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A New Theoretical Foundation for the Polarized-Oriented Multilayer Theory of Cell Water and for Inanimate Systems Demonstrating Long-range Dynamic Structuring of Water Molecules

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Abstract: Over the centuries, a vast amount of evidence has been gathering that layers of water sometimes measuring tens of thousands of water molecules thick exhibit altered properties in consequence of exposure to some solid surfaces. Yet, a clear cut theory based on the laws of physics that would predict this kind of long range dynamic ordering of water molecules has been long missing.

It is thus with great joy that I announce that a new theory has been developed, which offers theoretical confirmation of the phenomena of long-range dynamic structuring of water by appropriate solid surfaces and which gives clear cut quantitative answers to some key questions about the phenomenon. Thus, for example, under an ideal condition, an idealized checkerboard of alternatingly positively-, and negatively-charged sites of the correct size and distribution could polarize and orient deep layers of water molecules *ad infinitum*. Based on the quantitative data thus obtained and a relevant simple statistical mechanical law, the new theory predicts that a thin layer of water held between two juxtaposed ideal or near-ideal NP surfaces will not freeze at any (attainable) temperature.

On the other hand, water polarized and oriented by an ideal or near-ideal NP-NP system may also not evaporate at temperature hundreds of degrees higher than the normal boiling temperature of water.

Both predictions have been confirmed (retroactively) by experimental observations made in the past, accidentally or by design. In a following paper, I will demonstrate that the conclusion reached from the study of the two-dimensional NP surface can be smoothly passed on to the living cells. In the living cell, only one-dimensional linear chains of fully extended protein chains exist. Nonetheless, by proper orientation and distribution, they can achieve similar though less intense water polarization-orientation—as experimentally demonstrated worldwide during the 40 years past.

TEN YEARS after an early embryonic version was presented at a Symposium on Phosphorus Metabolism in Baltimore (Ling 1952), a theory of cell and subcellular physiology made its debut (Ling 1962.) It bears the title: "A Physical Theory of the Living State: the Association-Induction (AI) Hypothesis." Three years later in 1965 the Polarized Multilayer Theory of Cell Water (now renamed Polarized-Oriented Multilayer Theory, though still represented by the same short name, PM Thoery) was added (Ling 1965, 1969, 1972, 1972a, 1993, Ling *et al* 1993.) The association-induction hypothesis then became in essence complete and, as such, unifying.

Part of an original figure from the 1965 paper is reproduced as Figure 1 here to show very succinctly how the PM theory began. Further developments of the AI Hypothesis (before and after its completion) and results of its world-wide testing from before-1952 to early 2001 have been reviewed in three monographs published respectively in 1984 (Ling 1984), 1992 (Ling 1992) and 2001 (Ling 2001.) The present communication describes results of a recent effort further to strengthen the theoretical foundation of the PM theory. Under normal condition, this is perhaps all I need to say in an introduction. Unfortunately, the time is not normal. And, accordingly, more needs to be included in the introduction.

The time is not normal because a man-made information embargo has blinded the world of biomedical science to most, if not all, the propitious new developments as well as to the disproof of the century-old membrane theory (Wu and Yang 1931, Kaplanskii and Boldyreva 1934, Nasonov and Aizenberg 1937, Kamnev 1938, Cohn and Cohn 1939, Heppel 1939, Steinbach 1940) as well as its later modified version called the membrane pump theory (Ling 1962, Chapter 8; for a later review, Ling 1997.)

Withholding vital knowledge from other researchers, teachers and generations after generations of students worldwide is a very grave offense with foreboding implications for the long term well-being and even survival of our species. And it would take the concerted efforts of many good people over a long period of time to set it right again. But before the eventual lifting of the global information embargo, and in order that the reader of

Symbols and Abbreviations: a, amount of water (or other gas) adsorbed per unit weight of adsorbent; α, polarizability; d, distance between nearest-neighboring N and P site of an NP surface; δ, distance between a flat and a curved glass surface; E, (negative) adsorption energy or (negative) interaction energy of water molecules; $E^{(i)(j)(k)}$, (negative) adsorption energy of water molecule located at the ith row, jth and kth column; E^n, (negative) adsorption or interaction energy of water molecule polarized by, but far from an idealized NP surface; ε_i, the ith quantum-mechanically allowed energy level; k, Botzmann constant; μ, the permanent dipole moment; μ, total dipole moment equal to the sum of permanent and induced dipole moment; N, a negatively charged site; P, a positively charged site; O, a vacant site; NP surface, a checker board of alternatingly P and N sites; idealized NP surface, see Figure 6; NO surface, a checkerboard of alternatingly N and O sites; PO surface, a checker board of alternatingly P and O sites; NP-NP system, a system of juxtaposed NP surfaces; NO-NO system, a system of juxtaposed NO systems; PO-PO system, a system of juxtaposed PO system; NP-NP-NP system, a system of a matrix of parallel arrays of fully extended linear chains carrying properly spaced N and P sites; p, vapor ressure; p_o, vapor pressure at full saturation; p/p_o, relative vapor pressure; P_o, (molecular) orientation polarization; P_d (molecular) distortion polarization; (p.f.), partition function, equal to $1 + \exp(-\varepsilon_1/kT) + \exp(-\varepsilon_2/kT) + \ldots \exp(-\varepsilon_r/kT)$; $(p.f.)_v$, partition function of water vapor; $(p.f.)_l$, partition function of liquid water; $(p.f.)_s$, partition function of solid ice I; r, distance between nearest neighboring water molecules; T, absolute temperature; T_m, melting temperature (of water); T_b, boiling temperature (of water); T_{mp}, melting temperature of polarized-oriented water; T_{bp}, boiling temperature of polarized-oriented water; u_f, enthalpy of fusion; u_v, enthalpy of vaporization; u_{fp}, enthalpy of fusion of polarized-oriented water; u_{vp}, enthalpy of vaporization of polarized-oriented water.

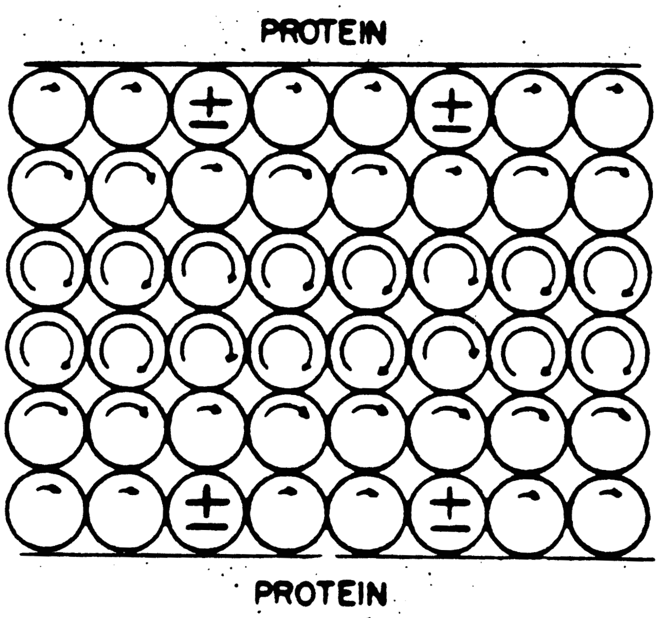

FIGURE 1. A section of the original graph that launched in 1965 the polarized multilayer theory — now modified to read polarized-oriented multilayer theory of cell water. In this theory, all cell water is dynamically structured. The decreasing length of the curved arrows in each water molecule indicates diminishing degree of motional freedom as one moves away from the protein surface — a concept that is contradicted by more recent evidence indicating a more even degree of polarization and orientation (See Discussion.) The figure also hinted at dipolar sites of proteins as the seat of polarization and orientation of cell water. This concept was more fully developed later (Ling 1970, 1972.) In this later view, backbone (dipolar) NH and CO groups offer the most important seats of water molecule polarization and orientation (modified after Ling 1965, by permission of New York Academy of Sciences,USA.)

this paper would be able to evaluate progress described below, it would be necessary to add something specific to this introduction. That something specific comes under two headings: (i) a summary of the PM theory and (ii) a short history of the investigation of multilayer adsorption of water vapor and other gases.

A summary of the PM theory and results of its 40 some years of world-wide testing

As extensive evidence reviewed in the three monographs mentioned above indicates (Ling 1984, 1992, 2001), the bulk-phase cell water does not exist in the form of normal liquid water — as widely believed and taught as truth even to this day. Instead, the weight of existing evidence suggests that the bulk of water in a typical living cell assumes the dynamic structure of polarized and oriented multilayers.

According to the AI Hypothesis, this dynamic structure and its propensity to undergo reversible changes enable cell water to play key roles in physiological activities at the most basic cell and below-cell level (Ling 2001, Chapters 14–15.) Many distinctive attributes of the living cells, — which in the conventional view of the living cell have been delegated to a host of often disconnected causes (e.g., the sodium pump, Dean 1941; tetracycline pump, Hutchings 1969; arrow-poison pump, Ehrenpreis 1967, etc.) — may simply reflect various aspects of the polarized-oriented cell water and other adsorptions on cell proteins (Ling 1993, 1997; Ling *et al* 1993.)

According to the PM theory, the assumption of the distinctive dynamic structure by the cell water results from its interaction with some intracellular proteins. More specifically, the dynamic structure of cell water results from its direct or indirect interaction of cell water with the positively-charged NH groups (P sites) and negatively-charged CO groups (N sites) on the "backbones" of a pervasive matrix of fully-extended proteins. These P- and N-site-bearing proteins and the water molecules with which they interact constitute what is called a NP-NP-NP system. To explain what "NP-NP-NP system" stands for, I shall begin with its prototype or classic NP system and NP-NP system.

Electrical polarization and directional orientation of multiple layers of water molecules may occur under the influence of one or two (juxtaposed) checkerboard(s) of alternately positive and negative sites. See Figure 3 below for earlier publication of the same idea. Figure 2d shows two juxtaposed polarizing-orienting surfaces in what I call a NP-NP system.

Thc NP-NP-NP system mentioned above is a variant of the classic NP-NP system (Ling 1980-1981.) As such, a NP-NP-NP system exists in the form of properly spaced, orderly sequence of (free) N and P sites carried on a parallel array of fully-extended protein(s) or other linear water-polarizing-orienting polymer chains (See below and another new publication, Ling 2004a.) Parenthetically, water molecules may also be polarized and oriented in multilayers by a NO system or a PO system, in which electrically-neutral O sites replace properly-spaced electrically-charged P or N sites of a classic NP system respectively (Figure 2e, 2f.)

The aggregate physical impacts of the NP sites on the bulk-phase water may be somewhat arbitrarily divided into three components: to enhance the average water-to-water interaction of (all) the water molecules in the system (Component 1); to reduce the translational as well as rotational motional freedom of the water molecules (Component 2); and to prolong the stay or *residence time* of each water molecule at a specific preferred location (Component 3.) In statistical-thermodynamic terms, each of these three components refers respectively to a rise of the (negative) energy (or more precisely, enthalpy) of the system, a fall of its thermal entropy and a decrease of its configurational entropy.

In testing a theory on a subject as complex as life, cell physiologists do not have the luxury of following the footsteps of physicists, who have the freedom to choose the simplest system to study. Instead, cell physiologists must develop their own strategy best suited to cope with very complex systems. One of these involves a well-orchestrated study of suitable inanimate models side by side with their living counterparts. Vastly simpler in its makeup and usually more tolerant of harsh treatments, the inanimate models more readily reveal what are more important, and what are less important in producing the attribute, which the most cogent model and its living counterpart share. A cogent inanimate model which behaves like its living counterpart is called a *positive model*. A *negative model*, though sharing some attributes of the positive model, either does not, or does weakly what the living cell and its positive model does strongly — because in its makeup, a negative model does not possess one or more key qualifying attribute(s) demanded by the theory.

And if a theoretically predicted attribute is confirmed in both the living cell-protoplasm and a positive model but not or significantly less in the corresponding negative model, we

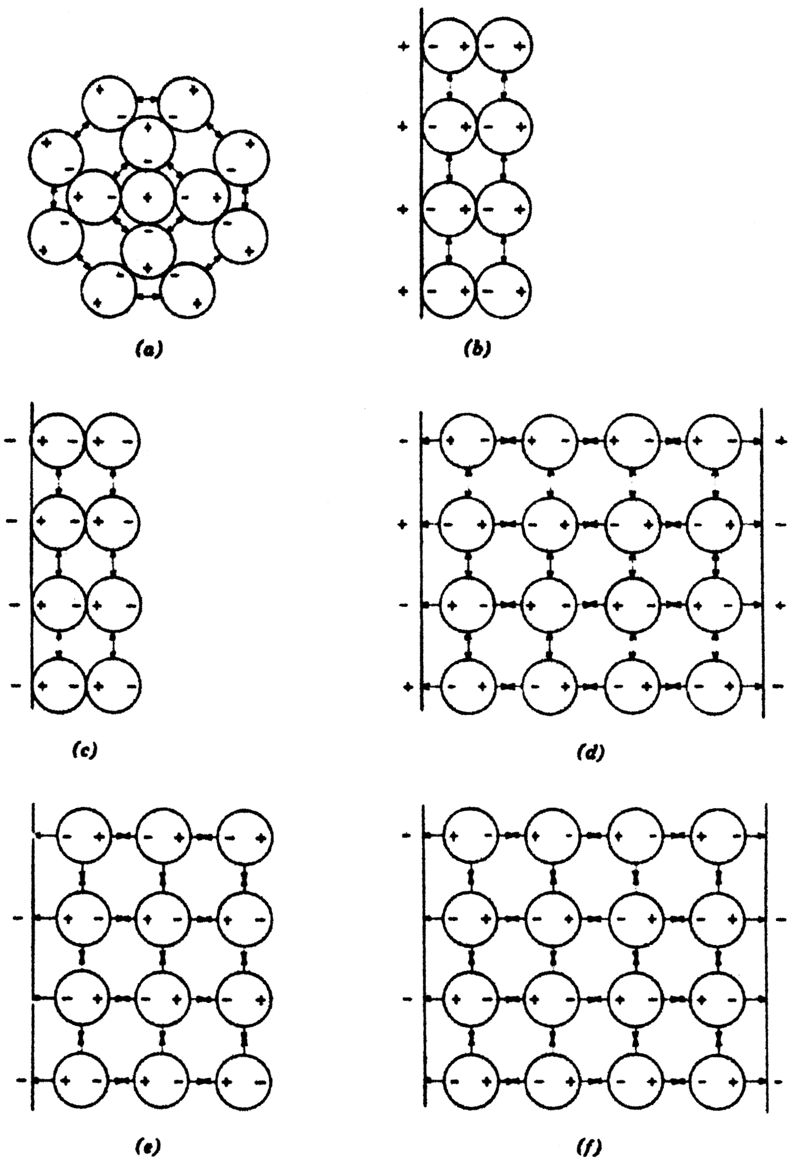

FIGURE 2. Diagrammatic illustration of the way that individual ions (a) and checkerboards of evenly distributed positively charged P sites alone (b) or negatively charged N sites alone (c) polarize and orient water molecules in immediate contact and farther away. Emphasis was, however, on uniformly distanced bipolar surfaces containing alternatingly positive (P) and negative (N) sites called an NP surface. When two juxtaposed NP surfaces face one another, the system is called an NP-NP system (d). If one type of charged sites is replaced with vacant sites, the system would be referred to as PO or NO surface (e). Juxtaposed NO or PO surfaces constitutes respectively an PO-PO system or NO-NO system (f). Not shown here is the NP-NP-NP system comprising parallel arrays of linear chains carrying properly distanced alternating N and P sites. Note how directions of paired small arrows indicate attraction or repulsion (modified after Ling 1972; reprinted by permission of John Wiley & Sons Inc.)

would call the combination a *triple confirmation*. A triple confirmation offers the reassurance that the investigator has probably been on the right track.

