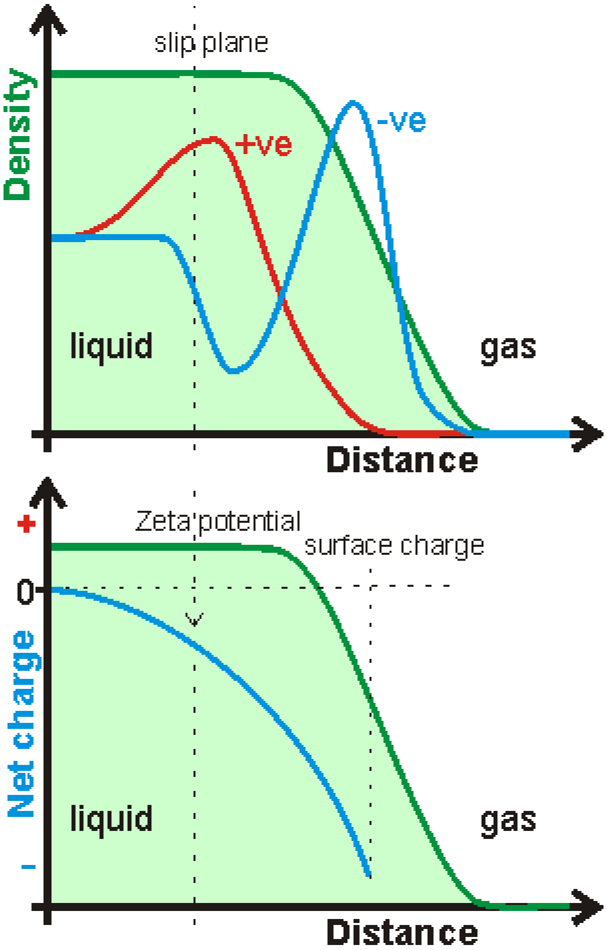
Interfacial water and water-gas interfaces

The surface of water

Interfacial water molecules at the gas-liquid surface have a strong attraction towards the bulk liquid causing a high surface tension. Gas at air-water and other gas-water interfaces behaves like a flat hydrophobic surface[g] with the difference that the van der Waals interactions between the liquid and gas surfaces are negligible. The surface will be strongly attracted to probes approaching from the gas side at distances of about a micrometer and jumping into contact when still over 100 nm distant [1294], thus showing the long range nature of the attractive van der Waals forces. The structure of the surface is not completely understood but some information has been determined.

The necessarily under-coordinated water molecules at the surface form an icelike, low-density phase that is hydrophobic, stiffer, and thermally more stable than the bulk water [2004]. Hydrogen bonding in the surface is stronger than in the bulk [1261] (and this has an effect on the osmotic pressure) but some hydrogen bonding is lost, giving a more reactive environment [594] and greater ice nucleation [914]. The increased strength of surface water hydrogen bonds is partially due to the reduced competition from neighboring water molecules [2030] but has little effect on their vibrational lifetime [1262]. This stronger bonding is due to lower anticooperativity and compensation for the increased chemical potential on the loss of some bonding. The diffusion within the surface is increased for some molecules (in the surface) but decreased for others and depends on the number of hydrogen bonds and size of the water clusters [1263]. The O···O distance, between surface water molecules, within 2-3 nm from the surface, expands by 5.9 % at 25 °C. Analysis of simple thermodynamics[c] shows the surface probably has considerable structuring, having identical density to that of bulk water at just under 4 °C. In addition, the surface water structuring varies less with temperature than the bulk. Refractive index study of the water-air surface reveals it to be about 1.7 nm thick at 22 °C and more dense than the bulk liquid (that is, it behaves like water at a lower temperature) [1482]. Recent vibrational spectroscopy shows this surface to be relatively homogeneous [1468a,c] although this work is questioned [1468b]. About a quarter of the water molecules each have a 'dangling' O-H group [415,1613] pointing at a slight angle out of the water [594, 1261], in an opposite manner to that at water-hydrophobe surfaces, creating a slight negative charge on the surface.[a]

