# Experimental Studies on Exclusion Zones in Water

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*A dissertation submitted for the partial fulfilment*
*of BS-MS dual degree in Science*

Under the guidance of
**Dr. Ananth Venkatesan**

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# Certificate of Examination

This is to certify that the dissertation titled **"Experimental Studies on Exclusion Zones in Water"** submitted by **Vivek Shukla** (Reg. No. MS16073) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: 09.05.2021

# Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Ananth Venkatesan at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Vivek Shukla
(Candidate)

Dated: May 09, 2021

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Ananth Venkatesan
(Supervisor)

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# Abstract

Surface effects on the contiguous aqueous process are typically thought to be confined to a few water-molecule layers. On the other hand, older research indicates a wider impact. According to this study, colloids suspended in aqueous solution are withdrawn deeply and widely from the surface of hydrophilic surfaces. Normally, this exclusion zone is of the order of 100 $\mu$m. Tissues, polymers, monolayers, beads, and solutes of various kinds, have all been found to have exclusion zones of this range. The scale of this changed zone is astounding, and it has far-reaching consequences for surface–molecule interactions in a variety of fields in biology, physics, and chemistry, including cellular identification, biomaterial–surface antifouling, bioseparation technologies, and others. Solute–free zones, also known as ”exclusion zones,” are also found next to various metals. These unexpected interfacial exclusion zones may provide new insight into electrochemical processes at metal interfaces.

# Chapter 1

# Introduction

## 1.1 Recent attempts to account for water’s behavior

Over the past three decades, there has been a sustained research activity in how water molecules behave. The seminal and pioneering work of some prominent research labs of how water molecules interact with one another are presented as follows.

- Frank and Wen developed the ”flickering cluster” concept in 1957. Clusters of water molecules form from the surrounding water in this model. Positive feedback causes clusters to expand to a critical size before dispersing spontaneously. The clusters ”flicker” and everything happens on a time scale of $10^{-10} to 10^{-11}$ seconds.

- Liquid water, according to Martin Chaplin, is made up of two groups of nanoclusters that are intermixed. One of them is more stable and well-structured. Water molecules quickly transition between these two stages, but the average number of molecules in each group remains constant under any given set of conditions.

- Anders Nilsson and Lars Petterson suggest a paradigm in which two types of water coexist: ice-like clumps and a disordered form surrounding it.

- Emilio del Giudice’s model is distinguished by a much broader clustering size. He proposes domains of water, based on quantum-field theory.

- Water, according to Gene Stanley, has two distinct states: low density and high density. In supercooled water, the difference is most noticeable. Water with a low density has an open tetrahedral structure, whereas water with a high density has a more compact structure.

- Pershin, Shinitzky and Scolnik have proposed two-state design which highlights the possibility of mirror images of water molecules. They assume water molecules to be left handed and right handed.
- Rustum Roy, a late materials science pioneer, proposed the most structurally complex model, based on water exchange mechanism and water's heterogenous nature.

The most of these structures have one thing in common i.e. multiple states. While the general consensus is that liquid water has only one state, these models theorise an additional state.

## 1.2 Exclusion Zones in Water

Professor Gerald H. Pollack's laboratory at University of Washington, proposed that water molecules assemble into liquid crystalline arrays near hydrophilic surfaces, which can project spontaneously far from their nucleating surfaces. These liquid crystals, including ice crystals, exclude a wide range of compounds, from macroscopic colloidal particles to submicroscopic solutes. The term "exclusion zone" was coined because of the importance of this obstructive aspect.

The literature presented ahead builds on the proof for long-range ordering by revealing an EZ structure that looks eerily like ice. It is not, though, ice. The driving force for the EZ's accumulation of organised water turns out to be a type of energy that is normal in daily life and easy to comprehend.

Stacked dipoles were first considered, while creating a structural model of the exclusion zone. However, dipoles remain persistently neutral, they cannot account for the net charge of the exclusion zone. As a result, the dipole model was found to be ineffective. The honeycomb sheet model looked more promising, with its hexamers out of sync with those on neighbouring sheets. Because of its resemblance to ice, this model could account for the EZ's net charge.

Local charge in this stacked sheet model is determined by the density of electronegative oxygen atoms. As a result, local electrical potential will range from exceedingly negative

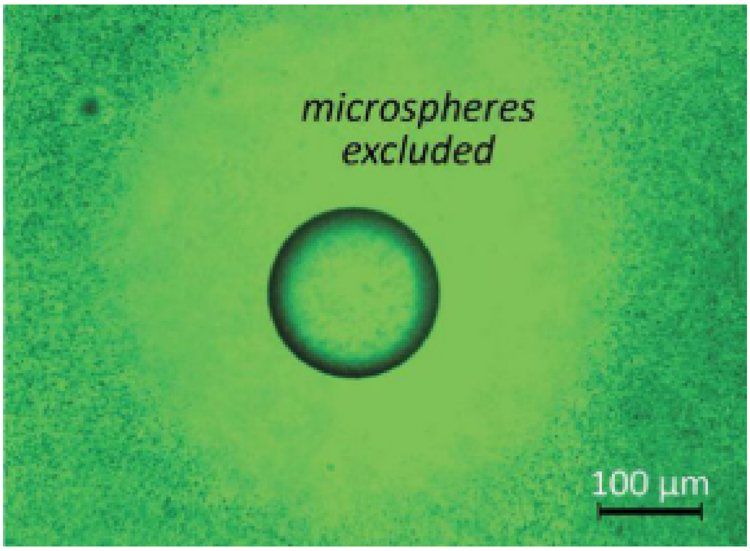


Figure 1.1: In an optical microscope, microspheres are seen being excluded from the vicinity of a charged gel bead.

to zero, even also into the positive values seen in certain exclusion zones. All types of exclusion zones can be accommodated by the basic structural structure.

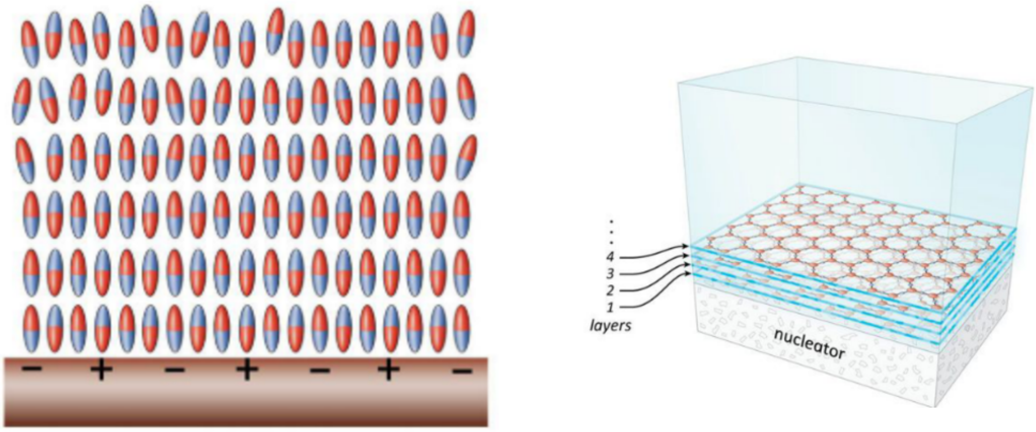


Figure 1.2: Water ordering model of stacked dipoles. Honeycomb planes shape from bulk water. EZ development begins on a hydrophillic surface and continues layer by layer. [14]

The hexagonal lattices in generic EZs are complete. Real EZs are less regular as they may lack oxygen and hydrogen atoms in places that represent the charge distribution of the nucleating surface, and they may be eroded. Exclusion zones seem to be large enough and distinct enough to be considered a different water phase. This ”fourth phase” is only now being recognised. The proposed EZ model’s ice-like properties are a key function. The EZ would have to meet certain conditions to count as a phase, it would have to be distinct and spatially bounded, and it would have to exist in a significant quantity. For the three classical states of water, these conditions seem to be met. They apply to the EZ as well: exclusion zones are bounded, have a distinct form, and can project up to a metre from a surface. The EZ seems to be as eligible for consideration as a process as ice. How does a structure made up of millions of layers of water molecules stretch millions of layers away from a nucleating surface? Hence, a system made up of stacked planes rather than stacked water dipoles was suggested. Each plane is large, and the larger the structure, the less thermal disturbance there is. As a result, any detrimental effects in the planar stack should be much less prominent than in the dipole stack.

Finally, the proposed structure explains why solutes are excluded and exclusion zones are formed. They exclude because solutes can only penetrate the EZ lattice through the hexagonal openings, and those openings are small. The actual stumbling block is even more formidable: the effective openings are narrower than the planar hexagonal openings since successive EZ planes are out of register. Since the lattice is so close, it is highly exclusive to solutes. Protons and smaller bodies are the only ones tiny enough to pass through.

