

## **THE STRUCTURE AND PROPERTIES OF VICINAL WATER: LESSONS FROM STATISTICAL GEOMETRY**

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In earlier works the properties of water near surfaces (vicinal water) have been shown to differ from those of the bulk. For instance, the density of water in 14 nm diameter silica pores is 3% lower than that of the bulk, while the heat capacity is 25% greater than that of the bulk. Etzler has proposed a statistical thermodynamic model for vicinal water which has predicted previously unmeasured thermodynamic properties of vicinal water. This model is based on earlier calculations by Stey, who found the distribution of single particle enthalpies in liquid water to be bimodal. Here we explore the microscopic implications of Stey's distribution. Specifically, it is found that the distribution of molecular (Voronoi) volumes is bimodal in SPC/E water at 298 K. This result is consistent both with the earlier work of Stey and with Röntgen's hypothesis (1892), which states that water exists in "bulky" and "dense" states. Furthermore, the results of this work are probably relevant to the understanding of liquid water at negative pressures and at supercooled temperatures.

### **1. Thermodynamic properties of vicinal water**

#### *1.1. Overview of experimental data*

For at least 300 years, several natural philosophers have realized the fundamental involvement of water in significant biological and technological processes. It has also been recognized that water exhibits a number of unusual properties (e.g., the density maximum at 4°C). Despite the considerable efforts of able investigators, the understanding of bulk liquid structure is still incomplete. The structure of liquids near interfaces is even less well understood. Indeed, many fundamental measurements remain to be made. Ignorance of the state of interfacial liquids has surely hampered the full understanding of many colloidal and interfacial phenomena, which are so important to science and technology.

As early as 1912, Hardy [1] recognized that interfacial liquids might be modified by proximity to solid surfaces. Early notions regarding the state of liquids at interfaces have been reviewed by Henniker [2]. More recently Drost-Hansen et al. [3–6] have reviewed the properties of vicinal water and

their biophysical significance. Etzler [7] has recently reviewed the current understanding of vicinal water structure.

Peschel and Adlfinger [8] as well as Low [9] have measured the viscosity of water in small pores and found it to be larger than that of the bulk. Derjaguin and co-workers have also reported elevated viscosities for interfacial water. (See for instance, ref. [10].)

Etzler and Fagundus [11] have measured the density of water in silica pores and found it to be 3% smaller than that of the bulk at 298 K. Low [9] has reported similar results for water in clays. From the work of Etzler [11], Low [9] and Peschel [12], it appears that significant vicinal structuring extends 3–6 nm from a surface, and that this structuring decays in an approximately exponential manner.

The heat capacity of water near a variety of materials has been measured by Braun and Drost-Hansen [13] and by Cianci [14], who found the heat capacity to be about 25% greater than that of the bulk and independent of the specific physico-chemical details of the surface. Etzler [7] has more recently reviewed the comparative properties of water adjacent to a variety of materials. These results indicate that the properties of vicinal water, at least to a good first approximation, do not depend on the precise physico-chemical details of the interface.

Vicinal water appears to undergo structural transitions near the “Drost-Hansen transition temperatures” (i.e., near 15, 30 and 45°C); thus the temperature dependence of many phenomena related to the structure of vicinal water is unusual. Peschel and Adlfinger [8] have observed maxima in the viscosity for water between quartz plates at the above temperatures. Wiggins [15], Hurtado and Drost-Hansen [16], and Etzler and Liles [17] have found a non-van 't Hoff temperature dependence for ion selectivity coefficients. Maxima in the selectivity coefficients were observed at the Drost-Hansen transition temperatures. Recently, Etzler [18] measured the temperature dependence of the heat capacity of water in silica pores as a function of temperature and observed heat capacity “spikes” near the Drost-Hansen temperatures. The molecular details of the vicinal water structural transitions are unknown. In this paper, the Drost-Hansen transitions will not be discussed.

### *1.2. Model for vicinal water*

In order to understand the unusual character of vicinal water, Etzler [7, 19, 20] has proposed a statistical thermodynamic model for vicinal water. Here, we explore some statistical thermodynamic notions and their relation to both vicinal and bulk water structure.