However, a failed model study (followed by a prompt and judicious response) may prove equally important in the long run. For it tells the investigator that it is time to consider seriously other alternative explanations. A scientific revolution with its usual sequel of rapid progress may then follow.

For testing the PM theory specifically, we have elected two kinds of inanimate models, referred to respectively as (positive) *extroverts* and (negative) *introverts* (Ling 1992 p. 107.) Extroverts include isolated proteins that by nature or for other reason exist substantially in the *fully extended conformation* (Ling 2004a.). This may result from an unusual amino-acid-residue composition (for details of the introduction of this interpretation, see Ling 1978; Ling *et al*, 1980; Ling 1992 p. 81) (e.g., gelatin, containing an abundance of non-helix-forming amino-acid residues proline, hydroxyproline and reluctant helix-forming glycine — see Eastoe and Leach 1958). Or it may occur on exposure to NH- and CO-group-exposing denaturants (e.g., urea, Ling 1992 Figures 5-6 and 5-7). *Extrovert* models also include other linear polymers carrying properly spaced atoms with available *lone pair* electrons (e.g., oxygen atoms in poly(ethylene oxide) or PEO for short.) A (concentrated) aqueous solution of PEO constitutes a NO-NO-NO system.

In contrast, *introvert* models, which include most globular proteins like native hemoglobin, act differently. With most of their polypeptide chains NH and CO groups neutralized and shielded in forming intra-molecular H bonds, they do not alter the property of bulk-phase water or do so only weakly (Ling 1992, pp.107–110; Ling and Hu 1988.)

As shown in the following, the PM theory of cell water has witnessed world-wide triple confirmation on all eight major physiological traits investigated in depth thus far.

(1) (Lengthening of) NMR rotational correlation time (τ_c) (Cope 1969; Hazlewood *et al* 1969, Damadian 1971, Ling and Murphy 1983); (2) (lengthening of) Debye reorientation time (τ_D) (Clegg *et al* 1984; Kaatze *et al* 1978); (3) (reduction of rotational diffusion coefficient from) Quasi-elastic neutron scattering (Trantham *et al* 1984; Heidorn *et al* 1986; Rorschach 1984); (4) vapor sorption at near saturation vapor pressure (Ling and Negendank 1970; Ling and Hu 1987); (5) freezing point depression (Chamber and Hale 1932; Miller and Ling 1970; Ling and Zhang 1983); (6) swelling and shrinkage (Ling 1987; Ling and Ochsenfeld 1987); (7) osmotic activity (Ling 1992 p. 101; Ling and Walton 1976); but above all (8) solute distribution, which could and did yield unequivocal, quantitative data on the amount and the mutual interaction energy of altered water in a sample (see below; also Ling 1965, 1970 and 1972; Ling and Hu 1988; Ling and Ochsenfeld 1989; Ling 1993 and Ling *et al* 1993.)

As mentioned above, I have divided the impact of a NP system/NP-NP system or their variants on the bulk-phase water into three components. Based on this system, one may say that studies (1), (2) and (3) listed above have confirmed the predicted motional restriction of water molecule (Component 2.) Study (4) has confirmed the increased localized residence time (both Component 1 and Component 3.) Studies (5) and (7) have confirmed the predicted enhanced water-to-water interaction energy (Component 1 and Component 3.) Studies (6) and (8) have confirmed both Components 1 and 2.

The combination of these eight sets of mutually supportive triple confirmations, offers strong confirmation of the PM theory in specific and the AI Hypothesis in general. However, there are other challenges that so far have not been fully met by investigators primarily interested in cell water. As will be made clear below, recent progress to be described below has changed all that.

Beyond the introvert and extrovert models, there are other inanimate systems discovered or created by workers in a different field, and yet exhibit behaviors and properties, which often in grossly exaggerated manner resemble those of *bona fide* positive models of the PM theory. It is conceivable that further attention to these *inadvertent positive models* may offer insight, which in its milder form seen in the more familiar extrovert models, might be masked and therefore undetectable.

Thus, many such inadvertent models for the PM theory can be found among widely scattered older reports, which describe layers of water hundreds, thousands and even tens of thousands molecules deep that are profoundly altered in their properties by contact with a foreign surface like glass (for a rich collection of these highly provocative findings reported before 1949, see "The Depth of the Surface Zone of a Liquid", a fine critical review by J.C. Henniker of the Stanford Research Institute published in the *Review of Modern Physics*, 1949. See also Drost-Hansen 1971; Israelachvili and Adams 1976; Peschel and Belouscheck 1979; Deryaguin 1933, 1987; Deryaguin and Landau 1941.) Anticipating a more detailed discussion below, I mention very briefly just one striking example published 7 years after the Henniker review.

Prof. Takeo Hori of the Institute of Low Temperature Science of the Hokkaido University, Japan showed that water films, thousands of molecules thick, would not freeze and turn into ice at a temperature as low as –90° C, if that water is held between two polished glass surfaces (Hori 1956; Ling 1970, 1972.)

The relevance of this reported "nonfreezing water" to our study of water in living cells would become self-evident from two well-established facts: (1) Human embryos, like all other living beings, are largely made of water. (2) Human embryos can be kept for a long time at liquid nitrogen temperature, (which could be as low as −195.8° C) and then promptly resume normal development into healthy human beings by merely thawing and warming to normal body temperature (Polge *et al* 1949, Rall 1987, Wennerholm *et al.* 1998.)

With both facts in mind, one sees that *being alive* is cogently modeled not only by inanimate systems existing at an ambient or body temperature, it can also be cogently modeled by inanimate systems existing at a severely cold temperature.

Hori's non-freezing water between polished glass surfaces has yet something else to offer. That is, other than serving as an appropriate model for cell water in the cold, it is also in fact a highly instructive inanimate model of even broader significance. For unlike the living cell itself and the extrovert models we studied extensively thus far, all of which represent the derivative NP-NP-NP systems, non-freezing water film held between polished glass surfaces represents a *bona fide classic NP-NP system.*

A short historical background of the PM theory of cell water and model systems

The physical phenomenon *adsorption* is, according to the AI Hypothesis, central to all basic physiological phenomena. The word and concept of, adsorption, was first introduced by Gehler (1825) but soon forgotten. It was reintroduced by H. Kayser 46 years later at the suggestion of Emile Du Bois-Reymond, one of the four great physiologists of the mid-19th Century nicknamed the *Reductionist Four* (McBain 1932 p. 7.) As if they were one, Du Bois-Reymond and his friends vigorously fought for their belief that the laws governing the behaviors of the dead world, also govern the living (Rothschuh 1973.).

In its modern definition, adsorption signifies the *association* of molecules and ions with solid surfaces, macromolecules or other fully or partly immobilized systems. For this reason, the title, association-induction hypothesis begins with the word, *association*. The second word, *induction* or electric polarization, is also portrayed in the polarization (and orientation) of cell water. But that is not all it signifies. For in the AI Hypothesis, induction is a part of the general molecular mechanism of information and energy transfer over distance in living cells (Ling 1962, Chapters 5, 6; Ling 1984, Chapter 7; Ling 1992 Chapters 6, 7 and Ling 2001, Chapters 14, 15.)

A shirt may smell of tobacco after a party. That is an example of adsorption of odorous gaseous products of burning tobacco on the cellulose of a cotton shirt. But historically, it is burned cellulose of wood, or charcoal that has been the favorite material for studying this phenomenon of adsorption. Thus students once attending classes in the 19th century, and even later years might have witnessed a dramatic laboratory demonstration introduced by Abbé Fontana of Italy in the 18th century. A piece of glowing charcoal was plunged into a pool of mercury. Thus cooled, the charcoal was allowed to float up into an inverted gas-filled glass tube. The subsequent rapidly rising level of mercury in the glass tube eloquently demonstrates the strong affinity of charcoal for gases of all kinds previously introduced into the glass tube (McBain 1932 p.1.)

To explain gas adsorption by charcoal, two kinds of theories were introduced known respectively as the *condensed thick film theory* of the old physicists and the *capillary condensation theory* of a later crowd.

In the condensed film theory, long-range attractive forces emanating directly from the solid surface hold deep layers of gas molecules captive on or near the solid surface (Saussure 1814; Polányi 1914.) This view, according to McBain, was eventually abandoned because no such long-range force could be found. Direct forces between molecules and even ions are short in reach, rarely going beyond one or two molecule diameters. However, in more recent years Israelachvili and his coworkers (Israelachvili 1985, 1987; Israelachvili and Adams 1976) appeared to have introduced their version of direct long-range force on distant water molecules that seem to resemble in appearance at least the old condensed thick film theory (Compare Figure 7 of Israelachvili's 1987 paper with Figure 136 in McBain's 1932 book.) (See Discussion.)

For a long time, the most popular view on the adsorption of deep layers of water vapor and other gases was the *capillary condensation theory* (Zsigmondy 1911.) As well known then, when a glass capillary is dipped into water, the water level inside the capillary rises to much higher than that outside the capillary. Since charcoal is highly porous and presumably contains many fine interstices behaving like the enclosed narrow spaces in glass capillaries, it was postulated that water and other gases would condense inside these internal capillaries just as water does in regular stand-alone capillaries. Eventually, this model too was abandoned. The interstices in charcoal were found to be only molecular in dimension and thus far too narrow to act like glass capillaries in sucking up columns of water (Coolidge 1926.)

Then Irving Langmuir dramatically revolutionized the basic concept of adsorption by his theory of *localized monomolecular adsorption* (Langmuir 1918, 1921.) That is, each adsorbed gas molecule does not just freely roam around in the vicinity of the solid surface but occupies a specific location or *adsorption site* on the surface for a finite lifetime (until it leaves). Langmuir introduced a mathematical expression of his concept later known as the *Langmuir adsorption isotherm* or simply *Langmuir equation*.

The Langmuir equation predicts that the uptake of a gas is strong at lower vapor pressure, becoming weaker and weaker as the vapor pressure increases until it becomes flat altogether. Thus, as a whole, the adsorption curve looks like a lying-down inverted letter, J. The sorption of CO_2 in charcoal follows this pattern (Zeise 1928.) The adsorption curve of water vapor in charcoal, on the other hand, looks more like a flattened letter S (Coolidge 1927; McBain 1932 Figure 52.). That is, weak uptake occurs at low vapor pressure followed by abruptly stronger uptake at higher vapor pressure.

While the condensed thick film theory and the capillary condensation theory were holding sway, other scientists offered what were at the time less popular ideas. One is called the *laminated or enchained multimolecular film theory*. In this, a series of monomolecular layers of gas molecules collect on the solid surface such that each layer is adsorbed on the layer immediately beneath it except the last one, which adsorbs directly on the solid surface. Among the earliest advocates of this theory was the same H. Kayser of Germany (1881), who as mentioned earlier, reintroduced the concept of adsorption. Another 38 years later, de Boer and Zwikker further pursued this line of thinking.

