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## The Structure of Liquid Water; Novel Insights from Materials Research; Potential Relevance to Homoeopathy

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# The Structure of Liquid Water; Novel Insights from Materials Research; Potential Relevance to Homoeopathy

## Abstract

This paper provides an interdisciplinary base of information on the structure of liquid water.

## FUNDAMENTAL RESEARCH

### The Structure of Liquid Water; Novel Insights from Materials Research; Potential Relevance to Homeopathy\*

Rustum Roy<sup>1</sup>, W.A. Tiller<sup>2</sup>, Iris Bell<sup>3</sup>, M. R. Hoover<sup>4</sup>

**Key words:** Water, Structure of water, Epitaxy, Succusion, Nanobubbles, Colloids.

This paper provides an interdisciplinary base of information on the structure of liquid water. It begins with a synthesis built on the information base on the structure<sup>5</sup> of noncrystalline, inorganic, covalently-bonded condensed liquid phases, such as SiO<sub>2</sub>, S, Se, P, and H<sub>2</sub>O, which exists in the materials science literature. The data for water are analyzed through the prism of well-established algorithms in materials research: the connection of properties to structure; the pressure-temperature (P-T) phase diagrams; the phenomenon of epitaxy; the phenomenon of liquid-liquid phase separation; the stability of two phase colloids; and, the recently discovered effects of weak magnetic and electric fields on the structure of simple inorganic oxides. A thorough combing of the literature of the condensed matter properties reflecting structural features of essentially pure water obtained via the normal processes of preparing homeopathic remedies, provides another rich data base.

The examination of these data through the standard materials science paradigms leads to the following conclusion: Many different structures of liquid water must exist within the range of observations and processes encountered near ambient conditions. A typical sample of water in these experimental ranges no doubt consists of a statistical-mechanical-determined assemblage of monomers and oligomers (clusters) of various sizes up to at least several hundred H<sub>2</sub>O units. The importance of the structural similarity of SiO<sub>2</sub> and OH<sub>2</sub> is very relevant to the structure of the latter as well as to the probability of epitaxy in controlling

at least the region contiguous to the silicate glass surfaces of many common containers.

The most distinctive feature of bonding in liquid water is not only the "well-known hydrogen bonds, but the necessary presence of a wide range" of van der Waals bonds between and among the various oligomeric (cluster) structural units. It is this range of very weak bonds that could account for the remarkable ease of changing the structure of water, which in turn could help explain the half-dozen well-known anomalies in its properties. In its subtler form such weak bonds would also allow for the changes of structure caused by electric and magnetic fields and by radiation of all kinds, including possibly so-called "subtle energies", which are the basis of an enormous range of claims about specially "structured" water.

This paper does not deal in any way with, and has no bearing whatsoever on, the clinical efficacy of any homeopathic remedy. However, it does definitively demolish the objection against homeopathy, when such is based on the wholly incorrect claim that since there is no difference in composition between a remedy and the pure water used, there can be no differences at all between them. We show the untenability of this claim against the central paradigm of materials science that it is structure (not composition) that (largely) controls properties, and structures can easily be changed in inorganic phases without any change of composition. The burden of proof on critics of homeopathy is to establish that the structure of the processed remedy is

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5. The term structure is used as in all materials research to designate the 3D arrangement of atoms or molecules, not the chemical usage of the term describing the structure of a single molecule or oligomer. ©2005 Matrice Technology Limited Materials Research Innovations 9-4: 1433-075X

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not different from the original solvent.

The principal conclusions of this paper concern only the plausibility of the biological action of ultradiluted water remedies, they are based on some very old (e.g. homeopathy) and some very new (e.g. metallic and nanobubble colloids) observations which have been rejected on invalid grounds or due to ignorance of the materials research literature and its theoretical basis. This constitutes an excellent example of the common error in rejecting new scientific discoveries by using the absence of evidence as evidence for absence.

## Introduction

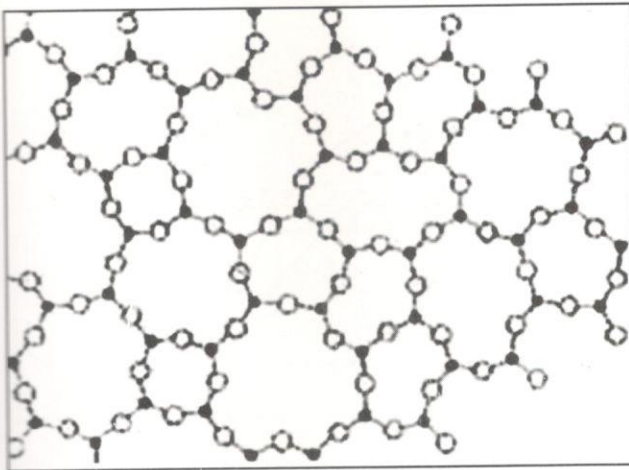
The “structure of liquid water” receives some 8 million hits on Google and the “structure of water” over twice as many. Any contribution that can be made to this vast body of knowledge is sure to be marginal. This paper does not report any such incremental advance with ultraprecise measurements about the structure of oligomers, femtosecond spectroscopy of bond breakage or phase transitions in glassy water. Instead, it examines the literature to establish only one proposition, that pure, thermodynamically stable or metastable liquid water can have more than one 3-D condensed matter structure. While we assemble here various sets of relevant data and lines of argumentation, by a coincidence, at the same time as this paper was first presented orally (April 2004), Kawamoto *et al.* published their paper providing the experimental proof of this assertion [1, 2]. Of course solid crystalline water has been known to exist in nearly ten different structures, and workers such as Angell and DeBenedetti and Stanley have given us an extraordinarily precise and interesting picture of certain metastable liquid waters, or metastable solid glasses of water with different properties and structures [3, 4]. These observations mimic the same phenomena known for generations in H<sub>2</sub>O’s close relative, SiO<sub>2</sub>. This paper brings together a very wide range of disparate observations on water (and other liquids which share one or more structural or bonding parameters) to support the case that water can indeed have its properties and hence its structure changed rather easily in non-linear ways without any change of composition.

The structure of crystalline inorganic matter which became a major pillar of the physics and chemistry of solids was based on the discovery by von Laue and the Braggs, father and son, of the diffraction of X-rays by the periodic array of atoms in crystalline solids. It remains the sine qua non of characterization in

contemporary materials research. The Braggs were followed by the schools of V.M. Goldschmidt (including Barth, Lunde and Zachariassen in Oslo), and Linus Pauling in California, who applied this new tool of X-ray diffraction (XRD) to a very large number of the common (crystalline) solids in the world of inorganic science and technology. Thus was born the extremely reliable science of crystal chemistry: the relationship of structure to composition as a function of the most powerful intensive thermodynamic variables: temperature, and pressure (see books by Goldschmidt; Pauling; Evans; and Muller and Roy [5–8]). The term structure is unambiguously defined in crystal chemistry as the position in 3-D space of each atom or ion typically with a precision nowadays of say  $\mu$  0.01 nm.

What immediately will catch the attention of an interested observer is the ratio, in inorganic crystal chemistry books, of the space devoted to solids as compared to liquids. It approaches 100:1. And thereby hangs our tale. Why? Water as a liquid is the most common phase on the surface of the earth, followed by ice. A very distant second is crystalline SiO<sub>2</sub> as quartz (one of the dozen structurally different forms of SiO<sub>2</sub>). The fact that we know the precise details of the structure of each form of crystalline SiO<sub>2</sub> while we have only the most rudimentary understanding of liquid SiO<sub>2</sub> is due to a fundamental lack in our arsenal of tools for determining the structure of liquids. The fact that low viscosity liquids sustain a continuous rapid movement of the atoms and/or molecules contained in them is not the defining difficulty. The effective tool of XRD is totally lacking for all noncrystalline (i.e. aperiodic) matter whether solid or liquid. The only tool which can now be used definitively and directly (albeit partially) to show the structure of non-crystalline solids (e.g. glasses) is transmission electron microscopy (TEM) and this cannot **easily** be directly used on liquids. Thus it is not surprising that many scientists, due either to ignorance or powerlessness, hold the naïve view that all liquids, like most crystalline matter, are more or less completely homogeneous in structure down to the unit cell, atomic or molecular level, and they exhibit structural characteristics in accord with the **random network** model, **one** of the two models developed nearly a century ago, for glasses [9]. This model of the “structure of glass” starts with that of the structurally homogeneous crystalline materials (i.e. those in which a structural element, the unit cell, is repeated throughout the sample in all 3 dimensions), and moves the atoms or ions from their normal sites, required for periodicity, by bending or stretching the bonds. This so-called random network model taken from Zachariassen’s original paper is shown in Fig. 1 [9].<sup>6</sup>

6. For several of the figures from older papers, we have chosen to reproduce after modification the original figures from the papers.

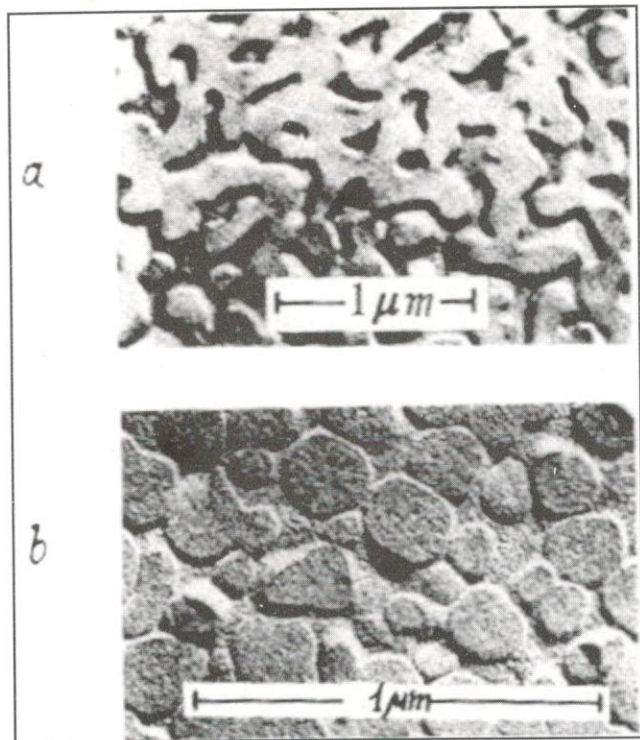


**Fig. 1:** The classical picture of the "Random Network Structure" as presented by Zachariasen in 1932, which has become "established" as the structure of glass on the basis of model fitting on x-ray scattering data. The key assumption (unrecognized by others for 7 or 8 decades) of this model is that the structure of all glasses is "homogeneous" in the same ways as crystals are.

This now outdated image, based on no direct data from other methods, has dominated the thinking of the physics and chemistry community ever since, and it became their "working model". Opposed to this "homogeneous structure" was the early "crystallite" theory (Prins which posited that small 5—50 Å fragments of various crystalline structures floated in a monomeric sea [10]. For over half a century, international conferences have periodically revisited the question of homogeneous (random-network) or heterogeneous (crystallite) structures for glass (frozen liquids). By the 1980s, the definitive relevant data came not from XRD but from transmission electron microscopy (TEM) in common alkali boro- and aluminosilicate glasses (Mazurin and Porai-Koshits; Fig. 2 is taken from their work) which showed the heterogeneous "nano-structure" of many, many transparent glasses which have even 2 or 4 separate phases [11]!! (A phase is defined as a region of characteristic structure or composition separated by a surface.)

The existence of the entire glass-ceramic industry depends on this incipient nanoheterogeneity or actual phase separation in glass, and the myriad TEM images from Corning (Beall and Pinckney) shows the true nanocomposites that result [12]. The existence and high probability of nanoheterogeneity in most strongly bonded glass and liquid structures are now established as the "standard model".