Stanley and Teixeira [21] have proposed a bond percolation model for bulk

water. This model considers the molecules to be distributed over five hydrogen-bonding states (0, 1, 2, 3, or 4 hydrogen bonds). The hydrogen-bonding state of a given molecule is of course ephemeral; hydrogen-bond lifetimes are envisioned to be on the order of 1 ps. Stanley and Teixeira have used their model to understand the properties of supercooled water. While it may not be essential in this paper to consider hydrogen-bonding classes, such classifications have been useful for discussion.

Stey [22] has calculated the single particle enthalpy distributions for water and a variety of other liquids. (See refs. [7, 19, 20] for further details regarding his calculation.) The enthalpy distribution is calculated in a model independent manner (i.e., no particular intermolecular potential function is assumed). In order to calculate the enthalpy distribution, it is necessary to determine the empirical heat content equation for the material in question. From the heat content,  $\langle H \rangle$ ,  $n$  moments of the distribution,  $\langle H^n \rangle$ , are calculated using the following relation:

$$\langle H^n \rangle = [-(\delta/\delta\beta) + \langle H \rangle] P^{n-1} \langle H \rangle, \quad (1)$$

where

$$\beta = 1/kT, \quad (2)$$

with  $k$  Boltzmann's constant and  $T$  the absolute temperature. Inversion of moments can then be used to calculate the distribution of single-particle enthalpies. In general, this inversion is not possible using less than an infinite number of moments. Stey has, however, shown that if the solutions are restricted to thermodynamically meaningful solutions (i.e., those with Boltzmann tails), then only a small number of moments is required for a convergent solution. In contrast to the enthalpy distribution function found for more simple liquids such as ammonia, Stey found the distribution function for water and deuterium oxide to be bimodal. Recently, Wynne [23] has confirmed and extended Stey's calculations. Wynne also has observed a bimodal enthalpy distribution for liquid Ga near its freezing point. The low enthalpy peak in Stey's distribution appears to represent 4-hydrogen-bonded or "ice-like" water molecules. Based on thermodynamic arguments independent of those presented here, Ubbelohde [24] has postulated the existence of "pre-nucleation clusters" in some liquids. The calculations of Stey and Wynne appear to be consistent with Ubbelohde's earlier arguments. The results of some of Stey's calculations are shown in fig. 1.

Single particle parameters can be related to thermodynamic quantities: isobaric heat capacity  $C_p$ ; isothermal compressibility  $\beta_T$ ; and isobaric expan-