What de Boer and Zwikker did was to offer for the first time an analytically-derived isotherm for the S-shaped adsorption of neutral gas molecules on solid surfaces. They gave their theory the title, *Polarization Theory* (de Boer and Zwikker 1929.) Furthermore, they pointed out how a checkerboard of alternatingly positive and negative sites on the surface of a salt crystal might enhance multilayer adsorption of gas molecules. To give due credit for this then-original concept, I have reproduced two of their original figures (their Figure 3 and 4) as Figure 3A and 3B respectively in the present paper. Shortly after de Boer and Zwikker published their paper, Bradley derived two similar adsorption isotherms one for gas molecules *without* a permanent dipole moment, the other one for gas molecules *with* a permanent dipole moment (Bradley 1936a, 1936b.). These three isotherms, (one) by de Boer and Zwikker and (two) by Bradley, can all be written in the form:

$$\log_{10}(p_o / p) = K_1 K_3^a + K_4, \qquad (1)$$

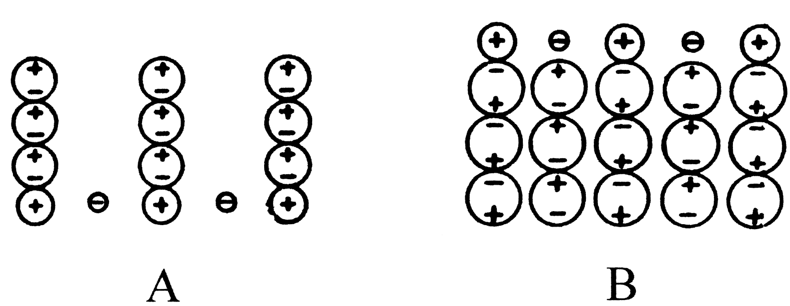

FIGURE 3. Reproduction of figures presented in the paper by de Boer and Zwikker in 1929, showing their vision of a checkerboard of alternating negatively-charged and positively-charged sites and two different ways as to how gas molecules might adsorb on them as polarized multilayers. These checkerboard of alternating positively-charged and negatively charged sites are what later I call the NP surface, a concept of considerable importance in the subsequent developments of the PM theory. The reproduction of their figures reminds us of the contribution de Boer and Zwikker made in 1929. A and B are respectively what they labeled as Figure 3 and 4 respectively in their original paper.

where a is the amount of gas taken up by a unit weight of the absorbent, p is the existing gas pressure and p_o the pressure of the gas at full saturation. Thus p_o/p is the reciprocal of the relative vapor pressure, p/p_o. The respective meanings of K_1, K_3 and K_4 are different in each of the isotherms. In all, they are constants at a fixed temperature. Equation 1 can also be written in the double log form:

$$\log_{10} [\log_{10} (p_o/p) - K_4] = a \log_{10} K_3 + \log_{10} K_1. \qquad (2)$$

If a set of numerical values can be found respectively for K_1, K_3 and K_4 such that the experimentally measured amounts of water sorbed (a) at different relative vapor pressure (p/p_o) can be shown to be rectilinearly related to the reciprocal of the modified relative vapor pressure (i.e., that represented by the entire left-hand-side of Equation 2), one then regards the data as fitting the theoretical isotherm shown as Equation 1 (or 2.)

As mentioned, de Boer and Zwikker envisaged in 1929 a surface of salt crystals as a checkerboard of alternating positively- and negatively-charged sites (Figure 2c and Figures 3A and 3B.) These fixed electric charges then induce electric dipole moments in a layer of gas molecules in immediate contact with the charged sites of the salt crystal surface. The induced dipole moments thus generated in the first layer of adsorbed gas molecules in turn induce dipole moments in the second layer of gas molecules and this process repeats itself many times until a deep layer of adsorbed gas molecules is achieved. To repeat, in the de Boer-Zwikker polarization theory, the force holding layers of gas molecules away from the solid surface is entirely attributed to the *induced dipoles* and to nothing else beyond the induced dipoles.

de Boer and Zwikker knew, of course, that many gas molecules like (vapor) water possess *permanent dipole moments*, which arise from the asymmetrical distribution of the positive charges (carried on the hydrogen atoms) and the negative charge (carried on the oxygen atom) in a water molecule. But they decided to ignore these permanent dipole moments, arguing that thermal agitation makes their orientation near the salt crystal surface constantly changing. In Part I of his 1936 paper, Bradley also ignored the permanent dipole moment but for a less controvertible reason — he was addressing in that paper specifically *only* gas molecules without a permanent dipole moment (e.g., argon.) But in presenting a **general theory** for gases of all kinds in Part II of his paper, Bradley did take into account the permanent dipole moments.

Brunauer, Emmett and Teller (the Teller of the H bomb fame) (1938) took issue with de Boer and Zwikker's Polarization Theory as well as Bradley's theory on sorption of non-polar gases on salt crystal surfaces. Brunauer *et al*'s main criticism centers on the dimensionless term α/r^2 — where α is the *polarizability* of the gas molecule and r the distance between the nearest neighboring adsorbed gas molecules. They showed that even in gas molecules with a very large polarizability like argon, its α/r^2 is still too low to allow a propagation of electric polarization to beyond the first layer. However, they did add this. "...if the adsorbed gas has a large permanent dipole it is possible that many layers may be successfully polarized by the mechanism of de Boer and Zwikker. This case has been treated by Bradley" (Brunauer *et al* 1938, p. 311.)

That, however, was all Braunaer *et al* said on the subject of adsorption of gas molecules with permanent dipole moment. Nor to my knowledge have de Boer and Zwikker nor Bradley responded to Brunauer *et al*'s criticism.

Meanwhile, Brunauer, Emmett and Teller (1938) had introduced a theory on multilayer gas adsorption of their own. In time this theory has become broadly known as the BET theory after the first letters of the three authors's respective names. Cassie (1945) and later Hill (1946) made improvements on the BET formulation of multilayer adsorption of gas molecules.

Now, in Bradley's multilayer adsorption theory for polar gas molecules, the gas molecules adsorbed at low as well as high vapor pressure are polarized respectively by the solid surface charges and by neighboring water molecules. In the BET theory, on the other hand, only the small number of gas molecules in direct contact with the adsorption sites is adsorbed, the remaining great majority of gas molecules is simply normal liquid water and as such not additionally polarized on account of their (non-immediate) propinquity to the solid surface.

Thus, although the authors did not make this point clear, the BET theory in fact represents a return to the capillary condensation theory (minus pores and interstices) as envisaged by Coolidge (1926, 1927, see also McBain 1932, p. 147.) In this connection, a new question arises, Have Brunauer and coworkers by at once endorsing Bradley's theory, (in which all adsorbed molecules are polarized) and advocating their own BET theory, (in which only gas molecules immediately in contact with the solid surface are polarized) contradicted themselves? As far as I know, they have not publicly provided an answer to this question.

Actually, this conflict does exist. But it might be readily resolved by making an additional assumption. That is, gases without a permanent dipole moment like argon follow the BET theory. (For reservation on account of some additional theoretical problem with the BET theory, see Cassie 1945, p. 450.). Gases with a large permanent dipole moment like (vapor) water follow the Bradley isotherm. In fact, experimental support for this dual assignment already exists in the literature.

In 1965 I analyzed Bull's data on the adsorption of water vapor on two proteins, collagen and sheep's wool (Bull 1944). At low vapor pressures, the data can be described well by the BET theory. At vapor pressure higher than 50%, however, theory and data diverge sharply (Ling 1965.) In contrast, at low as well as high vapor pressures, water sorption on both collagen and sheep's wool fit the Bradley isotherm.

Similarly, if one views together the incisive findings of Benson, Ellis and Zwanzig (1950) on one hand and Hoover, Mellon and their coworkers (1950) on the other, one also finds support for this duality.

Thus, Benson and Ellis showed that the adsorption of non-polar gases like nitrogen on frozen-dried (lyophilized) proteins follow the BET theory (Benson and Ellis 1948.) Furthermore, the amount of gas taken up depends entirely upon the state of division of the frozen-dried (or lyophilized) proteins, the finer the division, the higher the uptakes.

In contrast, the adsorption of water molecules (with its large permanent dipole moment) on the same lyophilized proteins is, firstly, several orders of magnitude higher than the uptake of non-polar gases (Benson *et al* 1950.) Secondly, the uptake of water vapor is totally independent of the state of division of the proteins — in diametric contrast to the uptake of non-polar gases. Instead, the uptake of water vapor is entirely dependent upon the chemical structure of the protein. What is that structure favoring water adsorption as polarized multilayers? To that question, Hoover and Mellon have also provided a clear answer.

Hoover and Mellon (1950) studied the sorption of water by polyglycine and silk on one hand and by wool and ovalbumin on the other. At vapor pressure from 0.05 to 0.95, all four sets of data fit a simplified version of the Bradley adsorption isotherm. Now, as potential water-adsorbing sites, polyglycine has (virtually) only the positively-charged NH groups and negatively-charged CO groups on its backbone. Yet the maximum uptake of water vapor by polyglycine matches that of sheep's wool, which carries as potential water-adsorbing sites both backbone CO and NH groups and polar side chains including β- and γ-carboxyl groups, ϵ-amino groups and hydroxyl groups, for example.

Such a comparison led Hoover and Mellon to conclude that the major seat of water adsorption on proteins is the positively charged NH and negatively charged CO groups of the protein backbone. Their conclusion is in harmony with a similar but earlier view of Lloyd herself (1933) and of Lloyd and Phillips (1933) and with a later view of Ling in his PM theory, according to which the NH and CO groups of the backbones of a parallel array of fully-extended protein chains polarize and orient the bulk of cell water (Ling 1970, 1972.)

In summary, the two sets of experimental data described briefly above also verify the idea that the BET theory is applicable only to the adsorption of non-polar gases. For polar molecules like water, the BET theory is not applicable while the Bradley theory is.

In further testing the PM theory of cell water, Ling and Negendank (1970) demonstrated that the equilibrium water contents of surviving frog muscle cells at different relative vapor pressure ranging from near-zero (4.3%) to near saturation (99.6%) fall into two fractions. A small fraction (5%) of the cell water begins and completes its strong adsorption at very low vapor pressure (apparently all on polar side chains, see Leeder and Watt 1974.) This fraction can be described by a Langmuir monolayer adsorption isotherm. The remaining 95% of cell water follows the Bradley adsorption isotherm all the way up from 4.3% to 99.6% relative vapor pressure (Figure 4.)

This work of Ling and Negendank represents the first of its kind on the water vapor sorption of surviving (frog muscle) cells from near zero to 99.6% saturation. Furthermore, the data (Figure 4) shows that fully 3/4 of the water uptake of these cells occurs at above the relative vapor pressure of 95%, which is the upper limit of the great majority of earlier publications on water sorption *in vitro* on proteins and polymers.

Moreover, the water vapor uptake of frog muscle cells matches quantitatively McLaren and Rowen's data on the water sorption of poly(glycine-D,L-alanine), which like polyglycine mentioned above carries its water adsorbing sites almost exclusively in the form of backbone NH and CO groups (McLaren and Rowen 1951.) This quantitative matching between the water uptake of polyglycine-D,L-alanine and that of surviving frog muscle shown in Figure 5 was one of the earliest evidence I cited in support of the PM theory that the bulk of cell water is adsorbed on the backbone NH and CO groups of a matrix of *fully-extended* intracellular proteins chains (Ling 1972, p. 697.)

Further confirmation of the dipolar backbone NH and CO groups as the primary seat of water sorption — but especially the carbonyl oxygen atoms with its lone pair electrons — came from Ling and Hu (1987.) They demonstrated that at physiological relative vapor pressure (0.996), the uptake of water vapor by frog muscle also matches that by poly(ethylene oxide) (and other oxygen-carrying linear polymers,) on which the only hydrophilic groups are the oxygen atom with its lone-pair electrons.

Seen side by side with other data like those of Hoover and Mellon discussed above, Ling and Negendank's finding represented a step forward in verifying the PM theory. Indeed, on various occasions of the past, the Bradley isotherm (with the explicit endorsement of Brunauer, Emmett and Teller) has been cited as the theoretical-physical foundation of the PM theory.

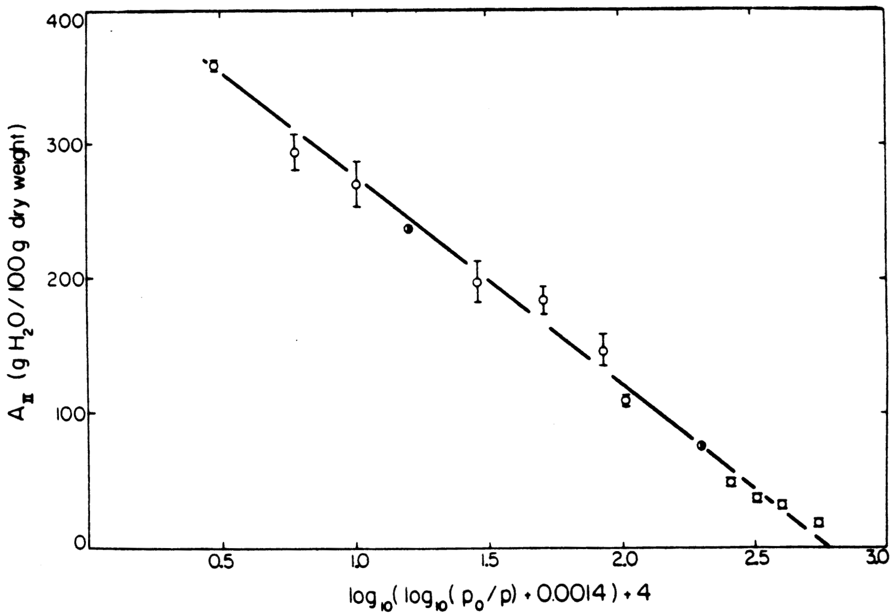

FIGURE 4. Water sorption isotherm of isolated surviving frog muscles. Data on 95% of the muscle water. The remaining 5% of muscle water is completed at very low relative water vapor pressure (p/p_0); it is described by a Langmuir adsorption isotherm and has been subtracted from the total water uptake to yield the data points plotted in the graph. Straight line plot indicates obedience to the Bradley isotherm. Half filled circles were from time course studies. (From Ling and Negendank, 1970.)

However, as the mounting experimental evidence has all but established the general validity of the PM theory of cell water, the Bradley theory, in comparison, has slowly fallen behind as a sort of a limping ally that is helpful but also hard to defend with conviction. And unless strengthened by new development, this weak theory might actually become a handicap for future progress. But before entering into a detailed analysis of my reasons for this concern, I would like to cite what another scientist did and did not do that might shed some light on the issue.