In 1960, Roy introduced the thermodynamic argument for using metastable immiscibility as an indicator of the parent liquids likely nanoheterogeneity

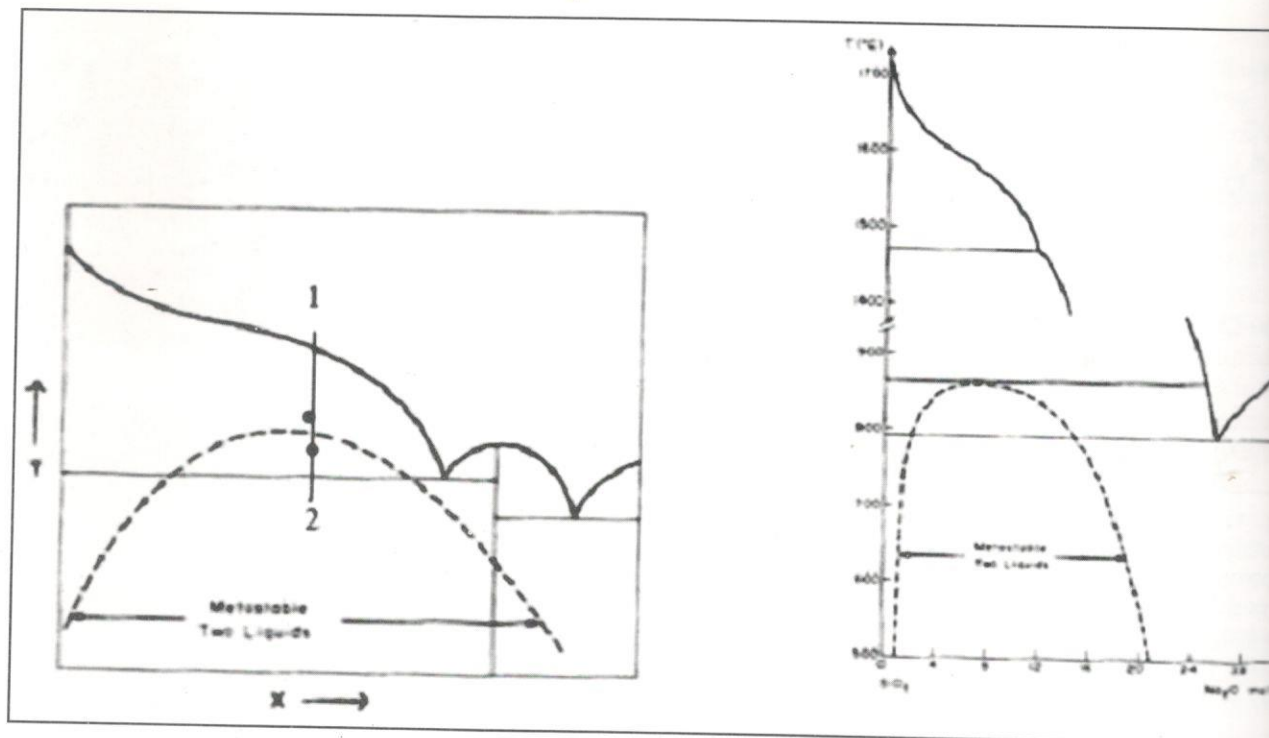


**Fig. 2:** In sharp contrast with the hypothetical calculations based on Zachariasen's random network theory, is the direct TEM evidence. Shown are some examples of binary and ternary glasses, some quenched, some heat-treated which clearly show actual phase-separation. One can confidently assume that in many if not most glasses and in many liquids, structural (-composition) fluctuations must exist as precursors to such phase separation (after Mazurin and Porai-koshits) [11].

[13]. Actual unmixing is a later stage in the development of heterogeneity, liquids manifesting their nascent heterogeneity by actually separating into different phases in their supercooled regimes (see Fig. 3). The structure of the liquid, say at point 1, can be inferred to have had nascent heterogeneity or proto-phase separated regions or clusters, which actually form say, at point 2. The thermodynamics of the non-ideal liquidus shape provides an indicator of possible phase separation (of course, this is in a 2-component system and easier to image).

The inherent "tendency" to inhomogeneity has since been greatly extended and completely verified in hundreds of cases (see comprehensive summary by Mazurin and Porai-koshits) [11, 15]. **Today, extensive and definitive experimental evidence exists for great heterogeneity of nano- or microstructure, indeed for a multiplicity of distinct regions, even Gibbsian phases in at least hundreds of common quenched liquids or glasses.**

An important observation about possible water structure and the kinetics of bond breakage, etc., and



**Fig. 3:** The first presentation by Roy (1960) of the theoretical argument that the non-ideality of the liquidus (clearly shown its shape) indicated that the liquid phase itself was “heterogeneous” in structure, and could be induced to phase-separate a temperature region where it was metastable (left hand figure) [13]. Poraikoshits and Averjanov experimentally demonstrated exactly such an example in 1968 [14].

their relevance to structure can be drawn from the phase diagrams in Fig. 3. This is the phenomenon of “consolute points” as appears at the top of the (metastable) two liquids region in the left-hand phase diagram. First we note that phase relations involving consolute points in unmixing liquids are quite common in simple binary systems involving water, e.g. the classic examples of phenol and water, nicotine and water, etc., treated in detail by Ricci in his textbook on the phase rule [16]. Immediately above the consolute temperature we have a single phase; immediately below there are two phases of infinitesimally different composition. Hence below the consolute temperature it is absolutely certain that we have two phases with different structures which are stable together “forever”. Now consider what changes when we go infinitesimally above the consolute temperature at exactly the same temperature? The key logic of this paper proposes that the structure of this liquid is nano-heterogeneous, containing regions, or clusters, or “oligomers”, reflecting the different structures which form just one degree Celsius below the consolute temperature. This is evidenced by the gentle continuous slope of the highly non-ideal shape of the liquidus curve.

Turning from the possible nanoheterogeneity of structure, to kinetics, we examine the argument that the “rapid breaking and remaking of bonds” excludes the possibility of different structures co-existing in liquid

water. One can safely assume that these kinetics do not change just because phase separation may be involved at essentially a single temperature. Obviously these very fast kinetics of breaking and re-formation of bonds are irrelevant since they take place within each structural arrangement of units, without statistical affecting the structure of the units themselves.

In the long tradition in classical chemistry and materials research circles, it has been assumed, and hence become a part of the canon, that liquids of fixed composition could not occur in two phases. This assumption has been disproved experimentally since the 1970's. It was then shown that in P-T (pressure-temperature) space, even in the liquid-stable region (not just metastable glasses), one finds a variety of different structures in liquids, in oxide melts, and even in monatomic systems such as elemental S, Se and Te [17–19]. Figure 4 shows the phase diagram for S with distinct phase regions for several different liquids taken from their work. In the jargon of the two decades later work on polyamorphism of H<sub>2</sub>O-glass, this is polyamorphism of stable liquids of S, Se, Te. We show later (Fig 6) how this key finding has specifically been extended to H<sub>2</sub>O itself.

In Fig. 4, the left image shows the P-T phase diagrams for sulfur (S) by Vezzoli *et al.* in with 12 crystalline phases [17]. Note the clear discontinuities

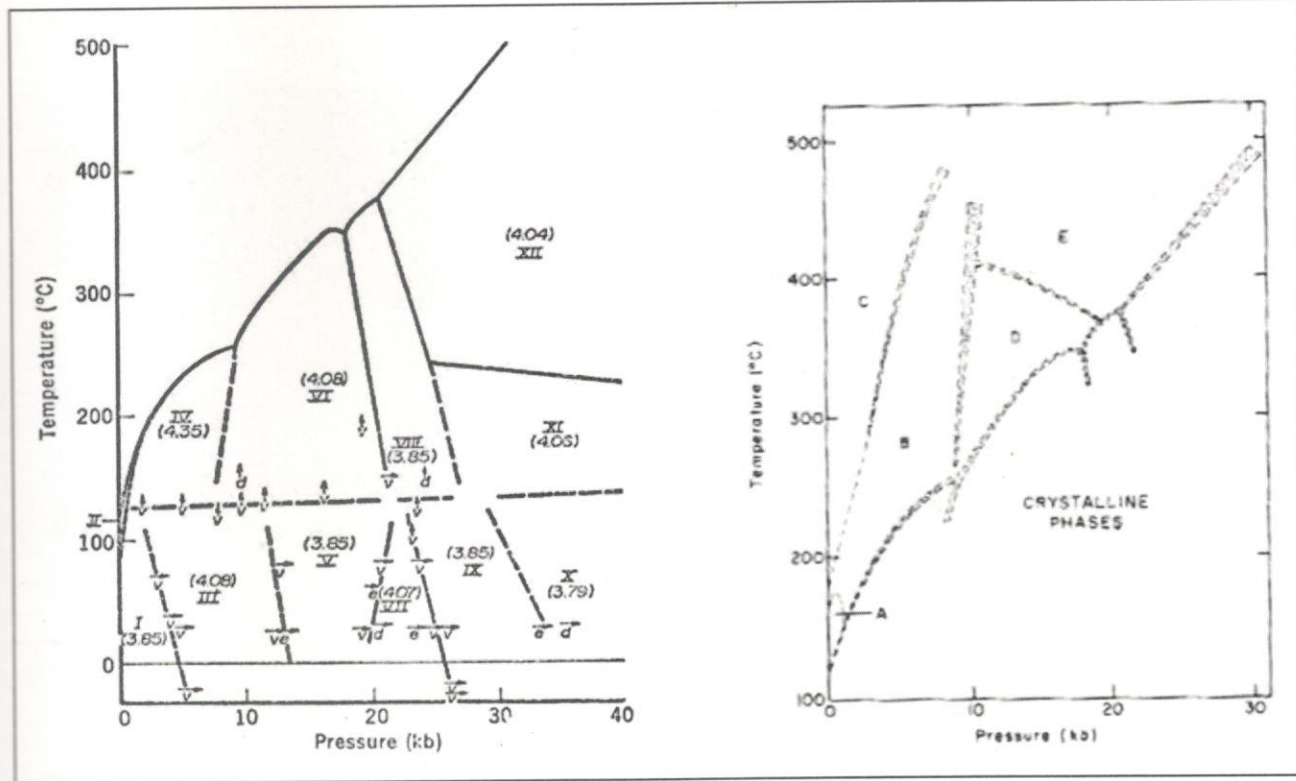


Fig. 4: P-T Phase Diagrams for sulfur (S). On the left is the sublucidus region showing the many crystalline structures. On the right is the liquid stable region showing at least 5 different liquid structures separated by a phase boundary.

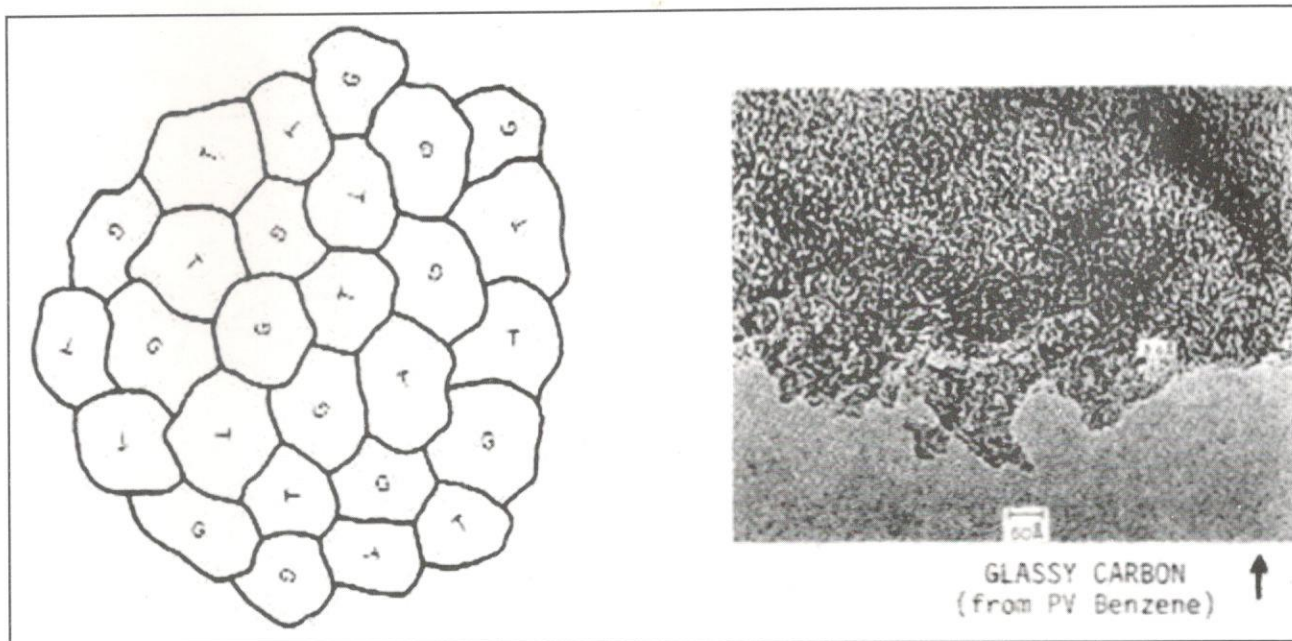
in the liquidus. The right half from the paper by the same authors shows the phase diagram of the liquid-stable region [20]. At this time (1969) it was universally accepted that only one liquid phase was possible. Yet the authors provided, probably for the first time ever, experimental evidence for differently - structured liquid phases A, B, C, D, E separated by somewhat fuzzy (second order?) P-T boundaries. Another relevant example, albeit metastable, is that of glassy carbon. TEM studies (Fig. 5) show that in glassy carbon, interlocking mixtures of 1–2 nm regions of SP<sup>2</sup> bonded graphite are mixed with SP<sup>3</sup>-bonded diamond regions [21].

As we will see later, the relevance of this line of argument by analogy has now been established beyond any doubt. That different structures of stable liquid water exist has now been fully confirmed experimentally by Kawamoto et al. using the very same P-T equilibria approach for water itself (See Fig. 6) [22].

We turn next to the very close crystallographic relationships in structure between silica and water as noted by Bernal and Fowler as early as 1933 [23]. They already assumed the existence of three “nano-regions” with structures analogous to SiO<sub>2</sub>- quartz and SiO<sub>2</sub>- tridymite. Weyl and Marboe and many others have developed these structural affinities between solutions

in H<sub>2</sub>O and SiO<sub>2</sub> [24]. (See Eitel for a general discussion [25].) Unknown to most readers concerned with biological effects, ordinary water forms (noncrystalline) glass fairly easily, e.g. by emulsions being poured into liquid N<sub>2</sub>. Unfortunately, many recent papers on H<sub>2</sub>O glass appear to have missed the enormous literature on SiO<sub>2</sub> which in crystalline and glassy forms is so similar to water. In spite of the debates recorded in Mazurin and Porai-koshits, for pure silica glass, a tetrahedrally coordinated, quenched liquid, with structures like water (but much more viscous), is implicit (see e.g. the work by Patel et al., Konnerth and Karle, and Roy: i.e. that SiO<sub>2</sub> glass also consists of regions with different packings or structural units [11, 26, 27, 28]).

