

Supercooled Water. Considerations About the System Organization of Liquid Water

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Summary. Supercooled water shows increasing values in heat capacity, free energy difference (in relation to ice) and compressibility as the temperature is lowered, whereas the density is decreased. After careful consideration of the boundary conditions, as they are required for the preparation of supercooled water, the reorganizations within the liquid were investigated and the changes in differentiations examined. Different groups of water molecules are distinguished, namely those at the interface, around dissolved gas molecules, around hydrophilic solutes and the vast majority of the remaining water molecules. It is emphasized that all of these groups are required for the existence of liquid water. Their continuous interrelations are described by the introduction of "hierarchic levels", as they are characteristic for a system organization.

The highest hierarchic level is that of the interface, the forces of which regulate and control the exchange of matter and energy both with the environment and within the liquid phase. Subordinated to this level is that of the dissolved gas molecules and their surrounding water molecules. In both of these levels the dynamic aspects are highly developed. Subordinated to this level is that of the hydrophilic solutes and their surrounding water molecules. Their unavoidable presence in liquid water is evidenced by the self-ionization equilibrium. The lowest level is that of all of the other water molecules, which provides some kind of more static boundary conditions for the exercise of the better developed dynamic features of the higher levels.

In order to obtain supercooled water, the dynamic features must be improved in the higher hierarchic levels, whereas in the lower levels the more static features should remain as small as possible. The former is achieved by certain cooling modes, by increased surface area, by hydrophobic environment and by increasing gas concentration in the liquid. On the other hand, the concentration of hydrophilic solutes must be minimized (the purity of water enhanced). The metastable state is dynamically better maintained, the better the system organization is developed. The state of supercooled water approaches that of optimal system organization in the temperature range between -20° and -30°C .

Keywords. Supercooled water; Anomalies of water; Liquid state; System organization; Dynamic aspects of order.

Unterkühltes Wasser. Betrachtungen über die Systemorganisation von flüssigem Wasser

Zusammenfassung. In unterkühltem Wasser nehmen die Wärmekapazität, die Differenz der freien Enthalpie in bezug auf Eis und die Kompressibilität mit sinkender Temperatur zu, während die Dichte abnimmt. Unter Berücksichtigung aller Randbedingungen, unter denen Wasser unterkühlbar ist, wurden die Reorganisationen innerhalb der Flüssigkeit untersucht. Die Eigenschaften von Wassermolekülen an der Phasengrenzfläche, in der Umgebung von Gasmolekülen, in der Umgebung hydrophiler Teilchen und der großen Zahl der übrigen Wassermoleküle sind unterschiedlich. Ihre kon-

tinuierlichen Wechselbeziehungen werden durch Einführung „hierarchischer Ebenen“ beschrieben, wie sie für eine Systemorganisation charakteristisch sind.

Die höchste hierarchische Ebene ist diejenige der Moleküle an der Phasengrenzfläche, deren Kräfte den Austausch von Materie und Energie sowohl mit der Umgebung als auch innerhalb der flüssigen Phase regulieren und kontrollieren. Dieser Ebene untergeordnet ist diejenige der gelösten Gasmoleküle und der sie umgebenden Wassermoleküle. In diesen beiden Ebenen sind die dynamischen Aspekte hoch entwickelt. Dieser Ebene nachgeordnet ist diejenige der die hydrophilen Bereiche umgebenden Wassermoleküle. Die niedrigste Ebene ist diejenige aller anderen Wassermoleküle, welche eine Art statischer Randbedingungen für die Ausübung der in den höheren Ebenen besser entwickelten dynamischen Aspekte bieten.

Um unterkühltes Wasser zu erhalten, müssen in den höheren hierarchischen Ebenen die dynamischen Eigenschaften verbessert werden, während in den unteren hierarchischen Ebenen die Differenziertheit so klein wie möglich bleiben soll. Ersteres wird durch Vergrößerung der Oberfläche, bestimmte Abkühlungsbedingungen, hydrophobe Umgebung und durch zunehmende Konzentration an gelösten Gasen erreicht, letzteres durch Erhöhung der Reinheit (Minimierung der Konzentration hydrophiler Teilchen). Der metastabile Zustand wird umso besser dynamisch aufrechterhalten, je besser seine Systemorganisation entwickelt ist. Der Zustand des unterkühlten Wassers kommt der optimalen Systemorganisation im Temperaturbereich zwischen -20° und -30°C am nächsten.

Introduction

In order to understand supercooled water, we have to be aware of the fundamental differences between liquid water and ice. Both from the phenomenological and from the molecular point of view a liquid may be considered in a state somewhere between that of the solid and of a gas. For the description of crystalline systems the model of the ideal crystal is used and for the description of gaseous systems the model of the ideal gas. Each of these models describes an extreme case, obtained by the elimination of the dynamic or the static aspects respectively. Because a liquid is somewhere *between* a solid and a gas, it is virtually impossible to present a model for a liquid which would completely lack either the static or the dynamic aspects.

In the absence of an ideal model for a liquid, chemists try to account for the actual material properties by considering molecular properties. For example, Eisenberg and Kauzmann write [1]: “In order to interpret the properties of steam, ice and liquid water, we must understand the water molecule”. Apart from the fact that properties of “single” molecules are different from those in the more complex relationship [2, 3], it must be borne in mind that the molecular concept has been advanced in order to consider the quantitative (stoichiometric) relationships [4] without providing an understanding for the qualitative changes in the course of chemical interactions [2–4]. Molecules completely lack material properties, such as temperature, color, strength, vapour pressure etc. and have instead molecular properties, such as dipole moment, bond length, donor- and acceptor properties etc. [2, 3, 5].

These facts led Bailar and al. [6] to the following statement: “In spite of the convincing nature of the general qualitative picture and the extensive range of physico-chemical measurements, which have been made on water, including in recent years numerous spectroscopic studies, it remains unfortunately true that no satisfactory detailed molecular picture has yet emerged. The present situation is too confused to be briefly summarized, and the same statement is even more true for efforts to give a molecular interpretation of the role of the solvent in solute-solvent interactions in water”. Primas [7] makes the following statement: “It is

indeed impressive how many experts have the absolute faith that say, the behaviour of liquid water will be reduced to interacting H₂O-molecules some time in the future... Even though the current paradigm commands it, it is pure science fiction that substances can be described in terms of molecules... Our main thesis is that the richness of chemical phenomena renders it impossible to discuss them exhaustively from a single point of view. The molecular view is just one of these and has no privileged status”.

