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THEORETICAL STUDIES OF COMPLEX SYSTEMS: WATER, PORES AND THE HYDROGEN FUEL SYSTEMS

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1 Water

The molecular diffraction form factors of water [1] impose restrictions on the sharpness of the angular correlations of liquid water that can be measured by X-Ray or neutron diffraction. Realistically, the largest angular term measurable is the octupole or hexadecupole. On the other hand, fully analytical models are needed to study transformations and phase behavior of water and solutions near electrode interfaces and in pores. The xyz-octupolar model of water [2] is simple and analytical. It is fully consistent with the diffraction experiments. The rather excellent agreement of the structure obtained from this potential and experiment (Blum et al.) [3] is a consequence of this fact. Several groups have in recent times used this model to study complex biological systems.

Substantial Progress has been achieved in the formulation of rather accurate analytical theories for complex angular dependent potentials: While in the past we used a perturbative method such as the GMSA, a new and very accurate method is the ESMSA [7, 8] which interpolates between high and low density systems has used to study electrolytes in pores [6]. The application to the water problem is underway.

2 Pores

In the past we have studied flexible polyelectrolyte chains [9, 10]. The equations are explicit, have the correct asymptotic limits for infinitely long chains [11] and yield the best agreement with computer simulations. A solution for flexible rings has also been found. With the new method stiff chains are tractable.

The first step in the formulation of an asymptotically correct theory of charged pores, is the solution of the linearized Poisson-Boltzmann equation (PBE) for a charged torus in an ionic solution. It has been achieved using the perfect screening theorem [12]. We get

$$\zeta(R,\theta) = \sum_{\ell} \varphi_{\ell}(R) P_{\ell}(\cos\theta) \tag{1}$$

Where is the Legendre polynomial $P_{\ell}(\cos\theta)$ with $\cos\theta = \sqrt{\frac{z^2}{R^2+z^2}}$. $\varphi_{\ell}(R)$ is a function of the distance R to the axis of the torus. This solution is valid for the general torus (oblate and prolate). We have done extensive Monte Carlo simulations of charged rings in an electrolyte. The comparison of theory and carefully controlled simulations is amazingly good [6]. We believe that this is a consequence of the fact that the analytical solution interpolates between exact asymptotic limits in this model, and is contained in the EMSA approximation.

3 The hydrogen fuel cell

We have refined our model for the hydrogen evolution on Pt(111) in the presence of SO_4H_2 [13, 14, 15, 16], and adjusted the position of the spike in the voltammogram to the flipping point of the water. The position of the turning point was previously treated as an adjustable parameter. This new choice of the flipping point of the ad-water at the PZC (point of zero charge) makes the model much more robust and coherent. This work has been presented at the International Fischer Symposium, a manuscript was submitted as a report DOE/ER/15422-1 and has been published in a special issue of the Journal of Physical Chemistry B [17]. This new parameterization clarifies some issues related to the mechanism of hydrogen oxidation and will be addressed in future work.

In the early stages of this project we tried with N. Marzari to compute the ex-situ structure of the bisulfate-water $\sqrt{3} \times \sqrt{7}$ (0r also $5/2 \otimes \sqrt{7}$) phase, seen by STM. However, we were unsuccessful in reproducing the known structures of the phase, even though we used state of the art pseudopotentials. There are various possible reasons why this happens, but the most obvious one is the environment of the electrode surface. This means that we need a theory that is able to include the local microfield as a function of the applied potential and electrochemical environment, and hence, we need to fully develop the density functional of a real molecular solvent solution in the double layer. Because of the recent advances in density functional theory (cited above) this is very feasible.

4 Classical Density Functional

The goal of this project is to develop a classical functional density theory capable of treating water and ionic solutions near charged electrodes and pores. The general theory of Yukawa fluids is useful in formulating such a density functional. A step in this direction is the new scaling mean spherical approximation for the ion-dipole mixture [18]. We have reformulated the solution of the multiyukawa closure of the Ornstein-Zernike equation [19, 20, 21], and in particular found a new solution of the one component Yukawa fluid [22], which satisfies correct symmetry requirements. In collaboration with J.A. Hernando of the Comision Nacional de la Energia Atomica, Argentina, we have solved the multicomponent, multidensity Yukawa mixture [20].

5 Miscellaneous

5.1 Other Federal Support

(Participant) NSF/CIRE/PUMP/DMR-04 project UPENN-MRC (sponsor: NSF).

5.2 Graduate Students

5.2.1 Past

: Andres Enriquez. (Ph. D., 2006)

5.2.2 Current

1. Melvin Arias
2. Domingo Perez
3. Ramon Mundaray
4. Jose Guerra
5. Ernesto Ulloa
6. Diego Rodriguez (M.Sc. , 2007)

5.3 Expenditures and Justification

The largest expenditures were equipment (2 workstations) and salaries of students. At the beginning of the project there were only 2 students and now there are 6 students in my group. The rate of expenditures was slow in the beginning of the project, in the last year my group increased considerably. Although there are some funds left in the budget, because of the large number of students in my group we could easily spend all of the remaining funds in a period of about 6 months. I would like to ask for a no cost extension if possible.

6 Publications and Awards

6.1 Awards

2003 Joel H. Hildebrand Award in Theoretical and Experimental Chemistry of Liquids.

6.2 Publications

1. C.M. Carlevaro, L. Blum and F. Vericat, Generalized Mean Spherical Approximation for a model of water with dipole, quadrupole and short range potential of tetrahedral symmetry, J. Chem. Phys. **119**, 5198 (2003).

2. L. Blum, N. Marzari, and R. Car, On the Mechanism of the Hydrogen/ Pt(111) fuel cell. J. Phys. Chem.B, **108**, 10960 (2004) (Frank Stillinger issue).

3. A.Enriquez and L. Blum, Scaling in Complex Systems: Analytical Theory of Charged Pores, Molecular Physics, **103**, 3201 (2005), B. Widom issue, (physics/0505009 v4).

4. L. Blum and M. Arias, Structure of Multi-component/Multi-Yukawa mixtures, J. of Physics, (Condensed Matter), **18**, S 2437, (2006), ArXiV (cond-mat/0602477).

5. L. Blum and M. Arias, Thermodynamics of the soft and extended soft mean spherical model, Mol. Physics, **104**, 3801 (2006) (2006 Liblice Conference Issue.)

6. A. Ruas, O. Bernard, B. Caniffi, J. P. Simonin, P. Turq, L. Blum and Ph. Moisy, Uranyl(VI) Nitrate Salts: Modeling Thermodynamic Properties Using the Binding Mean Spherical Approximation Theory and Determination of Fictive Binary Data. J. Phys. Chem. B **110**, 3435 (2006).

7. C.Santangelo and L. Blum, Interaction Between Two Rows of Localized Adsorption Sites in a 2D One-Component Plasma, Cond. Matter Physics, **8**, 325 (2005) D. Henderson issue, . (cond-mat/0412597 v1).

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