That scientist is the reviewer, J.C. Henniker mentioned earlier. In his 1949 review, he stated on page 323 of Volume 21 of the *Review on Modern Physics* that the "theoretical basis for adsorption in multilayers is firm. The isotherm of Brunauer, Emmett and Teller is based on more than one layer and is experimentally justified." But in my view, this is, strictly speaking, not entirely correct. The bulk of the deep layers of water found near (appropriate) solid surfaces, with which Henniker's review dealt, exhibits properties exquisitely different from those of normal liquid water. In contrast, (and as made clear above,) in the BET theory the bulk of water collecting on solid surfaces is simply normal liquid water. But more relevant to the question here on the strength and weakness of the Bradley isotherm, is its total omission. That is, Henniker made no reference to Bradley's theory of multilayer adsorption at all — even though it was up to now the only published theory of multilayer adsorption of gas molecules with large permanent dipole moment, and even though it was explicitly endorsed by Brunauer, Emmett and Teller in the same paper in

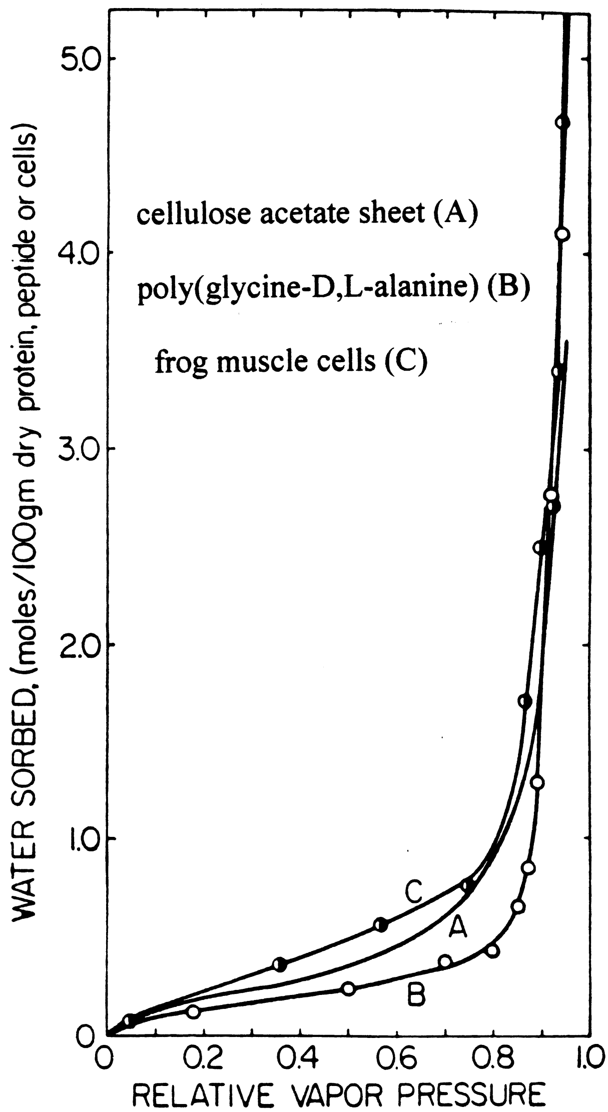

FIGURE 5. The strikingly similar steep uptake of water molecules at relative vapor pressure close to saturation of surviving frog muscle cells (marked C) and of the synthetic polypeptide, poly(glycine-D,L-alanine) (marked B, data of McLaren and Rowen, 1951), one finds evidence that the backbone NH and CO groups (which are virtually all the functional groups that can interact with water molecules in this synthetic polypeptide) are the major seats of (multilayer) water adsorption in living cells as suggested in the polarized-oriented multilayer theory of cell water. The third curve from unpublished work of Palmer and Ling shows that water taken up by commercial cellulose acetate sheets are similarly adsorbed on dipolar sites — a matter of great significance because later work of Ling (1973) shows that the permeability of this membrane strikingly resembles the permeability of a live membrane (inverted frog skin.) (Figure reproduced from Ling 1972; reprinted by permisssion of John Wiley & Sons Inc.)

which Brunauer, Emmett and Teller presented their own BET theory, which Henniker gave admiring recognition.

One possible explanation for this omission is that it was deliberate despite Brunauer, Emmett and Teller's endorsement. Thus, Henneker himself might have discovered that the Bradley isotherm has problems that Brunauer, Emmett and Teller had overlooked.

Now that we have reason to believe that the BET theory is only applicable to non-polar gases, the theoretical foundation for the adsorption of multilayers of polar gases like water is thus less firm than Henniker's statement cited above appeared to indicate. Perhaps this unstated uncertainty is also what prompted Henniker to say early in his review that "A basic theoretical treatment has not been attempted in this paper,..." Subsequent history, however, shows that neither Henniker nor anyone else has to my knowledge written such a basic theoretical treatment, nor even a follow-up of Henniker's masterful review — notwithstanding new observations of deep layers of altered water on solid surfaces like those described by Hori continued to accumulate.

Whatever the true reasons might be for the less than enthusiastic subscription to Bradley's isotherm, the net result is that the study of long-range water adsorption on solid surface has become more and more shunted to the side line. That one of the chief advocates of the concept of long-range water interaction, the talented and capable B.V. Deryaguin, has suffered a setbback — for making the (honest) mistake of believing in the existence of (non-existing) "polywater" — might have added another confusing and false reason for skepticism toward long-range water adsorption. But in my view, things may change and change soon. It is too exciting to stay suppressed for long.

The difficulty that had thwarted de Boer & Zwikker as well as Bradley

The weakness and even downright failure of the de Boer-Zwikker and Bradley theories do not reflect on the authors's knowledge and skill. Rather, in my view it is an almost inescapable consequence when a capable physicist attempts to achieve the same level of sophisticated mathematical formulation they have been accustomed to in dealing with simpler subjects, in dealing with a problem that is, by nature, unalterably complex.

And in order to make things manageable mathematically, de Boer and Zwikker decided to throw the permanent dipole moment out of the window — with disastrous result. Of course, Bradley did not throw the permanent dipole moment out of the window. He threw out something else. Namely, the fixed negatively charged N sites on the surface of salt crystals.

His explanation for this omission was that the anionic N site are too large, a lame explanation at best, not to mention that his announced intention was to write a *general theory* for gas adsorption on various salt crystals some with large and others with small anions. This omission of the N sites does not end up with what I call a PO system, which would be still relevant. Rather, it became what I would call a PP system, in which all surface sites are positively charged P sites with lateral repulsion between nearest neighboring adsorbed gas molecules. All in all, this elimination alone has created a model no longer compatible with adsorption on most salt crystal surfaces as Bradley intended to do or with the classic NP and NP-NP systems of the PM theory.

As Bradley pointed out himself, numerical fitting of experimental data to his isotherm (Equation 1 or 2) does not prove that the data follow the theory. Nor does fitting the Bradley isotherm provide answers to various important questions. Thus, fitting the isotherm does not tell us why the permanent dipole moment is so vital that its elimination has invalidated both the de Boer-Zwikker and Bradley's own isotherm for non-polar gas adsorption. Nor does fitting the Bradley isotherm offer even a hint if this theory can explain the polarization and orientation of all of the cell water — let alone the truly long-range impact of polished glass surface on water molecules thousands of molecules thick as reported by Prof. Hori. In general, fitting the Bradley isotherm does not provide quantitative data on the adsorption at all.

Now, to seek new ways to find answers to these important questions, we must first determine what specific obstacle has prevented de Boer and Zwikker as well as Bradley from producing a more powerful theory. And why did Brunauer, Emmett and Teller not take notice of the weakness of the Bradley isotherm for polar gases and give their unqualified blessing? And why did Brunauer, Emmett and Teller not derive a theory better than the BET theory they introduced, which cannot explain multilayer adsorption of water molecules and other polar gases?

A careful reading of the papers from de Boer and Zwikker and from Bradley shows quite clearly that they were plagued by the effect of thermal bombardment on the orientation of the permanent dipole moments of the gas molecules. It is the *uncertainty* thus created by heat on the orientation of the permananent dipole moments that has undermined the theory of de Boer and Zwikker as well as of Bradley.

A shortcut to a simple but more rewarding new theory

I now suggest that there is a short cut to get around the difficulty that had so far hampered all workers on multilayers adsorption of polar molecules on salt crystal surface. That short cut is *via* lowering the temperature of the model to one or two degrees above absolute zero.

For at this low temperature, the kinetic energy of the water molecules kT approaches zero and the thermal bombardments, to all intent and purposes, come to a stop. And in that quiet setting, electrostatics in all its simplicity and certainty takes over. If I am not wrong, quantitative knowledge on the polarization and orientation of water and other polar molecules on solid surfaces that have eluded de Boer-Zwikker and Bradley might be within reach. However, for this near absolute zero strategy to work, water must not freeze as the temperature is brought down lower and lower. For the moment, one must take it on faith. Rigorous proof will come later (p. 117.)

Theory

As well known, as yet no widely-accepted theory of the structure of liquid water exists. There is no shortage of theories. But at the current state of their developments, these models are too complex, As such, they do not lend themselves readily to helping me solve the very simple specific problems of the PM theory

As mentioned above, I chose a much simpler approach. The tetrahedral structure of water molecules, the H-bonds formed among them and many other related advanced knowledge on liquid water and protein structure will be shelved for now. In their place, each water molecule is treated as a simple dipole possessing a permanent dipole moment of 1.86 Debye (1.86 x 10^{-18} e.s.u., Moelwyn-Hughes, 1964; see also Sänger and Steiger 1928; McClellan 1963; Eisenberg and Kauzmann 1969, p.12) and a polarizability of

1.444 x 10^{-24} cm^3 (Conway 1952). This approach is nothing new to the reader. For example, it is that underlying the development of the de Boer-Zwikker as well as of the Bradley multilayer adsorption isotherm.

I began by considering an infinitely broad but thin solid sheet. The upper surface of this solid sheet is perfectly smooth and fully covered with a checker board of alternatingly positively-charged and negatively-charged sites, called an *idealized NP surface* as illustrated in Figure 6 and more fully described in the paragraph following the next one.

The other surface of the thin solid sheet is in intimate and full contact with a metallic conductor which is cooled by a powerful but carefully-controlled refrigeration system. The surface of the sheet carrying the N and P sites faces an open space filled with a flowing stream of *pure* water vapor at a pressure and temperature just below the triple point (Figure 7.) As the solid sheet and its N and P sites are being cooled by conduction (only), water molecules that have condensed on the NP surface are rapidly cooled to a lower and lower temperature. The perfectly orchestrated condensation and cooling of water molecules continue until an infinitely deep layer of condensed water chilled to the temperature close to absolute zero is obtained.

Each of these N sites on the *idealized NP surface* is separated from its nearest neighboring P sites by a distance, d. For an idealized NP surface, d is or close to 3.10 Å. We chose this d value because it is equal to what we can figure out to be the average distance

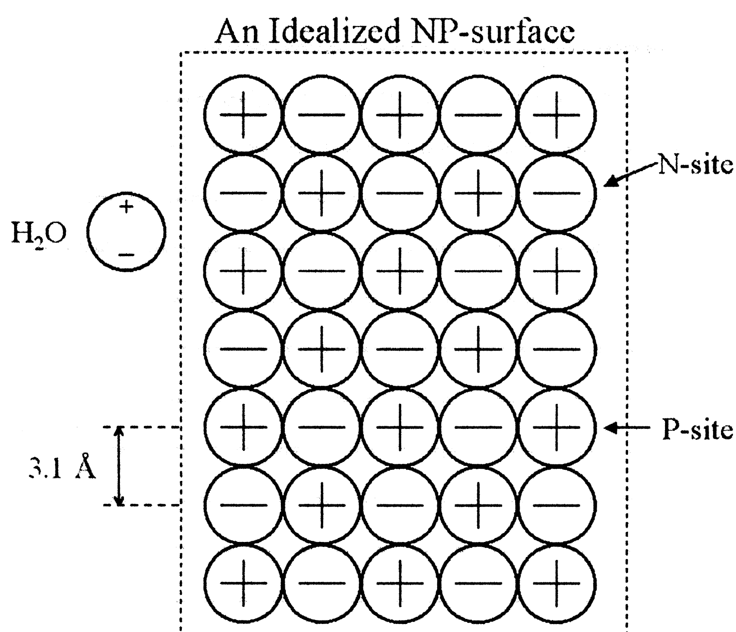

FIGURE 6. An idealized NP surface. The distance between a pair of the nearest-neighboring N and P site in the idealized NP surface is represented by the letter d and it is equal to r, the average distance between two nearest-neighboring water molecules in normal liquid water and is estimated at 3.1 Å .

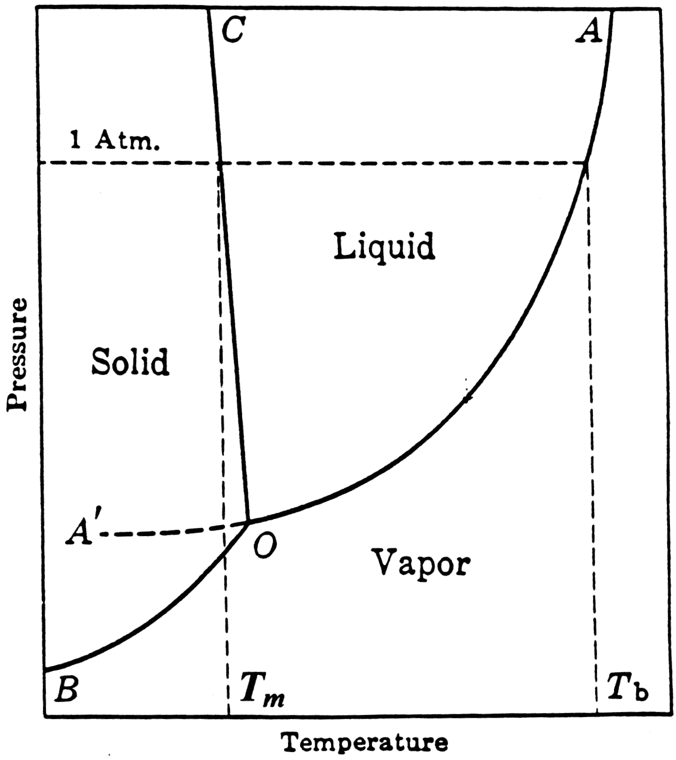

FIGURE 7. A phase diagram, showing solid-liquid-vapor equilibria. T_m and T_b are respectively the melting temperature and the boiling temperature. O represents the triple point. The sharpness of the transitions demonstrate intensely (auto)cooperative nature of the transitions (Modified after Glasstone, 1946; Ling 1980.)

between one liquid water molecule to its immediately neighboring water molecule and called r. The distance r is obtained by taking the cube root of the "unit cell volume" of each liquid water molecule, which in turn is obtained by dividing the molar volume of water equal to 18.016 cm^3 by the Avogadro number, 6.023 x 10^{23}.