In liquid water the molecules appear to be embedded within a fluctuating network, and hence they are in states of tension that vary from place to place and from time to time. It is impossible to observe the properties of such molecules and all of the experimental data obtained for liquid water, such as heat capacity, compressibility, density, thermodynamic and structural data, refer to the so-called “diffusionally averaged structure” [1], corresponding to averaged relaxation times of 10^{-11} s. On these grounds it has been assumed that in a fluid the movements of the molecules are irregular. This statement may be questioned both on philosophical and on experimental grounds, for example by the results of Laser investigations [8]. The latter suggest the need to approach a liquid from a non-statistical point of view [8] and to try to disclose some of the informations disguised in the statistical results. Therefore it appears necessary to extend the molecular concept, in order to learn to understand changes in qualities of material systems related to the behaviour of the molecules *within* the actual relationships of the system under consideration. In order to find the necessary differences in properties, equality considerations are no longer useful and similarity considerations are needed [9, 10].

In particular, we even have to consider results which are “anomalous” or “curious”, precisely because they do not meet the expectations according to theoretical considerations or model assumptions. They indicate shortcomings of our interpretations rather than inadequacies of nature [2, 3, 9]. As all observable and measurable things have the remarkable ability to maintain their chief characteristics under varying conditions, they must be subject to system organizations [9].

In order to obtain insight into the system organization of supercooled water, we suggest to start by summarizing the experimental results [11, 12].

Experimental Results

Temperature Range of Supercooled Water

The conditions under which supercooled water can be obtained have been extensively investigated. Experiments were made (i) in glass, quartz and silica capillaries of various diameters (range between 10 μm up to test-tube size [14–23]) partly coated by hydrophobic substances [20], (ii) on droplets placed on different solid surfaces (ranging from 3 μm to 50 μm) [24–28], (iii) on suspensions of droplets at the interface of immiscible liquids (mean diameter between 50 μm and 2.5 cm) [27–34], (iv) on emulsions (diameter of droplets about 4 μm) [11] and (v) in the cloud chamber (droplet diameters below 1 μm) [31–34]. The freezing points obtained as a function of the mean diameter of the capillary tubes are shown in Fig. 1 and those as a function of the mean diameter of the droplets in Fig. 2. The data are difficult to compare, because different experimental conditions were used (nature of the adjacent phase, purity of the sample and cooling mode).

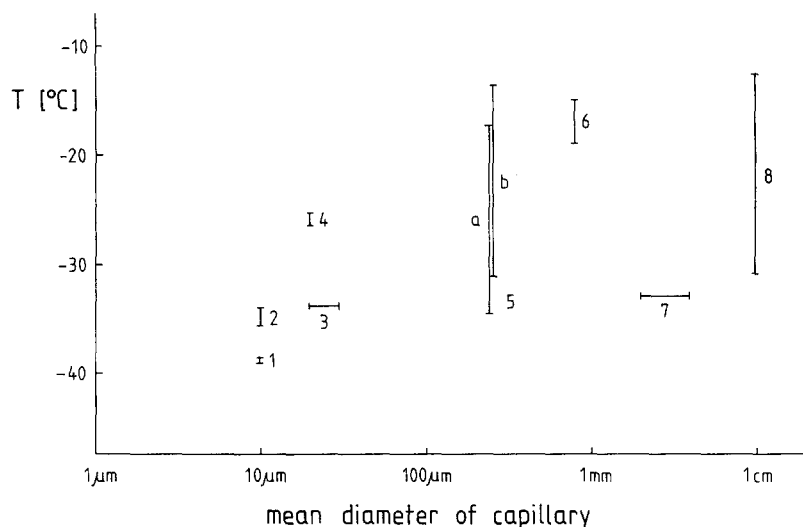


Fig. 1. Logarithmic plot for freezing temperatures of supercooled water in different capillaries in relation to their diameters; 1: glass capillaries (\varnothing 10 μ m) [21], 2: capillaries (\varnothing 10 μ m) [14–17], 3: Pyrex capillaries (\varnothing 25 \pm 5 μ m) [39], 4: Pyrex capillaries (\varnothing 20 μ m) [23], 5a: glass tubes coated by hydrophobic substances (\varnothing 250 μ m) [20], 5b: uncoated glass tubes (\varnothing 250 μ m) [20], 6: glass tubes (\varnothing 0.8 mm) [18], 7: quartz tubes (\varnothing 2–4 mm) [22], 8: glass tubes (\varnothing 1 cm) [19]

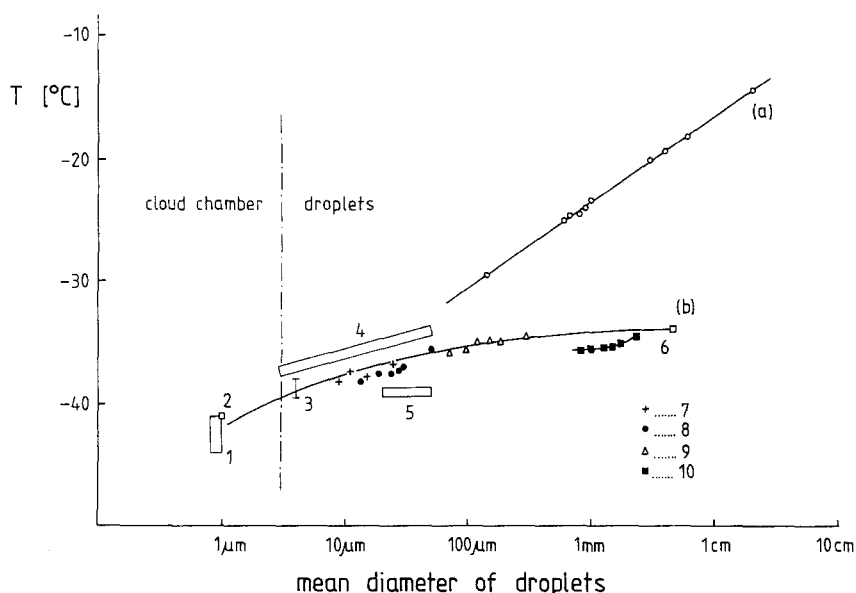


Fig. 2. Logarithmic plot for the relation between mean values of freezing temperatures and mean droplet diameter; a: Bigg's relationship ("heterogenous nucleation") [27]; b: Curve partly according to Langham and Mason ("homogeneous nucleation") [29, 34]; 1: cloud chamber experiments ($\varnothing < 1 \mu$ m) [31, 32] 2: cloud chamber experiments ($\varnothing \approx 1 \mu$ m) [33, 34] 3: freezing of a Rasmussen-Mac Kenzie emulsion (water in *n*-heptane + sorbitan tristearate, mean particle size 4 μ m) [11] 4: droplets condensed on colloidal films supported by highly polished metal surfaces (\varnothing 3–50 μ m) [25] 5: emulsion in silicone oil (\varnothing 20–50 μ m) [24] 6: water drops (\varnothing 4–6 mm) suspended between mercury and a silicone liquid [30] 7: droplets condensed on a metal surface and covered with silicone oil [26] 8: water droplets condensed on a silicon oil surface and covered with liquid paraffin [28] 9: droplets at the interface of liquid paraffin and carbon tetrachloride (median values) [29] 10: analogous to 9 (lowest values) [29]