By applying pressures of ≈ 200 kbar to SiO<sub>2</sub>-glass at room temperature, Bridgman and Simon first established that SiO<sub>2</sub> glass could easily be prepared and retained under laboratory p and t conditions in two very different structures [29]. Cohen and Roy in a series of papers then definitively established this phenomenon of unambiguous structural change with pressure, as a general property of virtually all strongly bonded glasses [30–32]. Thirty years later, apparently unaware of the early work, confirming the parallel between SiO<sub>2</sub> and H<sub>2</sub>O, Angell et al. and Kieffer via their data for glassy water: the latter saying that the evidence “provides



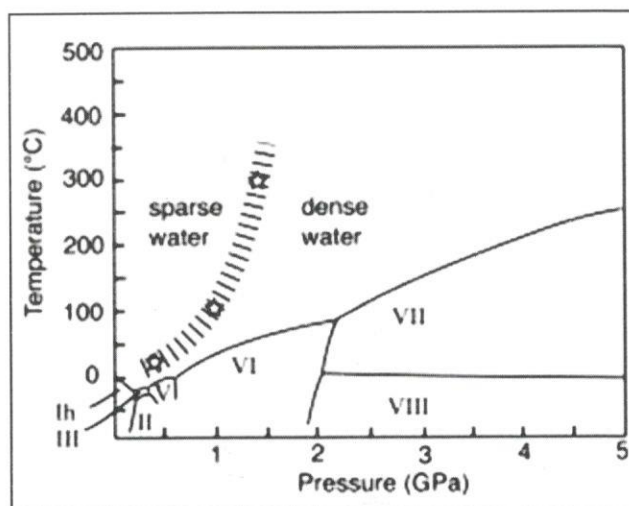
**Fig. 5:** TEM image and model thereof of glassy carbon structure showing 1 nm intergrowth of diamond-like and graphite-like regions after Noda and Inagaki [21].

strong support for the concept of polyamorphism, i.e. different non-crystalline structures in structures of glassy water” [3, 33].

While this “nano-scale heterogeneous” perspective on water, and the possible “phase behaviour of metastable water” itself have recently also started to appear in the literature, the possible extension to “stable water” via this early very rich and relevant background given here is hardly known and never referenced [34, 35]. Recently Soper, Tulk *et al.*, and DeBenedetti and Stanley explicitly accepted nanoheterogeneity in glassy H<sub>2</sub>O [4, 36, 37]. They also infer that there are discontinuous steps and first order transitions among “distinct metastable forms” in the changes from one to the other, in H<sub>2</sub>O”glass. The paper by Kawamoto *et al.* (see Fig. 6) shows the existence of (so far only) two “polymorphs” of stable liquid water in a P-T diagram exactly parallel to those for S, *etc.*, discussed above [22]. This occurs not in glassy or metastable water, but in liquid-stable water. Thus they take this line of argument (via exactly analogous P-T equilibria studies,) to the same conclusion we have derived from the data cited above on the P-T diagrams for S, Se, Te, *etc.*: that the presence of different crystalline structures are excellent hints for potential differences in liquid structures.

The significance of these data on the thermodynamics of liquid water, following the earlier studies of S, Se, Te, *etc.*, can now be summarized, although they may not be obvious to those unfamiliar with this branch of thermodynamics. It has been an

established part of conventional thermodynamics (as see in any textbook on phase diagrams) that the gas and one liquid stable regions of a fixed composition can only have one phase, in contrast to solids where one can, and often does, find even a dozen phases. There are no phase transitions of liquid A ↔ liquid B at a fixed composition. Hence **these data—the extensive earlier work and now the paper on water—require a major re-thinking on the structure(s) of water.**



**Fig. 6:** The paper by Kawamoto *et al.* shows a projection of at least two water structures into the stable liquid water region exactly analogous to Fig. 4’s experimental data on several liquid structures in liquid sulfur some 35 years earlier [22].



These data also provide some important indications on the kinetics of change of such structures. The conventional wisdom typically uses the argument that if new clusters (or nano-"structures") form they must be very transient because "the lifetime of a bond can be estimated by the two relations:

$$\tau = \tau_0 \exp \left[ \frac{Q}{RT} \right]$$

where  $\tau_0$  is the vibration period ( $=h/kT \cdot 1.6 \times 10^{-13}$ s at room temperature). Inserting data for the bond energy of typical hydrogen bonds one gets a lifetime of an average single hydrogen bond of about a microsecond. (For a strong covalent bond it jumps to 106 + years.) However, this is not what is at issue. Consider some of the larger oligomers shown in Martin Chaplin's website reference (Figs. 8 & 9) containing say 200 H<sub>2</sub>O molecules [38]. These presumably do not completely break up and reform via some cooperative bond breakage every microsecond. The Kawamoto *et al.* phase diagram (Fig. 6) proves that at least for the duration of the experiment (minutes-hours) under the P-T conditions specified there are structurally distinct phases, with characteristic properties, which make the phase boundary detection possible [22]. Likewise, the analogy of H<sub>2</sub>O to the other liquids described is not that their strongest covalent bonds are identical but that the bonds holding such clusters together are likely to be more similar because they enable one to study closely analogous phase changes in the same P-T range, with temperature as the principal bond-breaking vector.

The intuitively reasonable concept of continuing the structures of the crystalline phases into the liquid phase was the basis of Bernal's connecting H<sub>2</sub>O and SiO<sub>2</sub> [23]. Konnert and Karle identified explicitly the tridymite structure of SiO<sub>2</sub> as being present in SiO<sub>2</sub> glass [27]. Robinson's two state model for water is based on dense and less dense ice, and recently Beneditti and Stanley suggested that fragments of two different crystalline ice structures must persist into the liquid water region [4, 39]. The point being made here is that the obviously relevant kinetics are those of the persistence of structural elements (crystalline form determined clusters, non-heterogeneous regions, etc.) under near ambient conditions. It is absolutely certain that at least some of these are reasonably long lived, since they give us the distinctive properties.

One can therefore summarize that the actual experimental data, ranging over 50 years, on the structure of many glasses and liquids shows the following:

a. The ubiquity of nanoscale heterogeneity in the

structure of many covalently bonded liquids

b. That such heterogeneity on the nanometer scale is the rule rather than the exception for the structure of all strongly bonded liquids (i.e. principally excepting ionic and metallic melts).

Roy summarized the case for this "nano-heterogeneity" as the most generalized model for glasses in a review paper on the structure of glasses and their nucleation and crystallization [15]. Figure 7a, taken from his paper (confirmed by the later data such as those of Mazurin and Porai-koshits), presents a very crude schematic visual image which should replace Fig. 1 in our memories, as a closer approximation to reality for the "structure of (most, covalently bonded) liquids" [11, 15].

Strikingly similar is the cartoon image (Fig. 7b) from the major text on Electrochemistry by Bockris and Reddy [40].

Such liquids as the ones we are dealing with, similar to H<sub>2</sub>O, consist of statistically distributed molecular aggregates of different sizes, structures and (where relevant) compositions. Furthermore, it is also thoroughly established, that major changes of such structures (i.e. the 3-D arrangement of such aggregates or clusters in space) readily occur as a function of temperature and pressure for all common glasses (even of monotonic glasses). Many of these fine-structure changes in such glasses remain stable (i.e. exhibit a kind of memory) for years. Following the discovery by Bridgman and Simon with extensive work by Roy and Cohen and Cohen and Roy showed that the density and refractive index of SiO<sub>2</sub>-glass and indeed glasses of all compositions examined and, hence their structures, were a continuous function of pressure, and that these high-density solid forms could be recovered and retained metastably under room temperature ambients for years [29—32].

The appropriate question is on the longevity of particular structures, and the statistical distribution of particular structures, and the statistical distribution of such as a function of temperature. Relevant data which bear on this question, but obviously provide no quantitative answers, are the facts that the concentration of the different clusters or fragments resembling "dense ice" which must be present in all water samples at say 3 or 4°C, is very much higher than that present at room temperature. And these clusters do not disappear because of various bond breakage phenomena. They are of course in thermodynamically stable equilibrium. (i.e. last forever).

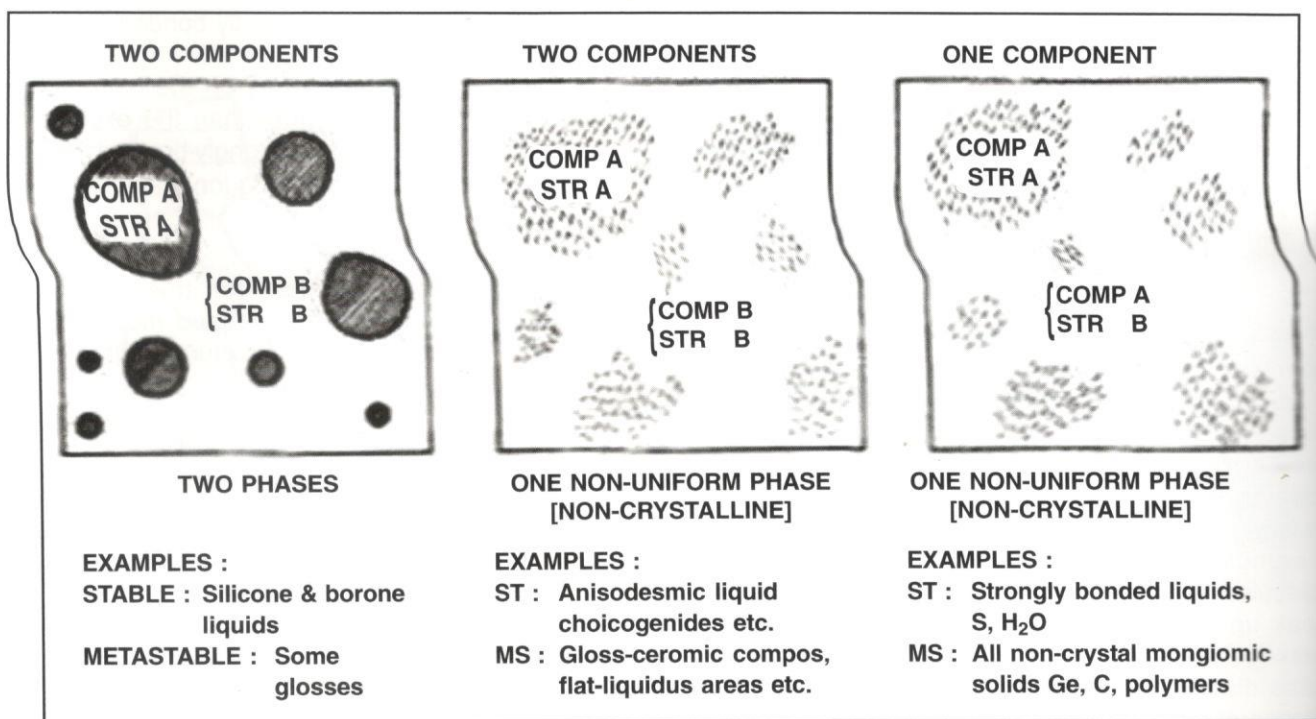


Fig. 7.a: The cartoon version of the more generalized structure of glass clearly indicating its heterogeneous (with respect to structure or structure and/or composition) nature from Roy [15]. Note that water is mentioned in the third column. This is the new minimalist schematic representation of the structure of water.

### Deconstructing the terminological confusion around the term “structure of water”

The sections above have adduced evidence from, and hence have been written in, the “language” of materials science. Strangely, however, in spite of some 17 million hits on Google for “structure of water,” materials scientists rarely study this most common material. The structure of water has been largely the province of chemists, and the reader must understand the differences in language and approach between these two communities. The vast majority of papers on the “structure of water” in the chemical and biochemical

literature start (and most often end) with statements and claims about what **molecules** exist in the water on the basis of particular, increasingly specialized, tools. The prominence of hydrogenbonding in the molecules is regularly commented on.

The very first (cited from July 25, 2004) reference listed on the Google list is (in our opinion) one of the very best and most comprehensive and most valuable reviews of this topic ever devised. It is a website by Martin Chaplin, of London’s Southbank University which contains an enormous, complex, and well organized review of the entire field (<http://www.lsbu.ac.uk/water>) [38]. Navigating through data from several dozens of papers, each only a click away it is fair to say that Chaplin presents others’ data on some hundreds of “structures of water” molecules. A small selection is assembled in Figs. 8 and 9 just to illustrate the ambiguity in the chemical literature associated with the term “structure of water”.