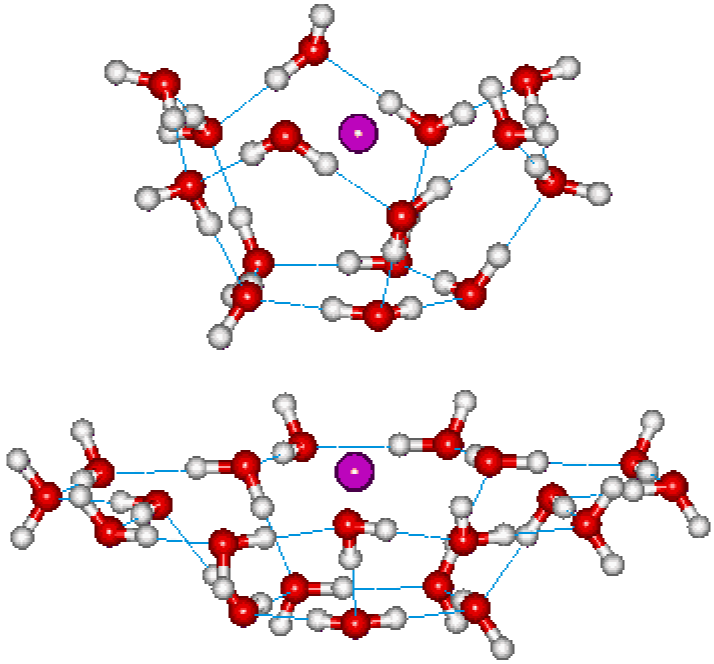
The density, dielectric (permittivity, [738b]) and dipole moment of interfacial water change from their bulk water values to that of the gas over a distance of less than about a nanometer. Thus water's solvation and dissociation properties also change at the interface, with ions and hydrophilic solutes generally being less soluble but non-polar gasses more soluble [1259]. Ions, including hydrogen and hydroxide ions, and other solutes will behave differently at the surface to their behavior in the bulk. Perhaps the most important property of the surface, after the surface tension, concerns how it affects the local ion distribution. Some ions prefer the surface as shown by their effect on the surface tension (Jones-Ray effect) [674] and bubble coalescence. Both OH^- [1025, 1266] and H_3O^+ [1308] can sit at gas/water interfaces, although clearly not at the same time due to their rapid recombination to form H_2O within this lower dielectric interface. As OH^- ions are preferred over H_3O^+ ions (above about pH 3-4),[f] this generally reinforces the interface's negative charge compared with the bulk.



The 'natural' state of such interfaces appears to be negative [1266,1433, 1477, 1591, 1905, 1951],[e] as at hydrophobic surfaces [1347,1607]. The interactions of ions [1351], and particularly H^+ and OH^- ions [1641], with the interface has been reviewed . Chaotropic ions with low surface charge density and/or high polarizability (such as Cl^-, Br^-, I^-, HO_2^- and $O_2^{\cdot -}$, but see ion effects in foams) will favor the gas-liquid interfaces [928a] as they only interact weakly with water but are influenced by the highly polarized surface. Aqueous radicals also prefer to reside at such interfaces [939], as do some molecular species that prefer to hydrogen bond on the outside of clathrate-like structures; superoxide[h] for example [1260]. The presence of radicals at the surface is further shown by their release when microbubbles collapse [2068]. Excess electrons have been found to be stable at the surface of ice for several minutes [1836].

Small cations (kosmotropes, but see ion effects in foams) are found away from the interface towards the bulk where their requirement for efficient hydration may be satisfied. Such cations only approach the interface in response to the surface negative charge. An exception to this is the oxonium ion, which has a much stronger preference for the surface than other small cations [1500]. In acid solutions, oxonium ions(H_3O^+) point away from the surface as they only poorly accept hydrogen bonds (but strongly donate three), with their oxygen atom pointing at the surface [1308]. This encourages these ions to sit in the surface layer [1308] in the absence of competing anions such as OH^-(see interfacial ions), and can lead to the charging of hydrophobic surfaces in acid solution [1584]. Mostly however at neutral pHs, there is a lower concentration of hydrogen ions than anions at the surface.

The zeta potential[b] of the surface of water is considerable and changes markedly with solute concentration (-65 mV for deionized water [1264], -46 mV for 0.1 mM NaCl, -18.8 mV for 0.1 M NaCl [1265]). This give a surface charge density varying from about an electron per 1000 nm^2 for pure water to about an electron per 10 nm^2 for 0.1 M NaCl (using the equations from [1267]). The charge at the surface of deionized water with air is similar to that found on small oil droplets in water [711c].