With regard to the purity of the sample, kinetic interpretations have been provided. A distinction is made between “heterogeneous nucleation” and “homogeneous nucleation” (Fig. 2) [20, 29]. Within each of these groups the liquid range that can be obtained is greater the smaller the diameter of the capillary tube and the smaller the drop size. The lowest temperature which has ever been obtained in capillary tubes is -39°C [21], in emulsions -40°C [11] and in cloud chamber experiments -44°C [31, 32]. It has further been shown that in a capillary tube of given diameter the freezing point is lowered as the capillary is coated by a hydrophobic layer. For example, in uncoated tubes the freezing points are between -13.9 and -31.7°C and in hydrophobically coated tubes between -17.5° and -34.7°C (Fig. 1) [20].

Molar Heat Capacity Under Constant Pressure

Below 37.5°C the heat capacity under constant pressure of liquid water is found to increase slightly as the temperature is lowered [35], but below 0°C it increases dramatically as the temperature is further decreased [36] (Fig. 3). At -35°C the c_p -value is by 34.7% higher than that of liquid water at its boiling point!

Wilhelm et al. [37] calculated the difference between the partial molar heat capacity of oxygen and nitrogen respectively in aqueous solutions at infinite dilution and that in the ideal gas state for different temperatures. The results presented in Fig. 4 show that the heat capacities of these gases are much higher when dissolved in water than in the gaseous state! According to the theorem of the additivity of heat capacities for solutions c_p is

$$c_p = \frac{1}{100} \cdot \sum x_i \cdot c_{pi},$$

where x_i are the solute concentrations in percent per volume and c_{pi} the heat capacities of the components. Thus, increase in concentration of dissolved gases leads to an increase in the heat capacity of the solution.

It is well known that the solubility of most gases in liquid water is increased as the temperature is lowered. For aqueous solutions data are available down to

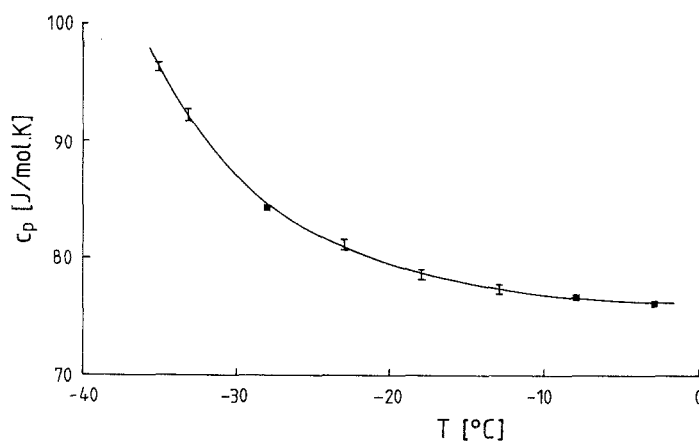


Fig. 3. Heat capacities of supercooled water from emulsion measurements (water in *n*-octane) [36]

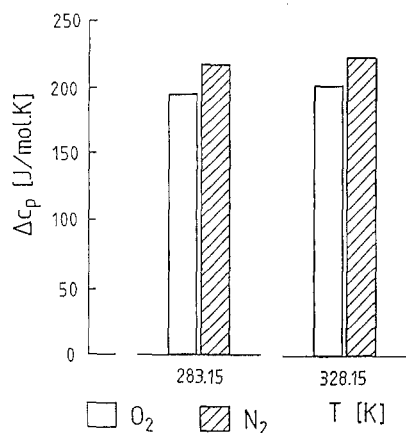


Fig. 4. Difference between c_p of O₂ and N₂, respectively, in aqueous solutions at infinite dilution and that in the ideal gas state [37]

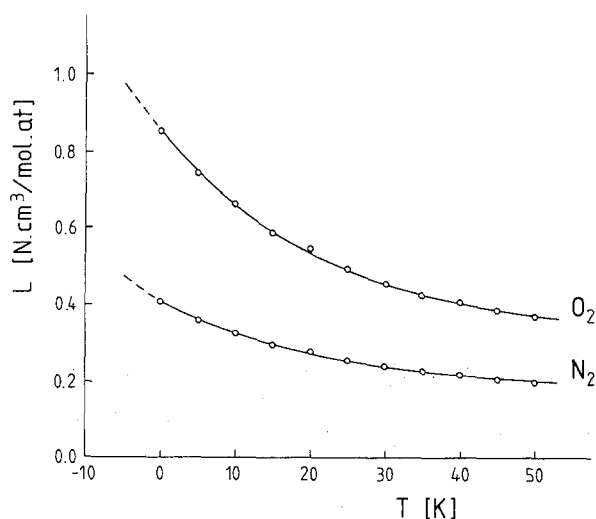


Fig. 5. Solubility of oxygen and nitrogen in water at different temperatures [38]

0°C. Fig. 5 reveals that the temperature coefficient of the solubility of oxygen and nitrogen respectively increases as the temperature is lowered. In Fig. 6 the c_p -values of water in the range from 37.5°C to 0°C have been plotted vs. solubility of nitrogen in water at different temperatures and in Fig. 7 vs. solubility of oxygen. In this temperature range the heat capacity of water appears related to the gas solubility. Unfortunately results of gas solubilities below 0°C are not available, and their measurement appears hardly possible. However, extrapolation of the curves in Fig. 5 suggests a further increase in gas solubilities with decreasing temperature in supercooled water. Thus, the heat capacity of a solution may be increased by increasing gas concentration also below 0°C.