Probably several hundred thousands of papers discuss the structure of the monomeric H<sub>2</sub>O molecule itself, and an equal number discuss some selection of the other molecules. The question is: Is it legitimate to use the term “structure of water” in presenting such images? It would certainly be more precise to call it the “structure of the water molecule(s).” But of course the rest of Chaplin’s references also address exactly the same subject and deal not with H<sub>2</sub>O but (H<sub>2</sub>O)<sub>χ</sub> trimers

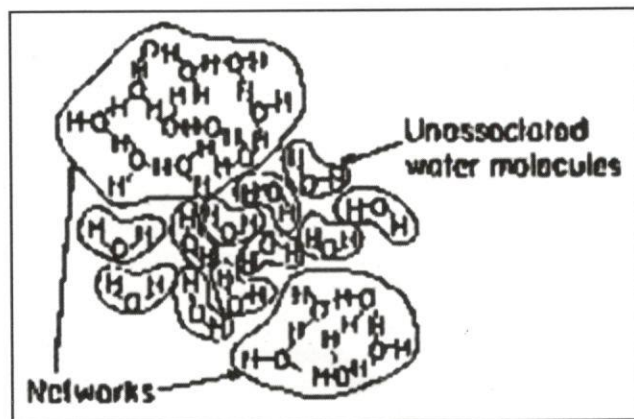


Fig. 7.b: A similar representation of the water structure by Bockris and Reddy [40].

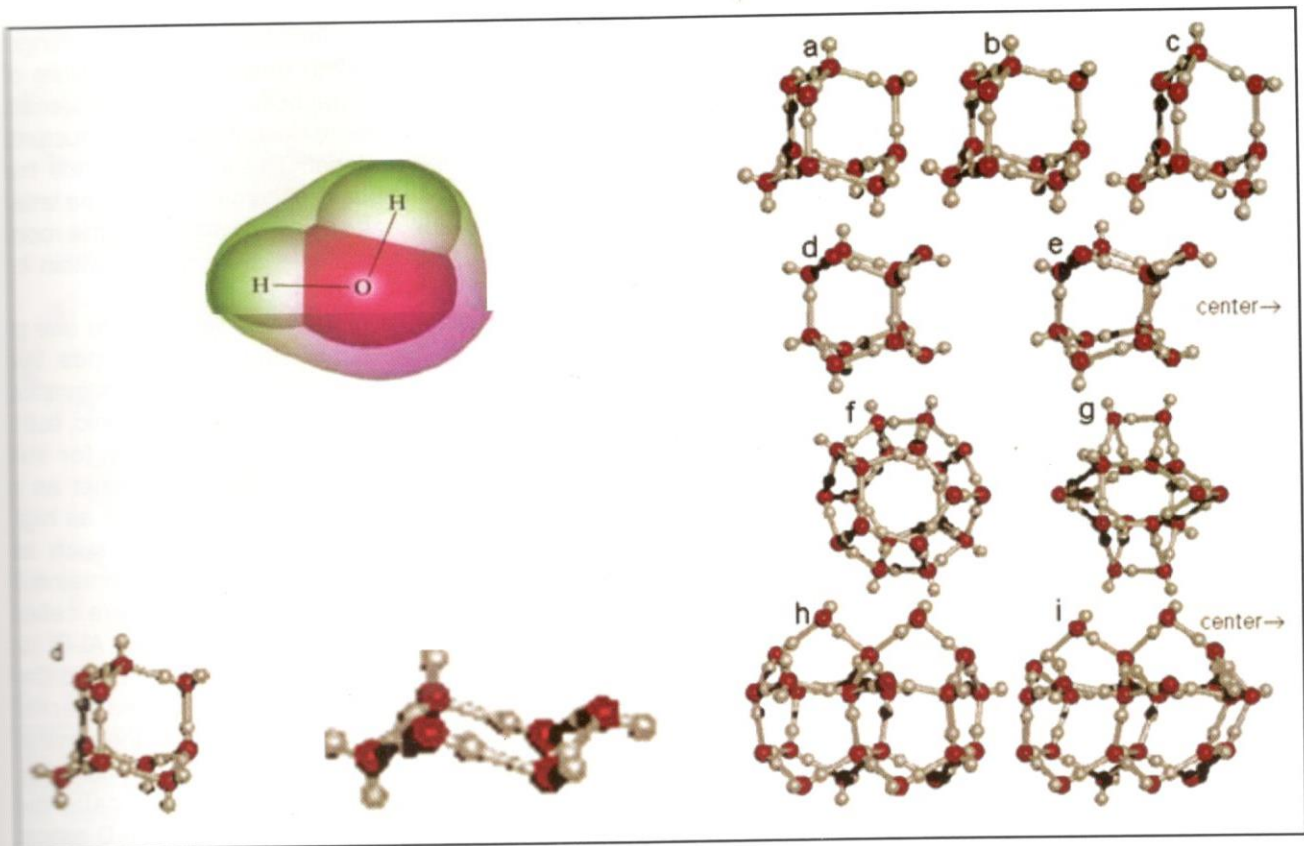


Fig. 8: The enormous variety of structures of the molecules in which almost certainly the chemical entity  $H_2O$  can exist. The well known  $H_2O$  monomer with its precisely defined tetrahedral angle is shown on the top left and below it a series of dimers, trimers, tetramers which can be constructed on paper from the relatively rigid  $H_2O$  molecule, and so on. Moderate sized molecules are on the right. See Chaplin 2004 (q.v.) for individual references for any particular structure pictured above [38].

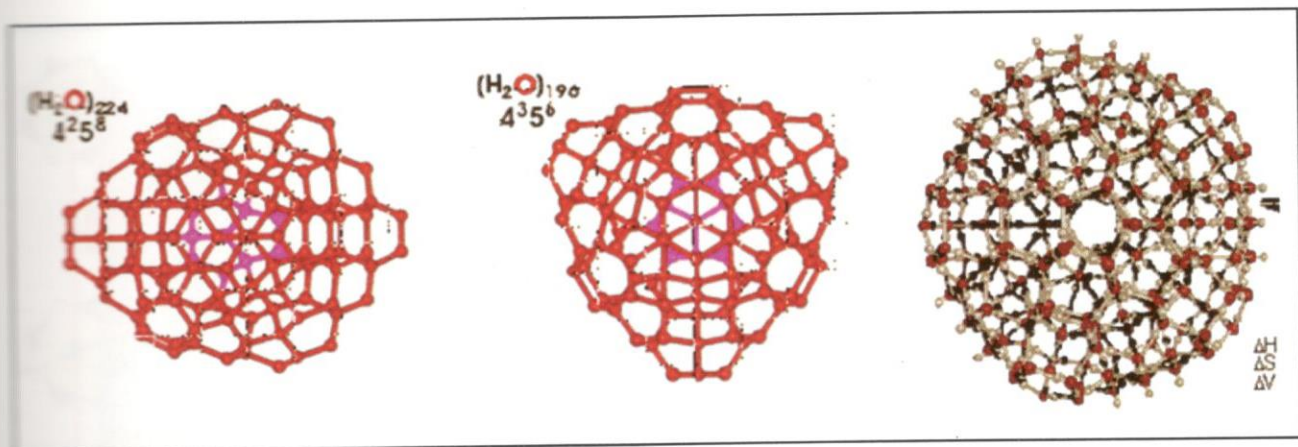


Fig. 9: This figure shows some of the larger polyhedra which are presumed to exist, largely on the calculation of likely structure of tetrahedrally bonded units. For refs. see Chaplin [38]. The relationship of the images of individual molecules, and how they are related to each other, in 3-D space, in liquid water, are rarely treated, the emphasis being on which units are present.

oligomers and polymers where  $x$  varies from 2 to say 250. Clearly water molecules appear in a whole range of sizes. The structure of a **condensed** phase, however, must surely also describe how these units are packed together. A very large number of similar papers in the chemical literature on the structure of water report the

presence of some particular complex oligomer or polymer detected by a particular experimental method under particular circumstances. But these papers do not specify how these molecules are arranged in space, nor do they address what other molecules may be present. Moreover, a very large number of these papers

deal with water vapor, not liquid water, a distinction easily lost in the reading.

A very large number of additional excellent and detailed papers have appeared which present evidence for the presence of specific molecular arrangements. An interesting cluster of these appeared recently in *Science*. Miyazaki et al. (*Science*, May 21, 2004) show infrared spectroscopic evidence for oligomers of different shape and sizes from  $n=4-27$  in  $(H_2O)_n$  [41]. Shin et al. (May 21, 2004) present intriguing IR data near the  $3.7\mu$  O-H stretching band in oligomers from 6-27, around the "magic number" of  $n=21$  [42]. From neither of these papers can one tell whether the authors believe that water—all waters under undelimited conditions—contain 100% of these molecules, or a majority. Nor is there any comment on how such clusters are distributed in space, or whether different size clusters are themselves formed into separate regions of the nano-heterogeneous bulk water.

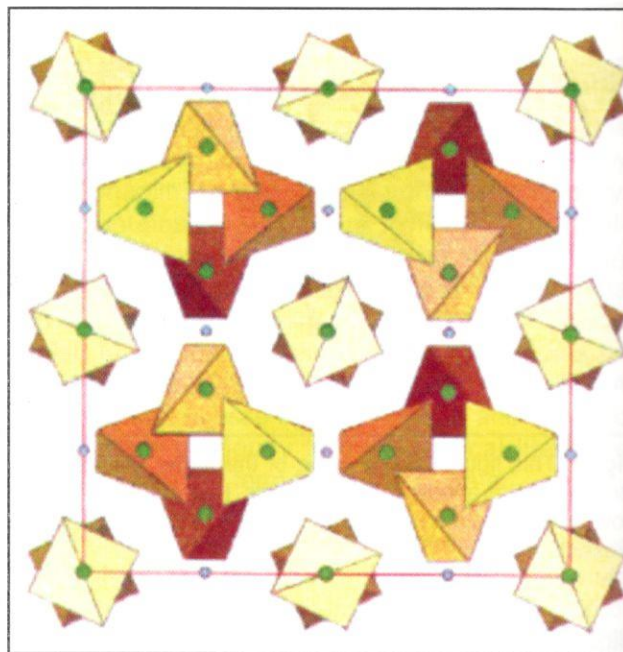
Some six months later, the October 22 and October 29 issues of *Science* carry several exquisitely detailed papers on water from senior authors. They discuss the energetics and dynamics of electron binding and transport in various cluster sizes, some of it in vapor samples. These processes are extremely rapid in the tens of femtoseconds. The papers do not consider any models with a distribution of cluster sizes, nor do they show how reproducible the data are with different water samples, even allegedly 'pure' ones, or prepared by different means. Wernet, et al. using XRD and Raman spectroscopy, supported the view favoring only ring and chain molecules, while J.D. Smith et al. used their total electron yield near-edge X-ray absorption time structure (TEY-NEXAFS) technique to come to very different conclusions that the water and ice H-bondings are very similar, and that the usually accepted 1-5 kcal/mole for the H-bond strength is consistent with their data [43, 44].

Somewhat analogous, albeit much less precise, measurements were made on nearest neighbor arrangements, 30-40 years earlier on (silicate) glasses by the then state of the art tools: optical, XRD, IR and Raman spectroscopy and EXAFS (Extended X-ray Absorption Fine Structure). None of these even hinted at the subsequently established nano-heterogeneities as the real structure of many glasses. Of course, the kinetics of bond making and breaking, are radically different. As discussed earlier, this complicates, but does not eliminate, the need to consider the model of nanoheterogeneity for the generalized structure of bulk water.

Clearly the origin of some of the inherent confusion in the field is based on the materials scientists' and the

chemists' use of the same term to mean different things. Chemists use "structure" to describe the structure of the molecules or 'structural building blocks.' Materials Scientists use "structure" to describe the 3-D structural architecture of the material. The former describe the size and shape of the bricks or cement blocks; the latter describe the shape and size of the walls and the room and how the bricks and blocks are arranged within it.

A single example of the materials science use of the term, may be used to illustrate the difference. We recognize that this example may be of limited relevance to the water issue, since it is crystalline and ionic, but it illustrates the difference in terminology for the nonspecialist. The structure of garnet, whether as a semi-precious mineral (e.g.  $Ca_3Cr_2Al_3O_{12}$ ) or as high tech magnetic materials (with a formula such as  $Y_3Fe_2Ga_3O_{12}$ ) is an example because it contains 3 different sized units or "molecules", which are called coordination polyhedra by crystal chemists, Al-O (or Ga-O) tetrahedra, Cr-O (or Fe-O) octahedra, and Ca O (or Y-O) cubes (see Fig 10). (These garnet "molecules" are somewhat analogous to the smaller "molecules" in water.) Figure 10 and Fig. 11, however also show what the materials scientist calls the "structure of garnet". It will be seen that, in 3-D space these polyhedra ("molecules") are not entirely separate but have a specific relation to each other. Indeed they interpenetrate completely sharing the same oxygen ions among the three cations. Moreover, this "unitcell



**Fig. 10:** Two of the "molecules" in inorganic materials illustrated in the garnet structure by the 4-coordinated (cornered) tetrahedral (colored yellow and orange in the middle of the four quadrants, and the 6-coordinated octahedra.

