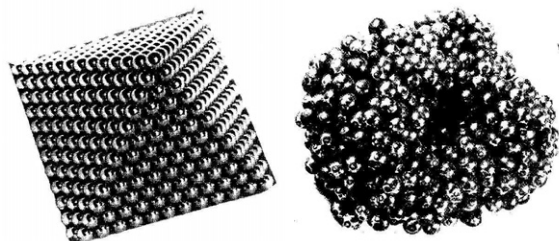
Figure 11. Bernal's key concept of the simple liquid as an irregular heap of molecules (right) in comparison to the regular pile of the crystal (left).
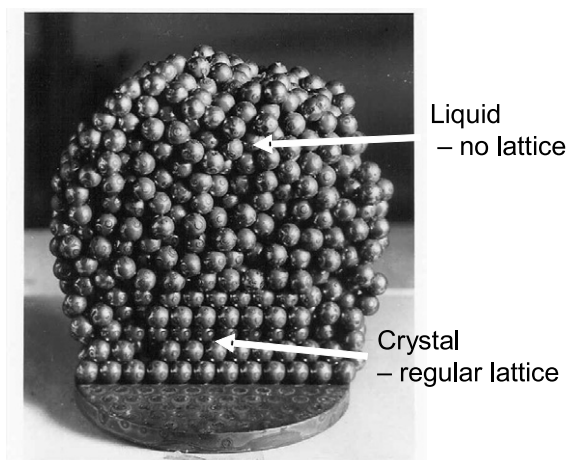

Figure 12. Bernal's model of a simple liquid (top) compared to the equivalent crystal (bottom).

model of an expanded heap built out of ping pong balls. It is photographed behind Birkbeck College and in front of the Torrington Square crystallography laboratory. I believe it is the model that was used in Bernal's 1962 Bakerian Lecture on the structure of liquids. Thanks to the far seeing powers that took over Birkbeck Crystallography many years ago, this model, as well as other historical ones that Bernal used to develop his concepts of liquids, no longer exists.
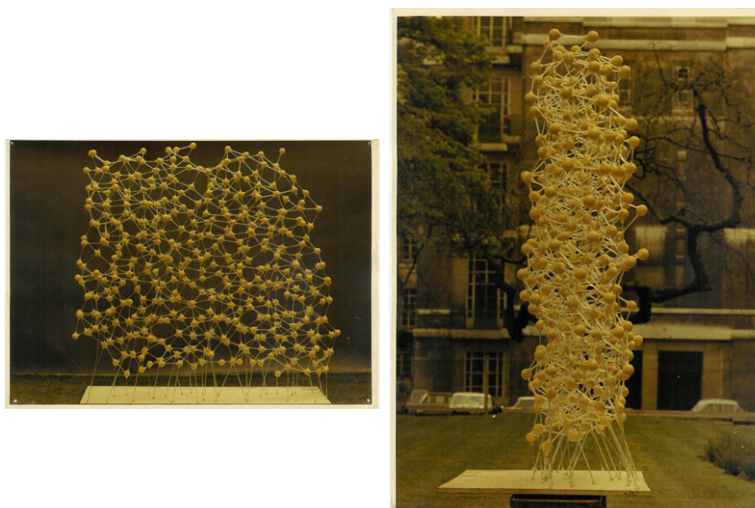

Figure 13. An early expanded model of the simple liquid (J L Finney private collection).

Figure 14 shows another expanded liquid model that does, I think, still exist. This is the one that Andrew Brown mentions in his biography of Bernal, for which the building had to be taken down before we could get the model out. It was eventually removed from Torrington Square when the building was demolished. Following a period of several years in a Plexiglass cage outside the new Crystallography Laboratory at Birkbeck, it subsequently spent some time
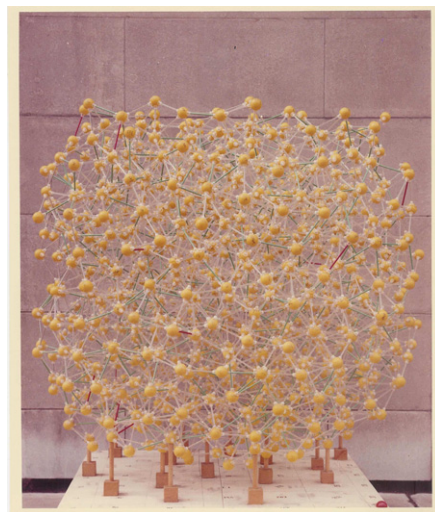
Figure 14. The last expanded model built of a simple liquid (J L Finney, Ph.D thesis, University of London, 1968).