Density and Isothermal Compressibility

Measurements of the density of supercooled water have been made in the range from 0°C to -34°C [39]. Fig. 8 shows that the density is drastically decreased, as

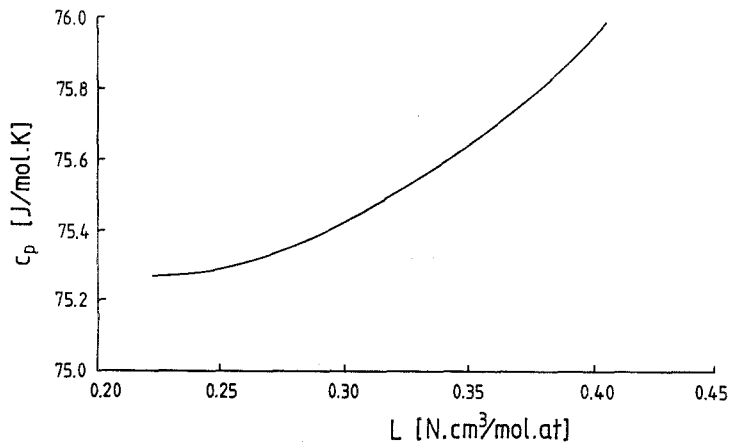


Fig. 6. Relation between the c_p -values of water at different temperatures within the range 0° to 35°C and the solubility of nitrogen in water at this temperatures [35, 38]

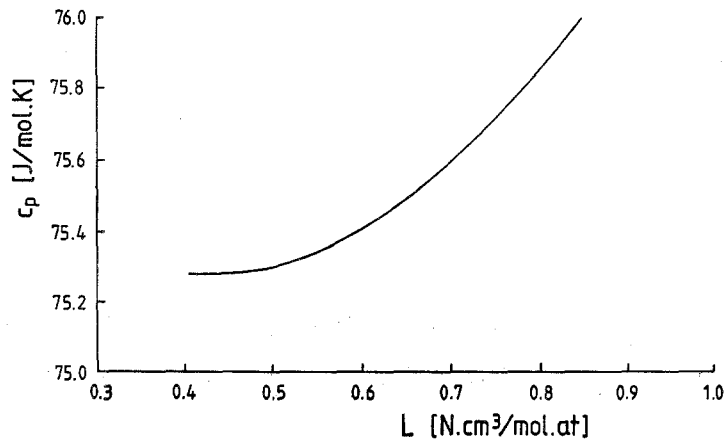


Fig. 7. Relation between the c_p -values of water at different temperatures within the range 0° to 35°C and the solubility of oxygen in water at this temperatures [35, 38]

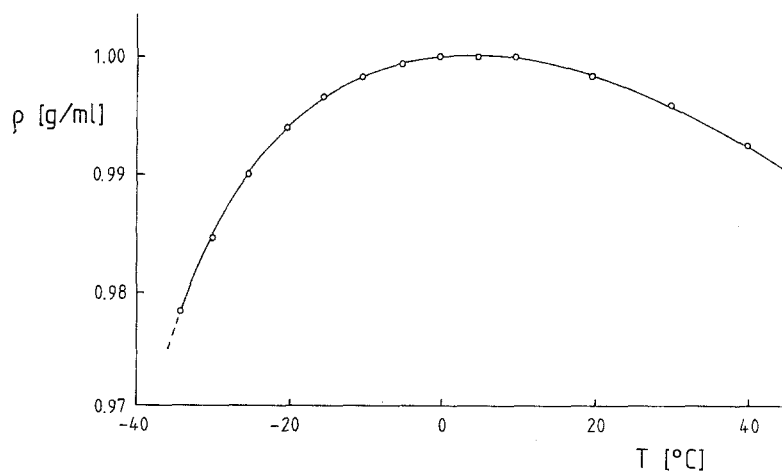


Fig. 8. Density of liquid water at different temperatures [39]

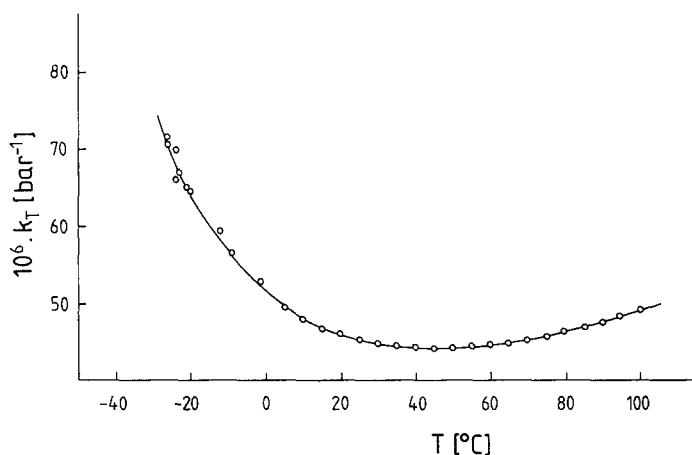


Fig. 9. Relation between isothermal compressibility k_T and temperature in liquid water. Values below 0°C according to results of Speedy and Angell [23]; data for temperatures above 0°C taken from the Handbook for Chemistry and Physics [35]

the temperature is lowered. At -34°C the density of supercooled water is almost the same as at $+70^\circ\text{C}$.

The decrease in density at decreasing temperature is paralleled by an increase in isothermal compressibility k_T of water.

Results of the measurements down to -26°C [23] show that the increase in compressibility is greater the lower the temperature (Fig. 9). At -26°C k_T for liquid water is by 45.2% higher than at 100°C ! Thus, the decrease in density is accompanied by an increase in isothermal compressibility k_T and hence by an increase in flexibility.

Free Energy and Entropy

For given temperature, values of the free energy difference between water and ice, ΔG° , have been calculated by Leyendekkers and Hunter [40] by extrapolation of the difference between the partial molal free energy of water in aqueous solution and the molal free energy of ice at the same temperature to zero concentration. The free energy difference for water in capillaries, $\Delta G^\circ_{\text{cap}}$, for emulsion water, $\Delta G^\circ_{\text{em}}$, were calculated from c_p -data [36, 41–43]. In the temperature range from 0° to -40°C both, $\Delta G^\circ_{\text{cap}}$ and $\Delta G^\circ_{\text{em}}$, are found between $+108$ and $+712$ J/mol (Table 1). The results show that (i) at a given temperature the free energy of supercooled water is higher than that of ice, (ii) the free energy differences between supercooled water and ice become greater, the lower the temperature.

The comparison of $\Delta G^\circ_{\text{cap}}$ and $\Delta G^\circ_{\text{em}}$ reveals that the free energy difference of water in emulsion is consistently higher than that “bulk” water [40]. In Fig. 10 the differences $\Delta G^\circ_{\text{em}}$ and $\Delta G^\circ_{\text{cap}}$ are plotted vs. temperature. The differences in free energy between water in emulsions and in capillaries are greatest between -20° and -37°C . According to the results of calculations by Leyendekkers and Hunter [40], the free energy difference $\Delta G^\circ_{\text{em}} - \Delta G^\circ_{\text{cap}}$ is proportional to the excess free energy due to a curved surface (Kelvin effect).