Next, I assume that each of the fixed N or P site carries one-half of a negative or positive electronic charge (1/2 x 4.804 x 10^{-10} e.s.u. = 2.402 x 10^{-10} e.s.u.) and that these electronic charges are each located d/2 or 3.104/2 = 1.552 Å from the center of the nearest water molecule. Furthermore, in my entire treatment, only electrostatic interactions between the nearest neighboring molecules or sites are considered. The justification for these choices will come later.

Let us first consider the successive layers of water in immediate contact with our idealized NP surface as the ith layers with i = 1, 2 and n. Next we focus our attention on a specific reference N site in the middle of the checkerboard of N and P sites and call the columns of individual water molecules going left-right from the reference N site as the jth and the columns of individual water molecules back and front from the reference N sites as the kth.

The immediately neighboring columns to the left and to the right of the N site are then referred to as the j−1 and j+1 column respectively. The immediately neighboring column to the front (toward the reader) and back of the reference N site as k+1 and k−1 respectively. The single column of water molecules going through the reference N site is then seen at once as j=0 and k=0. A water molecule designated 3(+2)(−4) is located in the 3rd row, the second column to the right and 4th column away (from the reader) from the reference N site. On the other hand, 2(0)(0) is the water molecule in the second row in the column j=0 and k=0.

In most cases, each water molecule is surrounded on all four sides by four other water molecules with their permanent dipoles oriented in the opposite direction to its own. And, with the exception of the water molecules in the first row, each water molecule is also in contact with two neighboring water molecules with their permanent dipole moment oriented in the same direction as its own, one in front of, or closer to the NP surface and another one behind it. As mentioned, there is an exception to this rule of four surrounding oppositely-oriented neighbors and two similarly oriented ones in front and behind. The exception is the water molecules in the first row. In this case, each water molecule faces either an N or P site on one side and oppositely oriented water dipoles on all four sides in the same row and only one water molecule oriented in the same direction in the row behind.

Now the electric field due to a point charge, ε, is ϵ/r^2, where r is the distance between the point charge and the point of measurement. The (negative) interaction energy of the negative electric charge on the N site with the permanent dipole, μ of an adjacent water molecule 1(0)(0) at a distance d/2 away — without taking into account the favorable induced dipole the point charge produces and interacts with — is $\varepsilon\mu/(d/2)^2$. And accordingly, it equals

$$(2.402 \text{ x } 10^{-10} \text{ x } 1.834 \text{ x } 10^{-18})/\ (1.552\text{x}10^{-8}/2)^2 = 2.838\text{x}10^{-12} \text{ ergs/molecule,}$$

equivalent to 40.82 kcal./mole. This is more than four times stronger than the (negative) water-to-water interaction energy in liquid water at its boiling point (9.7171 kcal/mole, Rossini *et al*, 1952.) Here we see how a fixed N (or P) site strongly adsorbs a water molecule and in so doing also orients the water molecule with the positive end of the water dipole facing the negatively-charged N site and the negative end of the water dipole pointing to the opposite direction.

This simple dipolar model offers other distinctive important insights. Thus, it shows without ambiguity not only the *attraction* among water molecules oriented the right way, it also provides a quantitative information on the *repulsion* a pair of nearest-neighboring water dipoles experiences for one another when they are oriented in the "wrong" way. Strong attraction for the right orientation coupled to strong repulsion for alternative wrong orientations ensures a specific, ordered and mutually enhancing or in *statistical mechanical* terms, (ferromagnetic or auto-) *cooperative* interaction among the assembly of water molecules (Ling 1980.)

(In contrast, if we had adopted a model in which each water molecule is linked to its neighbors by the formation of attractive hydrogen bonds, one would be hard-put to argue that the dissociation of such a bond and reorientation of the water molecules — which appears to be the only alternative action — can produce strong *repulsion*.)

Thus far, we have only dealt with the charge of an N-site interacting with a specific water molecule, 1(0)(0), in contact with the N site. Let us now go to the permanent dipoles and the induced dipoles belonging to all the immediately neighboring water molecules and find out about their respective parts in producing an even stronger induced dipole in that 1(0)(0) water molecule.

The alternatingly positive and negative fixed sites described above, produce induced dipoles of equal absolute magnitude for all water molecules in the same row, though oriented in opposite directions in adjacent columns. I shall designate these induced dipoles as $p^{1(0)(0)}$, $p^{2(0)(0)}$, $p^{3(0)(0)}$, $p^{4(0)(0)}$ etc. for the first, second, third, fourth, etc. water molecules from the N site in the column designated as j=0 and k=0. Now, the electric field created by one dipole on another one oriented in the same direction in tandem ($\rightarrow \rightarrow$) is $2\mu/r^3$ and that due to two dipole arranged in parallel but opposite directions ($\leftrightarrows$) is μ/r^3, where r is the distance between a pair of nearest-neighboring water molecules and it is equal to d, the distance between the nearest neighboring N and P sites. Taking these relationships in mind, one finds that the induced dipole in water molecule 1(0)(0) is described by the equation:

$$p^{1(0)(0)} = \alpha\varepsilon / [2\,(d/2)^2] + \alpha/r^3\,(2\mu^{2(0)(0)} + \mu^{1(-1)(0)} + \mu^{1(+1)(0)} + \mu^{1(0)(-1)}$$
$$+ \mu^{1(0)(+1)} + 2p^{2(0)(0)} + p^{1(-1)(0)} + p^{1(+1)(0)} + p^{1(0)(-1)} + p^{1(0)(+1)}), \quad (3)$$

where the first term on the right-hand side is the induced dipole due to the charged site N at a distance of d/2, the next five terms are induced dipoles due to the five immediately-neighboring permanent dipoles and the last five terms are induced dipoles due to the five immediately-neighboring induced dipoles. But since the permanent dipole moments, $\mu^{2(0)}$, $\mu^{1(-1)}$, $\mu^{1(+1)}$, etc. are all equal, equation (3) reduces to

$$p^{1(0)(0)} = 2\alpha\varepsilon/d^2 + \alpha/r^3\,(6\mu + 2p^{2(0)(0)} + p^{1(-1)(0)} + p^{1(+1)(0)} + p^{1(0)(-1)} + p^{1(0)(+1)}). \quad (4)$$

And for a water molecule in the second (and succeeding) row, the charge-dipole interactions due to the N (or P) site is not between nearest-neighbors and — following the rule adopted — ignored. In consequence, all water molecules in the second (and succeeding) rows are each surrounded on all six sides by other water molecules. We then have

$$p^{2(0)(0)} = \alpha/r^3\,(2\mu^{1(0)(0)} + 2\mu^{3(0)(0)} + \mu^{2(-1)(0)} + \mu^{2(+1)(0)} + \mu^{2(0)(-1)} + \mu^{2(0)(+1)}$$
$$+ 2p^{1(0)(0)} + 2p^{3(0)(0)} + p^{2(-1)(0)} + p^{2(+1)(0)} + p^{2(0)(-1)} + p^{2(0)(+1)}). \quad (5)$$

Again, since all the μ's are equal, we have

$$p^{2(0)(0)} = \alpha/r^3\,(8\mu + 2p^{1(0)(0)} + 2p^{3(0)(0)} + p^{2(-1)(0)} + p^{2(+1)(0)} + p^{2(0)(-1)} + p^{2(0)(+1)}). \quad (6)$$

The induced dipoles of water molecules belonging to the different rows were calculated and shown in the second column of Table 1. A striking feature of the results shown here is that as one goes farther and farther away from the surface of N and P sites, the induced dipole in the water molecules does not taper off to zero. Instead, it asymptotically approaches and eventually assumes a constant value, p^n described by the expression

$$p^n = 8\alpha\mu / (r^3 - 8\alpha). \quad (7)$$

TABLE 1

row (i)	p (Debye)	$\boldsymbol{\mu}$ (Debye)	E (10^{-12} ergs/molecule)	E (kcal/mole)
1	2.842	4.702	6.984	100.4
2	1.378	3.238	1.542	22.18
3	1.206	3.066	1.272	18.29
4	1.177	3.037	1.236	17.78
5	1.173	3.033	1.231	17.70
6	1.173	3.033	1.230	17.69
7	1.172	3.032	1.229	17.68
8	1.170	3.030	1.228	17.66
n	1.170	3.030	1.228	17.66

The computed induced dipoles (p), total dipole moment ($\boldsymbol{\mu}$, which equals the induced dipole moment, p, plus the permanent dipole moment, μ) and the (negative) adsorption energy (E) of water molecules in successive layers of water molecules in direction away from the idealized NP surface maintained at a temperature very close to absolute zero. E given in two units, 10^{-12} ergs/molecule and kcal/mole.

As shown in Table 1, the induced dipole at a position very far away from the idealized N-P sites and designated as the nth is equal to 1.170 Debye — to be compared with 1.86 Debye of the permanent dipole moment of a water molecule.

Since the induced dipoles p's of all the water molecules are oriented in the same direction as their respective permanent dipoles, μ's, one may define a *total dipole moment* of water molecule to be represented by the bold-faced Greek letter mu, $\boldsymbol{\mu}$ as the sum of induced dipole moment, p and the permanent dipole moment, μ:

$$\boldsymbol{\mu} = \mu + p. \tag{8}$$

Column 3 of Table 1 presents the total dipole moments, $\boldsymbol{\mu}$'s of the successive layers of water molecules calculated. With these data on hand, our next task is to evaluate the (negative) adsorption energy of the successive layers of water molecules.

As mentioned above, the (negative) energy of interaction between an electric charge ε and a dipole moment μ at a distance r apart is $\varepsilon\mu/r^2$, that between two dipoles μ_1 and μ_2 arranged in the same direction and in tandem is $(2\mu_1\mu_2)/r^3$ and that between two dipoles arranged in opposite directions in parallel is $(\mu_1\mu_2)/r^3$.

With these in mind and remembering to divide each (negative) water-to-water interaction term by 2 to avoid redundancy, we have for the total (negative) energy of water molecules of the first row in this ideal array and it is represented by $E^{1(0)(0)}$, where:

$$E^{1(0)(0)} = \varepsilon\boldsymbol{\mu}^1/\{2\,(d/2)^2\} + \{\boldsymbol{\mu}^{1(0)(0)}/2r^3\}(2\boldsymbol{\mu}^{2(0)(0)} + \boldsymbol{\mu}^{1(-1)(0)} + \boldsymbol{\mu}^{1(+1)(0)} + \boldsymbol{\mu}^{1(0)(-1)} + \boldsymbol{\mu}^{1(0)(+1)}). \tag{9}$$

Since the last four total dipole moments on the same row are equal in absolute magnitude as well as orientation, the total (negative) energy $E^{1(0)(0)}$ from Equation 9 can be written as

$$E^{1(0)(0)} = 2\,\varepsilon\mu^1/d^2 + \mu^{1(0)(0)}\,(2\mu^{2(0)(0)} + 4\mu^{1(-1)(0)})\,/2r^3, \tag{10}$$

or

$$E^{1(0(0)} = 2\,\varepsilon\mu^1/d^2 + \{\mu^{1(0)(0)}/r^3\}(\mu^{2(0)(0)} + 2\mu^{1(-1)(0)}). \tag{11}$$

The total (negative) adsorption energy of a water molecule in the second (and higher) row, $E^{2(0)(0)}$, is then

$$E^{2(0)(0)} = \{\mu^{2(0)(0)}/2r^3\}\ (2\mu^{1(0)(0)} + 2\mu^{3(0)(0)} + \mu^{2(-1)(0)} + \mu^{2(+1)(0)} + \mu^{2(0)(-1)} + \mu^{2(0)(+1)}). \tag{12}$$

Since the last four total dipole moments on the second row are identical, Equation 12 can be simplified into the following:

$$E^{2(0)(0)} = \{\mu^{2(0)(0)}/r^3\}\ (\mu^{1(0)(0)} + 2\mu^{2(-1)(0)} + \mu^{3(0)(0)}). \tag{13}$$

Like the induced dipoles moment, the total (negative) energy, E, also does not taper off to zero as one moves farther and farther away from the NP surface. Indeed as one moves farther and farther away from the polarizing N and P sites, the total (negative) adsorption energy of a water molecule, E^n, approaches and sustains a steady unchanging value, described by the following equation

$$E^n = \{4(\mu^n)^2\}\ /\ r^3\ . \tag{14}$$

Substituting (7) and (8) into (14), we have

$$E^n = (4\mu^2 r^3)/\ (r^3 - 8\alpha)^2. \tag{15}$$

The computed total (negative) energy of water molecules far away from the NP surface is listed in Column 4 of Table 1 in two units, respectively in 10^{-12} ergs/molecule and in kcal/mole. The data given in kcal/mole is also presented graphically and shown in Figure 8.

The implication of Equation 15 (and Table 1) is truly astonishing. It tells us that under an ideal condition described earlier, an idealized NP surface could strongly polarize and orient successive layers of water molecules *ad infinitum*.

Additional considerations and analyses of the theoretical model

In this new theory, the long-range impact on distant water molecules is not due to a propagated electrical polarization (induction) emanating from the electric charges at the N and P sites and proceeding through intervening water, molecule-by-molecule in the way first suggested by de Boer-Zwikker and also by Bradley. Nor can it be properly described

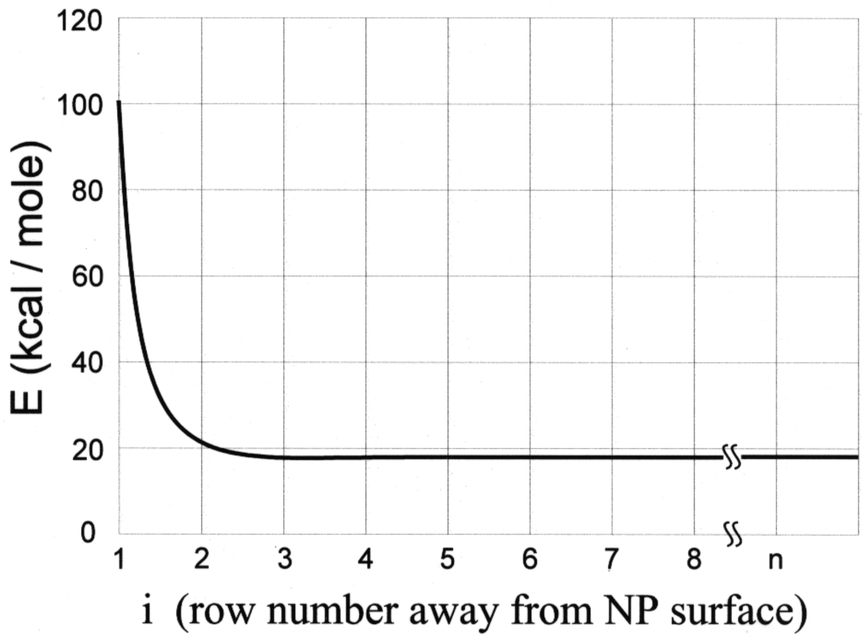

FIGURE 8. The theoretically computed (negative) adsorption energy of a water molecule, E, in one of successive layers of water molecules away from an idealized NP surface at a temperature very near absolute zero. Note that as the distance between the water molecule and idealized NP surface increases, the (negative) adsorption energy does not taper off to zero. Rather, it continues at a constant value described by Equation 15. For details on the makeup of an idealized NP surface, see Figure 7 and text.

as Brunauer *et al* did when they said that if a large permanent dipole moment is present in the gas molecules, then "many layers of the gas molecules will be successively polarized by the mechanism of de Boer and Zwikker."