on display at the Science Museum in London. Together with (I hope ...) some other smaller models that were associated with Bernal's imaginative early examination of the properties of liquid models, it was last heard of languishing at the back of a Science Museum store in a hangar at Wroughton in Wiltshire. I'm quite attached to it because it formed the basis of about half my PhD thesis.

Bernal had argued that he needed to understand simple liquids before he felt he could understand more complex liquids such as water. So now, with this simple model essentially verified and accepted as a model of simple liquids, how did he build on this to understand water?

The extension to water is essentially straightforward, at least conceptually. Referring back to the simple liquid model, we envisage the liquid as an irregular assemblage of atoms which has the correct density and in which the atoms interact with each other in a way that is consistent with the forces acting between them – the so-called potential function. In the simple liquid case, this intermolecular interaction is essentially isotropic or spherically symmetrical. The spherical atoms are in essence just packed together as in the heaps in figures 11 and 12 – a so-called random close packed structure of spherical atoms.

The water molecule is of course different. The 1933 paper concluded that the interaction between water molecules was relatively complicated, with each water molecule surrounded by, on average, four close neighbours in essentially a tetrahedral local arrangement (see figures 8 and 15).

We are now going to try to do the same with this tetrahedral motif, as Bernal essentially did with the simple liquid model. Can we join these water molecules together in a way which is liquid-like, and does not show crystalline order, but still fulfils the constraints the water molecule wants to fulfil at the local level? Which in essence means: can we build a random arrangement of water molecules connected together via the local tetrahedral motif of figure 15?

The answer is, of course, yes. Bernal could, and did. Figure 16 shows a laboratory model built by Bernal's group using just these constraints. In the figure, the black balls are the oxygen atoms of water molecules which are joined to other neighbouring water molecules through the small white hydrogens, with four water molecules surrounding each central water. Such a model
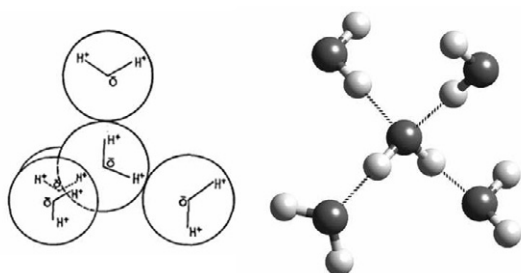
Figure 15. Two different representations of the basic tetrahedral motif in water (and ices). The left hand one is that from the 1933 paper.
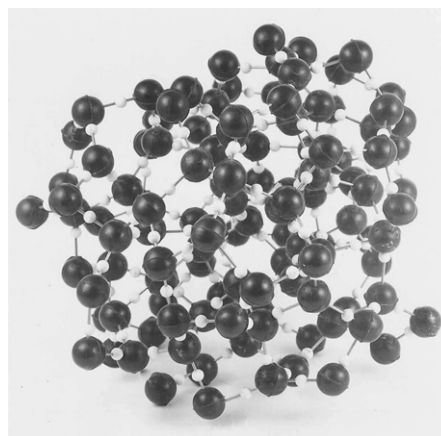
Figure 16. Bernal's realisation of a 'random network water model'.

is inherently non-crystalline, and can be constructed to have the density of water. In analogy to the simple liquid model being termed 'random packing', this water model is a 'random network'. A two-dimensional analogue is shown in figure 17, in which the connectivity is reduced from four to three and compared with the equivalent two-dimensional regular crystal. A similar three dimensional liquid/crystal comparison is shown in figure 18, in which only the connectivity between the water molecules is shown. One way of quantifying the difference between the two structures is to count the rings. The crystal – the ice in your freezer – consists of water molecules joined together to form six-membered rings. In the liquid water case, there is a range of rings from four- to seven-membered and above.
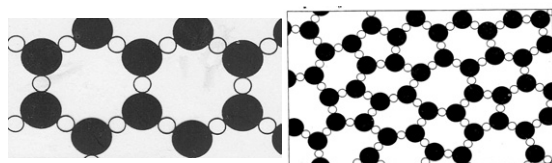