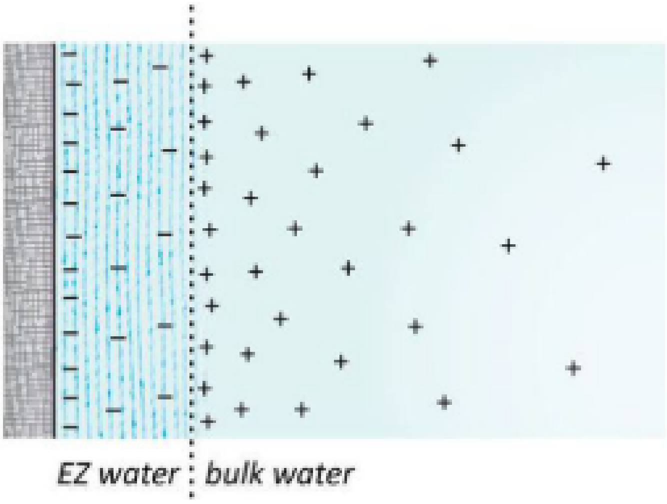


Figure 1.3: The EZ water battery is shown as a diagram. At the left is a hydrophilic surface. [4]

Protons, on the other hand, seldom exist as separate entities; instead, they attach to water molecules to form hydronium ions, which are much bulkier than protons and hence excluded. Protons are also released from those parent water molecules from where they can penetrate the EZ lattice and form ice later.Apart from those liberated protons, all solutes tend to be excluded, at least from lattice regions with no openings. The exclusion of even positively charged hydronium ions ensures that the electrical potential difference between the EZ and the water outside is maintained. Because of this, we can monitor the same potential difference over time. Most of what follows is affected by the continuous charge separation between the EZ and the bulk water zone beyond. A battery is made up of this charge separation.

### 1.2.1 A water battery

Exclusion zones exist in aqueous regions near hydrophilic surfaces. Those EZs are charge separators. A battery is made up of the separated charges. The EZ is one of the battery's poles, which is usually negative due to the abundance of oxygen atoms. The other pole is in the bulk-water region just beyond the EZ, and it normally consists of positive hydronium ions that can freely spread according to electrostatic laws. Many hydronium ions accumulate near the EZ boundary as they are drawn towards negativity.

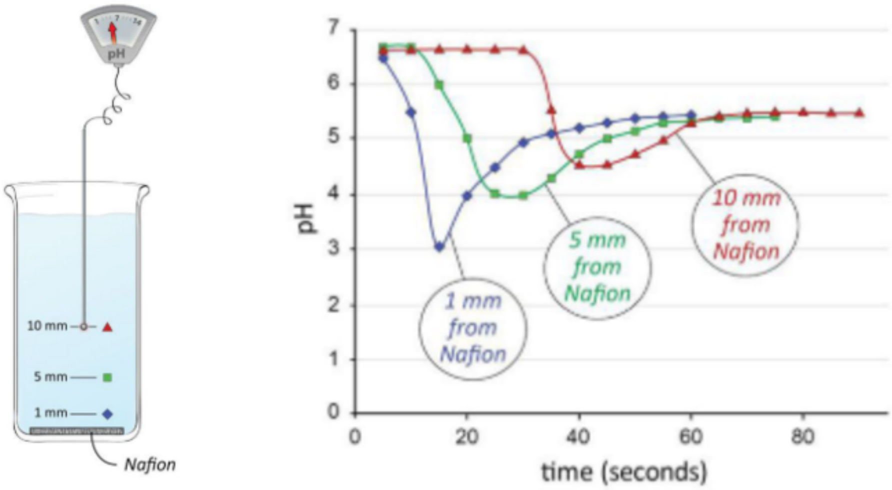


Figure 1.4: Following the addition of water to a layer of Nafion, the pH charge changes over time. As shown, pH was calculated at three points. [15]

### 1.2.2 Charging mechanism for this battery

Light energy, especially infrared, is used to establish the exclusion zone. And when the lights are switched off, infrared energy is visible. Acoustic energy may also be used for this purpose. These energies are likely to dissociate bulk-water molecules, allowing them to form the EZ. The freed water molecules are drawn toward the growing EZ by charge attraction and assemble onto the lattice. This causes EZ growth and charge separation as a result. The interfacial battery is charged in this manner.

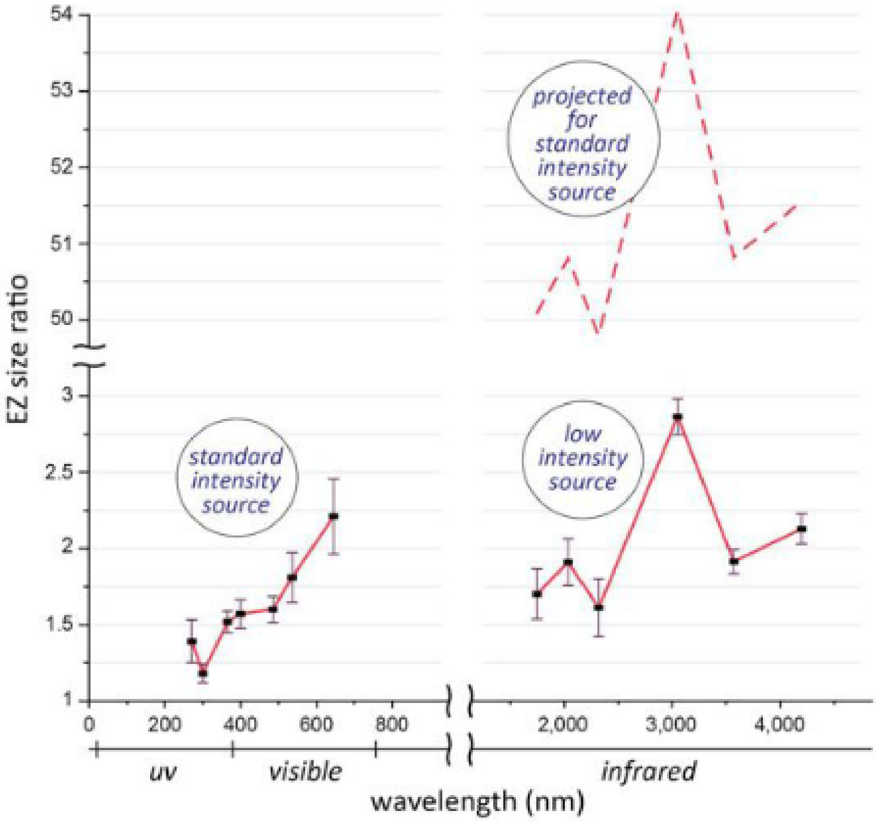


Figure 1.5: The wavelength of incident light has an effect on EZ growth. The EZ size ratio is the EZ size at the end of a five-minute time period. [15]

The EZ assembly method answers the question of how EZ charges can stack so tightly. Negative charges repel each other, so the EZ can fly apart naturally. Electron clouds, on the other hand, adhere each new element to the growing lattice, maintaining its integrity.

## 1.3 Alternative Expositions to EZ phenomena

Diffusiophoresis, proposed by Schurr and Vanderwaals forces have been sought as alternative explanations to the EZ phenomena.

### 1.3.1 Diffusiophoresis

According to Schurr (2013), forces resulting from concentration gradients of OH- or H+ and salt cause the EZ formation. Schurr refers to it as "long range chemotaxis," and it is a kind of diffusiophoresis, a more common and well-known phenomenon in colloid science. According to Huyghe, Wyss, and colleagues (2014), EZs are generated by a combination of ion exchange and diffusiophoresis. They point out that Nafion has a large supply of exchangeable protons available to swap with cations in the solution. An inhomogeneous distribution of ions (salt gradient) in the liquid will result from such an exchange.

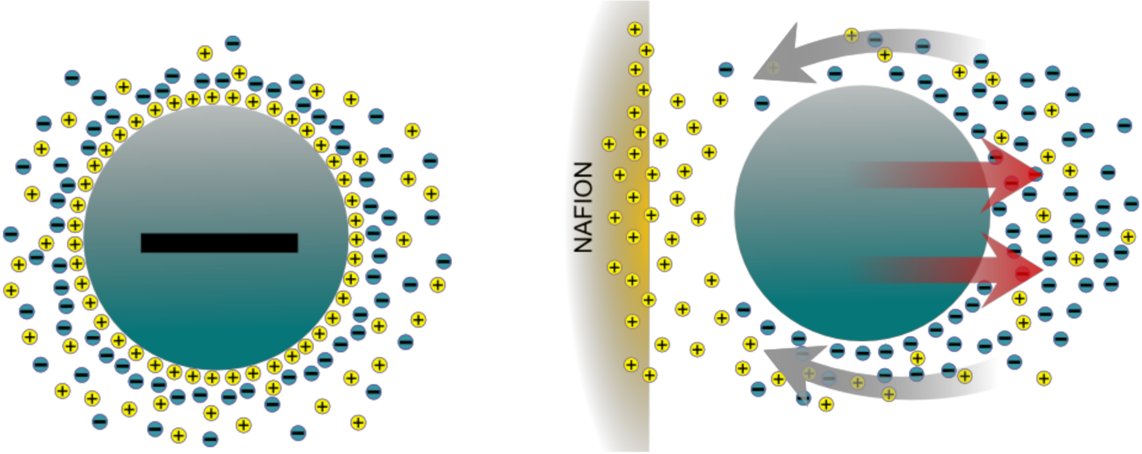


Figure 1.6: The figure shows homogeneous case on the left and heterogeneous case on the right, resulting to diffusiophoresis . [12]

A charged particle in an electrolyte solution will attract counter-ions through the effect of the local electric field, according to the diffusiophoresis principle. A symmetrical distribution of ions and counter-ions around the particle will be required in a homogeneous solution. T his will result in a uniformly distributed hydrostatic pressure with no fluid flow. However, when a proton donor such as Nafion is introduced, the resulting heterogeneous charge distribution results in an imbalanced arrangement of ions around the molecule.A fluid movement occurs as a result of the attempt to coordinate ions and counter ions, advancing the particles farther from the Nafion layer.