Rather, a long-range multilayer dynamic structuring begins with a concerted orientation (of the permanent dipole moment of a nearby water molecule) and electrical polarization (creating in the neighboring water molecule an induced dipole oriented the same way the permanent dipole is oriented by the N or P site.) Each of these components corresponds respectively to what is called *orientation polarization* (P_o) — due to spatial orientation of the permanent dipole moment of the molecule — and *distortion polarization* (P_D) — as in the Debye's formula for the total polarization of a polar molecule in an electric field (Debye, in "Polar Molecules" 1924.)

The (properly) oriented permanent dipole and the newly created induced dipole of the immediately neighboring water molecules in turn orient and polarize *their* nearest-neighboring water molecules. And this process spreads farther and farther outward until all the water molecules in the assembly have acquired a similar oriented permanent dipole moment and induced dipole moment in a perfectly orderly array.

This polarization-orientation *ad infinitum* under an indelaized condtion is possible only because the gas molecules involved have a large permanent dipole moment. This was probably what motivated Brunauer, Emmett and Teller to endorse Bradley's theory on gas molecules with large permanent dipole moments. It is more easily demonstrated here now that we have Equation 15. Set μ to zero; E^n, the (negative) adsorption energy of a water molecule far away from the ideal NP surface, becomes zero.

Note also that both the orientation component and the distortion component are of such a nature that they are highly *auto-cooperative* (Ling 1980.). That is, each time a water molecule is oriented and polarized in one direction, it will make all its six surrounding water molecules more likely to adopt the favorable low or high (negative) energy orientation. This three dimensional cooperativity provides the foundation for the stability of the dynamic structure formed. It is also the reason why multilayer water adsorption typically shows a pattern of *hysteresis*. Thus, the curve of *adsorption* of water is not identical to the curve of *desorption* but tends to occur at a higher relative vapor pressure as seen in many models studied (Anderson 1914 on silica gel; Urquhart and Williams 1924 on cellulose; Katchman & McLaren 1951 and Reyerson and Peterson 1953 on protein and virus.)

Next, I want to analyze and catalogue the assumed conditions in our specific model that have created in theory an endless polarization and orientation of water molecules. They fall into two categories.

The first five components listed below under Category A are essential and hence indispensable to produce in the idealized condition the *ad infinitum* polarization and orientation demonstrated theoretically above. The next two items listed under Category B, justified on the basis of the overall success of the effort built on these and the five other more essential conditions are less stringently required and can be changed (within limits) without serious adverse effects:

Category A

(1) a temperature very near absolute zero;

(2) a boundless, perfectly smooth surface carrying alternating P and N sites at the same distance, d, from all its nearest neighbors P or N sites;

(3) the distance, d is made equal to the average distance between nearest water molecules in liquid water r, obtained by taking the cube root of the average volume of each water molecule in liquid water, obtained by dividing the molar volume of water, 18.016 cm^3 by the Avogadro's number, 6.023×10^{23}, yielding a value of 3.10 Å. It is believed that this is the least arbitrary value of r one can find.

(Other values for comparison include twice the van der Waal radius of oxygen atom, 2 x 1.40 = 2.80 Å (Pauling 1960, p.260); the oxygen to oxygen distance in ice I, 2.76 Å (Eisenberg and Kauzmann 1969 p. 94); and a value of between 2.8 and 2.9 Å from the well-resolved peak of the X-ray radial distribution function of liquid water at 4°C. (Narton *et al*, 1967.)]

(4) an endless body of water in contact with the entire idealized NP surface;

(5) perfect insulation of the whole assembly from mechanical, acoustic, light, heat, gravitational and other perturbations from the outside.

Category B:

(1) Size and location of the negative and positive electric charge on the N and P sites are respectively set at one half electronic charge and d/2. No major difference is expected if the size is set at full electronic charge or much smaller than half electronic charge.

(2) Only the nearest neighbor interaction is considered. This is justified since $1/r^3$ decreases sharply as r increases. Due to the symmetry of the system, inclusion of the next-nearest neighboring interaction would only cause a uniform but small reduction of the energy terms, which for the quantitative accuracy we can expect to achieve is insignificant.

Two predictions from the present theory

If we designate each of the quantum-mechanically allowed energy states of water molecules as $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots \varepsilon_r \ldots$, and divide each of these energy levels by kT, (the average kinetic energy of each water molecule, where k is the Boltzman constant and T the absolute temperature,) then the sum $1 + \exp(-\varepsilon_1/kT) + \exp(-\varepsilon_2/kT) + \ldots = \sum \exp(-\varepsilon_r/kT)$ is called the *partition function* (p.f.) of the water molecules in that specific state, which could be vapor, liquid or solid ice (Rushbrooke 1949.)

In a mixture of liquid water and solid ice, the trend is for all the water molecules to exist as liquid water or as solid ice. Which way it goes at a given pressure depends on the temperature and its relationship to that specific temperature we call the melting point as illustrated in the Phase Diagram shown in Figure 6. This can be put into a more quantitative form if we designate the partition function of normal liquid water as $(p.f.)_l$ and that of solid ice (I) as $(p.f.)_s$ and u_f as the *enthalpy of fusion* and equal to the energy (or more precisely, enthalpy) difference between the zero energy level of the liquid water state and that of the solid ice (I) state. The melting temperature, T_m, is then described by the following equation (Gurney 1949, p. 129.)

$$T_m = u_f / \{k \ln [(p.f.)_l / (p.f.)_s]\}. \qquad (16)$$

Now, the melting point of normal liquid water is 273.15° K. u_f, the enthalpy of fusion of ice (I) is 1.4363 kcal mol^{-1} (Rossini *et al* 1952) or (divided by the Avogadro number) $1.4363 \times 10^3/(6.023 \times 10^{23}) = 2.39 \times 10^{-21}$ cal $molecule^{-1}$. The Boltzman constant, k, is equal to 0.330×10^{-23} cal $deg^{-1}molecule^{-1}$. Substituting the values of T_m, u_f and k into Equation 16, one finds that $\ln [(p.f.)_l / (p.f.)_s]$ equals 2.647.

Similarly, we can write Equation 17 for the boiling point of water, T_b, and its relationship to u_v and $(p.f.)_v / (p.f.)_l$:

$$T_b = u_v / \{k \ln [(p.f.)_v / (p.f.)_l]\}, \qquad (17)$$

where $(p.f.)_v$ is the partition function of water in the vapor state. T_b, the boiling point of water is 373.15° K. u_v, the enthalpy of vaporization is 9.7171 kcal mol^{-1} (Rossini *et al* 1952) or 1.6133×10^{-20} cal $molecules^{-1}$. Substituting T_b, u_v and k into Equation 17, one obtains $\ln [(p.f.)_v / (p.f.)_l]$ equal to 13.11.

Now, we are ready to calculate the theoretically expected freezing point and boiling point of water molecules polarized and oriented by an idealized NP surface. Table 2 shows that the average water to water (negative) interaction energy, E^n, far from the NP surface for d (=r) equal to 3.10 Å is 17.76 kcal mol^{-1}. We now want to find out what is the boiling point and freezing point of this polarized-oriented water with the aid of Equation 16 and 17.

TABLE 2

d	E	
(Å)	(10^{-12} erg/molecule)	(kcal/mole)
2.5	12.83	184.6
2.6	6.633	95.40
2.7	4.088	58.80
2.8	3.221	46.32
2.9	2.791	40.15
3.0	2.038	29.31
3.1	1.235	17.76
3.2	1.009	14.51
3.3	0.834	12.00
3.4	0.710	10.13
3.5	0.604	8.68
3.6	0.523	7.52
3.7	0.458	6.59
3.8	0.404	5.81
3.9	0.359	5.16
4.0	0.322	4.63

The computed (negative) adsorption energy, E^n, of water molecules at a great distance away from the idealized NP surface at a temperature very close to absolute zero. E_n given respectively n units of 10^{-12} erg per molecules and kcal per mole in the second and third column.)

To do that, we must first determine the enthalpy of vaporization of the polarized-oriented water far from the idealized NP surface, designated as u_{vp} as well as its enthalpy of fusion, designated as u_{fp}. Assuming that the enthalpy of water vapor to be negligible, u_{vp} would be simply 17.76 – 0 = 17.76 kcal mol^{-1}. On the other hand, u_{fp} would be the enthalpy of sublimation of ice-I, 11.30 kcal mol^{-1} (Eisenberg and Kauzmann 1969, p.101) minus 17.76 kcal mol^{-1} equaling –6.46 kcal mol^{-1}. Substitute these values of u_{vp} and u_{bp} into Equations 16 and 17 respectively, one obtains the boiling point of polarized-oriented water far from the idealized NP surface at 724°K or 451°C and a freezing point of –1228° K.

Now, we examine more closely the values of ln $[(p.f.)_v / (p.f.)_l]$ and ln $[(p.f.)_l / (p.f.)_s]$ used in the calculations above. You recall that implicit in the use of these respective values of 13.11 and 2.647 is the assumption that the partition function of polarized-oriented water far from the idealized NP surface is the same as that of normal liquid water. That, or course, is not true. That polarized-oriented water suffers motional restriction especially in translational and rotational motions. As a result, the number of allowed energy levels are fewer than in normal liquid water and the partition function of polarized-oriented water or $(p.f.)_{lp}$ is significantly lower than that of normal liquid water, $(p.f.)_l$.

One way of solving the problem would be to estimate how much is the difference. But that is not what we intend to do here. A look at Equation 16 and 17 readily reveals that a reduction of the value of $(p.f.)_l$ would make the estimated boiling point of polarized-oriented water even higher than 451°C and the freezing point of polarized-oriented water even lower than −1228°K. And that is all we need to know here to arrive at our first prediction:

Prediction 1: *The boiling point of polarized-oriented water would be at least as high or higher than 451°C.*

Prediction 2: *Under ideal or near-ideal condition, the polarized-oriented water can never be frozen.*

But to know by exactly how much is the freezing point of polarized-oriented water still lower than −1228°K adds no valuable information here either. For a freezing point below absolute zero is not possible, because to reach such a temperature, the assembly must go through the temperature of absolute zero. Yet according to the Third Law of Thermodynamics: "It is impossible by any procedure, no matter how idealized, to reduce any assembly to the absolute zero in a finite number of operations." (Fowler and Guggenheim 1960, p. 224.) This then leads to our second prediction.

Right away, this theoretical discovery has accomplished one important purpose. It justifies the assumption we made above that we can in theory create the idealized polarized-oriented water at a near-absolute zero temperature. For if the water freezes on the way toward absolute zero, we would not be able to continue and achieve what we did without engaging ourselves in unproductive, distractive arguments.

We now go back to Table 2. This table shows that the (negative) adsorption energy E^n of far-away water molecules given in Equation 15 exceeds the sublimation energy of ice-I, at 11.30 kcal mol^{-1} only if d is equal to the water-to-water distance r, estimated at 3.1 Å or lower but not much higher than 3.1 Å. Thus, if d is, say, 3.4 Å or even higher, freezing may take place. So clearly, a decisive factor in freezing or not freezing is the value of d. To produce non-freezing water, it must equal or at least be close to the water-to-water distance, r. And it must be *uniformly* so. These criteria are, of course, what make our idealized NP system ideal.

Our next task is to verify experimentally the two predictions. To do that , we must first resolve a set of problems.

Number 1 condition under Category A is a temperature of near absolute zero. We have just shown, absolute zero as such is impossible to achieve. However, liquid helium can provide a temperature close to −272.2° C, which is a little less than one degree above absolute zero or −273.16° C. Failing liquid helium, the next best would be liquid nitrogen offering a temperature close to −195.8°C., which is 69.3° C above absolute zero.

Essential conditions described under (2) and (4) under Category A are impossible to achieve. There is no such thing as a boundless perfectly smooth NP surface, nor an infinite body of water, nor perfect isolation from the external real world. But a practical substitute is a thin layer of water held between two juxtaposed smooth near-ideal NP surfaces — in other words, a near-ideal NP-NP system (see Figure 2d.) The juxtaposed NP surfaces conserve the polarization-orientation indefinitely. Being very thin, it is not difficult to keep it insulated from external disturbances. The thinness of the water layer also minimizes edge effects.

Finally, perhaps the most challenging of all is to find a real world replica of the idealized NP surface, where a checkerboard of N and P sites separated from each nearest neighbor by a distance close to if not exactly equal to the distance between two nearest neighboring water molecules. The best example one can imagine is the smooth surface of salt crystals. This is not at all new. de Boer & Zwikker were among the first to introduce such an idea (Figure 3.) One recalls that Bradley also explicitly dealt with salt crystal surfaces. But neither de Boer-Zwikker nor Bradley mentioned any specific salt crystals. Harkins demonstrated multilayer adsorption of water molecules on diastase or titanium oxide crystal (Harkins 1945.) Another attractive model is the cubic NaCl crystals. Unfortunately, it is water-soluble.