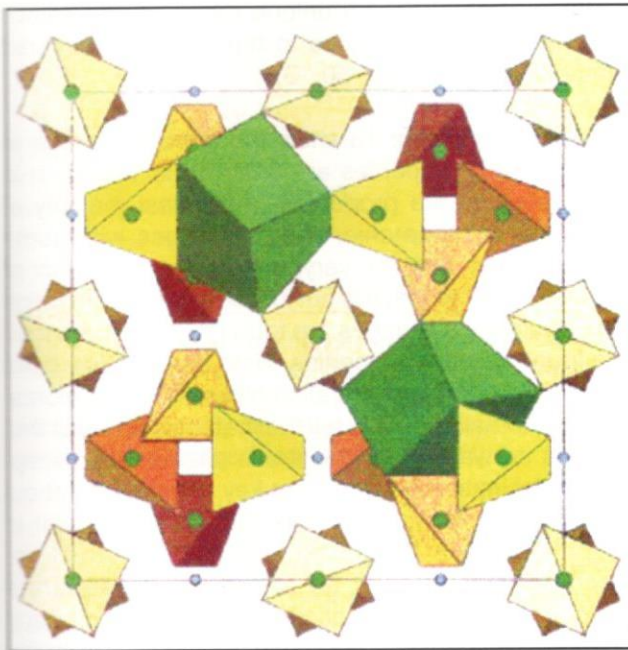


Fig. 11: The final “molecule” in the structure, the eight coordinated, or cornered, green cubes, is added, and knitted into a fixed position. The relationship of the atoms and polyhedra within the outlined (unit cell) boundaries are fixed; and repeated ad-infinitum in 3-D space, illustrating what materials scientists call “structure.”

is repeated precisely throughout the entire crystal, or stock- bottle or drum or tiny single crystal more or less exactly as shown.

How do we know? By the use of x-ray (or electron or neutron) diffraction, and transmission electron microscopy (TEM).

The TEM image in Fig. 12, by the leading nanocomposite lab in Japan, shows just how precisely materials scientists today can know the structure of (crystalline) materials [45]. Of course this is vastly simpler for a solid phase. One can literally define the position and composition of every atom, as shown in this TEM example, selected because it also shows what occurs when crystallinity or periodicity is lost. The so-called grain-boundary material is non- crystalline (glassy, liquid-like) and one can see immediately that all the atom by atom precision is gone. Instead we see the size and number of aggregates of various sizes without any regular arrays of atoms (cf – the cartoon version of Fig. 3 from 1971 [15]). That is precisely how every structure of covalently (strongly) bonded liquids, including water, is likely to appear.

Of course some of the best known water-structure research groups, such as that under

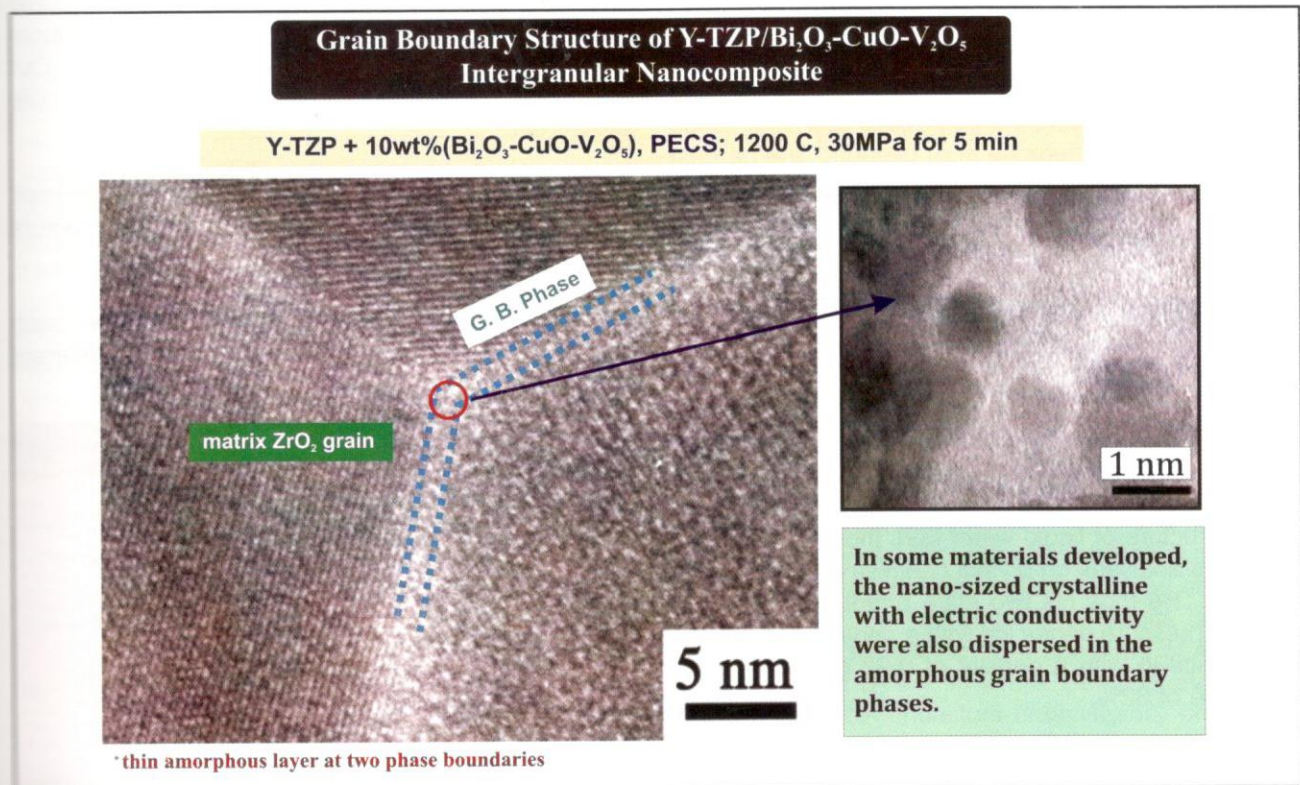


Fig. 12: Routine, typical TEM image of a complex crystalline composite at the nanometer level. Note the individual atoms all lined up in different arrangements, demanded by the structure. Specifically also note the intergranular matter, fuzzy and disordered. In the higher resolution blow up, one can see exactly what a typical, albeit multi-component, non-crystalline (like all liquids) area contains – disordered assemblages of different size (and composition, as revealed in the differences in contrast) typical of liquids. (From Niihara *et al*. [45]).

Nemethy and Scheraga and G.W. Robinson, had concluded on the basis of calculation that there was a “distribution” of two “states” or “five kinds” of molecules respectively, which varied with “P” or “T”, but no one ever described how they are distributed in space [39, 46].

#### Van der Waals bonds in Liquid Water Structure

A second aspect of the structure emphasized in materials research is the strengths of all the bonds involved. Some materials where all the bonds (and their strengths) are identical, say NaCl, are called isodesmic. In anisodesmic “structures”, different bonds have different strengths; e.g. in CaCO<sub>3</sub>, the C-O bond is much stronger than the Ca-O bonds. Much is made in the chemical literature of the (strong) hydrogen bonds in water. However, the significant role of the van der Waals bonds (the weak but ubiquitous inter-neutral molecule bonds in water) is ignored. A key principle in materials science is that the weakest bonds determine the (interesting) properties, while the strongest bonds determine the structure. An illustrative example exists in some common crystalline materials. Talc and graphite are both very soft made up of sheets, because the inter-plane forces are only van der Waals bonds and slide apart with finger pressure. Indeed, in graphite the in-plane covalent bonds are even stronger than in diamond, but the enormous anisodesmicity results from the very, very weak inter-plane bonds. This bond weakness also makes possible very soft phases and the entire world of different buckyballs and nano-tubes and their radical difference from diamond, the hardest material. The analogy to the rich diversity of structures possible in liquid water is obvious. Indeed the universally accepted presence of a wide variety of molecules in H<sub>2</sub>O no doubt contributes to the enormous range of van der Waals bonds present, with the weakest ones being most susceptible to change by very weak forces.

What is proposed here is in many ways simply a modification of G. Wilse Robinson’s series of papers developed to justify what he called the two-state model of the structure of liquid water [39]. Indeed, Robinson based his analyses on crystal chemistry and structure analyses. He took his two state prototypes as ice-II, the high pressure dense ice with a density of 1.18 gm/ml, and ice-Ih with a density of 0.92 gm/ml, a huge difference of 32%.

#### Water’s changing properties which demand a multi-structural model

The absolute reason why only models which posit a wide range of structure, and their distribution in space can have any value in describing the structure of liquid

water, is the wellknown unique range of anomalous physical property changes in the most encountered temperature range (0—50 °C).

Table I and Fig. 13 show the extreme degree to which water’s properties are anomalous. Note first in the figure that the properties of the vast majority of liquids have monotonic, linear, changes with some variable. Next, note the very, very different behavior of water. Next, note that it is not just one property in which very anomalous changes are found, but such changes are found in many properties. Note that the kink point or maxima or minima are all at different temperatures. These anomalies clearly tell the materials scientist that there is no way to achieve these phenomena except by a combination of two of our key conclusions about the structure of water. Across the transition point in properties there has to be a change of structure. Secondly, there must be several quite separate structural transitions to account for just the property changes noted. There is no prima facie way of telling whether such absolutely confirmed familiar behavior can be explained by complex rearrangement of just two (or five) states or clusters, or whether it requires simpler re-arrangements of many different states. The crystal chemical connection invoked by Robinson is certainly operative, but it is not necessary that water consists of a mixture of only “two states”, which by some juggling could be adjusted to try to explain the plethora of anomalies by utilizing only two structures. Our proposal is simply to posit that there are many possible structures.

On the basis of these well-established materials science principles, one can conclude that the structure

**Table I:** Changes in different water properties, each requiring a change of structure, each at a different temperature

Property	Comment
Density	Maximum at 4°C
Refractive index	Thermal maximum near 0°C
Thermal expansion coefficient	Changes from extremely high up to 6-7°C to low (normal) above 12°C
Isothermal compressibility	Minimum at 50°C
Isothermal piezo-optic coefficient	Maximum near 50°C
Specific heat of water	Minimum at 35°C

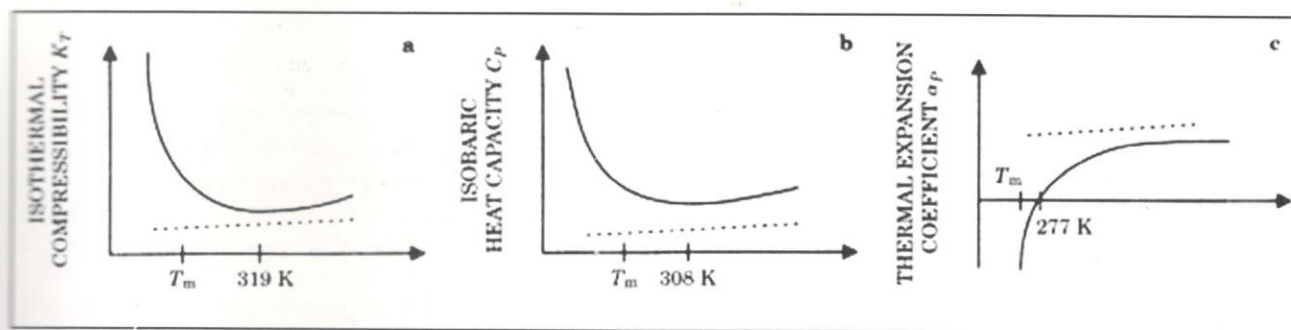


Fig. 13: Comparison of changes in normal (dashed lines) liquids with highly anomalous changes in water's properties as related to temperature. Such changes in property demand the existence of many structural changes of different kinds and at different temperatures. Notice in (a), (b) and (c), the radical difference from normal liquids. Notice the 308—319 K difference between (a) and (b). The most dramatic departure from typical liquid behavior is shown in (c). (Modified from DeBenedetti and Stanley (Physics Today 6 2003 p 41) [4])

of liquid water at say 25°C and 1 atm is a highly mobile assemblage of interactive clusters (dominantly perhaps of half a dozen different oligomers), with minor amounts of dozens of others, and possibly a few larger "polymers" in the 200-H<sub>2</sub>O range. What is very significant about this model is that this arrangement of a "zoo" of mixed sizes of molecules is also highly likely to be highly anisodesmic. First there will be a cluster of bond strength values around the typical hydrogen bond within the cluster, or in small molecules. But these intra-cluster bonds are likely to be much stronger than the inter-cluster van der Waals type bonds. Most interrogatory experimental tools may be inappropriate for making this distinction especially among its weakest bonds. Hence water is ideal for responses to small and large changes in all the intensive thermodynamic variables. Water is therefore probably the most easily changed phase of condensed matter known. It is this unique anisodesmicity, or structural and bonding heterogeneity, that helps explain its amazingly labile nature and hence the various extraordinary data, e.g. the clustering of water and solute in very dilute solutions reported by Samal and Geckeler, much of the ultra-dilution work, and the reported influences of very weak magnetic fields [47].<sup>7</sup>

This aspect of the materials science approach to the 3-D structure of matter is not the only highly relevant area of contemporary science which might have been overlooked by the chemical approach to water behavior. We discuss others below.