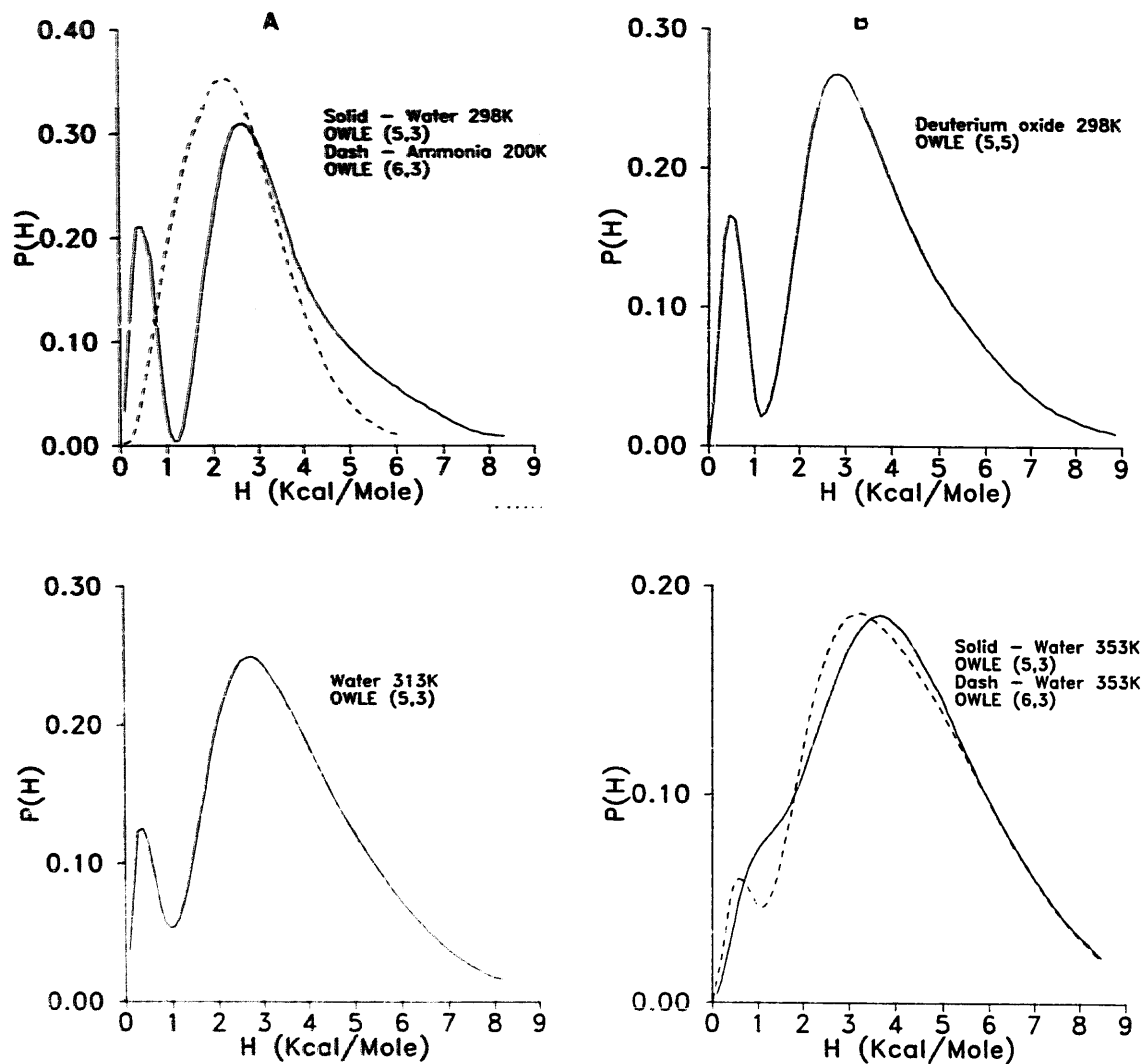


Fig. 1. The single particle enthalpy distribution of  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  and  $\text{NH}_3$  as calculated by Stey [22]. Probability of finding a molecule with enthalpy  $H$ ,  $P(H)$ , versus  $H$ .

sivity  $\alpha$ , via the following well-known expressions:

$$C_p = \sigma_h / RT^2, \quad (3)$$

$$\alpha = \sigma_v^2 / VRT^2 \quad (4)$$

and

$$\beta_T = \sigma_v^2 / VRT. \quad (5)$$

Here  $\sigma_i^2$  is the variance in the appropriate single particle parameter. The subscripts  $v$  and  $h$  refer to volume and enthalpy, respectively.  $\sigma_{v,v}^2$  is the

covariance between energy and volume. Below 4°C,  $\sigma_{\epsilon v}^2$  is negative suggesting the existence of low-energy-high-volume or “ice-like” states. The temperature dependence of  $\sigma_v^2$  is unusual in that it passes through a minimum near 290 K, whereas this function more typically monotonically increases with temperature. The observed minimum suggests that the distribution of molecular volumes may be bimodal.