However, there is another cubic salt crystal that has the same geometry as NaCl but hardly soluble in liquid water. That is silver chloride — especially large crystals artificially grown and used as lens for infrared spectroscopy, for example. In Figure 9, I reproduce (a modified version of) the silver chloride surface as given by Glaus and Cazzaferri (1999.) This may well be the best NP surface we know today. In his advanced textbook of inorganic chemistry, Moeller (1952, Table 18.5) gives the measured bond distance as 2.77 Å, the sum of ionic radius as 3.07 Å, which are close to the (r and) d value of 3.1 Å used in our computation.

Then there is Figure 10, which is a diagrammatic illustration of the surface structure of sodium silicate glass — a random network of silica oxide carrying negatively-charged

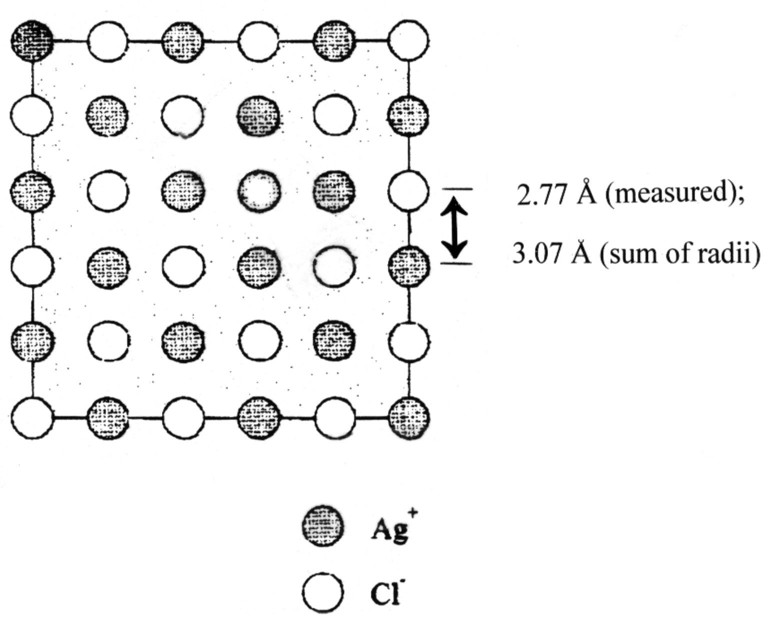

FIGURE 9. A diagrammatic illustration of the structure of the polished surface of silver chloride crystal and the distance between nearest neighboring Ag^+ and Cl^- ions from measurement of bond distance (2.77 Å) and from summation of atomic radii (3.07 Å.) (Modified after Glaus and Calzaferri 1999.) Reproduced with permission of J. Phys. Chem. ©1999 American Chemical Society.

free-hanging oxygen ions and positively-charged sodium ions (Pulker 1984.) All in all, the glass surface, though not nearly as ideal as the AgCl crystals, represents, nonetheless, an imperfect surface carrying alternatingly N and P sites. Since random network is only a postulation, and in Nature few things are truly random, the realistic surface of glass might be significantly closer to that of the AgCl crystal surface given in Figure 9.

In summary, we have with the aid of two sets of pictorial diagrams produced two specific model systems. They are the nearly ideal polished silver chloride crystal lenses with d close to 3.1Å. The more randomly oriented sodium silicate glass surface in contrast, may well have local areas with d-values at values both higher and lower than the ideal value.

Thus equipped, we return to where we started. Happily, here is where our good luck continues. For it turned out that the key experiments have already been done by scientists who had absolutely no idea that their findings were to play a key role in verifying a new theory of long-range polarization-orientation of water molecules by idealized NP surfaces. They only described their observations and their own reasons for making these observations.

Giguère and Harvey's accidental (retroactive) confirmation of the prediction that near-ideally polarized-oriented water between polished AgCl crystal lenses cannot freeze at subzero temperature all the way to the lowest temperature studied, i.e., –176°C.

That observation of singular value to the present work is that of Giguère and Harvey reported nearly half of a century ago in 1956. Its validity is enhanced by its chance discovery

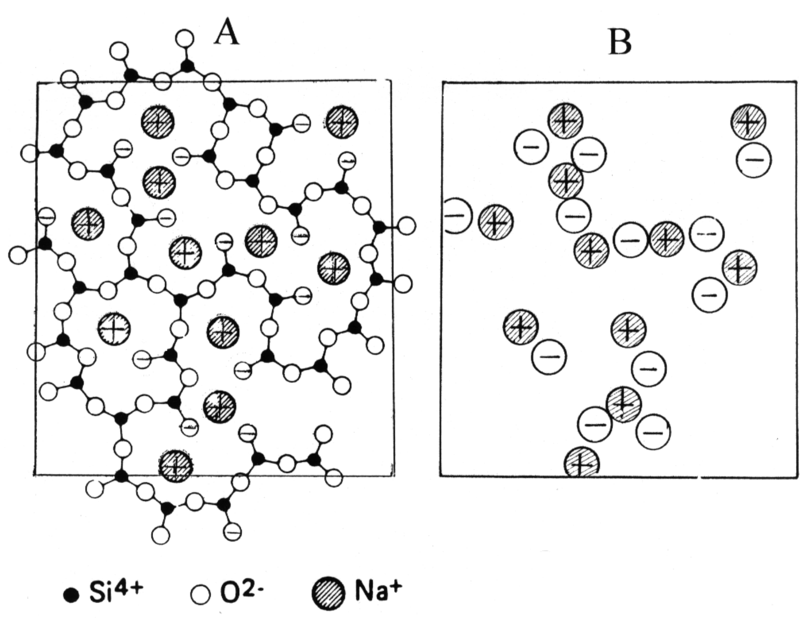

FIGURE 10. Visualization of the surface of sodium silicate glass based on the theory of random network of Zacchariasen (1932.) A. Picture from Pulker, 1984. B. Distribution of positive Na^{+} and negative oxygen ion on polished glass surface. Locations of ions from A. (Partly modified after Pulker, 1984. Figures reprinted with permission from Elsevier.

not expected at all and by its later independent confirmation by another scientist (See below.)

Giguère and Harvey placed a thin layer of water between two polished (transparent) AgCl plates. To their surprise, they discovered that as shown in their Figure 1 reproduced here as Figure 11, "essentially the same spectrum was obtained for all temperature studied even down to that of liquid air, confirming that no crystallization of water has occurred." (p. 801.)

They also pointed out that this phenomenon could be repeated any number of times under the same conditions (p. 801) and "Our films of water pressed between silver chloride plates could be warmed and cooled over a wide temperature range without significant alteration in their spectra" (p. 805.)

Giguère and Harvey (who have since either deceased, retired or otherwise beyond reach) made no mention of the exact thickness of the water film they studied. Luckily, I reached their one-time associate, Dr. Rod Sovoie, who kindly wrote me that the water film between the AgCl plates investigated by Giguère and Harvey was 10 micrometer thick. Thus, a water layer well over thirty thousand (30,000)-water-molecule-thick cannot be frozen even at the temperature of −176° C, when held between two polished AgCl crystals.

It seems that Giguère and Harvey's incidental discovery has confirmed the essence of our Prediction 2.

Before going on to our next set of experimental testing and its result, I would like to point out that the ideally polarized-oriented water cannot be classified as vitreous water because vitreous state is a free-standing phenomenon. The ideally polarized-oriented state of water is a direct consequence of the NP-NP system and without the NP-NP system, it will return to the state of normal liquid water.

A second point I want to mention concerns the reproducibility of the results reported by Giguère and Harvey. The fact that it was a totally unexpected and it could be repeated

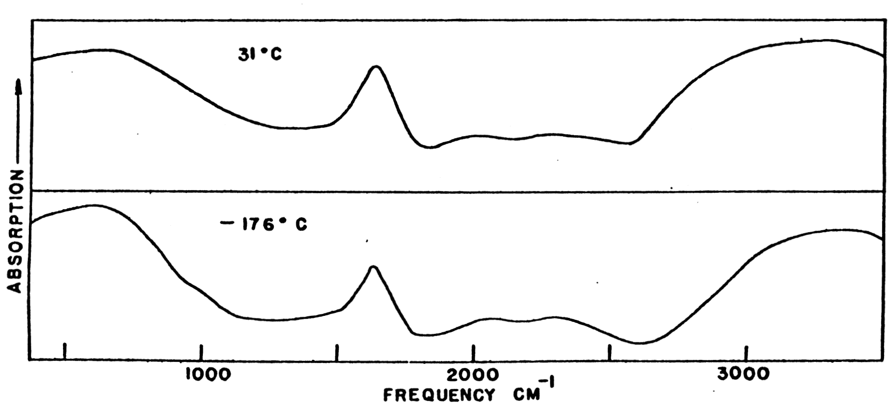

FIGURE 11. Infrared absorption spectrum of 10-micron-thick water film held between polished AgCl crystal plates. The two (indistinguishable) spectra were recorded respectively at ambient temperature (top, 31° C) and at liquid air temperature (bottom, −176°.) I am indebted to Dr. Rod Sovoie, the onetime associate of Drs. Giguère and Harvey, for the information on the thickness of the water films Drs. Giguère and Harvey earlier studied (from Giguère and Harvey 1956, by permission of *Canad. J. Chemistry*.)

any number of times the investigators chose speak volumes. However, in a 1982 review on “Supercooled Water”, C.A. Angell mentioned on page 57 of his review that a scientist named “Glew” had in a private communication told Angell that he (Glew) had made a similar obsevation. However, Angell and his coworker, Barkatt, failed to supercool water between glass surfaces below –28° C (–31° C for quartz plates). Since even normal bulk phase liquid water can be cooled to –40° C (Dorsay 1940; Hallet 1965; see also Figure 12 of the present paper) Angell and Barkatt’s difficulty in cooling water to –28° or –31° C could be from an inadvertent cause. If so, I suggest that this could be their inclusion of “a highly adsorbing dyestuff” into the water being cooled and that this dyestuff adsorbed onto the glass/quartz surface altered its water-polarizing-orienting attributes.

In harmony with this interpretation was Zocher and Coper’s demonstration in 1928 that by simply rubbing vigorously with filter paper the surface property of glass was profoundly altered. Other evidence in harmony with this interpretation comes from industrial processes conferring new surface properties to glass surface by coating it with diverse strongly-adsorbed chemicals (see Pulker “Coating on Glass” 1984.)

Another point I would like to make is to use the word “supercooling” with caution. Supercooling as such creates a *metastable equilibrium state*. The nonfreezing water between AgCl surfaces, in my opinion based on the theoretical reasoning, suggests that it represents a *true equilibrium state*.

Finally, to add still more to the significance of this retroactive confirmation of nonfreezing water held between polished AgCl crystal surface with d close to 3.1 Å I cite the work of Fox and Martin (1940), who also tried to study the infra-red spectra of liquid water and ice I as Giguère & Harvey did, but had not encountered unusual difficulties as did Giguère & Harvey. (See Fox and Martin’s Figure 3 on page 239 of their paper.) The main difference between Giguère & Harvey’s study and Fox and Martin’s lay in the nature of the absorption cells employed. The cells used by Giguère and Harvey comprised AgCl plates with cubic crystalline structure and near-perfect NP symmetry. In contrast, Fox and Martin used flurorite (CaF_2) plates, whose crystalline structure (see Pauling 1960, p. 534) is altogether different from that of the nearly ideal NP surface of silver chloride shown in Figure 9.

Hori’s “non-freezing” and “non-boiling” water between polished glass and quartz surfaces

As mentioned earlier, Prof. Takeo Hori of the Low Temperature Science of Hokkaido University published in 1956 an article in Japanese entitled “On the Supercooling and Evaporation of Thin Water Films”. It was translated into English for the US Army Snow Ice and Permafrost Research Establsihment in 1960 (Hori 1956.)

For the convenience of the reader, two key figures from Prof. Hori’s paper are reproduced here respectively as Figures 12 and 13. Figure 12 shows that water held between two polished glass plates 1/100 mm (or 10 micrometer) or farther apart, could be supercooled to as low as –30° C but no further and is therefore just like ordinary liquid water (Dorsay 1940; Hallett 1965). However, when the water film held between glass plates is below 1/100 mm or 10 micrometer in thickness, it frequently reveals no traces of freezing at temperature lower than –90° C...” (Hori 1960, p. 3.) At a distance of 1/1000 mm or 1 micrometer apart, there is no evidence whatsoever of freezing at –90°C even though a 1-micrometer layer of water is well over three thousand (3000) water-molecules thick.

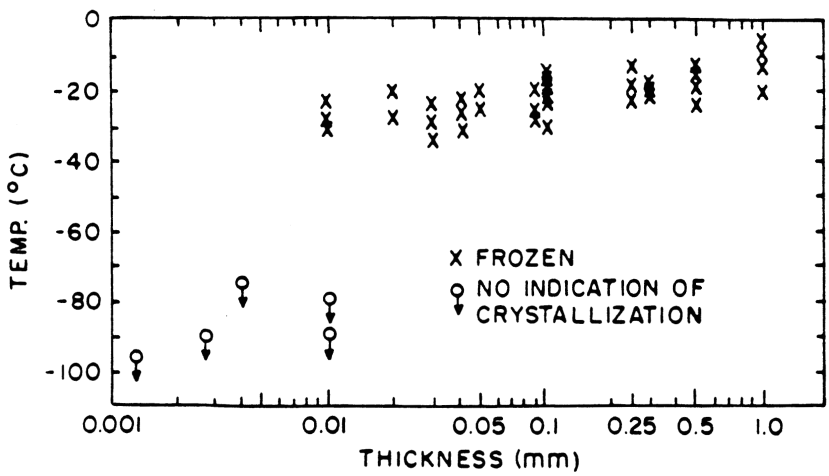

FIGURE 12. The influence of the thickness of water film (held between two flat polished glass or quartz plates) on the temperature at which freezing occurred or failed to occur. Prof. Hori pointed out that at a film thickness below 0.01 mm (or 100, 000 Å and thus more than 30,000-water molecules-thick), the water film frequently showed no trace of freezing at temperature as low as –90° C. Even in water films 0.1 mm thick, when freezing did take place, it took place only at isolated spots and not pervasively throughout. (from Hori, 1956, Institute of Low Temperature Science, (ALTS).)