#### a. The role of epitaxy

Epitaxy, a term which does not appear even in most technical dictionaries, is a phenomenon very well known, studied and used in dozens of everyday

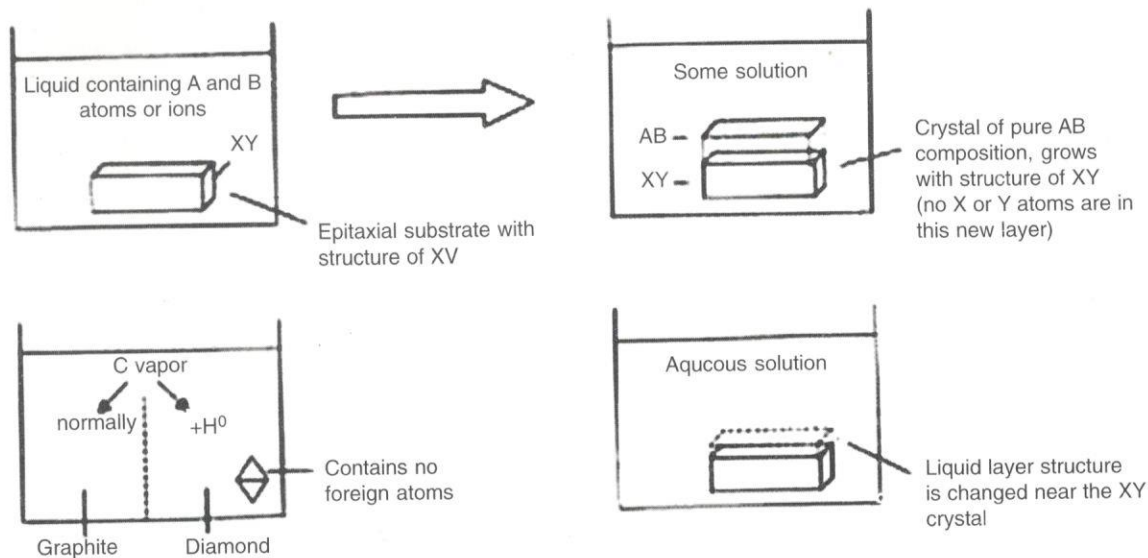
technologies in materials science (See Barker; Royer; Pashley [48—50]). Yet it is never invoked directly in the literature on potential interference in the data, or on the super-sensitive molecular structural studies of water. It is not even referenced by the strongest supporters of homeopathy. Epitaxy is the transmission of structural information from the surface (hence epi) of one material (usually a crystalline solid) to another (usually but not always a liquid) (See Fig. 14).

Subtleties of terminology appear in various papers, but it is structural "information" that is definitely transferred (for a recent example of the subtleties of the what and how information can be transferred in the preparation of certain industrially important phases, see Roy, Guo, Bhalla and Cross [51]. In most cases, no (zero) matter is transferred from solid to liquid, but even major structural changes and patterning information is certainly transferred, e.g. GeO<sub>2</sub> can be made to crystallize from aqueous solution in the quartz (SiO<sub>2</sub>) structure or the rutile (TiO<sub>2</sub>) structure (which is 50% denser), merely by using the appropriate epitaxial substrate. Hence it is clear that concentrations of the change agent or solute which **dissolves** in the liquid phase, being changed, whether above or below Avogadro's limit become wholly irrelevant, since it is zero. By providing a specific structure as a template (usually solid but sometimes liquid), one can induce an entire body of liquid (or even solid, see Liu et al.) to precipitate or crystallize in a pre-selected structure or morphology [52]. The seeding of clouds is epitaxial growth of crystalline-ice on a substrate of AgI, which has the same crystal structure. Seeding and epitaxial growth of semi-conductors is universally practiced in major modern technologies. Information and "memory" are transmitted from the seed or substrate to adjacent layers of the liquid phase, which can completely control

7. It is also plausible as reported by John Ives that especially with the succussing process, trace amounts of the glass (which is probably a complex aluminosilicate) are dispersed as nano-heterogeneities of silicate islands. ("Recent data on homeopathy research", Proceedings at the Whole Person Health Summit, Washington, D.C., April 2005)

# Epitaxy

- The transfer of the atomic structure of any “template” structure to a liquid *without any material transfer*.
- It is extremely common in materials science and technology.



**Fig. 14:** A cartoon model of epitaxial transfer of structural information from one crystal to another, and to the liquid adjacent to the crystal without any transfer of composition. The graphite to diamond “determined” by the presence of  $H^{\circ}$  but no H is left in the diamond.

the structure of what is formed from it. No chemical transfer whatsoever occurs.

In homeopathy, a specific material (animal, mineral, or plant source), is added to the liquid (water or water + ethanol). The preparation of the homeopathic remedy involves multiple serial dilution steps, each followed by multiple **succussions** (vigorous shaking or turbulence—by hand or mechanically). The resultant remedy is hypothesized to catalyze system-wide, hierarchically self-organized changes within a clinically ill person or animal [53, 54]. However, **this** paper is not concerned with any clinical effects whatsoever.

The only relevant question for us is, in what ways can the “active agent” change, affect or “imprint” the liquid structure [55]. The biochemical and medical community, unaware of the materials research field, assume that it is only the presence in solution of finite concentrations of the active agent that can affect a liquid. They are clearly wrong: structure can be transferred by epitaxy with no presence whatsoever of the controlling phase. We have established that the

structure of water can possibly be influenced by the structure of the solids with which it is in contact, including possibly the glass or polymer containers used to hold it in say IR or Raman spectroscopy. The thickness of the affected layer will of course be strongly influenced by the structural relations of the substrate and the liquid, and any generalization that is only a few atomic diameters neglects the key role of the structural affinity. The key thrust for future research will be to determine just how far the different epitaxial effects caused by the electrostatic force fields of the crystal extend into the liquid. Indeed, the reach of these changes in structure studied by NMR and IR spectroscopy have been recently claimed to extend from hundreds of angstroms to hundreds of microns or more [56, 57]. The authors use the term “contact with a solid phase” as necessary for this epitaxial transfer of information. The recent work by Samal and Geckeler also shows the most remarkable aggregation of solute+water clusters around a wide variety of solutes (from NaCl to DNA to fullerene complexes) which range into the micron size range as the specific chemical concentration goes down [47].



## **b. The colloidal state and its relevance to the structure of water**

The first well-established indications from materials science include: potential structural heterogeneity within virtually all covalent liquids, and the role of epitaxy in transferring structural information without involving compositional dissolution in the water at all. In addition to the above, materials scientists deal extensively with other phenomena which may prove to be relevant to the structure of a liquid phase, such as the formation of unexpected, novel colloidal suspensions. This is a much less explored area, but one with great potential [1].

A colloid is considered to be a two phase system usually consisting of finely divided solid matter ( $\approx \leq 100\text{-}1000\text{ nm}$ ) dispersed in a liquid. The term can obviously include both liquids and gases as the dispersed phase. The finely divided phase in a stable colloid consists of either positively or negatively charged particles, which of course keeps them from clustering and precipitating out. Can one see the significance of the colloidal state on the structure of water? (It is apocryphally reported that it was Einstein who in his work on Brownian motion, his most cited paper, commented on the fact that colloids are "atoms" (structurally different from the parent liquid?)).

First, the colloidal particles can exert a structural epitaxial influence on liquid layers (of unknown size) around them. Second, the very existence of a statistically periodic set of charged particles is also sure to affect the overall structure of the water. Of course, some of these effects may well be de minimis. Finally, again a major insight from materials science, the number of such nuclei, and the potential for epitaxy must—from classical nucleation theory—affect the ease of crystallization (and hence lowering the undercooling possible) and finally from epitaxial effects, the colloids should easily affect the morphology of the ice being crystallized.

The colloidal state also provides an excellent bridge to demonstrate the biological effects of ultradiluted water samples. It has been known for thousands of years that metallic silver had extraordinary antibacterial properties. These antibacterial properties of silver are utilized in many devices used in modern medicine from special stents to wound dressings. Colloidal metallic silver in pure water at 1 atom ppm concentrations is a powerful broad spectrum antibiotic. Data on one such colloidal dispersion is found in Table II. What is striking

is that this biological activity is comparable to the best known antibiotics and continues (even if slightly diminished) at 0.01 atom ppm or lower concentrations. Although not below the Avogadro limit, traditional chemical explanations of this effectiveness at such ultra-dilute concentrations have not been advanced.

Proposed mechanisms such as structural effects on the water can be seen as a bridge to the homeopathic regime. Ricci, in the standard text on the Phase Rule puts it thus: *Another non-uniformity possible in a homogeneous phase of an isolated equilibrium system free of the forces of gravitational and other such fields seems to be that of surface energy, if the phase is a subdivided one. The subdivided phase in a 2-phase colloidal system, for example, may not have the same surface development in all its pieces. But if there is such a thing as a reproducibly stable colloidal system, with an equilibrium state which is a function of T, P, and composition alone, independent of time and of the relative amounts of the phases, then this non-uniformity must be a regular one, following some statistical distribution fixed solely by these variables. If the colloidal system, then, is stable and in reversible equilibrium, the distribution of its surface energy must be assumed to be either uniform or a reproducible function of the stated variables [16].*

## **c. Other methods of affecting structure. The role of succussing<sup>8</sup>: pressure generation and nanobubble entrapment**

Pressure, after temperature, is of course the most important of the intensive thermodynamic variables in deciding what structure will form under new environments. Pressure is well known to have profound effects on crystalline H<sub>2</sub>O. Some 13 different crystalline H<sub>2</sub>O structures are known in a modest P-T region. We have shown as reported above, that while it is largely unknown among even materials scientists, it is fully established that all common glasses (frozen liquids) change structure (and their density and refractive index properties) continuously with pressure, and they can be retained in their new states rather easily<sup>9</sup>. There is no doubt that under the "normal" succussing procedures, very respectable pressures (say in the 10 kbar range) can be generated on the different size water droplets which result from the shaking. Reasoning from analogy with such similar liquids, there will, no doubt, be many different structures of water formed both by the pressures generated in succussing and in some combination with the epitaxy on any additives.

8. The process of agitating a liquid by rapping its container on a hard but elastic object thus causing high pressures and nanobubbles.
9. Scratching any glass surface with a ruby or diamond in a ring produces a substantial change in density in the glass particles produced.

**Table II:** Comparison of biocidal effectiveness (measured as the minimum inhibitory concentration MIC in ppm) of key antibiotics with ASAP-10, a colloidal silver prepared in a 11,000 volt AC field with a concentration of 1 atom per 106 molecules of H<sub>2</sub>O. (The MIC for the colloid applies in humans to topical applications) (Personal communication, Prof. R.W. Leavitt, Brigham Young University)

Organism	Antimicrobial					
	Tetracycline	Ofloxacin	Penicillin G	Cefaperazone	Erythromycin	ASAP
S. pyogenes	0.625/>5	1.25/2.5	>5.0	0.313/1.25	0.003/0.019	2.5/5.0
S. mutans	0.625/>5	2.5/>5.0	0.521/>5	1.25/>5	0.009/0.019	2.5/10.0
S.gordonii	0.156/0.625	2.5/5.0	0.009/0.039	1.25/1.25	00.005/0.019	2.5/10.0
S. pneumoniae	0.078/0.625	2.5/2.5	0.019/0.019	0.313/0.313	0.002/0.004	2.5/2.5
S. faecalis	0.313/>5	1.25/5.0	5.0/>5.0	>5.0	0.009/1.25	10.0/10.0
S. aureus	0.313/>5	0.417/0.625	2.5/>5.0	5.0/5.0	0.039/>5.0	5.0/5.0
P. aeruginosa	0.78/5	0.156/0.313	0.13/>5.0	2.5/5.0	2.5/>5.0	1.67/5
E. coli	1.67/>5	0.104/0.156	>5.0	0.625/>5.0	5.0/>5.0	2.5/2.5
E. aerogenes	>5	0.078/0.156	>5.0	2.92/>50	>5.0	2.5/2.5
E. cloacae	1.67/>5	0.156/0.156	>5.0	>5.0	>5.0	2.5/5.0
S. tiphimurium	1.25/>5	0.078/0.156	>5.0	1.25/2.5	5.0/>5.0	2.5/5.0
S. arizona	0.625/>5	0.078/0.078	>5.0	0.833/>5.0	4.17/>5.0	2.5/5.0
S. boycli	1.25/>5	0.078/0.156	>5.0	0.625/0.625	5.0/>5.0	1.25/1.25
K. pneumoniae	2.5/>5	0.417/0.625	>5.0	>5.0	>5.0	2.5/2.5
K. oxytoca	1.25/>5	0.104/0.156	>5.0	1.25/>5.0	>5.0	1.25/1.25

Finally, the "succussing" process itself must by its very nature produce a complete range of sizes of bubbles in the liquid. The size distribution of the bubbles will certainly include some nanobubbles – i.e. nanosize phase heterogeneities of mainly O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, plus possibly alcohol, the active ingredients, etc. Some of these bubble sizes will no doubt be well within the colloid range and therefore a water + gaseous and liquid colloidal inclusion would be formed, and it could be quite stable for very long periods. To the best of our knowledge this phenomenon – the creation of nanobubbles of air and their retention as "stable" colloids – has never been commented on, in either its influence on the structure of water or in the debate over the plausibility of homeopathy's claims of effectiveness.

There is no question of the plausibility of pressure induced changes during succussion. Such changes are well known in solid H<sub>2</sub>O, and Kawamoto has shown at least one phase boundary in liquid water at modest pressures [22]. Likewise the plausibility of nanobubble

formation is obvious. The question is whether they can survive. Objections based on the simple-minded calculations of high internal pressures of nanobubbles obscure their built in assumptions. Exactly the same objection was raised against the obvious stability and persistence at room temperature of several percent of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, etc. dissolved in SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, etc. glasses at modest pressures and temperatures which also "could not exist" using the same argument (See Faile and D. Roy [58]). The fact is they do. However, the work of Tyrrell and Attard at Australian National University has proved beyond any doubt that nanobubbles do exist and do persist [59]. (See Fig. 15 for a SEM photo showing the unevenly shaped nanobubbles)

These claims are further supported by extensive work in the Russian Academy of Sciences Institute for Physical Chemistry on what they term "bubstons" (bubbles stabilized by ions) under Prof. O. Vinogradova in the laboratory created by B.V. Derjaguin (See G.E.