As Stey’s distribution is bimodal, it is possible to consider the heat capacity of each peak separately using the following relation:

$$C_p = x_1 C_p(1) + x_2 C_p(2) + x_1 x_2 \Delta H^2 / RT^2. \quad (6)$$

Here, component 1 represents the low enthalpy peak. Etzler [19, 20] has previously estimated numerical values for the above quantities. It appears that at 298 K  $C_p(1) = 9.96$  cal/K mol,  $C_p(2) = 16.80$  cal/K mol and  $\Delta H = 2.55$  kcal/mol. Fig. 2 shows the hypothetical heat capacity of water as a function of both  $x_1$  and  $T$ . For water with a heat capacity near 1.25 cal/K g at 298 K, such as is found to be the case for water in 7 nm radius silica pores, the calculated value of  $x_1$  is 0.4, in contrast to the value 0.1 found for bulk water. Based on the increased hydrogen bond probability between water molecules adjacent to a surface, Etzler and Fagundus [11] have predicted the density of water in 7 nm

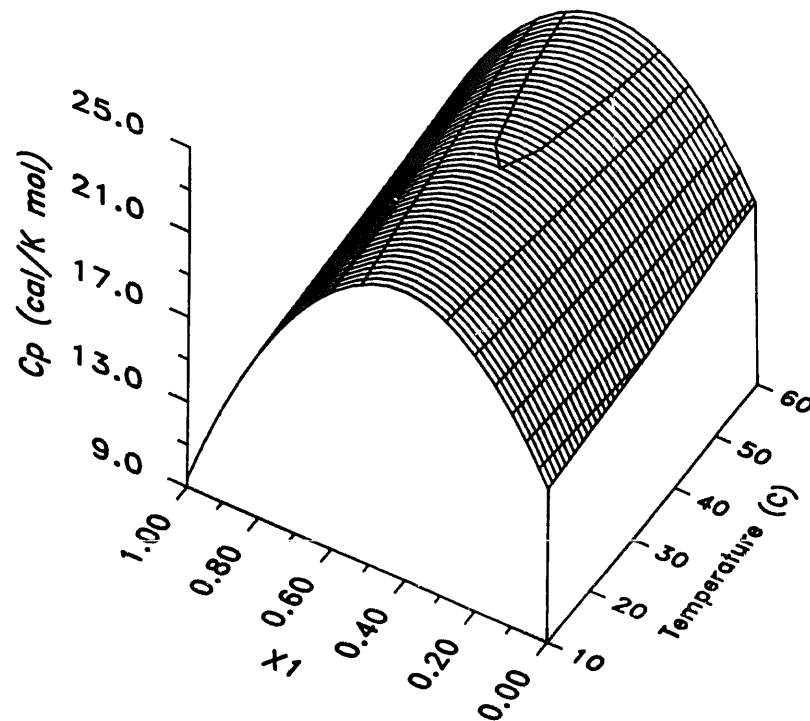


Fig. 2. The hypothetical heat capacity of water as calculated from eq. (6), plotted versus  $x_1$  and  $T$ . Note that  $x_1$  increases with proximity to a surface. Both dependences on  $x_1$  and on  $T$  have been confirmed experimentally [18, 20].

radius silica to be about  $0.97 \text{ g/cm}^3$ ; this prediction was confirmed experimentally. Again, fig. 2 shows the hypothetical heat capacity of water as a function of  $x_1$  and  $T$  as calculated from eq. (6). The parabolic dependence on  $x_1$  has been confirmed experimentally by Etzler [20]. If  $x_1$  increases as water approaches an interface, then the heat capacity will pass through a maximum value near  $1.25 \text{ cal/K g}$ . The heat capacity of water in silica pores of various diameters indeed exhibits a maximum value near  $1.25 \text{ cal/K g}$  near  $7 \text{ nm}$  pore radius, when  $C_p$  is plotted versus pore radius. The general increase in vicinal water heat capacity with increasing temperature has also been observed [18].

The earlier work by Etzler thus suggests that vicinal water differs from the bulk, in that hydrogen bonding between water molecules is enhanced by propinquity to an interface, and that this vicinal structuring extends  $3\text{--}6 \text{ nm}$  from the surface. Furthermore, it appears that the experimentally observed properties of water in silica pores may be interrelated using Stey's single particle enthalpy distribution function.

## 2. Microscopic implications of Stey's calculation

As Stey's bimodal enthalpy distribution has been shown to be useful for correlating the thermodynamic properties of vicinal water, it seems appropriate to explore the microscopic implications of these calculations more fully.