### 1.3.2 Van Der Waals Repusion for metal surfaces

The exclusion zone phenomena has been reported next to metal surfaces as well by the Pollack's group. There are possibilities that this exclusion zone phenomena near metals can be explained to some extent, by repulsive van der Waals forces. In this context, they can be Casmir-Polder forces.

Hamaker (1937) was the first to recognise that two objects of different compositions could experience a repulsive force when immersed in a liquid. Lifshitz established a complete theory for such forces in arbitrary dielectric media in 1954. If the dielectric susceptibility of the medium seen between two plates is intermediate, Lifshitz's equations provide for a repulsive force through them. Calculations based on the Lifshitz principle show that the slabs' finite size has no impact on their repulsion. Metals have an incredibly high dielectric constant due to the presence of free electrons. Water has a dielectric constant of 78, whereas a polystyrene microsphere has a dielectric constant of around 2.5. As a result, the metal-microsphere-water mechanism obeys the Casmir Pollard repulsion conditions.

# Chapter 2

# Non-Metal Hydrophilic Surfaces

## 2.1 Introduction

The properties of the near-surface aqueous region must be understood in order to consider how solutes interact with surfaces. Surface features inside such aqueous zones can be detected by solutes. Despite the fact that size-dependent depletion effects in colloidal systems studied in confined spaces can span many particle diameters, interactions are thought to fall off within nanometers of the surface. Solutes in this small zone are believed to be mostly blind to surfaces. The older literature, on the other hand, discusses the effect of surfaces over far longer distances. Numerous experimental studies showing remarkable long-range surface-induced ordering of different liquids, including water, are cited in a 1949 analysis by Henniker [3]. Nobel Laureate Albert Szent-work Gyorgyi's work on long-range water ordering is also noteworthy.

Two recent papers have raised the question of long-range effects once again. On theoretical grounds, Ling (2003) contends that water ordering could stretch virtually indefinitely under some ideal conditions, while Roy et al. (2005) argue for long-range ordering based on precedent in materials science. How water molecules could be restricted to achieve such order is one barrier to any thought along the lines of potential long-range water ordering. Water molecules can readily adsorb onto hydrophilic surfaces through hydrogen bonding, but due to the disruptive effects of thermal motion, additional ordering conferred by subsequent hydration layers that build upon the first is generally thought to quickly give way. Although there is sufficient experimental precedent for long-range ordering, there is no evidence that such ordering could apply over long distances.

To achieve such long-range stability, either the hydrogen-bond energy that holds molecules together must be higher than expected, or the thermal motion that tends to tear them apart must be weaker than expected. Observations on colloidal microspheres in aqueous suspension support the latter possibility i.e. random and crystalloid phases coexist in microsphere suspensions where the volume ratio is less than one.

Thermal motion is of the expected magnitude in the random phase, but in the crystalloid phase, even though microspheres are clearly separated from one another by many micrometres, r.m.s displacements are an order of magnitude lower. As a result, the destructive effects of thermal motion in ordered regions may be lower than previously thought, and this property may predispose molecules to long-range ordering.

Exploring the local disposition of solutes is one way to investigate the interfacial zone. Many solutes should be excluded if such interfacial water is truly in the ordered, liquid crystalline state. Colloidal solutes are removed from the near-surface zone of various gels by distances on the order of $100\mu$m.

## 2.2 Observations and discussion of the experiments

### 2.2.1 How general is exclusion zone phenomenon?

To prove the generality of this phenomena, various examples of exclusion are shown next to a number of surfaces. figure 2.1(a) depicts the behaviour of microspheres in aqueous suspension following exposure to a polyacrylic-acid gel surface for a few minutes. The microspheres were initially scattered in the aqueous process. They gradually converted away from the gel surface, forming a particle-free zone that expanded at a rate of $1\mu$m/s, eventually leaving a stable $250\mu$m-wide particle-free zone. Since the polyacrylic acid gel has a charged surface, comparable findings could be obtained for non-charged polyvinyl alcohol gels, meaning that surface charge is not needed for exclusion.

Exclusion does not occur only in the case of artificial gels, but also in the presence of biological tissues. Microsphere activity in the vicinity of a representative biological specimen i.e. a muscle is depicted in figure 2.2(b). Unlike particle-free exclusion zones found around artificial gels, the exclusion zone here was not absolute; it included certain microspheres, but in much lower concentration than in zones farther out. Using both microspheres and erythrocytes, exclusion areas have been seen adjacent to collagen gels and vascular en-

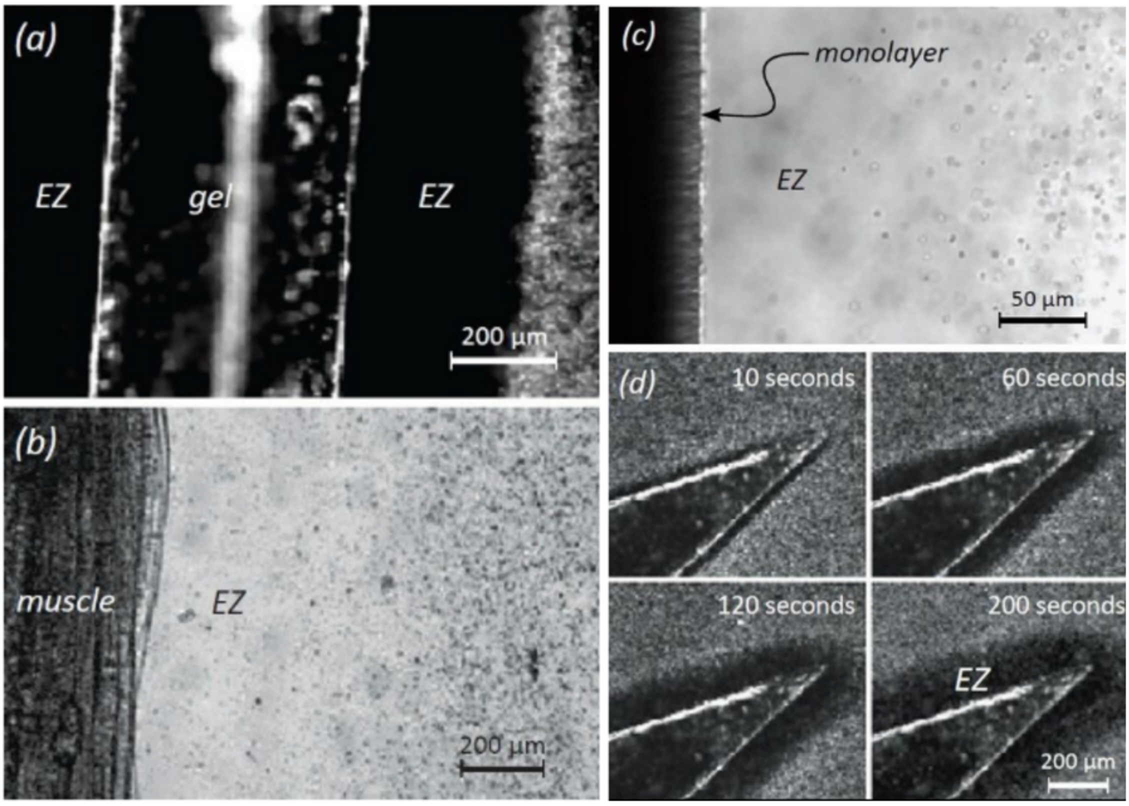
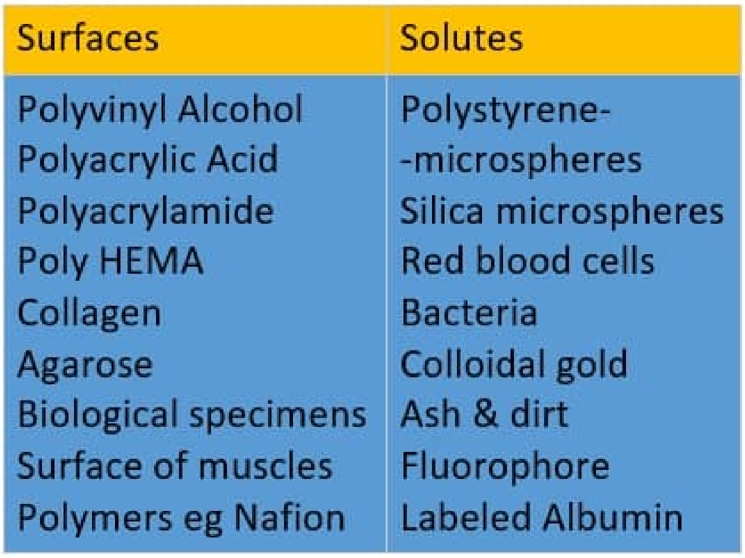


Figure 2.1: Exclusion besides (a) PAA gel, (b) a muscle, (c) a monolayer,and (d) Nafion polymer. [1]

dothelium as well.