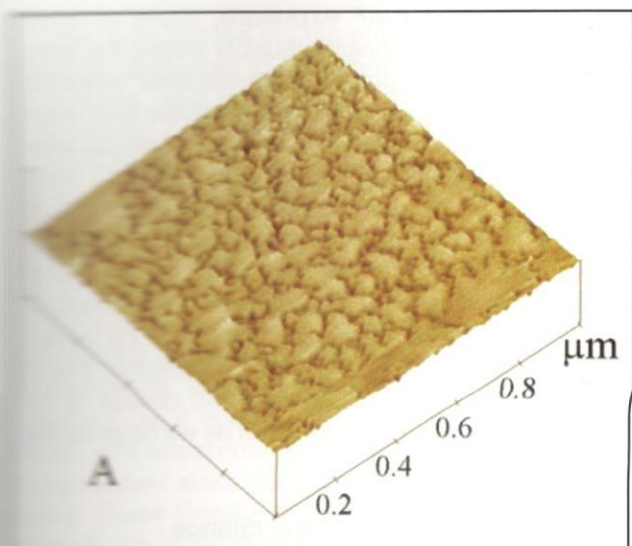


Fig. 15: Irregular nanobubbles shown as modified from paper by JMG Tyrrell and P. Attard [59].

Yakubov et al. who discuss the formation of these “stable microcavities” [60, 61]).

**4. The influence of magnetic and electric fields, and human “intentions” (subtle energies)**

In addition to those major important variables which can determine the structure of water, are the roles of electric and magnetic fields. This becomes even more interesting as the role of the molecular organization around electrons is highlighted (see October 2004 Science papers [2, 41, 42]). While the E or H fields contribute relatively little to the Gibbs free energy stability of most materials,<sup>10</sup> they become profoundly important when these effects can be “locked into” a material as, for example, ordered domains in a magnetic ferrite, or in the domain structure of ferroelectric transducers. All modern electronics depends on memories which utilize such materials. A considerable body of work now demonstrates the effects of magnetic fields on aqueous solutions. The effect of magnetic fields on the formation of scale in boilers has been established in an overwhelming mass of data (for a list of references, see Duncan [62]). In the laboratory, the influence of modest d.c. magnetic fields on the nucleation and growth of CaCO<sub>3</sub> (phases, sizes, morphology) in dilute aqueous solutions have been thoroughly studied and demonstrated by Higashitani et al, and Pach et al [63, 64]. The former demonstrates a strong memory effect in the constituent solutions exposed to the H-field. Tiller et al. have shown the remarkable effect of a static magnetic field on the pH of water in a conditioned space (Fig. 16) [65].

There has been very little study of the effects of magnetic fields on the structure of common crystalline solids. Since 2002, Roy et al. have demonstrated in a series of papers, wholly unexpected and dramatic effects of weak magnetic fields (< 0.5 gauss) at GHz frequencies [66—68]. These fields literally destroy the crystalline structure of even refractory solid oxides (melting points of near 1500 C°), such as Si, and classic insulators such as TiO<sub>2</sub>, all in a few seconds. These most remarkable structural effects had not, and could never have been, predicted by any theory in solid state physics. Reports, from Roy et al. include interesting *biological effects of such high frequency magnetic fields* [66—69]. Hence the reports of the effects of milli-gauss magnetic fields on “imprinting” water and aqueous solutions as reported by K. Mohri et al. are not surprising [70].

These data on the effects of such weak magnetic fields are an appropriate backdrop to the fact that Tiller’s conditioned water can have its pH changed by one unit by a modest static magnetic field (see Fig. 15). This suggests that “intention implantation”, or more generally “subtle energies”, can also change the properties, and hence the structure of water. Even more direct evidence is found in the literature as reported by Liu Zuyin [71].

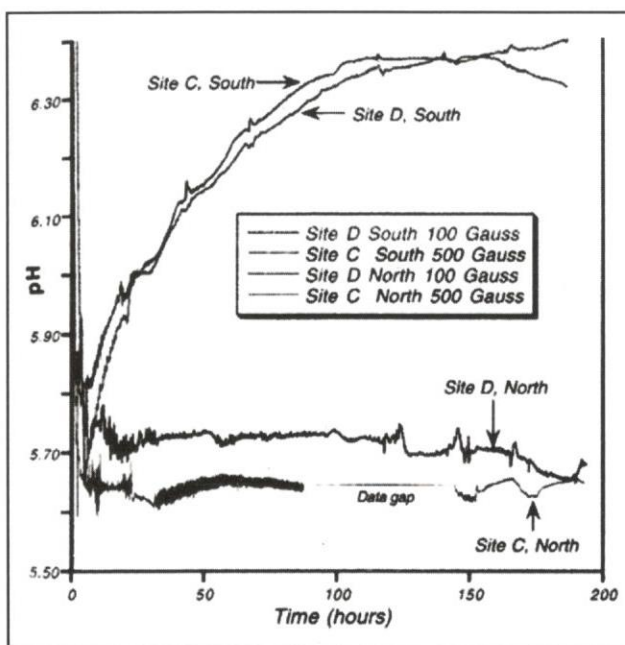
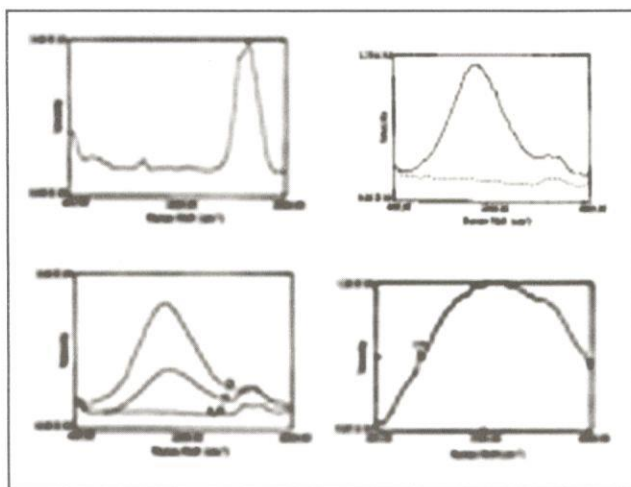


Fig. 16: The change in the structure of water caused by the subtle energies, as illustrated by the work of Tiller, Dibble and Kohane showing the change of pH of water only in space “conditioned” by subtle energies, caused by a static magnetic field with a specific N/S orientation [65].

<sup>10</sup>. They are not even mentioned in the standard textbook on the thermodynamics of the Phase Rule [16]!!

In Tsinghua University in Beijing, Raman spectra were taken of distilled water before and after implantation of “qi,” or intention, by Dr. Yan Xin, the best known of China’s Qigong grandmasters, from a great distance (10’s to 1000’s of km.). Figure 17 reproduces the major change in water structure as reflected in the Raman spectrum of before and after treated specimens [71]. These are truly remarkable results indicating that the structure of water—the major features easily measured by Raman spectra—is a very sensitive indicator of its physical environment including especially the role of magnetic and subtle energy fields. The most direct evidence, using infra-red spectroscopy (by E.G. Brame, an authority in that field) for the change of the structure of water by the “subtle energy” of healers hands in the U.S., has been presented by Schwartz *et al.* and Tiller [72, 73].

While such robust data are now appearing in the **materials field**, the effects of magnetic fields long reported in various other **health interventions** become much more plausible [74—77]. Further, any nano-scale heterogeneities, like the clusters or bubbles, have different electric and magnetic susceptibilities relative to the surrounding “bulk” water [78]. Thus, both electric and magnetic dipoles are induced at these interfaces [79]. For non-uniform fields, the nano-clusters and nano-voids will try to migrate towards the high-field regions of the bulk water under the influence of dielectrophoresis and diamagnetophoresis forces [80—83]. Abundant experimental data exist to confirm many unusual effects associated with electromagnetic fields (EMFs) and water. Surprisingly, when water is first



**Fig. 17:** The change in the structure of tap water shown in its Raman spectrum caused by the emission of qi (subtle energy) by Dr. Yan Xin from a distance of 7 km. The main O-H stretch frequency is very strongly reduced and the bending modes strongly enhanced (compare before and after Qi, left and right). The bottom left shows the reversion in about 2 hours as it relaxes. The bottom right shows the sample to sample variation possible.

degassed before EMF exposure, many of these unusual effects are absent plausibly linking the effect to our proposal of a probable “nanobubble” presence [84]. Direct electron microscope evidence also exists for magnetic field alteration of the Helmholtz layer thickness at solid/water interfaces [85, 86]. Most interestingly, Smith in his longterm study of coherence effects in water treated as a macroscopic quantum system, reports on the significance of the interaction of the magnetic vector potential with the chemical potential [44]. This interaction is relevant in the context of this paper to the extent that it is another line of evidence showing the unsuspected results of the complexity of the structure of water as we have defined the term.

#### e. The kinetics of structural change

A final important issue in attempting to bring some of the results into the context of current (not classical) physio-chemical thought, concerns the kinetics of any structural change. We have dealt in earlier sections with responses to specific objections. If indeed one were to imprint “epitaxially”, specific structured information on to a homeopathic liquid remedy, or expose it to a human intention field, *how long would such a (metastable) imprint last?* The fact that a phase is metastable gives no clue whatsoever as to its rate of reversion to the stable form. A diamond (a metastable phase in the room ambient) “is forever” the ad says; thermodynamics says: not so. But diamond persists for billions of years under a wide range of geological conditions, even under strong stresses, where it is metastable. The common assumption is that different compositions and structures in ordinary liquids (like water) will mix perfectly, “instantly”, or in seconds with stirring. This assumption has recently been questioned. Yamashita and Tiller have shown that times in hours are required [83]. In the careful work by Liu Zuyin at Tsinghua University, the meta-stable water state created by intention by Yan Xin, was followed by Raman spectroscopy and shown to take a few hours to return to “normal”. Recent results on the discovery of ortho and para water (the oxides of ortho and para hydrogen) by Tikhonov and Volkov not only expanded the possibilities of making different waters, but they clearly showed that the mixing kinetics, contrary to expectations, required months in ice and a half hour in water [87]. The most relevant to homeopathy parallel research is Tiller, Dibble and Kohane’s report on their ability not only to alter the pH of water by focused intention, but also to preserve the altered state over time and also over distances for weeks to months [65]. The study of the kinetics of structural change among the different water structures, some possibly containing 250 H<sub>2</sub>O molecule oligomers, now becomes the significant area for research.

We have pointed out the anisodesmic nature of a structure postulated to contain a variety of oligomers or clusters, and necessarily surrounded by some "monomeric" or similar matter. What is certain is that the intra-cluster bonds will be substantially different from the intercluster bonds. In an earlier section dealing with the thermodynamics of aqueous solutions with consolute points we made the case that the kinetics of bond breakage and formation (in pico and femtoseconds) have little or no bearing on the existence and stability of two structurally different liquid phases in equilibrium. The onomatopoetic conflation of bond "breaking", as if in a ball and stick wooden structural model, with actual change of structure (i.e. the change of equilibrium atom positions in space) is obviously wrong. These kinetics of structural changes of liquid liquid (A)+liquid (B) and of the survival at equilibrium of the liquid A and liquid B combination become the most relevant kinetics for a starting point to discuss how long the distribution of clusters changed by pressure, electric or magnetic fields or subtle energies will last under specified p, t conditions.

#### f. Experimental tools for determining the structure of liquids including water

The tools which have been most used to attempt to determine the 3-D structure of bulk matter are X-ray, electron and neutron diffraction. We recall that diffraction can be definitive for periodic crystalline matter but all of these tools are indirect for aperiodic glasses and liquids, requiring assumptions and models (see for example the review by Soper on the use of neutron diffraction [88]). Further we note that it was these very tools, which led the entire scientific world astray on the structure of most glasses (a "frozen" liquid) for 40 years by assuming the "homogeneous-structure" implied by the "random network theory". Most of these approaches, such as deriving the structure from the radial distribution function, from X-ray or neutron scattering, are only model fitting. None of these carry the definitiveness of diffraction from a periodic lattice, nor the "photographic" record of TEM.

Of the spectroscopic methods, i.e. X-ray, infra-red and NMR, on balance while they provide good information on nearest neighbor coordination, it is Raman that appears to pick up the changes beyond nearest neighbor distances best. The literature on NMR spectroscopic evaluation of homeopathic remedies versus controls, for example, has shown mixed results [55, 89]. The only other direct method for determining structure at the nanometer level or below is direct observation by transmission electron microscopy. It was this, in the hands of Mazurin and Poria-Koshits, which demonstrated the incredible heterogeneity of structure (and composition) in transparent, clear glasses [11].

Of course, these were all solids. Today we believe that this technique is an obvious but new, albeit experimentally difficult, possibility for studying water structure. The cryo-TEM approach to glassy water structure is now feasible, in principle, by quenching samples to liquid He (or N<sub>2</sub>) temperatures, coating the iceglass with an appropriate polymer and carrying out the TEM imaging at liquid N<sub>2</sub> or He temperatures as has been done on other samples (See Fig. 18). Indeed TEM images of crystalline and liquid samples in equilibrium at high temperature have recently been achieved. Clearly this could be a new approach to possibly settling some of the arguments on the structure of water and/or ultradilute—colloidal samples or homeopathic remedies, which may, for example, contain nanobubbles, that continue without resolution.