The isobaric partition function is given by the following relation:

$$q = \sum_i g_i \exp(-h_i/kT). \quad (7)$$

Here  $h_i$  is the enthalpy of the  $i$ th microstate.  $h_i$  can be considered to consist of an energy  $\epsilon_i$  and volume  $v_i$  "component", via the well-known thermodynamic relation

$$h_i = \epsilon_i + Pv_i. \quad (8)$$

The single-particle enthalpy distribution function calculated earlier by Stey may thus be bimodal through contributions of either or both  $\epsilon_i$  or  $v_i$ . Here we explore the possibility that  $v_i$  is bimodal.

## 3. Statistical geometry as a tool for liquid structure

An understanding of the packing geometry of molecules in liquids would appear to be critical to the understanding of liquid structure. Unfortunately,

the appropriate experimental information regarding the instantaneous three-dimensional packing of molecules in the liquid state is at the very best difficult to obtain.

Earlier, Bernal [26, 27] suggested the study of liquids by statistical geometric methods. He first studied the packing of steel spheres, and later used computer simulation techniques to study the packing of spheres interacting through simple potentials such as the Lennard-Jones potential. The geometry of Voronoi polyhedra [25] constructed around the molecular centers of mass were thought to be useful for the understanding of liquid structure and the properties of liquids.

Voronoi polyhedra [25] are polyhedra which represent all the space containing points which are closer to a selected molecule in a system than they are to any other molecule in that same system. The geometry of a polyhedron belonging to a given molecule in a liquid rapidly fluctuates due to molecular motion. At a given instant, the Voronoi volume represents the instantaneous molecular volume. Other properties of these polyhedra can also give insight into local molecular packing.

The use of Voronoi polyhedra and statistical geometric methods to study liquid structure has not received wide attention, although several publications have appeared in the literature over the last two or three decades. Here we will not attempt a comprehensive review on the use of Voronoi polyhedra to study liquid structure. Finney [28] has used Monte Carlo simulations of liquid Ar to generate Voronoi polyhedra statistics. Finney found that atoms in liquid argon behave very much as if they were random packed hard spheres.

Rapaport [29] has used Voronoi polyhedra to investigate the relationship between density fluctuations and hydrogen bonding in supercooled water. In this study, the MCY-CI potential was used for the simulated water under study. No clear relation between the number of hydrogen bonds on water molecules and local density was found. Rapaport's conclusions do not necessarily contradict the conclusions that will be drawn in this paper; we consider geometric relations not discussed by Rapaport.

#### 4. Present work

A computer program was developed to construct Voronoi polyhedra and to determine their properties. The algorithm for polyhedron construction was based on the work of Brostow [32]. The FORTRAN code is available for distribution from the authors.

Some of the properties of each polyhedron which can be computed are:

Voronoi volumes, number of polyhedra faces, area of each face and types of polygons (i.e., triangles, tetragons, etc.) represented in the polyhedron.

Molecular coordinates were obtained from a molecular dynamics simulation of SPC/E water at 298 K. Periodic boundary conditions were used. The molecular dynamics simulation was performed by Prof. M. Berkowitz at the University of North Carolina. The properties of 10 000 Voronoi polyhedra were obtained by choosing the eight water molecules closest to the center of the simulation volume, which contained 216 molecules. A total of 10 000 polyhedra were obtained from successive time steps. Each time step represented 1 ps. 3 such sets of polyhedra were studied; no significant differences were found between sets.