For 1$\mu$m carboxylate-functionalized microspheres that bear negative charge groups, an exclusion zone of 100$\mu$m can be seen. For amidine-functionalized microspheres, which have positive charge groups, a related exclusion zone was discovered. As a result, the polarity of the solute has no bearing.

Exclusion was also discovered near a hydrophilic monolayer. A half-cylindrical region on the outside of a glass capillary tube was filled with a COOH-terminus monolayer. There was no exclusion on the side without the monolayer, but there was distinct exclusion on the side with the monolayer, as seen in figure 2.1(c). The ionomer Nafion is used in a variety of applications, including electrodialysis as a proton-exchange membrane, fuel cells as a proton conductor, electrolytic cells as a separator, and mechanical actuators. It was chosen as a study subject because many of its functions are dependent on contact with water. Microspheres moved away from the edges of the Nafion layer at a rate of 2$\mu$m/s, leaving a 600$\mu$m exclusion zone in less than 10 minutes.



| Surfaces | Solutes |
|---|---|
| Polyvinyl Alcohol | Polystyrene- |
| Polyacrylic Acid | -microspheres |
| Polyacrylamide | Silica microspheres |
| Poly HEMA | Red blood cells |
| Collagen | Bacteria |
| Agarose | Colloidal gold |
| Biological specimens | Ash & dirt |
| Surface of muscles | Fluorophore |
| Polymers eg Nafion | Labeled Albumin |

Figure 2.2: Various solutes and solvents showing EZ phenomena.

The findings demonstrate that the exclusion mechanism does not necessitate the use of a gel; all that is needed is a surface with hydrophilic moieties.

### 2.2.2 Some particular physical aspects of the exclusion zone

The discovery of solute-exclusion zones is unprecedented to our knowledge, wherein some long-range results have been identified. Inter-facial effects are expected to range no farther than nanometers from surfaces according to normal DLVO theory, but the results above suggest repulsive interactions between surfaces and solutes reaching up to six or seven orders of magnitude further. Furthermore, it was discovered that both positively and negatively charged microspheres were excluded from the same surface in certain cases.

Another explanation is that the exclusion zone is a separate phase of water that keeps solutes out. The fact that solutes of various sizes and characteristics are omitted, ranging from colloidal microspheres to small molecular weight pigment, supports this theory.

### 2.2.3 Potential Measurement

To see if the solute-free phase is mechanically distinct from the solute-containing phase, measurement of potential gradients was done to see if there were any variations between exclusion and bulk water. The potential profile in the vicinity of Nafion and polyacrylic acid-gel surfaces was measured using standard microelectrodes. The potential difference was negligible since the probe tip was just outside the exclusion zone limit.

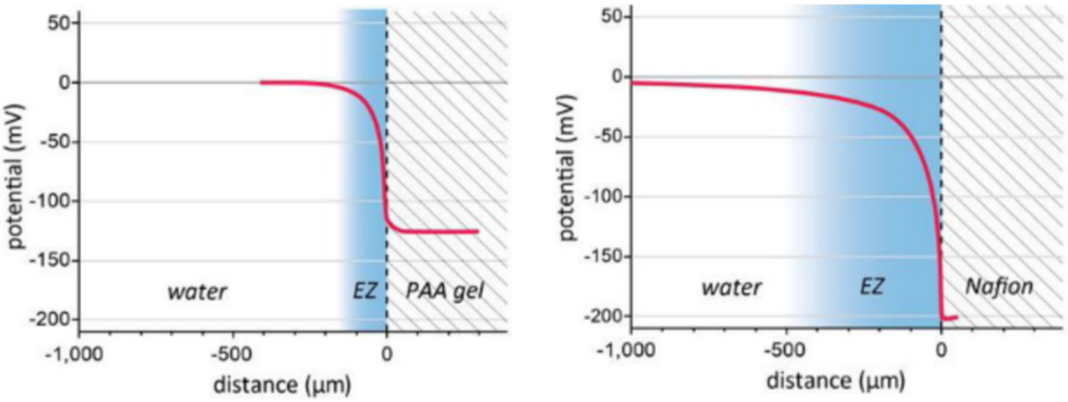


Figure 2.3: Near a PAA gel and a Nafion layer, electrical potentials were measured.

Negative potentials started to be registered as the probe got closer to the surface, and their magnitude grew as the probe got closer to the surface. The magnitude just outside the polyacrylic acid gel was 120 mV, and it remained stable at that value as the probe progressed within the gel. The magnitude increased to (negative) 160 mV at the gel surface in the case of Nafion. Non-zero potentials could be observed far from the surface of both cases: within 200 $\mu$m in the case of the gel, and often beyond 1 mm in the case of Nafion.

As a result, sustained potential gradients can be found within the exclusion region, but no such gradients can be found outside of it. Exclusion-zone molecules tend to be stable structures that are completely devoid of mobile charge carriers as a result.

### 2.2.4 Spectrophotometer

The physical character of the exclusion zone was also investigated using UV–Vis absorption spectrum measurements. One of the four vertical faces of a regular cuvette was bonded with a sheet of Nafion, which was then filled with distilled, deionized water. The Nafion surface was parallel to the optical axis when the cuvette was placed. Incident light was passed through vertically focused slits mounted before and after the cuvette, as shown in figure 2.4(b). The spectrum was flat far from the surface, as shown in figure 2.4(a), with no noticeable difference between the measured spectrum and a blank water sample. As the illuminated window got closer to the Nafion, however, a peak appeared at 270 nm. With increasing proximity to Nafion, the peak grew larger and gradually dominated the spectrum.

As a result, the interfacial zone's absorption characteristics vary significantly from those of the bulk zone.

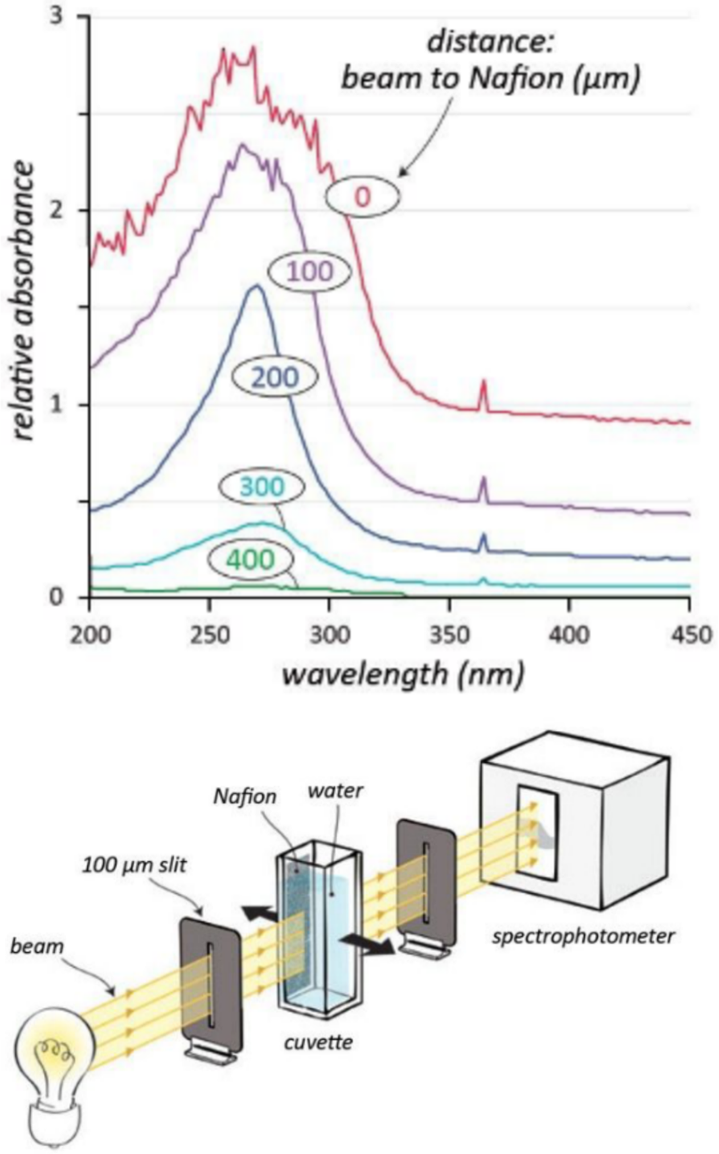


Figure 2.4: Absorption of light measurements. Probing water at different distances from the Nafion surface is made easier by moving the cuvette laterally. At different distances from the Nafion-water interface, the absorption spectrum was measured. [1]

### 2.2.5 Infrared Radiation Imaging

Examination of infrared emission with a high-sensitivity, high-resolution infrared camera was a third way to investigate the physical character of the exclusion zone. A Nafion sample was put in a shallow, water-filled chamber and left to equilibrate at room temperature for

1 hour. To minimise gradations in overall image brightness, infrared radiation from the sample was averaged over several image frames and high-pass filtered.

