The magnitude of the work function to bring an electron from a metal into the exclusion zone water layer making hydrophilic contact with the metallic interface is theoretically computed. The agreement with recent experimental measurements is satisfactory.

PACS numbers: 82.47.Jk, 82.47.Uv, 84.60.Jt

I. INTRODUCTION

When bulk water is in contact with a hydrophilic metallic interface, the water shows an exclusion zone ordered water layer that repels large objects such as colloidal particles and even heavy ions but can carry extra semi-conducting electrons\[1, 2\]. The exclusion zone layers are sensitive to electromagnetic radiation\[3\] at least when in contact with hydrophilic organic substrates. The same should hold true for metals. While there are many works on the water-metal interface without considerations of the layer of exclusion zone water, the understanding how electromagnetic radiation with a metallic surface immersed in water remains incomplete\[4–11\].

The situation changed when experiments\[12\] were performed yielding data on the work function required to bring an electron from the metal into the water. Our purpose is to theoretically explain the magnitude of the work function required to bring an electron from a metal into the exclusion zone water layer making hydrophilic contact with the metallic interface. The agreement between theory and experimental data is satisfactory.

II. POLAR WATER MOLECULE

Water molecules in the ideal vapor phase have a static polarizability\[13\] of the form

$$\alpha_T = \alpha_\infty + \frac{\mu^2}{3k_B T},$$

where

$$\alpha_\infty \approx 1.494 \times 10^{-24} \text{ cm}^3,$$

$$\mu \approx 1.855 \times 10^{-18} \text{ Gauss cm}^3.$$  

The value of the dipole moment is often incorrectly associated with a thermal mean dipole moment but this must thought through more carefully since in virtue of tumbling motions the thermal dipole moment is null. The polarizability is given in ideal gas statistical thermodynamics

$$p_n = e^{(F - E_n)/k_B T},$$

wherein \(p_n\) is the probability of the molecule being in state \(|n\rangle\) and \(d_{nm}\) are the electric dipole matrix elements.

Define the restricted double sum

$$\sum_{nm} = \sum_{nm} \text{ restricted by } |E_n - E_m| \ll k_B T.$$  

Eqs.\(1\) and \(2\) imply

$$\mu^2 = \sum_{nm} p_n |d_{nm}|^2 \equiv |\langle d \rangle|^2 < \langle |d|^2 \rangle.$$  

with the inequality applying in virtue of the finite but small value of \(\alpha_\infty\). Eq.\(1\) defines the experimental electric dipole moment \(\mu\) of a single water molecule given that \(\langle d \rangle = 0\) due to parity and/or time reversal symmetry.

III. EXCLUSION ZONE WATER

Metal surfaces tend to be hydrophilic. Water is a liquid ferroelectric\[14\]. The mean polarization

$$\mathbf{P}(r) = \left( \sum_k \mathbf{d}_k \delta(r - r_k) \right)$$

is the order parameter for ferroelectricity in water. The water layer adjacent to the metal is thereby ordered with a structure in the polarization \(\mathbf{P}\) characteristic of a ferroelectric boundary. The ferroelectric order is illustrated below in FIG.\(1\). Large objects of micron length scales are excluded from the ordered layer since such objects would destroy the polarization which would require a positive free energy to destroy ferroelectricity\[15, 16\]. Also excluded in the ordered water layer are positive ions and some other effectively large charged objects.

What does exists in the ordered exclusion zone water layer are extra electrons described in chemical terms as \(OH^-\). Some protons \(H^+\) get absorbed into the metal leaving behind a net negatively charged exclusion zone.
FIG. 1: Shown in a schematic fashion is the up-down ordering of the dipole moment per unit volume $P$ near a boundary of a liquid ferroelectric\[10\]. This is the ordered structure of the exclusion zone hydrophilic layer near a liquid ferroelectric water metallic interface.