Nonetheless, compared to the inability of a 10 micra thick water layer to freeze at –176° C, there is no question that a much more powerful and effective polarization-orientation of water molecules and over a much longer range was achieved by the more nearly perfect NP-NP system of AgCl plates than polished glass plates — further confirming the theory.

Let us now turn to the second figure reproduced from Prof. Hori (Figure 13). It shows the vapor pressure of water held between one flat polished glass plate (or quartz crystal plate) and a curved one on top of it — with a radius of curvature of 35 m. When water is introduced between the two surfaces, the distance of separation, called δ (not to be confused with d representing the distance between nearest neighboring water molecules in our study) varies from near zero at the center where the two plates meet to increasingly higher value toward the periphery of the water film. Viewed from the top, the water film shows a series of concentric light and dark bands or fringes which are known as Newtonian rings. From the location at a specific ring, the index of refraction of water or air between plates, the wave-length of the light, and its angle of incidence, the thickness of the film at that point, δ, could be determined with accuracy. To study the influence of film-thickness and of temperature on the vapor pressure of the water film, Hori placed the whole assembly in a vacuum chamber kept at different temperatures.

The water film at the periphery is relatively thick and the vapor pressure registered was not different from those of bulk-phase water at the same temperature. With time, this peripheral water evaporates away and the outer boundary of the water layer shrank toward the center of the water film. This continued until a final equilibrium position was reached,

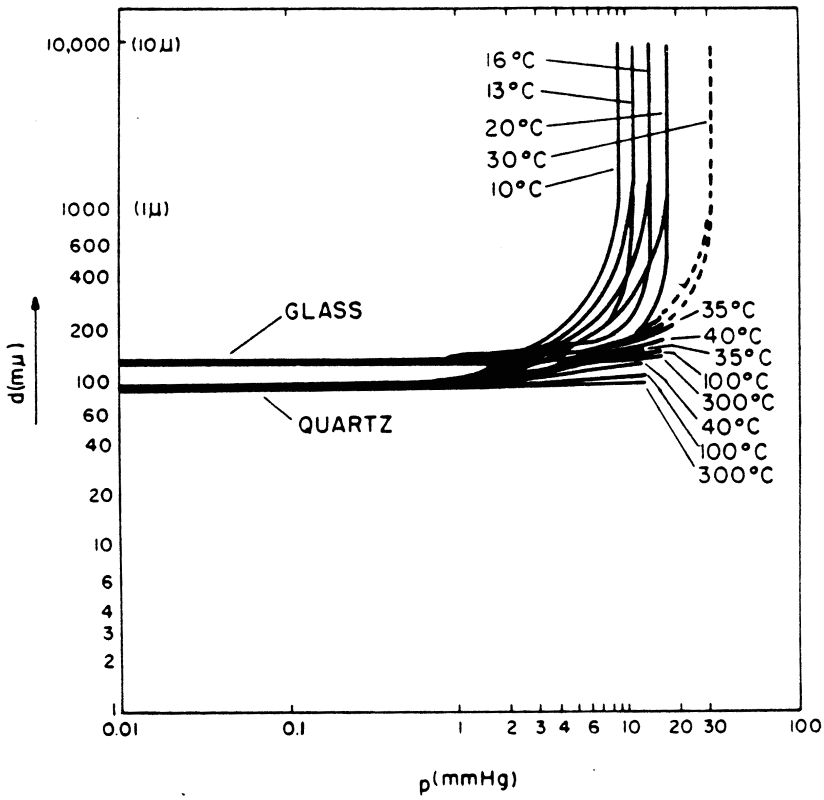

FIGURE 13. The vapor pressure (abscissa, in mm of Hg.) of water film at different thickness in units of mμ (or 10 Å) (ordinate). Water film of varying thickness was produced by placing water between one flat glass (or quartz) plate and another curved plate with radius of curvature of 35 m. The thickness mentioned above refers to the water film at the periphery of the doughnut-like ring of water. When the thickness was 1 μ or thicker, the vapor pressure was not different from normal liquid water. However, when the thickness fell to 90 mμ (900 Å or some 300 water molecules thick), the vapor pressure became zero even at temperature as high as 300° C. (From Ling 1972, redrawn after Hori 1956, Low Temperature Science.)

from then on net loss of water came to a halt. It is at this point that the vapor pressure dropped to zero.

Hori found that in the case of quartz crystal plates, when δ reached 90 (±20) millimicra (equivalent to about 300 water molecule thick), the measured vapor pressure became zero and there is "absolutely no evaporation even in a vacuum" at a temperature as high as 300° C (p. 5). But when the flat plate and curved lens are glass, the critical δ is 140 ±20 millimicra, (roughly equivalent to 500 water molecules thick), at which there is zero vapor pressure even at 300°C. Both sets of data affirm the first prediction that the ideally or nearly ideally polarized and oriented water would not boil at a temperature of 430° C or higher.

Discussion

A critical theoretical confirmation of the hypothesis of propagated short-range electrical polarization-orientation in the dynamic structuring of water in living cells and in a wide range of inanimate systems

The entire history of the study of the adsorption of multilayers of water molecules in living cells and in a wide variety of inanimate systems has been plagued by the absence of a physical theory that can unequivocally tell us how deep a layer of water molecules can be influenced by a solid surface under the best of conditions. If I am not mistaken, that problem has now been resolved. That is, under the favorable conditions defined, an idealized NP surface can enhance the water-to-water adsorption energy *ad infinitum*.

This new insight has not only further solidified the polarized-oriented multilayer (PM) theory of cell water and the association-induction hypothesis of which the PM theory is an integral part, it has also given new life to the many exciting discoveries of the past that have been banished to dusty shelves seemingly forever.

Do we need a revival of the classic condensed film theory to explain long-range dynamic water structuring?

As mentioned earlier, in as far back as the early 19th century, investigators of the highest caliber had subscribed to the idea that solid surfaces may strongly attract gaseous molecules over long distances. As an example, van der Waal had suggested it to J. R. Katz for his extensive data on the adsorpton of water on proteins, nucleic acids and other biomaterials (McBain 1932, p. 451; Katz 1912, 1912a.) However, when McBain wrote his monograph in 1932, the majority of the "old physicists" had already abandoned this theory. Nonetheless, a small minority hung on.

In more recent years, one notices that Israelachvili (1985, 1987) and his coworkers appeared to have returned to the condensed film theory with a twist. That is, they offered direct electrostatic force to achieve the long-range ordering of water molecules. However, I am inclined to disagree.

My reasons for disagreeing are twofold. The first is the Law of Macroscopic Neutrality (For a lucid discussion on the subject, see Guggenheim 1950, pp. 330–331.) That is, isolated electric charges in chemically measurable concentrations can only be found during thunderstorms and in high energy physics laboratories. They do not exist inside living cells. As a rule, where there are negative electric charges, there are an exactly equal number of positive charges. When isolated electric charges are found at exposed surfaces, their number is so small that they would have little impact on the sorption of water, which as a rule occurs at high concentrations.

My second reason can be understood with the help of Figures 2a, 2b and 2c. Water dipoles polarized and oriented by a surface carrying electric charges of the same kind are oriented in the same direction. As such, these similarly oriented water dipoles strongly repel one another. That is why ions (Figure 2a) and other surfaces with one kind of electric charges (Figure 2b, 2c) cannot polarize and orient water molecules much more than one or two layers.

Do the N and P sites on the surface of AgCl plates and polished glass represented in Figure 9 and Figure 10 truly represent respectively isolated negatively- and positively-charged sites?

Not exactly. I have chosen for the sake of simplicity to do something that is not entirely correct. However, the harm such a deviation from truth might cause is more than made up by the clarity on the main message that this simple approach brings. In reality, sitting behind each N (or P) site in the near-ideal NP surface in Figure 10 is (respectively) a P (or N) site. And sitting behind that P (or N) site is another N (or P) site and this goes on and on. Indeed, an even more precise way of doing it would be to represent what we now call an NP surface, a N(P)P(N) surface or even N(PNPN...)P(NPNP..) surface. But that would be too cumbersome to be worth the effort. For, after all, the AgCl salt crystal and the sodium silicate glass are not two dimensional sheets but three dimensional solid structures, in which each N or P site is surrounded by neighbors of the opposite polarity.

As far as the polarizing and orienting influence on the adjacent water molecules is concerned, if we had in fact replaced each of the N and P sites with a dipolar site with the appropriate negative end or positive end facing the water molecules, the overall impact on the water adsorption would be a reduction in the reach of the polarizing and orienting force locally with no significant consequences beyond that. The pervasive short range nature of the interaction in fact calls for limiting the computation of interaction to those between the nearest neighbors of the N and P sites and among the water molecules

Does the specific nature of the solid surface including the pattern of electric charge distribution affect the long range ordering of adjacent water molecules?

Prof. Walter Drost-Hansen expressed the view again and again that "proximity to most (or all) 'solid interfaces' regardless of the detailed specific chemical nature of the surfaces" would produce what he calls "vicinal water", which he defines as "water near interfaces." In my view, this is not a very good argument. It seems circuitous.

Referring to this alleged indifference to the nature of the solid surface as a "Paradoxical Effect", Drost-Hansen tentatively suggested in 1991 that it is "external geometrical constraints that produced such an effect" (Drost-Hansen and Singleton 1991, p. 14.)

Even though Drost-Hansen and I share a belief in the existence of long range ordering of water, we are on opposite sides on how such a long-range effect is produced. And it is my obligation to express why I do not share his view.

In my opinion, there are legions of evidence supporting my position but one example that seems most appropriate here is the profoundly different infrared absorption spectra of water held at, or below its normal freezing temperature when placed between AgCl plates as shown by Giguère & Harvey (Figure 11) or between CaF_2 or fluorite plates as shown by Fox & Martin (1940.) One could not be frozen at −176° C, while the other was frozen to ice I without any difficulty.

The steepness of the drop of adsorption energy of water molecules moving away from close to the NP surface. Or put differently, the question of the homogeneity of the adsorpton energy of water molecules in a deep layer of polarized-oriented water.

When I first introduced the PM theory, I believed that water molecules in immediate contact with the polarizing sites on the proteins are more strongly acted upon and suffer greater motional restriction than water molecules farther removed. This view is indicated in Figure 1 by the decreasing size of the curved arrows in water molecules as one gets closer to the proteins. On the basis of this kind of reasoning, I believed then that this motional restriction, and hence reduction of entropy, was the main cause for the low steady level of sodium ion in cell water. As time went on, my ideas began to change. Thus, when I presented my quantitative theory for solute exclusion from living cells and model systems (Ling 1993), I solidified my later view that the cause for the partial exclusion of sodium and sucrose involves both enthalpic and entropic reasons.

As such, the idealized NP surface depicted in Figure 6 would be highly unstable. The positive and negative charges would neutralize each other and become non-polar. The real world NP systems like that shown in Figure 9 for AgCl is stable, because behind each N or P site, there is a P and N site respectively etc., etc. And it is the entire three-dimensional crystal that stays stable. Thus, what we draw as an N or P site is in fact a dipolar site with its respective negative and positive end facing the water molecules. Nonetheless, at least a layer of water molecules thirty thousand molecules thick has been made non-freezing by these banks of dipolar sites. This success provides indisputable evidence that what we call NP-NP systems but are in fact N(PNPN...)P(NPNP...)-N(PNPN...)P(NPNP...) systems really work.

The most outstanding difference between an isolated charged N or P site and their dipolar counterparts is the reach of their polarizing force. In the real world what we see as a NP surface is in fact dipolar or even multipolar. This recognition in turn leads one to believe that in the real world polarized-orientaed multilayers of water, the reach of each step of polarization orientation is short, even though the aggregate effect is long. Taking away the contribution from the longer acting isolated charges, the values of adsorption energy would end up being constant rather than steeply falling as implied in Figure 1 and shown in Figure 8. This idea of more constant water-to-water interation energy is also in harmony with the assumption of uniform water-to-water interaction energy of all water molecules in the theory of solute exclusion mentioned earlier (Ling 1993), which, in turn, is backed up by its success in explaining the size-dependent solute exclusion in frog muscle cells and model systems (Ling *et al* 1993.)

The reduced average kinetic energy of water molecules in polarized-oriented multilayers like those shown between polished AgCl plates and between polished glass surfaces.

It is known that the individual water molecule in a pool of pure liquid water is in possession of an average kinetic energy equal to kT, where k is the Botzmann constant and T the absolute temperature. At 25° C, this amounts to 3.90 x 10^{-14} ergs per molecule or 592 gram-calories per mole. This average kinetic energy arises from the constant bombardments each water molecule receives — from other water molecules. However, placed between suitable NP-NP systems of AgCl, glass or quartz plates, the water molecules are greatly restricted in their motion. Accordingly, the average kinetic energy must be reduced from that in normal liquid water, further enhancing the stability of the dynamically structured water.

How do you bridge the gap between conclusions derived from two-dimensional NP surfaces on bulk phase water to water in living cells, which contain only one-dimensional protein chains?

I have used the symbol NP-NP-NP system to describe how parallel arrays of fully-extended protein chains could function like a two-dimensional NP surfaces. But admittedly that was just a vague stipulation — even though a vast amount of experimental data can be explained on the basis of that postulation. However, new progress made recently has provided more insight into the problem. I intend to publish soon another paper on the subject.

However, this much can be said here. First, Hori's work shows that while irregularity in the N and P site distribution on glass and quartz surface weakens long-range water polarized-orientation of water, it does so modestly. Second, the excess (negative) water-to-water interaction energy in living frog muscle (estimated at 126 cal mole^{-1}, Ling *et al* 1993) amounts to less than 2% of the excess (negative) adsorption energy of distant water produced by the idealized NP surface ($17.76 - 9.72 = 8.04$ kcal mole^{-1} or 8,040 cal mole^{-1}). Taken together, these two sets of facts provide generous margins for effective polarization-orientation of all the cell water by a relatively small amount of intracellular proteins that assume the fully-extended conformation of an NP-NP-NP system.

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