The partial derivative of the free energy differences $\Delta G^\circ_{\text{em}}$ and $\Delta G^\circ_{\text{cap}}$ respectively according to temperature provides the values for the entropy differences

Table 1. The free energy differences between supercooled water and ice at different temperatures for emulsion water and water in capillaries, respectively, according to calculations of Leyendekkers and Hunter [40]

T (°C)	ΔG_{em}° (J/mol)	ΔG_{cap}° (J/mol)
-5	108.2	108.1
-9	192.3	192.0
-10	213.0	212.5
-11	233.5	233.0
-12	254.0	253.2
-13	274.3	273.4
-14	294.4	293.3
-15	314.4	313.1
-20	412.3	409.6
-22	450.4	447.0
-25	506.3	501.7
-26	524.6	519.6
-27	542.7	537.3
-30	595.8	589.3
-32	630.0	623.0
-33	647.1	639.6
-35	680.2	672.1
-37	712.3	703.8
-40	758.4	749.8

ΔS_{em}° and ΔS_{cap}° . The plots ΔS_{em}° and ΔS_{cap}° vs. temperature (Fig. 11) show that the entropy differences decrease when the temperature is lowered. In the temperature range between -20° and -30°C the entropy difference between water in emulsion and in capillaries is greatest. At given temperature in the supercooling region the values of ΔS_{em}° is always higher than the value of ΔS_{cap}° .

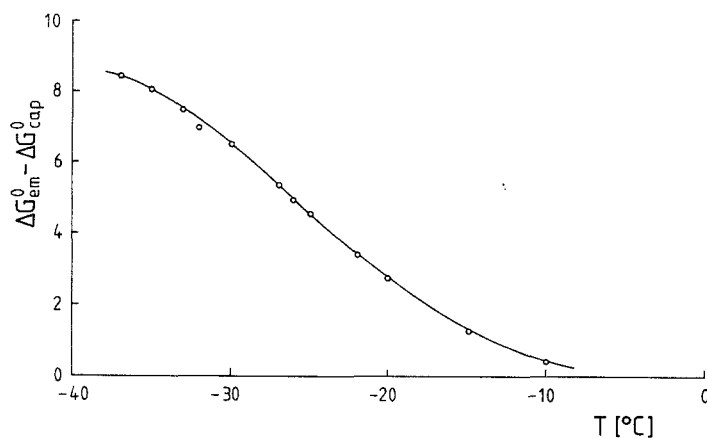


Fig. 10. Differences between free energy of water in emulsions and in capillaries at various temperatures in the supercooling region. Data from Table 1 are used [40]

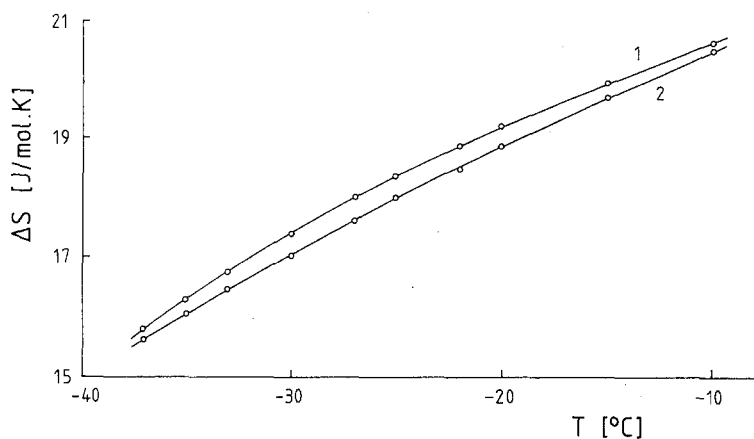


Fig. 11. Differences between entropy of supercooled water and ice vs. temperature according to calculations of Leyendekkers and Hunter [40]. Curve 1 refers to tiny water droplets in emulsions, curve 2 to water in capillaries

Discussion

The Role of Unavoidable Solutes

The high values in heat capacity (Fig. 3), entropy (Fig. 11), free energy (Table 1) and compressibility (Fig. 9) as well as the low values in density (Fig. 8) are expressions of highly developed dynamic features, for which a molecular interpretation on statistical grounds cannot be given. In order to go beyond the consideration of the statistically valid aspects, we have to consider the actual differentiations in the liquid and, first of all, to understand the role of the so-called impurities in solution.

Different kinds of solute molecules or ions may be distinguished from each other as well as from water molecules. Most of the studies in solution chemistry are concerned with the properties of solutes in solution, and numerous experimental techniques are available in order to investigate thermodynamic, structural and kinetic properties.

A distinction may be made between hydrophilic and hydrophobic solutes. Hydrophobic solutes, including most cations and anions, are known to attract water molecules which are arranged around the solute in a characteristic way. Due to the self-ionization equilibrium in liquid water, hydrated hydrogen ions and hydrated hydroxide ions are always present, so that it may be supposed that the presence of hydrophilic solutes is an existential requirement for liquid water [44].

Hydrophobic solutes, such as gas molecules, are known to rotate or to librate within voids of the water structure [45, 46], which, according to the results of X-ray crystallographic investigations on crystalline "gas-hydrates" are greater than required for the accommodation of the solute molecules [47–50]. Their highly developed dynamic properties are reflected in the c_p -values, which are higher than in the gas phase (Fig. 4). Carefully "degassed" water still contains about 10^{-6} mol gas per litre, and hence the presence of gases appears to be a condition for the existence of liquid water.

Differentiation of the Water Molecules

If the presence of both hydrophilic and hydrophobic solutes is required for the existence of liquid water, we have to investigate the question in what ways the liquid system is influenced by them. Hydrophilic solutes are known to rearrange the water molecules in their immediate environment, and this range is called hydration shell.

The water molecule is "open" towards all sides. It may act as a strong electron donor (base) through its oxygen atoms and as a strong electron acceptor (acid) through its hydrogen atoms. Such donor-acceptor interactions [51] are involved in solvent-solvent as well as in solute-solvent interactions, and they are of importance for the establishment and for the maintenance of the three-dimensional network, that is extremely flexible and adaptable. Statistically, each oxygen atom is surrounded by four other oxygen atoms, interconnected by so-called "hydrogen bonds". Because the local structural features are influenced by their molecular environment, an enormous variety of local arrangements is bound to exist within the liquid structure [10, 44, 52].