Atomic force microscopy at air/water interfaces has indicated that the surface polarization causes the presence of nano-sized clusters of water[d] within about 250 nm of the interface [738]. The reduced density and stronger hydrogen bonds within the surface will both contribute to the stabilization of water clusters; particularly that of ES over CS full and partial clustering. Small gas molecules bind to these surface clusters due to multiple van der Waals dispersion interactions, and good fit, between the gas molecules and the clusters without the possibly negative influence caused by the necessary closure of the clusters within the bulk. This offers an explanation for the greater solubility of the hydrophobic gasses at the interface as they can occupy clathrate-type water dodecahedra.

This is also supported by the exceptionally small difference in surface density from the bulk density as shown by theabnormally large pressure coefficient of the surface tension ($= \left(\frac{d\gamma}{dP}\right)_{TAn} = \left(\frac{dV}{dA}\right)_{TPn}$) [1280] at ambient temperature.

Interestingly, the air-water interface may give rise to chiral selectivity and recognition [1285]. The surface may therefore act, as the isotropic bulk cannot, as a mechanism for the choice of chirality early in the formation of life's molecules; for example, the D-series of carbohydrates and the L-series of amino acids.

Recently, it has been discovered that the charge on the interface affects the freezing point of supercooled water [1737]. On a surface with no electric field, water droplets were found to freeze at around -12.5 °C. On a positively charged surface, however, the freezing point is raised to -7 °C, while if the surface is negatively charged the droplet does not freeze until the temperature reaches -18 °C. Whether this strange behavior is due to the reversal of the charge of the natural negatively-charged surface destroying the water clustering has yet to be determined. [**Back to Top** ▲]

Footnotes

[a] The sign convention for the surface potential is generally taken as measured from the air into the solution; therefore a positive potential means the bulk is positively charged and the surface is negatively charged. Not all workers follow this convention. [Back]

[b] Zeta potential (ζ) reflects the charge on a moving charged particle that remains when countercharges are left behind, beyond the slip plane. It is easily determined from the movement of such particles in an electric field and depends on the dielectric constant and viscosity. [Back]

[c]

Thermodynamics of the liquid-gas surface for water

At the liquid-gas surface the following thermodynamic relationship holds:

$$dG = -SdT + VdP + \gamma dA + \Sigma_i \mu dn_i$$

where G, U, S, T, V, P, γ, A, μ and n_i are the thermodynamic quantities, Gibbs (free) energy, internal energy, entropy, temperature, volume, pressure, surface tension, surface area, chemical potential and number of moles of substance i, respectively.

From the properties of the differential: $\left(\frac{dG}{dA}\right)_{TPn} = \gamma$

, $\left(\frac{dV}{dA}\right)_{TPn} = \left(\frac{d\gamma}{dP}\right)_{TAn}$ and $\left(\frac{dS}{dA}\right)_{TPn} = -\left(\frac{d\gamma}{dT}\right)_{PAn}$.

Also there is the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ (see for example [1287]).

Although $\left(\frac{dV}{dA}\right)_{TPn}$ has units of length, this may be misleading. It is better to consider its reciprocal $\left(\frac{dA}{dV}\right)_{TPn}$ as a measure of a difference in density between the surface density and bulk density.

As H = G +

TS, $\left(\frac{dH}{dA}\right)_{TPn} = \left(\frac{dG}{dA}\right)_{TPn} + T\left(\frac{dS}{dA}\right)_{TPn}$ then $\left(\frac{dH}{dA}\right)_{TPn} = \gamma - T\left(\frac{d\gamma}{dT}\right)_{PAn}$ (surface enthalpy).

From inspection of the surface tension changes with temperature, it is clear that this term (the surface enthalpy) is always positive.

As H = U + PV, $\left(\frac{\partial H}{\partial A}\right)_{TPn} = \left(\frac{\partial U}{\partial A}\right)_{TPn} + P\left(\frac{\partial V}{\partial A}\right)_{TPn}$

Also, $\left(\frac{\partial U}{\partial A}\right)_{TPn} = \left(\frac{\partial U}{\partial V}\right)_{TPn} \times \left(\frac{\partial V}{\partial A}\right)_{TPn}$ where $\left(\frac{\partial U}{\partial V}\right)_{TPn} = \Pi_i = \text{internal pressure}$.

Therefore, $\left(\frac{dH}{dA}\right)_{TPn} = (\Pi_i + P) \times \left(\frac{dV}{dA}\right)_{TPn}$

The internal (cohesive) pressure (Π_i) [1279] is the work required to increase the volume at constant temperature, external pressure and solute concentrations, having the same units as pressure.