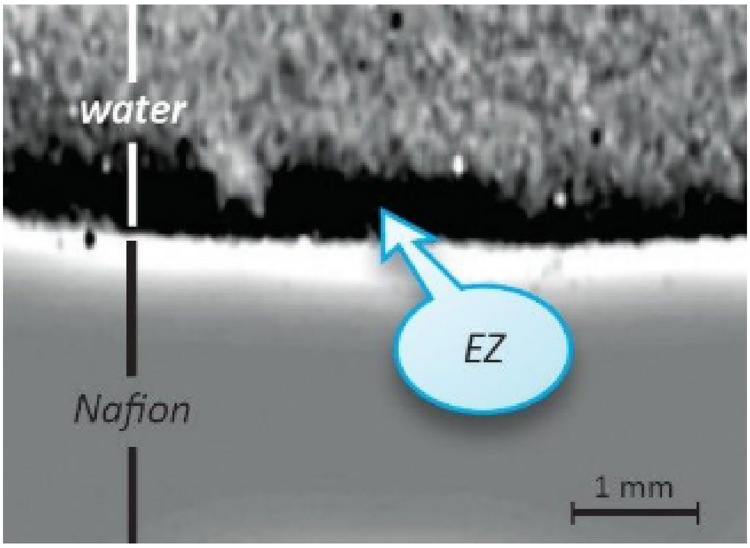


Figure 2.5: Nafion's infrared emission image, next to water. [2]

The results show that the aqueous region directly adjacent to the Nafion radiates very little (dark), while the aqueous region further away radiates normally (bright). The dark zone extends 0.3–0.5 mm from the sample surface, which is equivalent to the exclusion zone's dimension. Temperature and structure influence the intensity of infrared radiation. The former is unlikely to play a significant role because it is difficult to imagine sustained temperature gradients over limited spatial regions, particularly when records are averaged over long periods of time. As a result, the (dark) non-radiating area appears to lead to a more stable structure with a lower emissivity, resulting in less radiation than ordinary bulk water.

### 2.2.6 Magnetic Resonance Imaging

Magnetic resonance imaging was used as the fourth process, where a map of apparent transverse relaxation time (T2) was obtained from a multi-echo imaging sequence.

The apparent T2 value in the gel is 30.2 +/-0.3 ms, 27.2 +/-0.4 ms in the bulk water phase, and 25.4 +/-1 ms in the interfacial area. The interfacial area has a thickness of about 60 $\mu$m, which is comparable to the size of the exclusion zone found with the specific gel (PVA). The apparent T2 in the gel phase was significantly shorter than that in the bulk water phase for lower resolution images obtained on such specimens. Water molecules at the interface seem to be restricted.

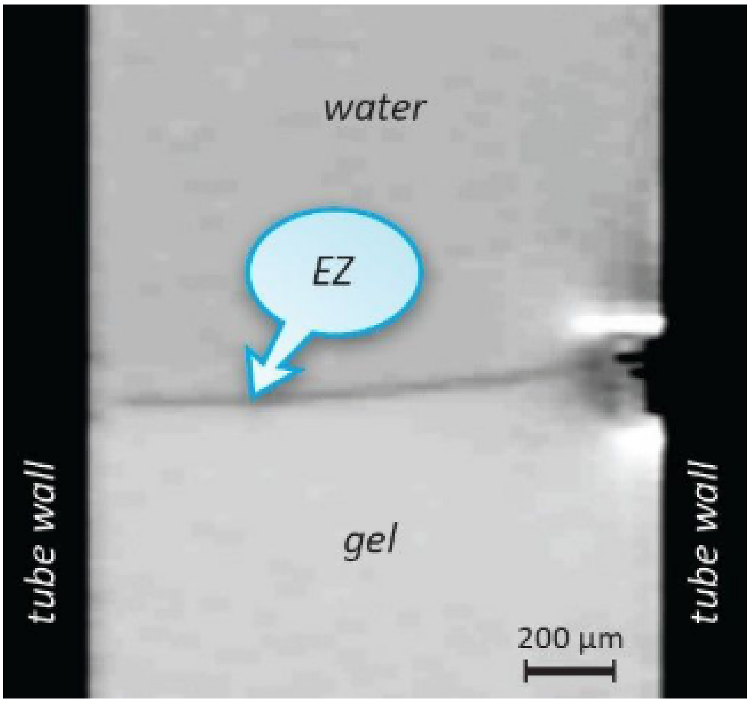


Figure 2.6: Relaxation times on an MRI chart. PVA gel was used in the lower half, while water was used in the upper half. More molecular restriction is shown by the dark band corresponding to the gel's EZ. [2]

The evidence provided shows that water in the interfacial region differs from bulk water in many ways, and that this region stretches over vast distances. Furthermore, the findings of both IR imaging and MRI strongly indicate that water molecules in the interfacial zone are much less mobile than water molecules in the bulk phase.

## 2.3 Conclusions

The discovery of vast zones of water with restricted mobility has far-reaching implications for biology, biotechnology, and other fields. Indeed, the probability of water being influenced by surfaces raises the issue of complementary entities such as enzymes–substrates, antigens–antibodies, and so on being recognised over long distances.

The current findings foreshadow the restriction process and point the way for a better understanding of the origins of low friction. Understanding that even relatively dilute suspensions of colloidal solutes converge into quasi-regular arrays may be due to the abundance of mobility-limited water surrounding these particles in the field of colloid chemistry.

If this is the case, water organisation around charged surfaces could be a key factor in biological and bio-inspired self-organization. The existence of solute-exclusion zones around gel beads in various popular bioseparation technologies, such as chromatography, raises questions about the conventionally accepted separation mechanism; understanding the function of solute exclusion could lead to significant technological advances. Finally, the exclusion phenomenon observed here may be the source of anti-fouling agents against various biofilm formations and their applications to common biomaterials.

In conclusion, hydrophilic interfaces play a larger role than previously thought. Solutes in aqueous suspension are extensively removed from the vicinity of several interfaces, and the evidence provided here supports the theory that such exclusion results from long-range restriction of water molecules nucleating at the interface and projecting deep into the aqueous phase, as in liquid crystals.

# Chapter 3

# Metal Surfaces

## 3.1 Introduction

There has been an increased recognition that more attention needs to be paid to the area of interaction of water with metal surfaces. In just the past few years, not only this has emerged as a phenomenon of exceptional interest for research work in the first few water layers adjacent to metal surfaces, but also has raised a number of open questions regarding metal surfaces.

Literature survey ahead is aimed to look at and identify positively charged exclusion zones of a significant size next to a variety of reactive metal surfaces. Such zones did not appear in nobler metals like platinum and gold. The existence of these zones may have a direct impact on our understanding of electrode materials, electrochemical processes, and biochemical reactions on metal surfaces.

## 3.2 Literature Review of experimental procedures

In this section, I present an overview of literature of work done on metal surfaces. Zinc, aluminium, tin, lead, tungsten, copper, platinum, and gold were among the metal foils used. The thickness of each of the metal foils varied from 0.125 mm to 0.25 mm. The experiments were conducted at room temperature. [6]

Various 1-$\mu$m diameter functionalized microspheres were used to measure the extent of the exclusion zone. Carboxylate, polystyrene, amino, amidine, and fluorescent amine-modified microspheres were among the microspheres used.

## Observations

The rate of EZ growth varied depending on the type of metal. The exclusion zones are visible next to metal surfaces which are reactive while, metals such as platinum does not show any exclusion zone.