#### g. Data from the literature on homeopathy consistent with the newer materials science models

This paper has attempted to review the literature on the structure of water through the prism of materials science, hence focusing on that literature. Of course large amounts of very relevant research also exist in the homeopathy literature, and in the following section we attempt merely to connect the two approaches.

The central thrust of this paper, which has presented an argument that nullifies the simpleminded argument of "zero concentration of solute, hence no possible effect," is that it is structure NOT composition which has the effect. When we turn with that lens to

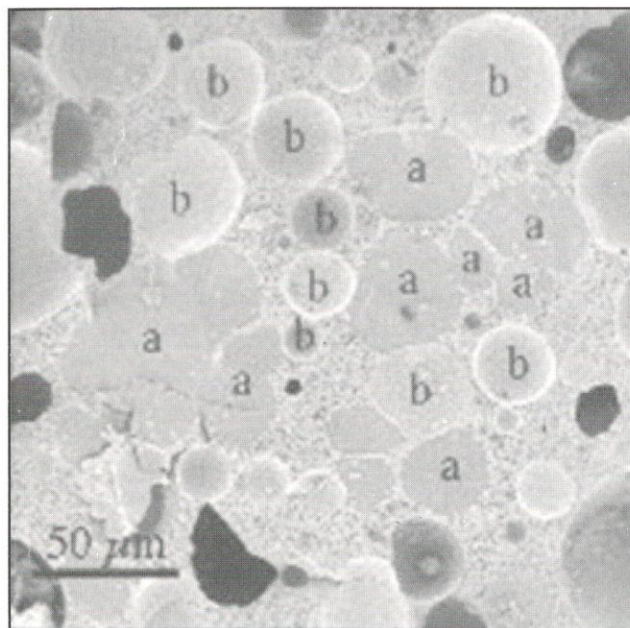


Fig. 18: Cryo-TEM of microstructure of ice-cream consisting of three phases: water, fat, and air. (From Hans Wildmoser [90])

the homeopathy literature one can find much supportive data not only on effectiveness, but on possible mechanisms, and the relation to structures when liquid homeopathic remedies are subjected to marked changes in pH or x-rays after extreme cooling [91—93]. Clinicians also claim that homeopathic remedies are destroyed by exposure to high heat and/or strong magnetic fields. On the latter topic, a growing number of randomized controlled and observational clinical studies as well as basic science studies on animals, plants, and cells suggest that homeopathic remedies can indeed exert biological effects [55, 94—109]. At the same time skeptics in the field correctly point to inconsistencies and replication failures—albeit hardly unique to this field—that raise important concerns about the reliability of phenomena that homeopathic remedies may induce [110—114]. Recent conceptual advances in the field, e.g., understanding the patients' and other living organisms' responses to remedies as manifestations of nonlinear system dynamics, may lead to new insights into some of the bases for variations in reproducibility [53, 55].

However, these references are only cited for completeness, and they are not in any way involved in the data or argument of the present paper, which is limited to the fundamental chemistry and physics of pure water and the remedies themselves. To take one example, the recent calorimetric thermodynamic study by Elia and Niccoli demonstrated with high reproducibility that mixing a base (sodium hydroxide) with a homeopathically prepared agent diluted beyond Avogadro's number and shaken vigorously (dose of 12 C, diluted to 10-24 and succussed) generated a pH-dependent excess of exothermic heat release in comparison with diluted control solutions prepared **with succussion** [91]. They noted a pattern of apparent pH-dependent disruption of order in the test solutions, analogous to that seen in protein denaturation. In a very recent paper, the same authors, accurately, make the point that virtually no "physico-chemical measurements", other than their own, have been made on such diluted and succussed solutions [92]. They then extend their property measurements to include electrical conductivity and show again the influence of composition, dilution, and succussion on these properties [92]. These findings are similar to those in a number of other studies indicating the essential role of succussion, not merely dilution, in preparing active remedies. In this paper we have shown that a possible key as far as changing the structure of water is concerned, is the pressure, and nano-bubbles generated in the succussion process. It is important to emphasize that the proper control solutions include not only untreated, unsuccussed solvent, but also succussed solvent without the initial addition of any remedy source materials to address possible artifacts

generated by the shaking of the liquid *per se* within the test container itself. Obviously chemical contamination from the container material could itself serve as a "remedy". This is particularly relevant in the materials science perspective, since that includes the "poly-water" error of the 1980's caused by contamination from the glass containers. If succussing is carried out in glass containers the likely possibility of contamination with small fragments of silicate materials exists. But the influence of these nano-fragments may really lie in the fact that they could serve as nucleating sites for particular water clusters.

In the recent homeopathy research literature, various investigators have also proposed structural models quite analogous to what ~~we~~ are proposing, involving formation of aggregates of water molecules or water clusters, possibly seeded by, but not requiring, the continued presence of, molecules from the original source substance, e.g. zwitterions or clathrates [55, 115]. Others have also proposed involvement of a coherent electromagnetic radiation field within the solvent that contributes order to the molecular motion [74, 116].

Del Giudice's concept of "superradiance" or a "coherence" in an electromagnetic field of molecular structural elements (extending even into the 100i range) is similar to some of our models. Clusters around certain foreign ions at great dilutions have been shown to grow to the micrometer range as shown in SEM photos with dilution [47]. These authors concluded: "It appears that there is an equilibrium in the solution between clusters and aggregates of clusters, which is dynamic and dependent on various factors such as concentration, solution history, time, temperature, etc." To which if one adds epitaxy, nanobubble, and pressure effects, we have an exact statement of our own position. This complex heterogeneity makes the equilibrium distribution more susceptible to change by magnetic or electric fields and by the total homeopathic preparation process, including succussion.

Other new data by Rey demonstrating that successfully diluted water solutions are indeed different from standards, comes from his recent work on the thermoluminescence of extremely diluted samples after X-ray irradiation of alkali halides [93]. This data again supports the case that extreme dilution + epitaxy + succussing, can plausibly result in a water with different structures, possibly containing a permanent nanobubble colloid, and it can have measurably different physical properties, a very plausible result from the viewpoint of materials science, and consistent with the extensive data from the homeopathy research.

## Conclusions

In 1971, Henry Franks, who was recognized as the leading researcher on water, wrote: "The current consensus view of water seems to be that water can be treated as a three dimensional hydrogen bonded network with the bond length and angles being increasingly distorted with rising temperature, but without a significant number of non-bonded H<sub>2</sub>O molecules!!" This shows a leaning to the random network homogeneous structure view.

F. Franks in his book "Water: Matrix of Life", in the chapter on "Structure of Water" devotes one page to diffraction methods, followed by nine pages of "theoretical" and "computational" approaches [117]. He ends with the quote from Henry Franks, cited above, and then goes on to say: "Almost three decades later,

progress has indeed been made, but it is probably clear that despite its molecular simplicity, water in the bulk liquid still presents major puzzles to physical and life scientists." In other words, we know a lot about the units present, but not how they are put together.

The key summary conclusion of this work is not inconsistent with some aspects of F. Franks, but takes the argument in a very different direction by pointing out the key role of the nanoheterogeneity of liquid water and the resulting ease of change of structure. The understanding and mental images of the structure of liquid water have been radically distorted in the minds of most scientists and (thence) the medical community. Liquid water (OH<sub>2</sub>) like its remarkably similar analogue SiO<sub>2</sub>, is not a homogeneous structure at the molecular level. It is a dynamic equilibrium among changing percentages

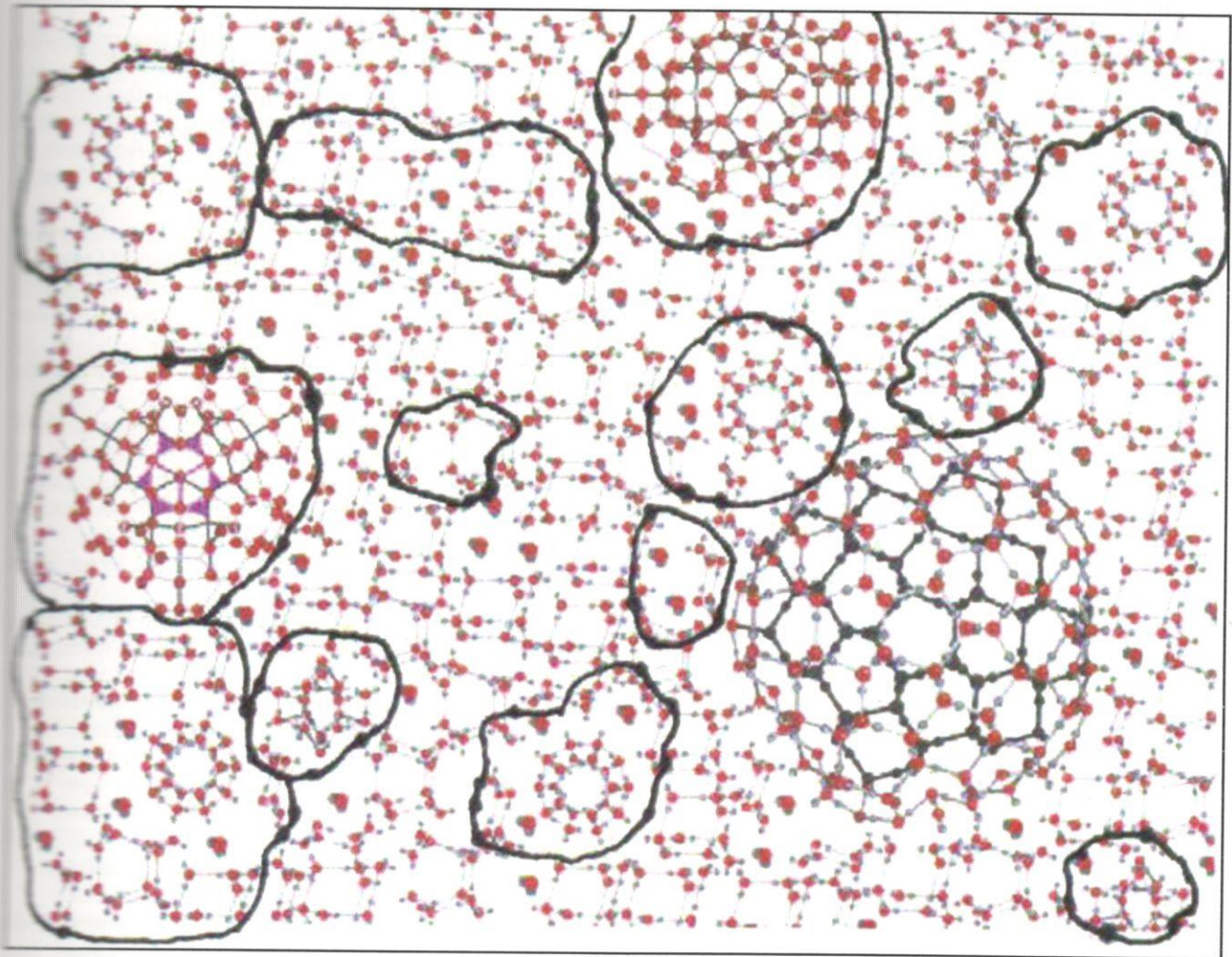


Fig. 19: Cartoon of schematic presentation of the kind of space-filling mixture of molecular units which must exist in some proportion of smaller 2-4 molecule clusters (Fig. 8) and other larger molecules up to the calculated 280 molecule units shown in Fig. 9, to emphasize the key element of heterogeneity of structure within water. Unfortunately, the figure cannot easily present the scaled spatial relations among the actual molecules, nor the probable clusters which are present because no such data exist. The forces between the clusters outlined in black must be very much weaker than the intracuster forces, although the bond terminations are not drawn thus.

of assemblages of different oligomers and polymer species. The structure (architecture) and these assemblages or units themselves are dependent on temperature (hence its many anomalous property-temperature relationships), on pressure, and on composition. The structure is thus more responsive to composition including very low levels of solutes, to magnetic and electric fields, and to "subtle energies."

This extreme structural flexibility certainly predisposes water to change by both epitaxy and succussion. The latter introducing the possibility of a stable nano-airbubble colloid. These last named factors provide a theoretical plausibility for the robust outcomes data of dozens of researchers in the homeopathic field, who have reached more or less similar conclusions by other routes.

The connection of the imprinting, via succussion and possible epitaxy, of the different specific homeopathic remedies on the structure of water eliminates the primitive criticism of homeopathy being untenable due to the absence of any remnant of the molecules. Structures change properties vastly more easily and dramatically than chemistry changes them. Beyond the homeopathic field, such an enormous structural pliability also provides a plausible framework for the claims of the most reliable workers in the field of "subtle energies" to be able to change the structure and properties of water.

While in Fig. 6 we had presented a very primitive 1971 version of nano-heterogenous liquids, in Fig. 19 we present a different still primitive image which we believe will be valuable to the reader to start connecting the chemical image of molecules to the materials scientist's necessary assemblage of molecules within a constrained condensed matter phase.

In conclusion, this paper has outlined testable hypotheses about the ability to alter the structure of water in the ultra-dilute regime, through epitaxy coupled with succussion (vigorous shaking) generating pressure and nano-bubbles leading to properties markedly different than those of untreated water.

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