## 5. Results and discussion

The distribution of Voronoi volumes in SPC/E water as a function of the number of polyhedron faces and the Voronoi volume are shown in figs. 3, 4 and 5. The number of polyhedron faces is related to the number of “important” neighbor interactions, and is a simple index of the polyhedron geometry. From the figures, it can be seen that the distribution of Voronoi polyhedra is bimodal. The high-volume peak occurs near  $0.031 \text{ nm}^3$ , approximately the mean molecular volume of water in ice. The precise relation

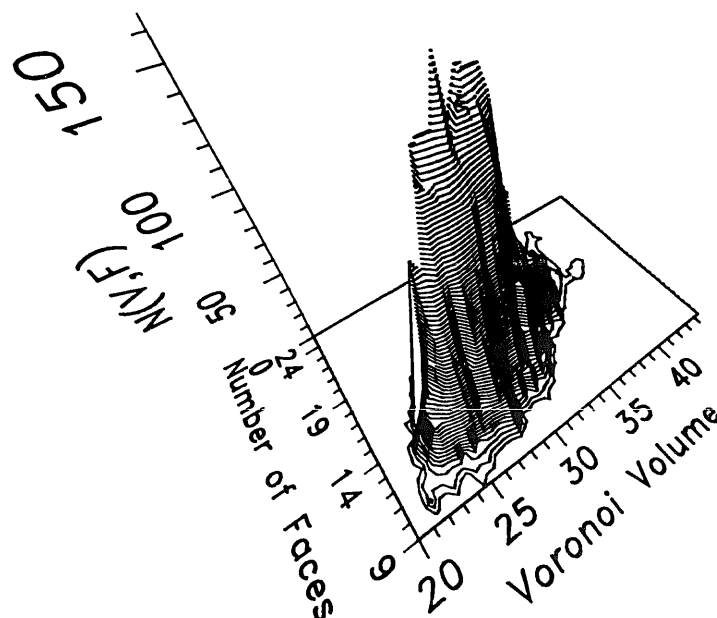


Fig. 3. Frequency  $N(V, F)$  for finding a Voronoi polyhedra in SPC/E water, as function of both Voronoi volume  $V$ , and with  $F$  number of faces. Units of the volume are  $1000 \text{ nm}^3$  or  $\text{\AA}^3$ .



