Self-generation of colligative properties in water [a]

Preamble

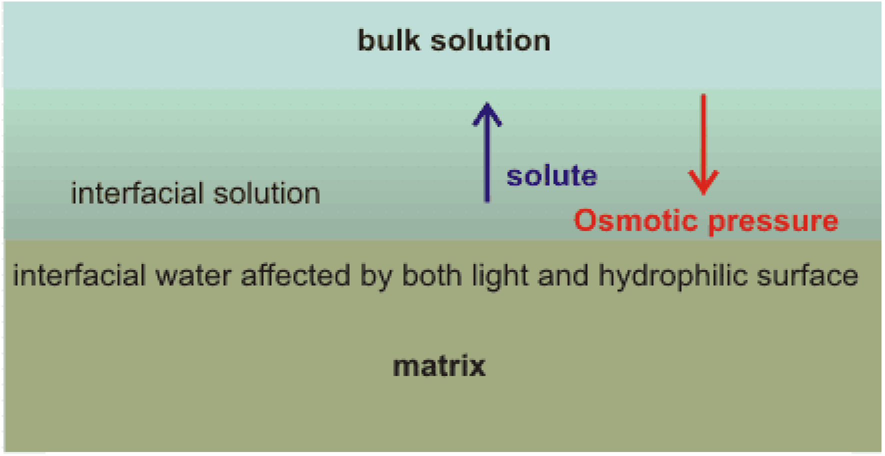
Although there is some contention amongst physical chemists over how to describe osmotic pressure, it is generally agreed that it is a reversible thermodynamic colligative property and correlates well with other colligative properties such as freezing point depression. As such, the osmotic pressure is thought ideally to depend on the number of dissolved 'particles' (e.g., molecules) present in a volume of liquid. It is, perhaps, unsurprising that ion exchange surfaces can generate very high osmotic pressures of over 100 MPa in water [1669], as they create high surface concentrations of counter-ions. Poly-ionic nanoparticles, with high surface area, produce such a great osmotic pressure that they can be used in practical desalination processes [1768a,d]. Likewise; polyelectrolytes may also produce high osmotic pressures between molecules [2006]. However, hydrophilic uncharged molecules, without any counterions, also produce similarly high osmotic pressures to polyelectrolytes between molecules [2006]. Also, it has been experimentally verified that uncharged hydrophilic particle surfaces generate high osmotic pressure, without the presence of counter-ions or solutes [1768b,c]. It is clear, therefore, that relatively small numbers of particles, far less than required by the 'conventional' colligative law, can generate high osmotic pressures so long as they possess extensive hydrophilic surfaces.

Much work has been done in the laboratory of Gerald Pollack (and confirmed by many other independent workers [2058]) concerning the mesoscopic properties of aqueous solutions next to surfaces [1328, 1740].[c] In essence, it has been found that the interfacial water next to ionic charged (e.g. polyacrylate) or neutral uncharged (e.g. polyvinyl alcohol) hydrophilic surfaces expel solutes to the bulk of the solution that may be several hundred microns away. These exclusion zones (named as EZ-water) can be visualized when low-molecular weight dyes, proteins, micron-sized microspheres or other solutes are used. With a laser tweezers system, the existence of force fields inside the solute-free exclusion zones have been found to reduce as a function of distance from the surface [1784]. Also the EZ-water seems to possess other physical properties such as absorption at 270 nm, greater density, greater viscosity and negative charge compared with the bulk water. Further, the efficient operation of uncharged hydrophilic reverse osmosis fibrous membranes (that function in spite of not possessing useful molecular-sized pores) show that they must present thick multimolecular layers of water that are relatively inpenetrable by low molecular weight salts and molecules. It has also been independently experimentally verified that uncharged but highly hydrophilic nanoparticles, with high surface area, produce such a great osmotic pressure that they can be used in practical desalination processes [1768a,b]. Also, uncharged hydrophilic polymers have been shown to generate greater than MPa osmotic pressures at nanoscopic distances [2006].

There is no generally-accepted explanation for these phenomena or properties. However, below I give a new explanation that is very simple, easily understood and potentially very important in a number of related fields.