The structural features around a cation are illustrated in Fig. 12. The intermolecular $O \cdots O$ -distances are shortest within the first hydration spheres, whereas the intramolecular $O-H$ -bonds are longer in the first hydration sphere, where the hydrogen bonds are shorter, more symmetrical, with wider $O-H-O$ -bond angles than in the subsequent hydration layers [10, 44]. Thus, the water structure is somewhat contracted in the surroundings of a hydrophilic solute, but in principle the structure of the whole liquid is somewhat affected. As the concentration of hydrophilic solutes is increased, the vibration spectrum of the solution corresponds to that of water at a higher temperature [53]. From this point of view the water structure appears to be "broken". A decrease in dynamic properties is indicated by the decrease in specific heat [54] as well as by the lowering of the vapor pressure. The lowering of the vapor pressure indicates that the structural contraction around the solute is also reflected in a structural contraction at the interface [52].

All of the said properties show (i) that the effects caused by the presence of solutes are "spread" over the whole liquid system, (ii) that the static structural features of the liquid are improved, and (iii) that its system differentiation is increased.

The situation is different for the structural effects caused by the presence of hydrophobic solutes. Their role has been neglected in most solution studies. Fig. 13 illustrates the changes in structural features around a void corresponding in size to those found in crystalline gas hydrates [9, 10, 44, 52, 55]. Like in the solid state, the bond lengths at the inner surface of a void are shorter and the adjacent bond lengths somewhat longer than in most other areas. The changes in the water structure extend in principle over the whole solution, leading to a loosening of the water structure: By increase in concentration, the vibration spectrum of the solution is changed and corresponds to that of water at a lower temperature [52]. The dissolved gases have greater c_p -values than in the gas phase (Fig. 4), and they give rise to an increase in vapor pressure. The decreasing values for density and surface tension point in the same direction, namely to a decrease in static features of the liquid.

The amplitudes of the librations of the gas molecules are confined by the flexible and yet somewhat resistant inner surfaces of the voids, which appear to provide

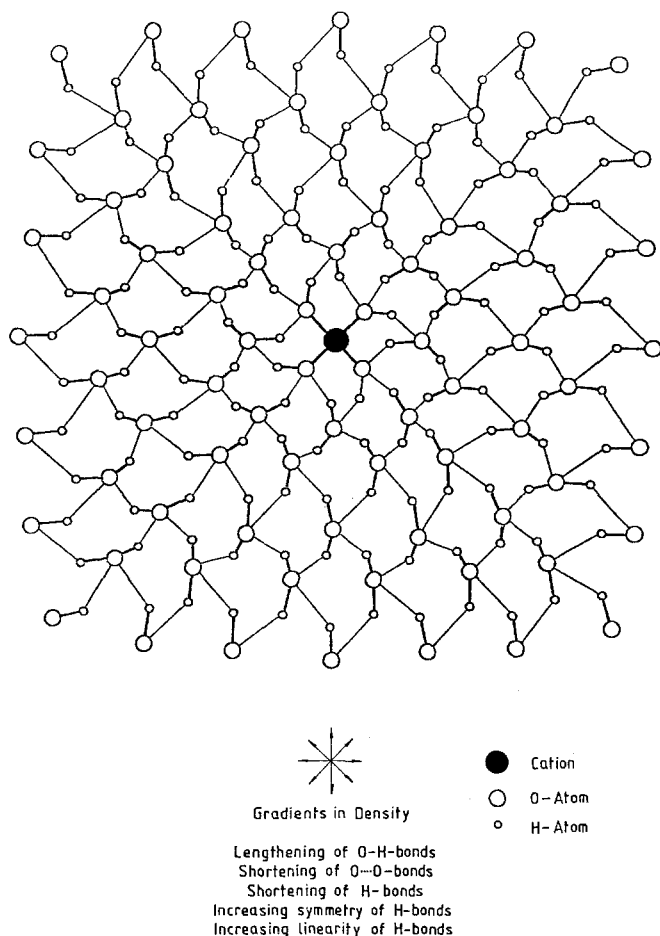


Fig. 12. Idealized illustration of the static aspects of order of the water structure around a cation [9]

more static boundary conditions for the motions of the highly mobile gas molecules [9, 56]. This means that the gas molecules are influenced by the vibration pattern of the liquid structure, which at the same time is dynamically maintained by the librations of the gas molecules, until a kind of “synchronization” is established between the oscillating pattern of the liquid solution structure and the motions of the gas molecules. Thus, the region around the gas molecules bear informations about the liquid and serve at the same time to maintain the dynamic features of the whole system.

The different effects of hydrophilic and hydrophobic solutes on the solution properties [9] have been summarized in Table 2.

By considering all experimental facts, the following conclusions may be reached:

1. Both hydrophilic and hydrophobic solutes are indispensable for the existence of liquid water.
2. The former contribute to structural contractions and the latter to conservation of the structural features of the liquid.

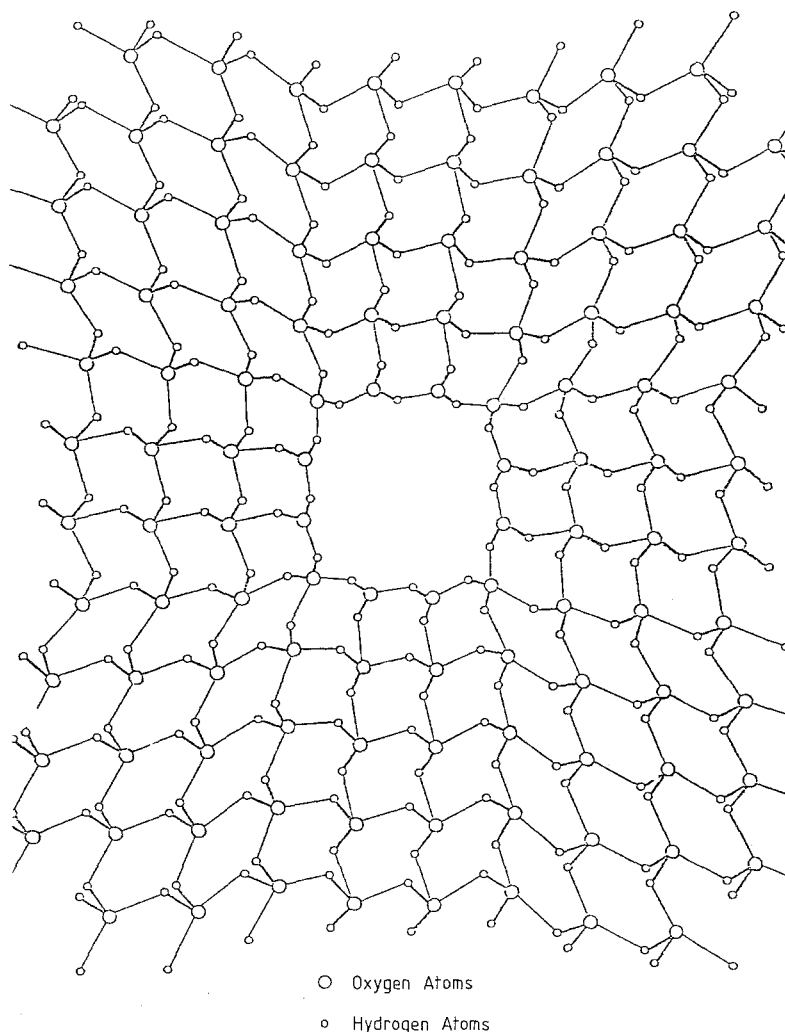


Fig. 13. Idealized illustration of the structural aspects of water in the neighbourhood of a hole corresponding in size to that found in gas hydrates [44]