As dU = TdS - PdV, $\left(\frac{\partial U}{\partial V}\right)_{Tn} = T\left(\frac{\partial S}{\partial V}\right)_{Tn} - P$, therefore $\left(\frac{\partial U}{\partial V}\right)_{Tn} = T\left(\frac{\partial P}{\partial T}\right)_{Vn} - P$ (see above),

and as $\left(\frac{\partial P}{\partial T}\right)_{VAn} = -\left(\frac{\partial P}{\partial V}\right)_{TAn} \times \left(\frac{\partial V}{\partial T}\right)_{PAn} = \alpha / \kappa_T$, the internal pressure may be calculated from (Π_i + P) = Tα/κ_T, where α is the coefficient of thermal expansion and κ_T is the coefficient of isothermal compressibility [1279].

It follows from

$$\left(\frac{dH}{dA}\right)_{TPn} = (\Pi_i + P) \times \left(\frac{dV}{dA}\right)_{TPn} \text{ and } \left(\frac{dH}{dA}\right)_{TPn} = \gamma - T\left(\frac{d\gamma}{dT}\right)_{PAn}$$

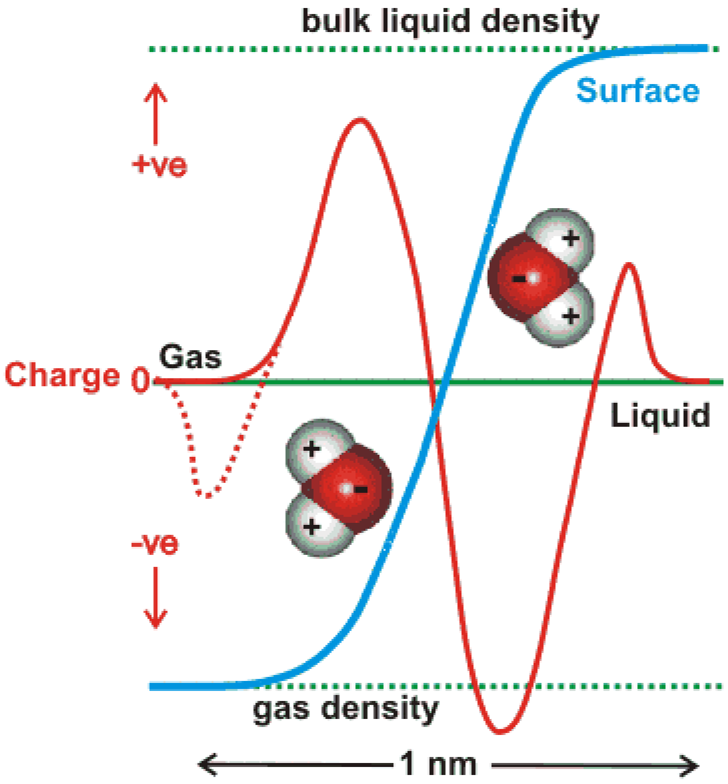
that

[1519]

$$\left(\frac{dA}{dV}\right)_{TPn} = (\Pi_i + P) \Big/ \left\{\gamma - T\left(\frac{d\gamma}{dT}\right)_{PAn}\right\} \text{ and } \left(\frac{d\gamma}{dP}\right)_{TAn} = \left\{\gamma - T\left(\frac{d\gamma}{dT}\right)_{PAn}\right\} \Big/ (\Pi_i + P)$$

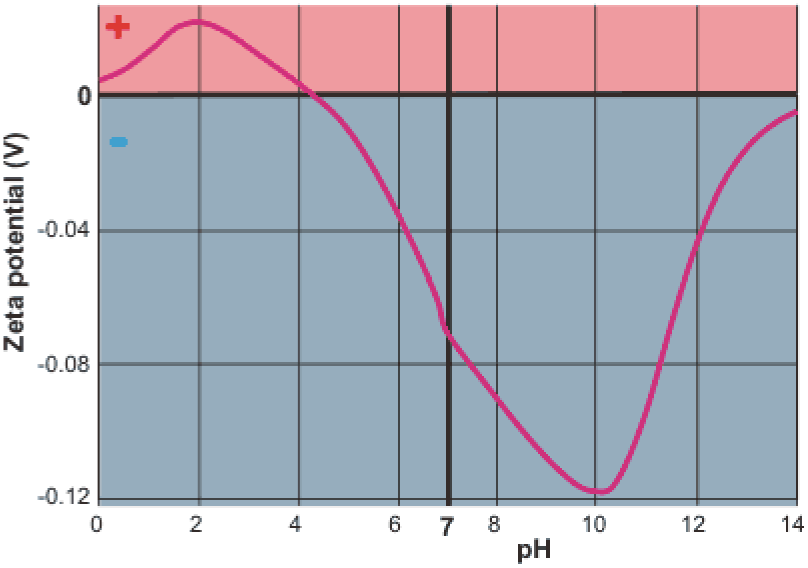
As $T\alpha/\kappa_T$ is zero at 3.984 °C, so is $(\Pi_i + P)$ and both are negative below this temperature, as must be $\left(\frac{dA}{dV}\right)_{TPn}$; Π_i is zero at 3.99 °C when cohesive and repusive components of the hydrogen bonding are equal. It follows that the densities of surface and bulk water are equal at 3.984 °C as, below this temperature, the surface density contracts relative to the bulk density (rather like what happens at the surface of hexagonal ice [937]). Thus below 3.984 °C, bulk liquid is less dense than the surface liquid whilst above this temperature the bulk liquid is more dense than the surface liquid. [Back] [**Back to Top**]