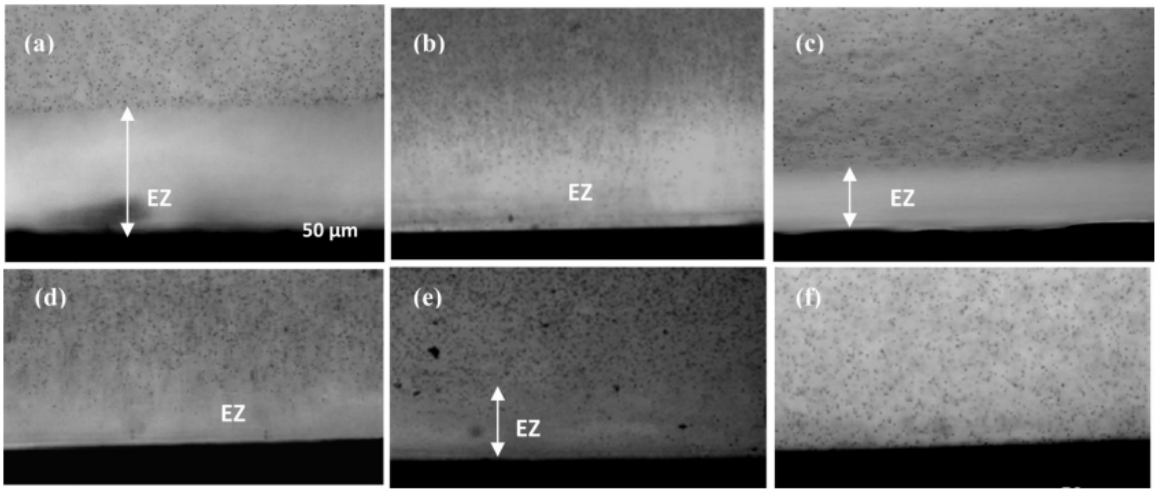


Figure 3.1: Exclusion zones next to different metal surfaces. (a) Zn (b) Al (c) Pb (d) W (e) Sn and (f) Pt. [7]

In certain areas, the EZ covered the entire zinc surface, while in others, microspheres collected near the metal surface between gaps. The results show that there is a lot of coverage, but it isn't total. Fresher samples, on average, appeared to have more full coverage than those that had been used and washed.

Microscopic measurements of the interaction between microspheres and surfaces near other reactive metal surfaces were made in addition to zinc. Exclusion zone width was in order of Zn, Al, Pb, Sn, W. Zinc had the largest size as well as fractional coverage.There was no EZ under the measurement conditions for gold and platinum.

The rate of growth of the solute-free zones varied depending on the metal. Figure 3.4 shows the rate of EZ growth near zinc as a function of time. The dynamics of EZ-growth were dependent on the metal.

Different types of functionalized microspheres were used to see whether EZ formation next to metal surfaces is an inherent feature of metal-water interaction, regardless of microsphere charge. Polystyrene which is negatively charged was used along with amino which is slightly negative at pH 5 and amidine which is positively charged at pH 8. The average EZ widths for the three microsphere groups were found to be approximately same i.e. on an

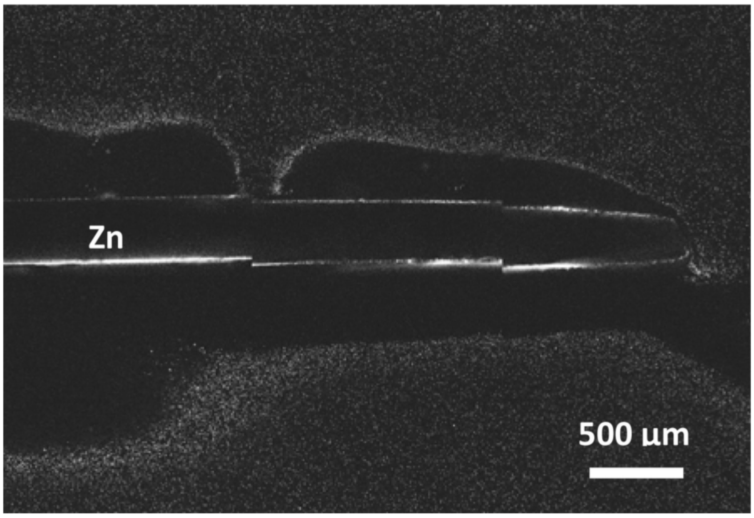
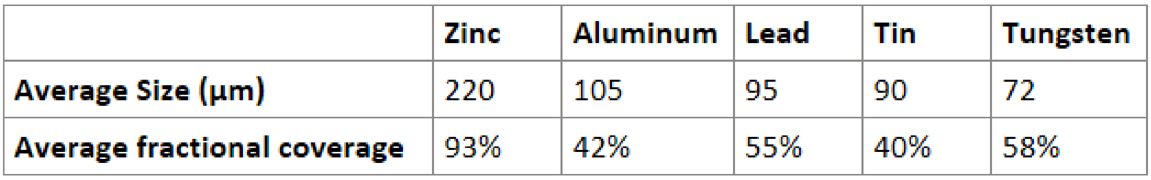


Figure 3.2: Picture of an exclusion zone near zinc taken with a confocal microscope. On one side of the zinc (below), the continuous EZ was seen, and on the other, the pockets of exclusion (above). [6]



| | **Zinc** | **Aluminum** | **Lead** | **Tin** | **Tungsten** |
|---|---|---|---|---|---|
| **Average Size (μm)** | 220 | 105 | 95 | 90 | 72 |
| **Average fractional coverage** | 93% | 42% | 55% | 40% | 58% |

Figure 3.3: With carboxylate microspheres, EZ width and fractional coverage were measured for different metals.

average of 220 m EZ width. As a result, the charge of the microspheres had only a marginal impact on the findings.

### 3.2.1 Electrical potential measurements

In the exclusion zones next to zinc and aluminium, the electrical potential distributions were calculated. Positive potentials started to register as the probe got closer to the zinc surface, with the magnitude increasing as the probe got closer to the surface. The potential was approximately +200 mV at the surface. The findings were less consistent in case of aluminium.

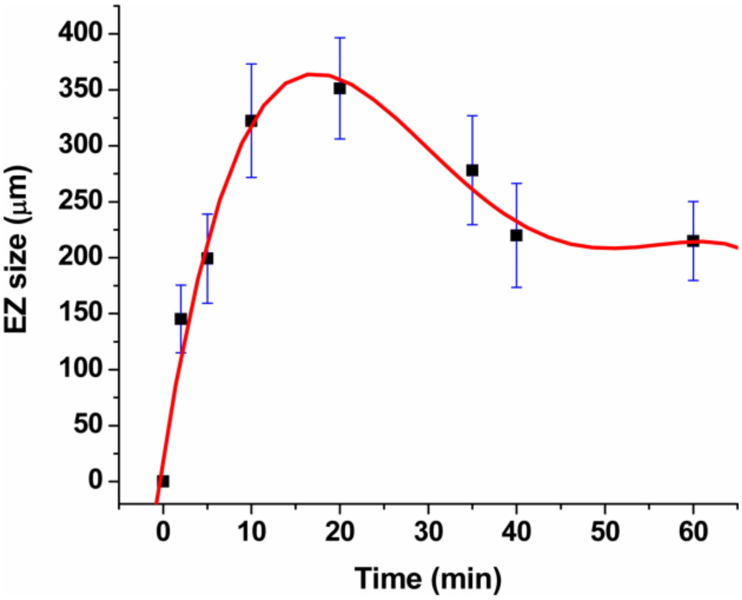


Figure 3.4: The width of the zinc EZ was measured over time using carboxylate microspheres. [7]

### 3.2.2 pH measurements

A pH indicator dye was used to visualise the pH distribution.Closer to the zinc surface, the dye colour (lines) is less intense, suggesting pH dye exclusion. Beyond these clearer areas, the colour is greenish or purplish, suggesting a high pH value. A pH probe was placed 5 mm beyond the metal surface to confirm the pH-dye effects, and pH values were also reported as a function of time, which showed that pH shifts were greater with zinc than with aluminium.

### 3.2.3 EZ and Oxidation

Since metals oxidise readily in the presence of water, a possibility of a connection between oxidation and the creation of exclusion zones was also looked. Surprisingly, the oxidation pattern matched the EZ distribution pattern very well. Oxidation strips were not present in cases where the exclusion zone remained consistent. Oxidation strips were seen in cases where pocket exclusion zones formed. As a result, there was a fair connection between the exclusion-zone trend and the oxidation pattern.

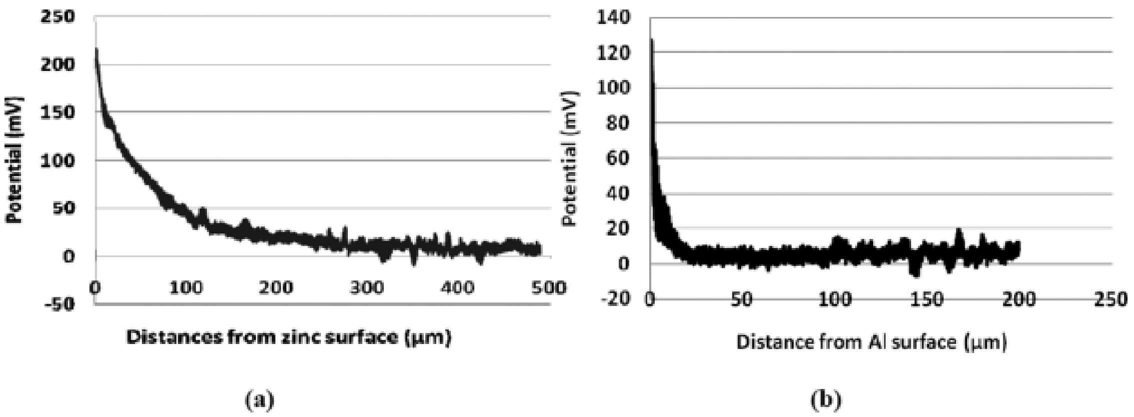


Figure 3.5: Potential distribution graph for zinc and aluminium [7].