Table 2. Actions of solutes on solution properties

Property	Hydrophilic solute	Hydrophobic solute
Surface tension	Increased	Decreased
Vapour pressure	Decreased	Increased
Density	Increased	Decreased
Specific heat	Decreased	Increased
Water structure	More dense	Less dense
Particle movement	One-dimensional	Rotation
Vibration spectra, correspond those of pure water at	Higher temperature	Lower temperature
Actions on the static aspects of "water structure"	Increasing	Decreasing
Actions on the dynamic aspects of "water structure"	Decreasing	Increasing

Another existential requirement for the liquid is its phase boundary, where the molecules are in states of higher energy (surface energy), under greater strain (surface tension and bond contraction [51, 57]) and dynamically considerably more active than all other solvent molecules [10, 56]. The highly developed dynamic aspects of the molecules at the interface may also be inferred from the high values in heat capacities of water films on solid surfaces, which are up to 20% higher than for the bulk liquid [58].

Apart from the said water molecules, the vast majority of water molecules is also required for the existence of the liquid. These "normal water molecules" are less differentiated and their dynamic properties less developed.

System Organization of Liquid Water

The continuous connectivity and cooperativity between all molecules of a liquid implies that each molecule has a different environment at any given time. It would therefore be impossible to find water molecules of exactly the same properties. A molecule that has additional properties is superordinated to a molecule devoid of such additional properties. Superordinations and subordinations are characteristic for a so-called "hierarchic order" or system organization [59, 60].

Because a system organization is not directly observable, we have to try to grasp the gradual transitions by introducing (artificially) discontinuities by means of abstractions. The results are called "hierarchic levels", which cannot be considered as entities themselves, but rather as parts of the whole within the whole [10, 61, 62]. (In one way or another, we are always forced to deal with "wholes" or "systems" in all fields of knowledge.)

The general aspects of the system organization of liquid water have been illustrated by means of a truncated pyramid [9, 10] shown in Fig. 14. The surface molecules are appropriated a prime position because of their major role in providing "the first line of defense", in communicating with the environment and by exerting the greatest influence both on the liquid under consideration and on its environment [9, 10]. Because an interface belongs to two phases and because the interface is dynamically maintained by the continuous interactions between them, it is bound

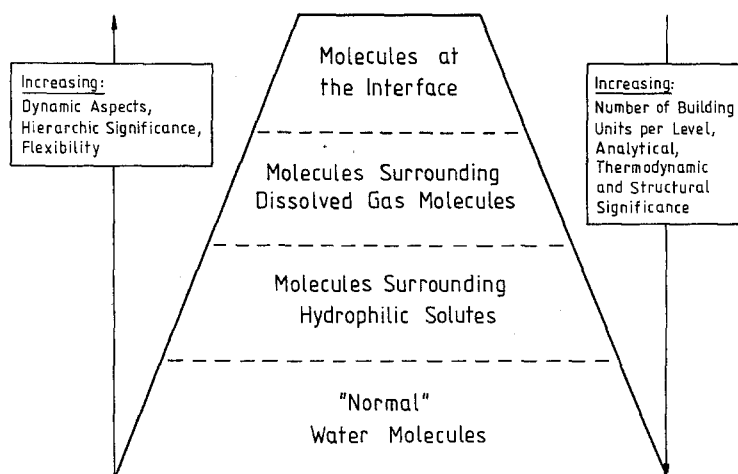


Fig. 14. Illustration of the system organization of liquid water

to be in a state of tension [62]. An electrical double layer is a necessity, because charge transfer involved in any molecular interaction leads to the pile-up of negative charges at the donor site and to a spill-over of negative charges at the acceptor site [51, 63]. The highly developed dynamic actions at the surface have a decisive influence on the properties of all other molecules of the liquid. The interface molecules are therefore considered as serving the highest hierarchic level of the liquid (that is accessible) [9, 10].

The dissolved gas molecules and their surrounding water molecules have highly developed dynamic properties, but smaller than the interface molecules. Because their actions seem to be under control of the interface, they are considered to provide the level immediately subordinated to the highest level [9, 56].

As pointed out, the water molecules in the surroundings of hydrophilic solutes have better developed static structural features (structural contraction of water molecules in the hydration shells and lowering of the vapour pressure). They are therefore subordinated to the water molecules around the voids. Because they have a decisive influence on the solution properties, they are superordinated to the vast majority of the “normal” water molecules. These present the lowest level, representing the thermodynamic and structural properties of the liquid. This assignment is implied when the “solvent structure” is considered as hardly changed by the presence of solutes.

It is important to realize that each of these hierarchic levels is mandatory for the existence of liquid water [9]. The highest level is dynamically most active, most resistant against changes from outside and responsible for maintaining the system properties. The lowest level is more passive and providing some kind of boundary conditions for the exercise of the dynamic actions of the higher levels, which in turn are responsible for the dynamic maintenance of the said boundary conditions. In other words: the higher levels provide suitable boundary conditions at the lowest level, which are “respected” by the highest levels.

System Organization of Supercooled Water

Now the point seems to be reached in order to account for the improvement in dynamic properties in supercooled water.

It has been shown for the solid state that the building units at the interface (serving the highest hierarchic level of the solid) may gain or lose considerable amounts of energy (per part) without losing their dominating properties. They retain more energy in the course of a cooling process [64, 65], and hence they remain dynamically more active at a lower temperature than would be expected from thermodynamic considerations [9]. Because these building units are not in thermal equilibrium, they have a kind of “primitive memory” to previous conditions. For example, after cooling they retain certain dynamic aspects from the state at higher temperature. This property is in agreement with the characterization of the highest hierarchic level given by Primas [66]: “A higher level in a hierarchy has always a much longer reaction time than a level classified as lower. This condition is necessary in order that a lower level is controlled by the dynamical variables of the higher level, and that the lower level variables adapt themselves immediately”.