[d] These clusters are apparently built up from ~100 H_2O molecule clusters; the same size that forms the core to the ESclusters in the icosahedral model of water [738b] and as found by X-ray analysis in Mo-based nanodrops. [Back]



[e] The charge on the surface of just theoretical water (H_2O, modeled without dissociation), gives a change in the charge across the surface dependent on the depth of the surface examined, as indicated opposite [1348a]. Thus overall it is negative (relative to a positive bulk) but where the very outer layer of the interface (next to the gas) is more positive [1348c]. It is probable that the outer (gas-facing) positive contribution is due to the almost-free singly linked water molecules compensating for the negative quadrupole and dipole contributions in the denser part of the surface layer [1348b]. A recent explicit *ab initio* electronic charge density study shows that a negative exterior surface may be present due to electron density 'leaking' into the gas phase (suggested by the dotted line opposite) and not because of any preferential orientation of water molecules [1721], although this may have a consequential orientation effect similar to the description above.

It should be noted that there is some dispute over the charge at aqueous surfaces [1205], with much of the extensive earlier work indicating that it is negative [1517]. Also, simulations have shown that NaOH solution surfaces are negative [1677]. The view prominent here [1591] is greatly influenced by the undisputedly negative zeta potential. Also there are good reasons to suppose that the surface negative region is actually a different aqueous phase, pehaps similar to a liquid crystal, that extends for up to hundreds of nanometers or even further [1328a]. It is possible that this aqueous phase is created by the higher osmotic pressure created at the surface (e.g. see [1669]) by an excess of longer-lived water clusters created there. [Back]



f There is some dispute over the charge on the surface at pH 7 [1205]. Shown opposite is the zeta potential in water with no added ions except the necessary H3O+and OH- [1853]. Oxonium ions (H3O+) may well favor the extreme outside surface layer. However this layer has low molecular density and any net acidity would be diluted by several orders of magnitude if the complete surface layer (that is, the molecules from the surface down to those showing 'bulk' properties) was to be considered. Surface H3O+ions may (preferably) evaporate from the surface [1883] leaving a negatively charged surface behind. Throughout this relatively large volume, hydroxide ions are preferred over oxonium ions. In small water cluster modeling H3O+ seems to prefer the outside of clusters [854] whereas OH- prefers a more central position [1828]. However such a small cluster modeling approach may not be applicable to extensive surfaces as optimal small clusters of just H2O do not seem to be present in bulk water. Studies with surface active pH sensitive dyes (e.g. [1947] can show the 'apparent' pH at the surface as different from the bulk pH but care must be taken over the conclusions as differences may be due to artifacts inherent in the determination. [Back]

[g] A water layer with a thickness of up to 35 nm exists at hydrophobic surfaces. This layer is characterized by a more ordered network of hydrogen bonds than liquid water [1714]. [Back]

[h] Superoxide ($O_2^{\cdot -}$) hydrates in a planar manner to H-O protons on four water molecules [2007]. It decays decays by reaction with its conjugate acid, $HO_2^{\cdot}$ ($O_2^{\cdot -} + HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + O_2 + OH^-$) in water at a rate constant of about $10^8 M^{-1} s^{-1}$ which gives a half life-period of about a second, when $O_2^{\cdot -}$ and $HO_2^{\cdot}$ are at micromolar concentration. [Back]

Source:http://www1.lsbu.ac.uk/water/interface.html