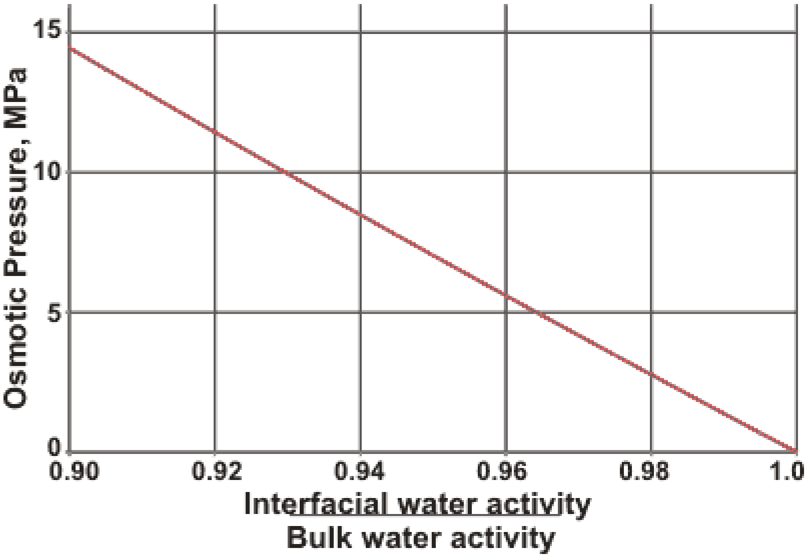
Proposal for the generation of osmotic pressure at aqueous interfaces

Wherever water is present in solution it may be considered as being either 'bound' or 'free', although there will be a transitional water between these states. When considering the colligative properties, 'water' is considered bound to any solute when it has a very low entropy compared with pure liquid water. Such water is considered part of the solute and not part of the dissolving 'free' water [1064]. As pure liquid water consists of a mixture containing low-density water, made up of extensively hydrogen bonded structures, and higher density water, consisting of much smaller less extensive clusters, the proportions of 'bound' or 'free' water in pure liquid water can vary; the strongly-bound larger clusters behaving like 'bound' water. In bulk liquid water, the relative concentrations of the two aqueous forms is of no consequence as all the water behaves the same throughout. If volumes of the solution contain different proportions of strongly and weakly hydrogen-bonded water molecules (or even more simply that there is more extensive clustering present), then these different volumes will show a difference with respect to their water activity and chemical potential. Normally any such instantaneous differences in water activity and chemical potential between different volumes within the same mass of liquid would rapidly cause liquid movement from one to the other in order to equalize these states and so remove the potential differences.



However, where there are surfaces interacting with the liquid water, the concentration of the more extensive hydrogen-bonded clusters may differ from the bulk values with the surface interactions preventing the potential equalization between bulk and surface volumes. When this occurs, the surface water has a lower water activity and chemical potential to the bulk, leading to differences in osmotic pressure, and other colligative properties.

The change in the chemical potential (μ_w) is $-\{RTLn(x_{ws}) - RTLn(x_{wb})\}$ (that is, a negative energy term is added to the chemical potential when $x_{ws} < x_{wb}$) where xws is the mole fraction of the 'free' water ($0 < x_{ws} < 1$) in the surface layer and x_{wb} is the mole fraction of the 'free' water ($0 < x_{wb} < 1$) in the bulk liquid.



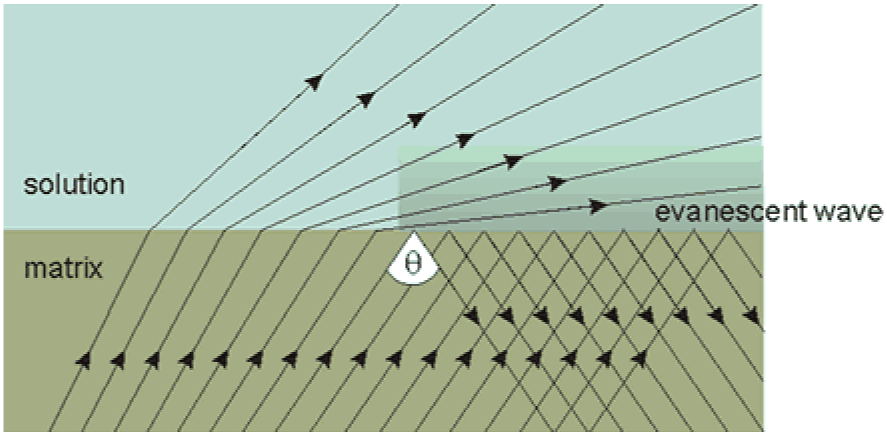
The generated osmotic pressure (Π) is given by,

$$\Pi = -(RT/V_M).Ln(x_{ws}/x_{wb})$$

where V_M is molar volume of water. Clearly quite small reductions in the interfacial water activity will give rise to large osmotic pressures.