It must be admitted that it seems more difficult to accept such effects for the

liquid state, because all results refer to the diffusively averaged structure [1]. Thus, a dynamically maintained local differentiation is not envisaged, although this is a condition for the application of the statistical method. Random distribution is not a fact, but the idealized statistical interpretation for the highly differentiated behaviour of the individual parts. Instead of applying a non-statistical approach in order to obtain access of the dynamically ordered individual relations, the statistical data are interpreted as showing even “chaotic character” (disordered motions). It is true that for us the motions appear chaotic, because we are unable to observe the individual (ordered) motions, but we must bear in mind that scientifically relevant results could not be obtained for a (completely) disordered system.

In order to understand the influence of the cooling mode on the preparation of supercooled water, we may again consult results obtained for the solid state. Extremely thin metal films are obtained by “rapid vapour quenching” procedures. Their outstanding dynamic properties (thin gold films are found to flow together above 200°C [67–70] are not obtained by a normal mode of slow solidification. For example, rapidly quenched cobalt shows at room temperature the structure of the high temperature phase (which is thermodynamically stable above 420°C) [71]. A well-known example is that of the so-called “martensitic transition”, which is of great importance in steel technology. When austenite that contains 2% carbon in solution is cooled below 903°C, ferrite and carbon are formed. However, when austenite is rapidly cooled, the solubility of carbon and a higher developed system dynamics is retained in metastable “martensite”, which has much higher strength and hardness than ferrite.

Just as in these cases the metastability is dynamically maintained by the actions of the highest hierarchic levels, rapidly quenched water is obtained in a glass-like form [72, 73], and hence it is more differentiated and dynamically better developed than ice obtained by a normal cooling mode.

In order to obtain supercooled water (rather than vitrified water), the temperature difference allowed for the quenching process and the cooling rates are more limited. It is therefore necessary to apply additional boundary conditions, which favour the incorporation of dynamic properties in the process of preparation.

Because energy at an interface is maintained dynamically by the oscillations of interface molecules, it seems obvious that the energy content of the interface is increased as the number of its building units is increased. Increase in the ratio interface area to volume will definitely strengthen the dynamic properties of the highest hierarchic level, and hence more energy may be retained in the course of the cooling process. As the ratio interface to volume is increased, supercooled water is obtained at lower temperatures (Figs. 1 and 2), the free enthalpy difference and the entropy difference between supercooled water and ice are greater for emulsions than for water in capillaries. According to the results in Fig. 10, the temperature coefficient for differences between free energies in emulsions and in capillaries is greatest in the range between -20° and -30°C . The differences in entropy are greatest in the same temperature range (Fig. 11).

These findings seem to indicate that the system organization is better developed in emulsions and best developed in the temperature range between -20° and -30°C .

Another important factor is the nature of the immediate environment, as expressed by Angell [11] as follows: “It has become quite clear, however, that crystallization of ice as it is normally observed is not a property of water itself,

but rather a function of solid surfaces, particulate or otherwise, with which it is in contact". It can be seen from Fig. 1 that in a capillary tube of given diameter the liquid is obtained at lower temperatures as the surface has been coated by a hydrophobic layer.

The lowest temperatures at which liquid water has ever been obtained, have been recorded in cloud chamber experiments, i.e. in extremely small droplets (diameter $< 3 \mu\text{m}$) in a hydrophobic gas-atmosphere. This is because (i) the interactions water-hydrophobic substrate are particularly weak, so that the liquid can retain its energy content and hence its individual properties reasonable well, and (ii) the dissolution of gases may be favoured. Unfortunately, no measurements have been made on gas solubilities in supercooled water. As pointed out in the section about molar heat capacity, the dramatic increase in heat capacity at lower temperatures may be related to increased amounts of dissolved gases.

However, one would also expect that the rate of dissolution of gases would be decreased as the temperature is lowered. On the other hand, increase in free surface area, the presence of hydrophobic boundary conditions and increasing loosening of the water structure will be in favour for the integration of gas molecules within the liquid structure. The loosening of the water structure is seen from the decrease in density (Fig. 8) and the increase in compressibility (Fig. 9), as the temperature is lowered. Thus, an increase in gas concentration is expected and subsequently a considerable improvement of the dynamic properties of the whole system.

The dissolved gas molecules have the remarkable ability to take over structural informations from the solution structure and to preserve this dynamically in their oscillation behaviour, in harmony with that of the solution. The dissolved gas molecules appear to maintain dynamically the structural features of the whole liquid system. Due to their oscillating properties, they seem to act as a kind of "dynamically maintained points of inner rest" or "synchronization nodes" within the oscillating network, and in this way to play a decisive role for the maintenance of supercooled water.

The considerably improved dynamic properties of the higher level (interface and voids containing gas molecules) have a decisive influence on the lower levels in improving their dynamic properties as well.

It has further been found that supercooled water can be obtained at lower temperatures, as the purity of water is improved [12, 29]. For this fact kinetic interpretations with regard to different modes of nucleation of ice crystals have been advanced. A distinction is made between "homogeneous nucleation" and "heterogeneous nucleation [20, 29]. The former is favoured by the presence of hydrophobic conditions [20] and the latter by that of hydrophilic solutes.

For the production of supercooled water highly purified water is also requested from the point of view of its system organization. This is because all contributions should be minimized by which the static aspects of the system, in particular those of the lowest level, are improved. Increased concentration of hydrophilic solutes leads not only to an improvement of the static structural aspects, but also to a decrease in dynamic properties, as by their presence the dissolution of gases may be hampered.

The above considerations lead to the following generally valid conclusion: *The system dynamics is improved by increasing differentiation in the higher levels and by decreasing differentiation in the lower levels.*

Conclusion

None of the observed properties of supercooled water is anomalous, as all of them are required for its existence.

Certain boundary conditions are required for its production, by which a considerable improvement of the system organization of liquid water is achieved. The system becomes energetically more differentiated and dynamically more active, so that the increase in static properties due to decrease in temperature is compensated by improvement of the dynamic aspects.

As the temperature is lowered below 0°C, the boundary conditions that are needed for the existence of liquid water are great differentiation of the highest hierarchic levels, and low differentiation of the lower levels.

This interpretation is, however, unfamiliar to scientists, in particular to experts in a certain field. It may be emphasized, however, that each material system is subject to a system organization, and that its investigation may open up entirely new aspects to science and technology. One of the examples is a new approach to metastable systems. The activation parameters appear to be increased as the system organization is improved, and hence measures to improve system organizations should be studied in more detail.

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