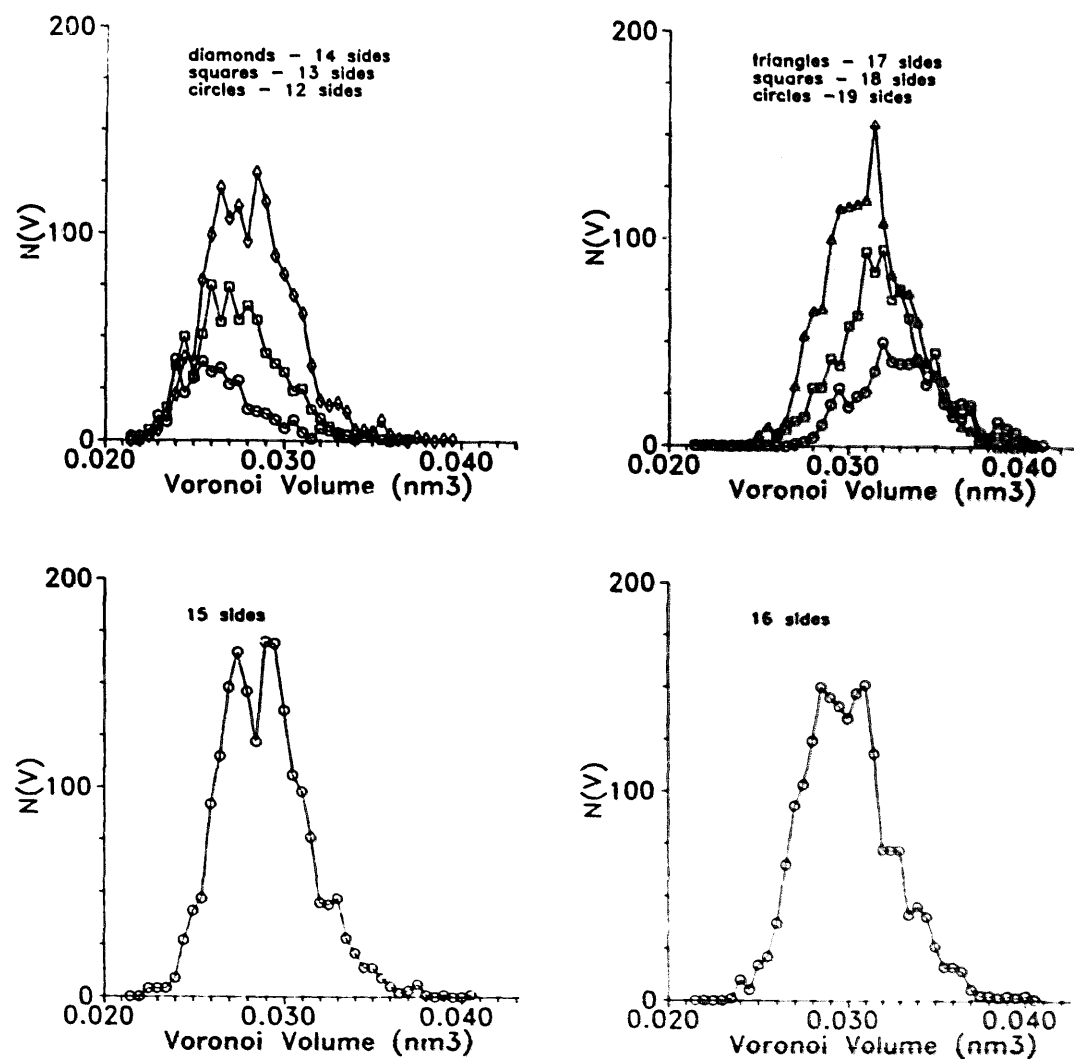


Fig. 4. Same as fig. 3 but in two-dimensional format.

between packing volume and hydrogen bonding is not clear from the distribution. If the volume distribution is considered to be composed of two component distributions, then these distributions must be highly overlapping; thus, for a given volume, it is not clear to which component a particular polyhedron belongs. It is, however, clear that one may indeed consider “bulky” and “dense” states within liquid water. At the end of the last century, Röntgen [30] suggested the existence of “bulky” and “dense” states in liquid water in order to account for the density maximum in liquid water.

The distribution of the number of polyhedra faces is unusual in comparison to that given by Finney [28] for argon. (See fig. 6.) In the case of SPC/E water, the most probable number of faces is 15–16, in contrast to 14 for argon. This result is consistent with rather long first neighbor distances and rather short first neighbor–second neighbor distances in water. The existence of high

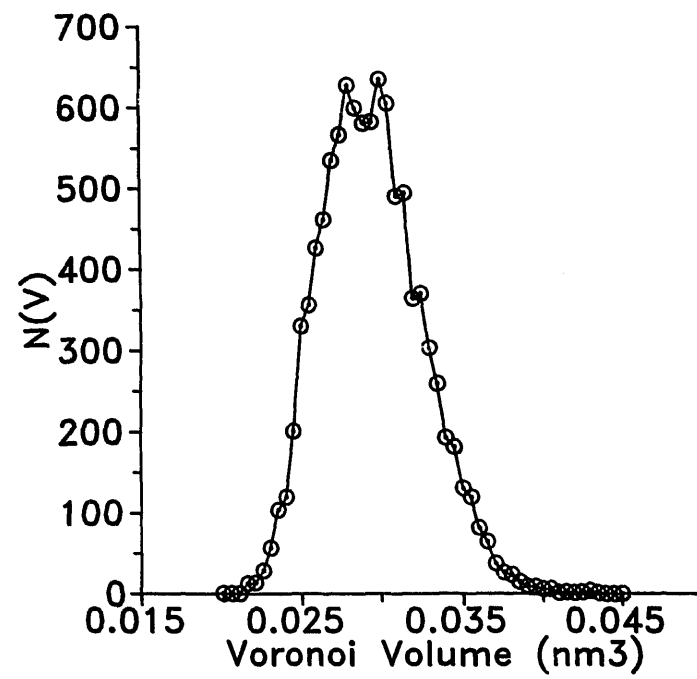


Fig. 5. Frequency for finding a molecule with Voronoi volume  $V$  in SPC/E water.

