Communication

Compelling Alternative Theories for Exclusion Zone Phenomena in Water and Other Liquids

Daniel C. Elton*

[1] Radiology and Imaging Sciences, National Institutes of Health Clinical Center, Bethesda, MD 20892, USA
* Correspondence: daniel.elton@nih.gov

Abstract: The existence of the exclusion zone (EZ), a layer of water in which plastic microspheres are repelled from hydrophilic surfaces, has now been independently demonstrated by several groups. A better understanding of the mechanisms which generate EZs would help with understanding the possible importance of EZs in biology and in engineering applications such as filtration and microfluidics. Pollack theorizes that EZ water exists in a new phase which has a layered structure. We note several problems with Pollack's proposed structure, some of which were noted in the 1960's when a similar structure was proposed for "polywater". We argue that Schurr's diffusiophoresis based theory presents a compelling alternative explanation for the core EZ phenomena, although there remain other findings from Pollack's lab it does not explain. Among other things, Schurr's theory makes predictions about the growth of the EZ with time which have been confirmed by Florea et al. and others. In this work we also introduce and explore a novel hypothesis - that some aspects of EZ phenomena may be attributable to repulsive van der Waals forces. Finally, we touch on several possible confounding factors that make experimentation on EZs difficult, such as charged surface groups, dissolved solutes, and adsorbed nanobubbles.

Keywords: water; exclusion zone; diffusiophoresis; repulsive van der Waals

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1. Introduction

Prof. Gerald Pollack's group has provided many convincing experimental demonstrations of an exclusion zone (EZ) in water whereby particles such as plastic microspheres are repelled from a surface.[1] For the case of highly hydrophillic surfaces these findings have now been reproduced by several independent research groups[2–7] and are considered to constitute a genuine physical phenomena which is need of a theoretical explanation. In this work we argue that Pollack's theory of a layer of ordered water is untenable. Instead, there are several other other plausible mechanisms by which the EZ phenomena can arise. In any given experiment, some or all of those mechanism may be present.

The dominance of Pollack's theory in the EZ literature has probably led many researchers to disregard the phenomena entirely. This is unfortunate since EZ phenomena may have important engineering applications in water filtration and microfluidics.[4] EZ phenomena have obvious importance to understanding biological systems, and Deryagin pointed out EZ water type phenomena in cells in 1986.[4,8]

2. Pollack's "fourth phase"

Pollack proposes that the EZ water is structured in hexagonal sheets, with the hydrogens lying directly between oxygens.[9] Furthermore, he proposes that when these sheets are stacked hydrogen atoms bond to the oxygens in neighboring layers, such that each hydrogen forms three bonds. Finally, he proposes that water forms H_3O_2- ions, which would result in a vast amount of negative charge per unit space, making the structure extremely unstable. Even if we ignore this possibility of charge build up, there are still serious problems with this structure. Hasted noted problems with such a hexagonal structure in 1971, noting that high energy cost of placing hydrogens between oxygens was enough to make such a structure explode if it were ever created.[10] Furthermore, Seggara-Martí et al. performed quantum chemistry calculations showing such a structure to be unstable.[11] More broadly speaking, there are no thermodynamic forces in the system to drive such a phase transition.

Exclusion zone phenomena have been observed in other polar liquids as well, suggesting that the phenomena is not tied to restructuring of the liquid.[12] If that were the case, we would expect EZ phenomena would be quite different between water, which supports low density hexagonal structures and hydrogen bonding, and other polar solvents which do not. An experiment which could falsify Pollack's theory would be to do x-ray crystallography of the EZ. This has not been done for EZ water but has been done for the electrically-induced water bridge which Pollack suggests is made of EZ water.[9] Both molecular dynamics and X-ray crystallography show that the internal structure of the water bridge is unchanged – implying that it is supported by enhanced surface tension rather than a change in internal structure.[13]

Other evidence that Pollack presents include optical birefringence,[9] and absorption at 270 nm. The optical birefringence has been shown to be an artifact of reflection from water-material interface.[7] As far as the absorption at 270 nm, results from Pollack's own lab show that a similar absorption peak is seen in salt solutions (LiCl, NaCl, KCl).[14] Thus rather than being indicative of a special phase of water, the absorption peak seems to indicate the presence of a salt gradient near Nafion.