At hydrophilic surfaces, interactions between the surface and neighbouring water molecules fix the localised hydrogen bonding and this, together with steric factors, increases the cluster extent and lifetime [2059].[b] As the 'free' water reduces as compared with its bulk value when the formation of longer-lived and more extensive hydrogen bonded clusters increases, so the water activity reduces and the osmotic pressure increases. Solutes next to the surface will move to equalise the water activity throughout the liquid. In other words, the increase in osmotic pressure next to the surface will displace solutes from the surface towards the bulk until its effect is equalled by the osmotic pressure of the surrounding solution or the system reaches a steady state. As the first effect of this solute expulsion is naturally the formation of an increased concentration band as expelled solute mixes with the prior solute concentration, the extent of the expulsion will affect the whole of the unstirred layer (~1-100 µm). Where hydrophilic microparticles or nanoparticles are suspended in aqueous solutions, their surfaces will necessarily cause mutually repulsive osmotic pressure effects that may result in the ordering of the particles within small volumes of the liquid [272a, 2060]

It should be noted that osmotic drive does not require a membrane to separate the two solutions [1744] provided there are two phases (e.g. [1669]). Here the two phases consist of the unstirred and stirred layers. In this context [1739], the affected aqueous layer behaves similarly to that described for exclusion zone (EZ) water by Pollack and may be a simple explanation of his experimental data [1740]. It also shows similarities with the experiments on autothixotropy [509, 1898,1975]. The increase in density at the interface, as found in EZ water, has been explained previously by the increase in clustering causing the water to behave as though it is at a lower temperature, which also explains the ease with which thissurface layer freezes. The presence of 270 nm absorption in the interfacial water, as described for EZ water [1328], has been ascribed to the delocalization of electrons within the extended clustering.[d] As the cluster lowest unoccupied molecular-orbital (LUMOs) are both huge and relatively low energy, these electron delocalizations are stabilized by the addition of an electron but not by protonation, so causing the charge separation seen at these interfaces [1744, 2061]. Other experimental properties of the EZ layers, such as the reduction in its thickness with particle size [2062] and with increased bulk ionic strength [1328b] are easily explained by the presented hypothesis, as the unstirred layer around particles is known to depend on the particle size and high bulk osmotic pressures will oppose the osmotic pressure at the hydrophilic surface

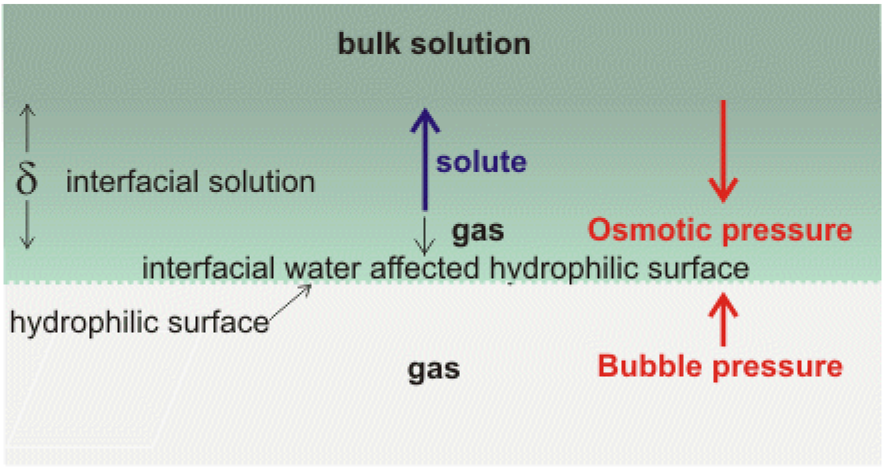


Another effect of interfaces is the formation of evanescent waves due to the internal reflection of electromagnetic radiation. The standing electromagnetic evanescent wave within the interfacial water is caused by impinging electromagnetic radiation and the angle at which total internal reflection occurs (θ). The standing electromagnetic wave produced will interact with water molecules to stabilise a standing wave of hydrogen bonded clusters that will alter the local concentration and extent of hydrogen bonded clusters so increasing the above osmotic effect, in agreement with the experimental data [1173,1589, 1741].

It appears that a similar effect on solutes to the one described for water may occur in other polar solvents that can form hydrogen bonds [1742]; thus reinforcing the likelihood that a mechanism is acting that does not depend on the specific properties of water, such as the here-described colligative thermodynamics.