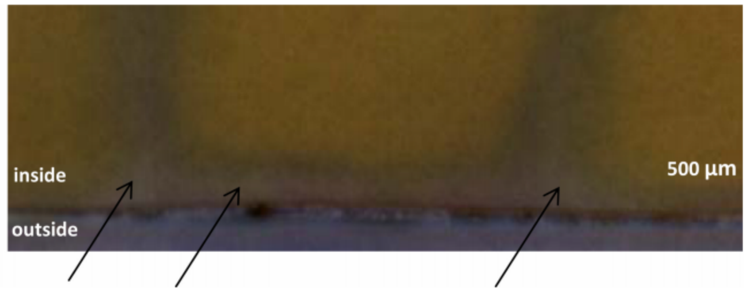


Figure 3.6: View of pH dye near a zinc surface at high magnification. Lighter regions are indicated by oblique arrows, suggesting dye exclusion. [7]

## 3.3 Conclusion

### 3.3.1 Exclusion zone next to metals

Exclusion zones occur next to a variety of metal surfaces were discovered. Zinc had the widest EZs and the most surface coverage of all of them. Other reactive metals had smaller areas and less coverage than the others. Noble metals like platinum and gold did not display apparent exclusion zones.

### 3.3.2 Charge separation mechanism

Positive electrical potentials were found next to zinc and aluminium in electrical potential measurements. If these are representative, these near-metal exclusion zones tend to be positively charged. As a result, the elevated pH values observed outside of those near-surface zones indicate a higher concentration of OH groups. Water molecules are initially neutral, but after some time, charges are separated.

There are no reactions at the metal surfaces when there is no separated charge, which is perhaps why noble metals are called noble. Since they don't react, they can also be used as electrodes. As a result, it appears that the difference between noble and reactive metals is whether or not they produce robust exclusion zones.

# Chapter 4

# Experiment

In this thesis work microsphere suspensions in water were infused around gels of various compositions. Solutes were kept out of areas that were 100 $\mu$m away from the gel base. The proof presented here demonstrates that solute-repulsion forces occur at far greater distances than predicted by standard theory. The findings suggest that solutes can interact over an unusually long range.

## 4.1 Methods and Procedure

Coated latex microspheres were analysed in the vicinity of polyvinyl alcohol gels to investigate the activity of solutes near hydrophilic surfaces. The gel was shaped around a glass cylinder in our setup. The cylinder was removed after gelation, leaving a 1 mm diameter tube. The optical axis was perpendicular to the cylinder axis and the tube was filled with an aqueous suspension of microspheres.

Polyvinyl alcohol (PVA) gels were made by freezing and deliquescing a 3/7 mixture of 10$\%$ PVA solution in water and 10$\%$ PVA solution in dimethyl sulfoxide (DMSO). A rectangular cube with a 1-mm cylindrical hole was created by injecting the mixed solution into a mould. Physical crosslinking was accomplished by freezing the solutions for 23 hours at 20 degrees Celsius, and then annealing was accomplished by exposing them to air at room temperature for 1 hour. This cycle was carried out four times in all. Finally, the gels were purified by immersing them in acetone and pure water five times each, and then storing them in a huge bath of pure water for at least two days. The resulting gels were translucent and had a refractive index that was almost identical to that of water.

Figure 4.1: The top right figure shows Polyvinyl alcohol (PVA), which is readily soluble in water and was used to make PVA gel. The bottom right image shows DMSO used. The left image shows 10% PVA solution in water and 10% PVA solution in dimethyl sulfoxide (DMSO), which was mixed further in 3/7 ratio to make a cylindrical gel.

Figure 4.2: The three images here are the gels made around a glass cylinder. The cylinder was removed after gelation. The optical axis of the microscope was perpendicular to the cylinder axis and the tube was filled with an aqueous suspension of microspheres.

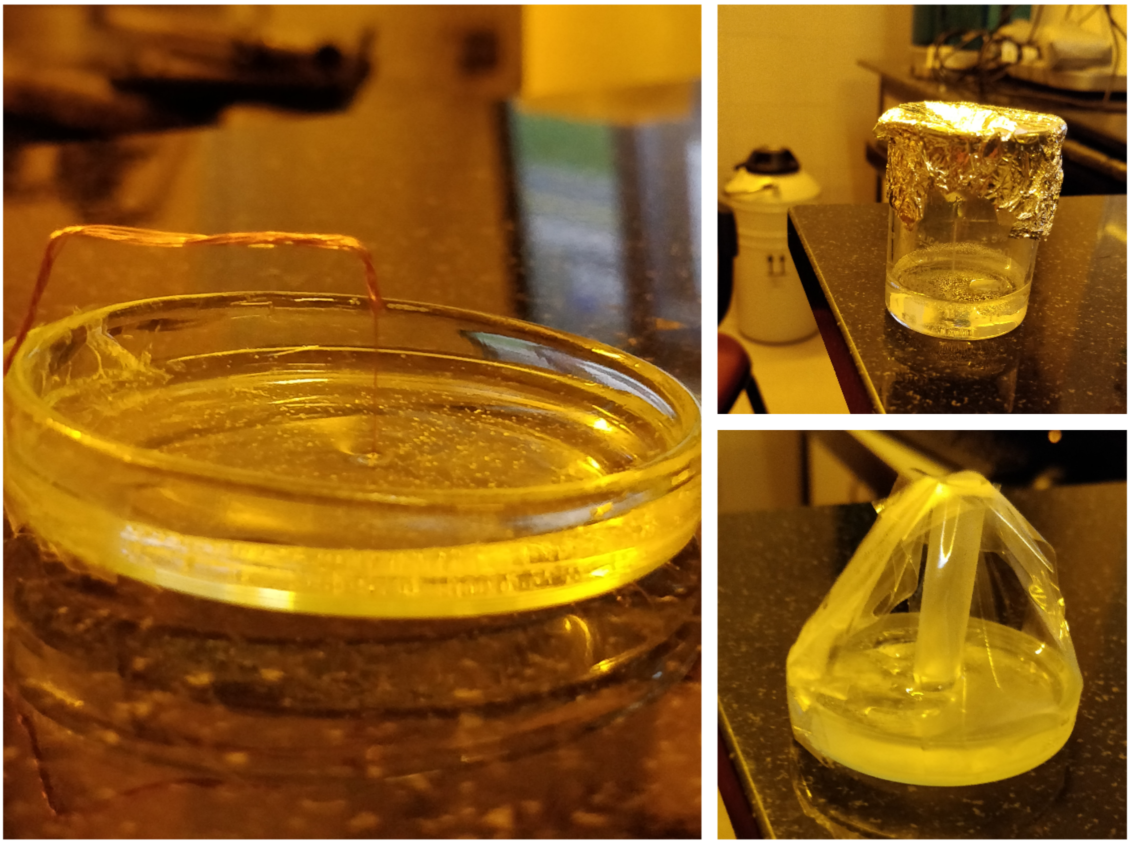


Figure 4.3: To reduce the diameter of the cylindrical hole, a wire was used as shown in figure on left. The 3/7 mixture was placed on magnetic stirrer using magnetic beads as shown in figure on top right. The bottom right figure shows the gel with a glass rod in the middle.

Polystyrene microparticles are colloidal particles with a negative charge. Polymerization of styrene under conditions that cause spontaneous coalescent bead formation produces the microparticles. When two chains react to form a sulfate-terminated polymer chain, polymerization is completed. These terminal sulphate groups are found on the particle surface, interacting with the aqueous phase.

Aqueous suspensions of latex beads were purchased Sigma-Aldrich, which were stored in the refrigerator until diluted for use in the tests. Microscopy was performed on a microscope stage with samples seen in bright field, typically with a 20x objective. Experiments were conducted at room temperature, with observations saved on a data disc.

Figure 4.4: Latex beads polystyrene.

# Chapter 5

# Results and Discussion

Microspheres were distributed non-uniformly in our experimental model. The area near the gel surface was almost entirely free of microspheres. Microspheres appeared evenly spaced and underwent fast thermal motion far from the surface. The distinction between exclusion and non-exclusion was usually clear—on the order of 10% of the exclusion zone's distance. The exclusion zone diameter for 2-$\mu$m carboxylate microspheres in pure water was normally 100 $\mu$m in the cylinder configuration.