TABLE I: Work Functions into the Vacuum and into Water

| Metal | $W_{\text{vacuum}}$ | $W_{\text{water}}$ |
|-------|---------------------|-------------------|
| Pt    | 5.5 eV              | 2.1 eV            |
| Au    | 5.2 eV              | 2.3 eV            |
| Cu    | 4.7 eV              | 2.1 eV            |

Experimental determinations\[12\] of the work $W_{\text{vacuum}}$ required to move an electron from the metal into the vacuum and the work $W_{\text{water}}$ required to move an electron from the metal into the exclusion zone layer of the water.

layer. But other extra protons yield a positive charge beyond the water metal interface exist above the boundary of the exclusion zone layer perhaps a few hundred microns away from the metal water interface. The negative charged region which is the exclusion zone layer increases with the incidence of electromagnetic radiation wherein a battery voltage exists between the positively and negatively charged regions within water.

IV. WORK FUNCTIONS

Experimental determinations were discussed\[12\] for the work required to move an electron from the metal into the vacuum $W_{\text{vacuum}}$ and from the metal into the exclusion zone layer of water, $W_{\text{water}}$. These measurements have been listed in TABLE I. The ordered polarized state of water has molecules which are in a coherer superposition of these two states\[17\] with matrix elements of the dipole moment $d_{10}$ which may be taken to be a real dipole vector. The state $|0\rangle$ is in an electronic $s$ state forming a scalar while the first excited state $|1\rangle$ is in an electronic $p$ state which is thereby triply energy degenerate forming an electric dipole vector. This dipole vector may coherently rotate within an ordered fluid domain.

V. CONCLUSION

Our purpose was to theoretically explain the magnitude of the work function required to bring an electron from a metal into the exclusion zone water layer making hydrophilic contact with the metallic interface. Under the assumption of quantum coherent polarization ordered domains\[14, 17\] in the exclusion zone layer, the agreement between theory and experimental data is satisfactory.

Acknowledgments

J. S. would like to thank the United States National Science Foundation for support under PHY-1205845.
[1] J. Zheng and G.H. Pollack, Phys. Rev. E 68, 3146 (2003).
[2] J. Zheng, W.C. Chin, E. Khijniak, E. Khijniak Jr. and G.H. Pollack, Adv. Col. Int. Sci. 127, 9 (2006).
[3] B. Chai, H. Yoo and G.H. Pollack, J. Phys. Chem B 113, 13953 (2009).
[4] P.A. Thiel and T.E. Madey Surf. Sci. Rep. 7, 211 (1987).
[5] M.A. Henderson, Surf. Sci. Rep. 46, 1 (2002).
[6] A. Michaelides, Appl. Phys. A 85, 415 (2006).
[7] A. Hodgson and S. Haq, Surf. Sci. Rep. 64, 381 (2009).
[8] S. Schnur and A. Gro, New J. Phys. 11, 125003 (2009).
[9] J.S. Filhol and M.L. Bocquet, Chem. Phys. Lett. 438, 203 (2007).
[10] J.M. Heras and L. Viscido, Appl. Surf. Sci. 4, 238 (1980).
[11] E. Langenbach, A. Spitzer, H. Luth, Surf. Sci. 147, 179 (1984).
[12] F. Musumeci and G.H. Pollack, Chem. Phys. Lett. 536, 65 (2012).
[13] P. Debye, “Polar Molecules” p 30, Dover Publications Inc., New York (1928).
[14] S. Sivasubramanian, A. Widom and Y.N. Srivastava, Physica A 345, 356 (2005).
[15] J.A. Gonzalo, “Effective Field Approach to Phase Transitions and Some Applications to Ferroelectrics”, World Scientific Singapore (1990).
[16] B.A. Strukov and A.P. Levanyuk, “Ferroelectric Phenomena in Crystals”, Chapt. 10, p 219, Springer Berlin (1997).
[17] G. Preparata, “QED Coherence in Matter”, Chapt. 10, World Scientific Singapore (1995).