Osmotic pressure stabilises nanobubbles

There is now much evidence that sub-micron-sized gas-filled cavities (often called nanobubbles) can exist for significant periods of time both in bulk aqueous solution and at submerged aqueous-hydrophobe interfaces. Their contained gas is in constant flux with gas molecules both leaving and entering continuously. The cavities are under excess pressure given by the Laplace equation ($2\gamma/r$, where γ is the surface tension and r is the cavity radius) as the surface tension causes a tendency to minimize their surface area, and hence volume. Nanobubbles grow or shrink by diffusion according to external pressure and the degree of over- or under-saturation in the surrounding solution, with the dissolved gas relative to the raised cavity pressure. As the solubility of gas is proportional to the gas pressure and this pressure is exerted by the surface tension in inverse proportion to the size of the bubbles, there is increasing tendency for gasses to dissolve as the bubbles reduce in size so accelerating the bubble-dissolution process. Such size-reduction is increased by the bubble's movement and contraction during this activity, which aids the removal of any gas-saturated solution around the cavities. Calculations show that nanobubbles should only persist for a few microseconds, in contrast to their long lifetimes (hours to days) as detected by light scattering or resonant mass measurement (bulk nanobubbles [1972]) or tapping mode atomic force microscopy (surface nanobubbles). Interestingly, these cavities (bubbles) are subject to Brownian motion, so behaving as though they have solid shells similar to solid nano-particles. Surface and bulk-phase nanobubbles can both give rise to the otherwise difficult to explain long range attraction between hydrophobic surfaces due to bridging nanoscopic gas cavities or the osmotic effect due to local nanobubble depletion.



Contributing to the stability of nanobubbles is the slow rate of gas diffusion to the bulk liquid surface from both surface and bulk-phase nanobubbles [1973, 1987]; in particular, nanobubbles in a cluster of bulk nanobubbles protect each other from diffusion by a shielding effect [2074]. Apparently there is a thick interfacial layer; a phenomenon experimentally supported by the higher forces required to penetrate greater depths of the nanobubbles' interface [1986,1987]. Here we assume that the cause of this layer is the high osmotic pressure produced beneath at gas liquid interface so both preventing the gas dissolving towards the bulk and driving any dissolved gas near the interface back into the nanobubble (see left). The depth of the 'unstirred' layer (δ) is approximately proportional to the size of the nanobubbles. This thickness will be substantially reduced by the mixing caused by any surface changes in the bubbles as they rise or change size.

The generation of the osmotic pressure at the surface is due to the necessarily under-coordinated water molecules at the gas-liquid surface forming an ice-like, low-density phase [2004] that has lower water activity than the bulk water. Hydrogen bonding in the surface is stronger than in the bulk [1261], due to the reduced competition from neighbouring water molecules, lower anticooperativity and compensation for the increased chemical potential on the loss of some bonding. A further reason for at least some of the stability of nanobubbles is that the nanobubble gas/liquid interface is charged[1591], expanding the surface and introducing an opposing force to the surface tension, so slowing or preventing the nanobubble dissipation. It is clear that the presence of like charges at the interface will reduce the effect of the surface tension, with charge repulsion acting in the opposite direction to the surface minimization due to surface tension. Any effect may be increased by the presence of additional charged materials that favour the gas-liquid interface, such as OH^- ions at neutral or basic pH [1591]. Recently, it has been proposed that the surface tension is reduced by the degree of supersaturation at the surface [2013]. As this supersaturation is prevented from equilibrating away from the bubbles by the imposed osmotic pressure, this introduces a further stabilisation effect on the nanobubbles.

[**Back to Top** ▲]

Footnote

[a] This theory [2057] was first presented at the international conference 'Water and Nanomedicine', Academy of Sciences and Arts of Republic of Srpska, Banja Luka, Aug. 30, 2011 [1772]. [Back]

[b] This agrees with the earlier proposition for long-range water ordering involving the partial alignment of water molecules induced by the surface [1328]. [Back]

[c] These ideas and experiments have been the subject to a critical analysis giving an alternative view involving concentration gradients [2036a] and this, in turn, has been mostly answered by Pollack [2036b]. [Back]

[d] An alternative view of the 270 nm absorption has been given in terms of an (improbable) highly charged extensive planar hexagonal ice-like model [2077]. [Back]

Source:http://www1.lsbu.ac.uk/water/colligh2o.html#nano