Figure 17. A two-dimensional analogue of ice (left) and liquid water (right) (adapted from Ziman J M 1979 *Models of Disorder* (Cambridge University Press))
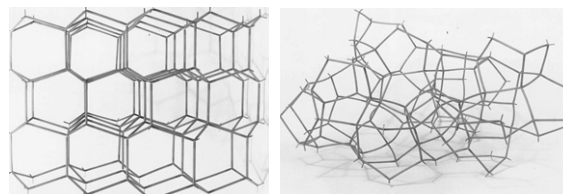
Figure 18. A 'spaghetti' visualisation of (left) normal (hexagonal) ice and (right) liquid water.

This random network model is different from the 1933 model in a very significant way. The earlier model was really a disordered crystal. It did give quite good agreement with experimental data, and allowed an explanation of some important properties of liquid water. In contrast, the later random network model – which Bernal never published in any detail – is, like the simple

liquid model, one which is inherently non-crystalline. Yet it fulfils the required local interaction geometry and models can be built which have the correct density. The model can also explain the essential physical properties of the liquid, for example the expansion on freezing to ice, the existence of a temperature of maximum density and other related 'anomalies', the mobility of hydrogen and structural changes induced by changes in temperature and pressure.

How well does this model explain the x-ray diffraction pattern from water?

Figure 19 reproduces a negative of Bernal's early calculation of what is called the radial distribution function of the random network model in comparison with the one obtained from the experimental x-ray data. In the figure, the smooth continuous line is the experimental data, while the histogram results from counting intermolecular distances found in the model. Although difficult to see, the comparison does look quite good. After smoothing the histogram data, the published comparison is given in figure 20. Here again, the agreement for the time is very good. The random network model does indeed seem to be essentially consistent with the experimental data.
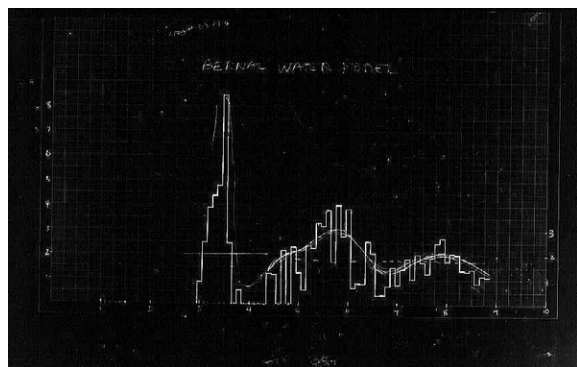