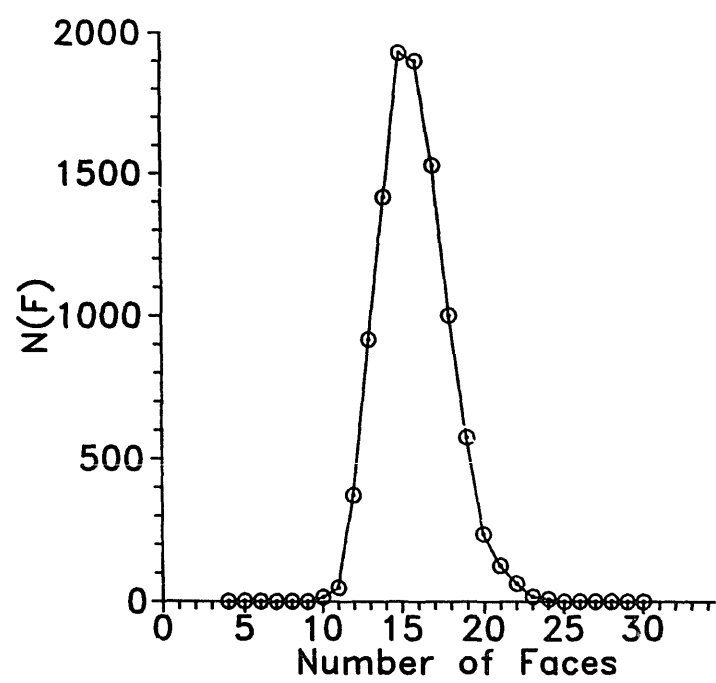


Fig. 6. Frequency,  $N(F)$ , for finding a polyhedron with  $F$  faces in SPC/E water. The most probable number of faces is greater than that found for liquid argon [28].

volume or “ice-like” states in the liquid thus does not appear to be unreasonable. The contrast between argon and water distributions suggests that the geometry of molecular packing in these two liquids differs in fundamental ways.

The geometry of the Voronoi polyhedra characterized by the two peaks in fig. 4, may be contrasted. Two groups of molecules will be considered: group I (molecular volume  $0.0265\text{--}0.0285\text{ nm}^3$ ) and group II (molecular volume  $0.0285\text{--}0.0305\text{ nm}^3$ ). The coordination number, which is the number of molecules closer to the given molecule than the distance of the first minimum in the radial distribution function, is skewed to lower coordination numbers for the high volume group (group II). Coordination number 4 is better represented in group II. The areas of polyhedron faces may be placed in descending order. The first neighbor can then be considered to be the neighbor responsible for the face which has the largest area in the Voronoi polyhedron. Face area is related to the importance of a particular molecule–neighbor interaction. In general, the first 4 neighbors result in significantly larger faces than the fifth or higher neighbors. For molecules in group II all polyhedron faces are somewhat larger suggesting stronger neighbor interactions in group II, the high volume group.

## 6. Summary and conclusions

The properties of water near interfaces are different from those of the bulk. Etzler [7, 19, 20] has proposed a model for vicinal water, which is able to correlate a number of thermodynamic properties of water in silica pores. This model has been based on a bimodal single particle enthalpy distribution calculated by Stey [22]. Here, we have explored some of the microscopic implications of Stey’s calculation, using a statistical geometric analysis of computer simulated water (SPC/E water). The statistical geometric analysis suggests, at least in part, that the bimodal character of Stey’s distribution results from the existence of a bimodal distribution of molecular (Voronoi) volumes. The calculated distribution is consistent with the notion that water molecules in liquid water may exist in so-called “bulky” and “dense” states. The existence of “bulky” and “dense” states was first postulated nearly a century ago by Röntgen [30], to account for the density maximum in liquid water near  $4^\circ\text{C}$ . Based on thermodynamic arguments, both Ubbelohde [24] and Frank [31] have postulated the existence of similar states. The properties of water near interfaces, and probably the properties of water at supercooled temperatures and at negative pressures, appear to be determined by relative populations of the “bulky” and “dense” states. The precise details of inter-

molecular interactions which produce bimodal distributions remain to be explored.

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