2.1. Learning from the polywater affair

Polymeric water ("polywater") was purported to be a special phase of water which formed when water was condensed into tiny capillary tubes with diameters smaller than 100 micrometers. Interestingly, the structure which was proposed for polywater is very similar to the the structure Pollack proposes for EZ water. The earliest papers on polywater phenomena originated from the group of Boris Deryagin at the Institute of Surface Chemistry in Moscow, USSR in the early 1960s.[15] In 1962 Fedayakin proposed that polywater had a honeycomb like structure with each oxygen bonded to 3 hydrogens.[16] Lectures by Deryagin in England and the United States in 1966, 1967 and 1968 drew the attention of Western researchers. Research interest peaked after a 1969 a paper by Lippincott et al. in *Science* which reported spectroscopic results which were said to provide conclusive evidence of a "stable polymeric structure".[17] Over 160 papers on polywater were published in 1970 alone.[18] However, by 1972 it became apparent that the observed phenomena were due to trace amounts of impurities,[19] some of which likely came from human sweat.[20] In some cases it was found that the sample tubes contained very little water at all. Altogether, over 500 publications were authored on polywater between 1963-1974.[18,21] Far from being just a historical curiosity, the polywater saga is something that EZ water researchers can learn from to avoid repeating the mistakes of the past. The polywater saga is an example of what Langmuir called "pathological science", whereby a community fixates on a particular theory while disregarding other explanations. Other features of pathological science are that the experimental evidence is often on the edge of significance, and that interest in the pathological theories persists for years after disconfirming evidence and better theories have been presented. There is a long history of pathological science regarding water, which is probably related to the fact that water's properties can change dramatically under the influence of trace solutes and dissolved gases which are hard to control experimentally.

3. Alternatives explanations for EZ phenomena

This section focuses on two alternative explanations to EZ phenomena, diffusiophoresis (long range chemotaxis), reported previously by Schurr, and the repulsive van der Waals forces, reported here for the first time. These theories are very compelling explanations for the growth and maintenance of the exclusion zone where plastic microspheres made of (possibly functionalized) carboxylate, polystyrene, amidine, or PTFE are repelled from various surfaces. Other related phenomena, such as anomlous flow or the expansion of the EZ with light require further explanation. To conclude this section we touch on other mechanisms which may play a role in EZ phenomena.

3.1. Diffusiophoresis

Schurr has developed a theory which proposes that the EZ formation is created by forces arising from a concentration gradients of OH^- or H^+ and salt. Called "long range chemotaxis" by Schurr,[22, 23] it is a type of a more general and well known phenomena in colloid science called diffusiophoresis. Florea et al. have performed experiments on the EZ, carefully measuring it's time course, and have shown that the data are fit by a model of diffusiophoresis.[4] Notably, these experiments were done with the hydrophilic surface horizontal, which avoids convective fluid motions due to the force of gravity which occur when it is vertical, as in many of Pollack's experiments. Pollack has responded to Shurr's work.[24] Figure 1 in his response arguably support the theory however, since it shows a large pH gradient, as indicated by a dye.[24] Figure 2 in his response is more difficult to understand, as the nafion surface is not flat but has corrugations and the EZ is not easy to pinpoint.

Apart from the experiments of Florea, there are theoretical reasons to suppose that a large concentration gradient would arrise near the surface of Nafion, the most popular surface used for generating EZs. Nafion is a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octene sulfonic acid which finds application in fuel cell technology. If the sulfonic acid part were allowed to dissolve into water it would be quite a strong acid, but this doesn't happen since it remains bonded into the copolymer. When Nafion is placed in water it quickly swells, resulting in a gell-structure with an extremely high surface area. In this structure all of the sulphonic acid groups are surrounded by water. The highly negative sufonic acid group dissociates water and adsorbs $H+$ ions, resulting in a very low internal pH for Nafion, as observed with indicators such as methylene blue.[25] Computational studies show it is energetically favorable for 2-4 hydronium ions to surround each sulfonic acid group.[26,27] Using methylene blue the internal acidity of Nafion has been estimated to be equivalent to 1.2M sulphuric acid.[25] The excess protons inside Nafion are of two types - "fixed" ions which cam "hop" between sulfonic groups, and "mobile" ions which can can freely diffuse away.[25,27] Thus water around Nafion becomes acidic, with a pH gradient approaching neutral (7) further away from the memberane. This is shown clearly in experiments by Pollack where pH sensitive dyes have been added to the water.[28] Elsewhere the pH of water around Nafion has been reported as being -6.[29]

3.2. EZs at metal surfaces and van der Waals repulsion

The theory of chemotaxis of Schurr presents a compelling theory of the EZ phenomena observed near Nafion. However, Pollack's group has also reported EZ phenomena near metal surfaces, although they are much smaller in size.[30] The EZ is largest for Zinc (220 μm), followed by aluminum, lead, tin, and tungsten (72 μm).[30] Notably, attempts to independently replicate these findings with aluminum and zinc have failed.[7] Pollack also reports EZ phenomena at the surface of platinum, but only after a voltage is applied.[31]. While water molecules adsorb onto surfaces like platinum,[32] and may dissociate on such surfaces in certain circumstances,[33] the expected gradient of hydronium ions as one moves away from the surface is expected to be small, if it exists at all. A so far unexplored possibility is that the exclusion zone phenomena near metals (and possibly other materials) may be partially explained by repulsive van der Waals forces (also called Casmir-Polder forces in this type of context). The possibility that two objects of different composition may feel a repulsive force when submerged in a liquid was first realized by Hamaker in 1937.[34] The full theory for such forces, for arbitrary dielectric media, was worked out by Lifshitz in 1954.[35] Lifshitz's equations allow for a repulsive force between two objects if the dielectric susceptibility of the medium between the two objects is intermediary between the two. Calculations using Lifshitz theory show that the finite size of the slabs does not effect the repulsion between them.[36,37] Having free electrons, the dielectric constant of metals is extremely high (for instance Milling take the dielectric constant of gold to be 300).[38] The dielectric constant of water is 78 and the dielectric constant of a polystyrene microsphere is about 2.5 (other plastic microspheres should have dielectric constants between 1.5 and 3). Thus, the metal-microsphere-water system obeys the conditions necessary for Casmir Pollard repulsion.