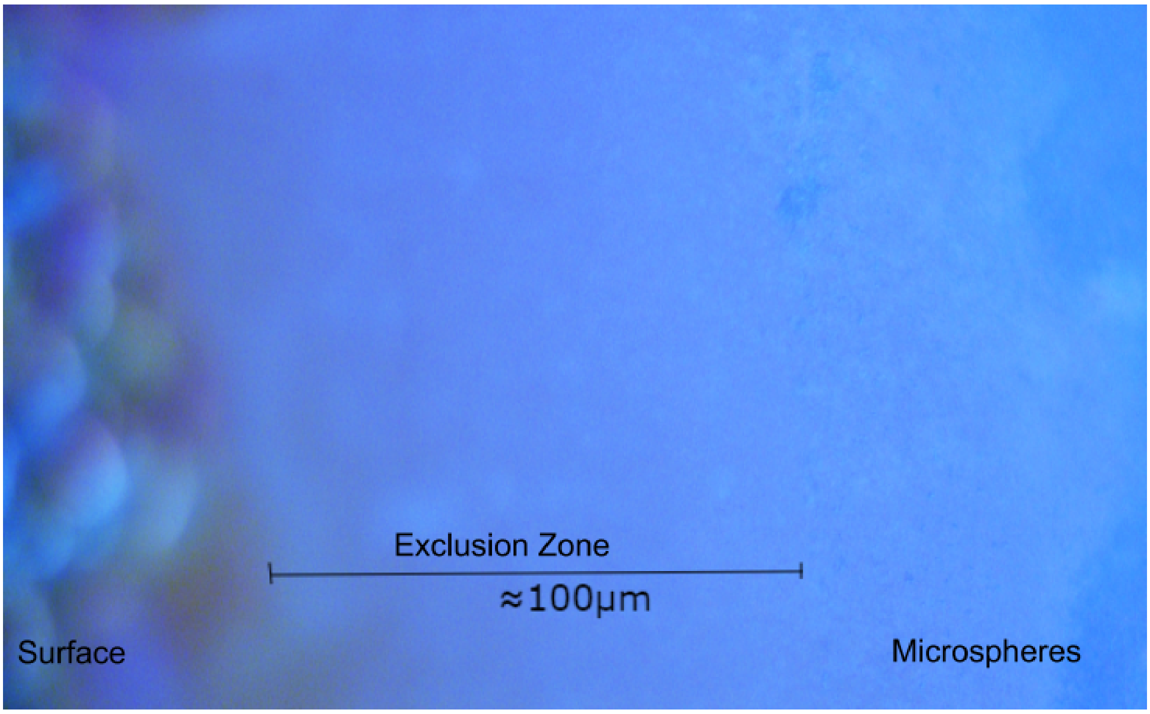


Figure 5.1: Results obtained using our configuration. The exclusion zone diameter for 2-$\mu$m carboxylate microspheres in pure water was normally 100 $\mu$m in the cylinder configuration.

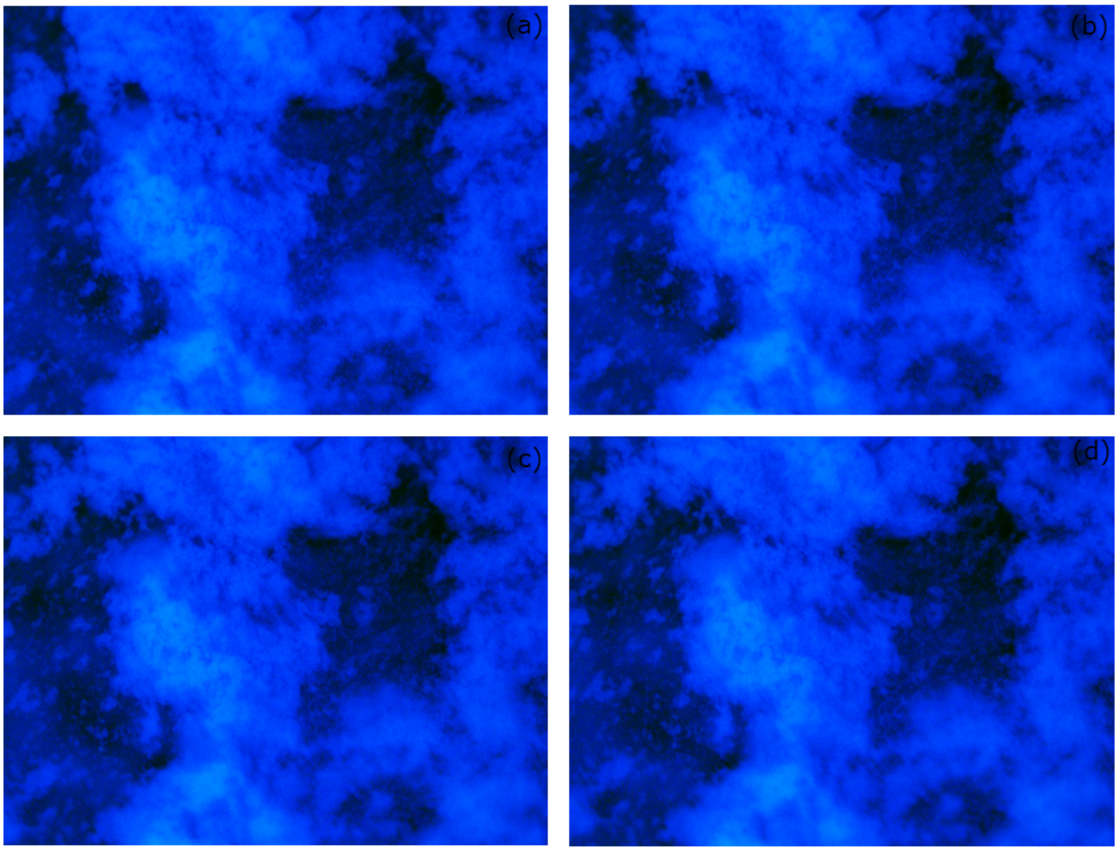


Figure 5.2: This figure shows a time series of particle movement over a period of time (a) 5 seconds (b) 10 seconds (c) 15 seconds (d) 20 seconds

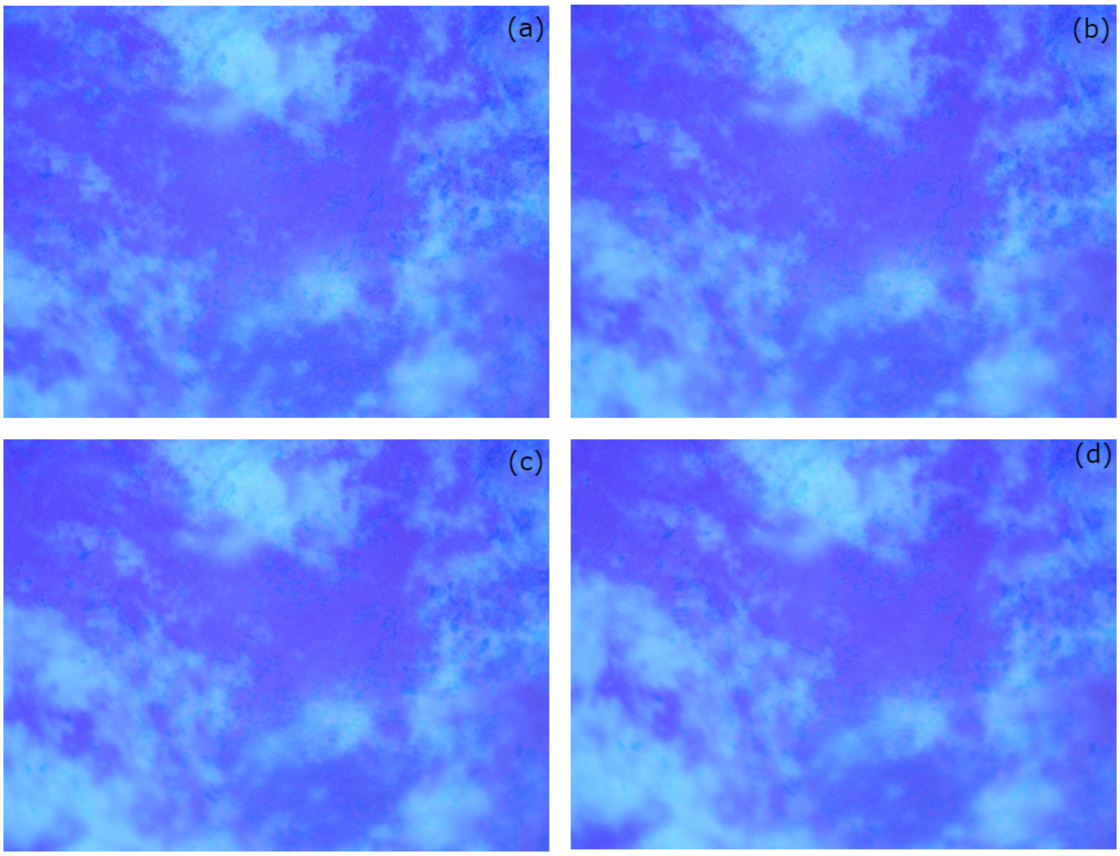


Figure 5.3: This figure shows a time series of particle movement over a period of time (a) 3 seconds (b) 5 seconds (c) 7 seconds (d) 10 seconds

# Chapter 6

# Conclusion

We looked at the effects of interfacial water on various non-metal hydrophilic surfaces in the previous chapters. A closer look at the data shows some large solute-exclusion zones (EZs) that stretch hundreds of micrometres below the surface. Various gels, polymers, monolayers, and biological specimens have been used as surfaces. The water in the exclusion zone is more ordered, it moves less than the bulk water and has physically distinguishable characteristics. The existence of interfacial exclusion zones adjacent to these surfaces also led us to study the exclusion zones coexisting with other solid surfaces, such as metals.

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