Figure 19. Bernal's first comparison of the experimental radial distribution function (curved line) with the prediction from his random network model (histogram).
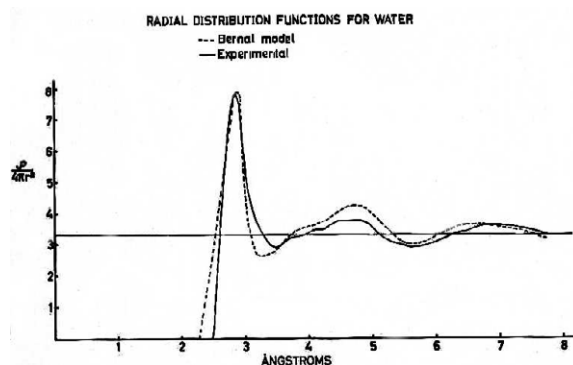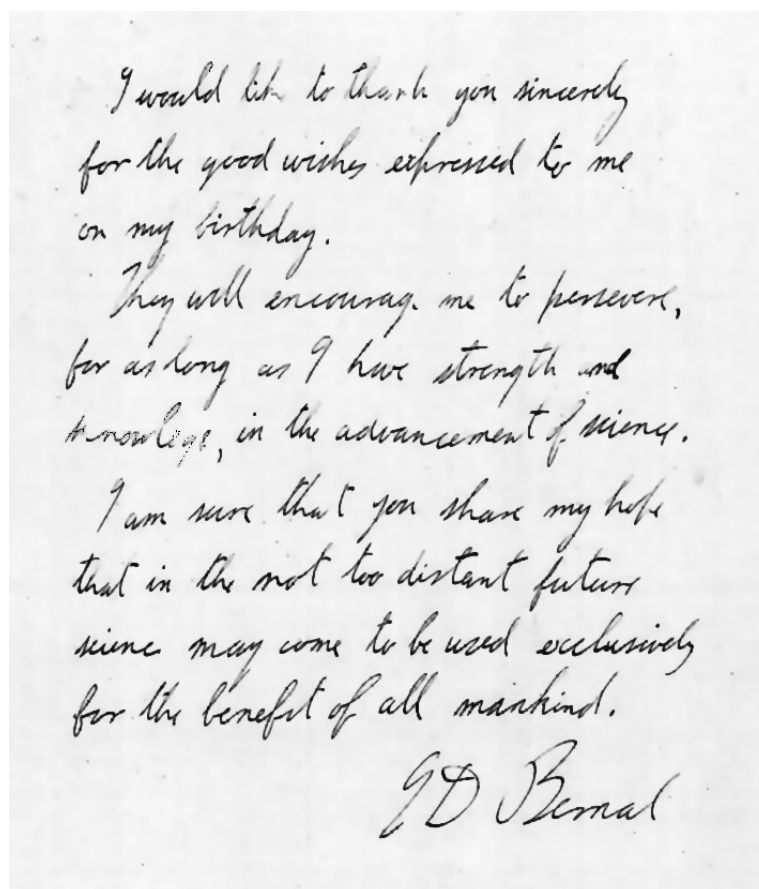

Figure 20. The experimental comparison after smoothing the model data.

Bernal's final view of the structure of water is essentially that of this random network idea. In this network of water molecules, each molecule interacts with its neighbours in an approximately tetrahedral geometry. The local near-neighbour coordination is ideally four-fold, though as we are dealing with a liquid and hence with a degree of disorder, we would expect some local variation in coordination, but with essentially an average coordination of four.

How do Bernal's ideas match up to modern ideas about water structure? [4] We now have far better experimental data than Bernal ever had access to, and consequently we do know what water looks like in some detail. In brief summary, just as the random sphere packing model contains the essence of simple liquid structure, so the random network model contains the essence of the structure of liquid water. State-of-the-art experimental data confirm the dominant tetrahedral local geometry, giving water the open structure that is central to explaining its so-called anomalous physical properties such as the temperature of maximum density. Real water seems to be a little more defective than the ideal model in terms of this coordination and its variation, with a significant amount of three-fold bonding found. As in Bernal's laboratory-built random network, there are significant distortions of bond angles away from the tetrahedral, and the experimental data allows the degree of distortion to be quantified. Real water also can be thought of as a mixture of rings of different sizes, with 4-, 5-, 6- and 7-membered rings dominating as in the simple model.

Figure 21. (J L Finney private collection)

4. Some concluding comments

Let me finish by summarising what I think Bernal did in his two bouts of working on water.

The 1933 paper is still regarded as seminal. Many of the ideas in it are still highly relevant. It set out the essential electronic structure of the molecule and the consequences of that for the way in which molecules interact with each other. He argued for the liquid structure being a disordered version of a similar tetrahedral structure known from silicate studies, and the structure which fitted the data best was one based on quartz. This idea explained many of the important properties of water, as well as giving good agreement with the experimental x-ray scattering data.

But over time he was not happy with the approach he took then. The model had too much order in it. It smacked too much of a crystal.

His second bout of work produced an inherently different model that did not suffer this major defect. Building on his work on simple liquids as irregular heaps of spherical models that gave rise to his random packing model of liquids, he developed a parallel 'random network' model that was consistent with the preferred tetrahedral local interaction expected between water molecules. This later model was also clearly non-crystalline. When checked against the available experimental data at the time, the model performed well and was able to explain the

main important physical properties of the liquid. Moreover it is consistent with the current state-of-the-art experimental work. Although this is not discussed above, this simple model has also helped us understand water's biological role.

I'll leave you with figure 21. It ties in more with Alan Mackay's talk, but it encapsulates the reasons he did science – including the work on water.

References

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