Most studies of the repulsive van der Waals force have used liquids other than water, likely due to the fact that water is easily contaminated with charge bearing solutes which can confound such experiments. The effect is also larger in nonpolar liquids than polar ones.[38] Munday et al. (2009) have reported a repulsive Casmir force between a gold plate and a silica sphere submerged in bromobenzene.[39] Similar repulsion has been found in follow up work with cyclohexane and other liquids.[40,41] Milling et al. (1996) measured the force between a gold sphere and PTFE block submerged in several liquids, including water.[38] While their results for water were neutral/inconsistent (both weakly attractive and weakly repulsive forces were observed), their theoretical calculation indicates that the vdW force in water should be repulsive.[38]

One issue with this theory though is that retardation effects can diminish the van der Waals force starting at just a few nanometers of seperation.[42,43] Retardation effects become important when the travel time due to the speed of light becomes similar the timescale (period) of polarization fluctuations which underlie the van der Waals force. Under retardation the force changes from falling as $1/r^7$ to $1/r^8$. However, Isrealachvili notes that here is also a non-retarded zero frequency component to the vdW force which persists to large seperations.[44] According to Isrealachvili, the actual progression of the vdW force may be from $1/r^7 \rightarrow 1/r^8 \rightarrow 1/r^7$.[44]

The growth of the EZ zone with laser light may be a similar type of induced van der Waals repulsion. It has been shown that the van der Walls forces between silver nanoparticles can be enhanced by radiation, since electromagnetic radiation induces fluctuating dipole moments in the particles. The possibility for light-driven enhancement of repulsive van der Waals forces has been shown theoretically by Rodríguez-Fortuño et al.[45] While these considerations are for metal nanoparticles, the polarizability of plastic (especially functionalized plastic) means such induced dipoles moments may be possible. Further theoretical study is needed to clarify this matter.

3.3. Other possibilities

Huszár et al. have investigated two other possible explanations for EZ-formation.[3]

- Dissolution of Nafion, during which polymer strands diffusing out of the gel push the beads away from the surface.
- A "brush mechanism" in which closely spaced long elastic polymer strands keep the beads away by entropic forces.

Close inspection of gell shows that it does not loose mass, and an AFM study of the surface shows that there are no long strands hanging out, so they ruled out both of these mechanisms.

Apart from these two effects, there are many other possible effects that can contaminate microsphere systems and confound experiments. Plastic nanospheres can be easily contaminated with charge bearing groups. In the case of PTFE these may include "residual carboxylic groups from the polymerization process".[38] Referring to research that uses plastic microspheres Horinek et al. note "these systems are notoriously plagued by secondary effects, such as bubble adsorption and cavitation effects or compositional rearrangements."[46] As an example, the discovery of an ultra-low frequency Debye relaxation in water was later show to be due to microbubble contamination.[47] There is also growing research showing that the removal of nanobubbles from water can be very challenging. This is especially true when they are adsorbed on surfaces. Results from Pollack's lab show that the absorption of light at 270nm can be suppressed by nanobubbles and/or dissolved gases.[48] Thus careful degassing should be a key part of any research on EZ water going forward.

Finally, we note that Chaplin has a theory which he calls "self-generation of colligative properties".[49] The basic idea is an osmotic effect can be generated near hydrophillic surfaces. Chaplin predicts that an even larger osmotic effect should occur near nanobubble's surfaces, due to "surface teathered" solutes near or on the nanobubble air-water interface.[50] Chaplin's theory will require carefully designed experiments to test.

4. Conclusion

In this communication we have argued against Pollack's hypothetical "fourth phase", noting several major problems with it. Schurr's theory of macroscopic chemotaxis presents a compelling alternative theory which can explain things which Pollack's theory cannot, such as the precise time course of EZ growth. We have also explored a novel hypothesis that some aspects of EZ phenomena may be attributable to repulsive van der Waals forces. Looking at the polywater affair as a historical reference, the research community should embrace these new theories and work on experiments to test them as well as experiments (such as x-ray diffraction) which would more conclusively falsify Pollack's theory. A better understanding of the mechanisms behind EZ phenomena will assist in understanding their possible roles in biology as well as their engineering applications.

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