

A Review: Emergence of a Stern Layer from the incorporation of Hydration Interaction into the Gouy-Chapman Model of the Electrical Double Layer by Brown et al [2]

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Abstract

This study investigates hydration interactions in the Gouy-Chapman model of the electrical double layer (EDL) as discussed by Brown et al. The goal is to reproduce their findings and extend the work by exploring additional system interactions or introducing new assumptions. The theoretical framework includes the Poisson equation, Boltzmann distributions, and hydration interactions modeled via a Yukawa potential. The study contributes to understanding specific ion effects and hydration interactions in charged interfaces.

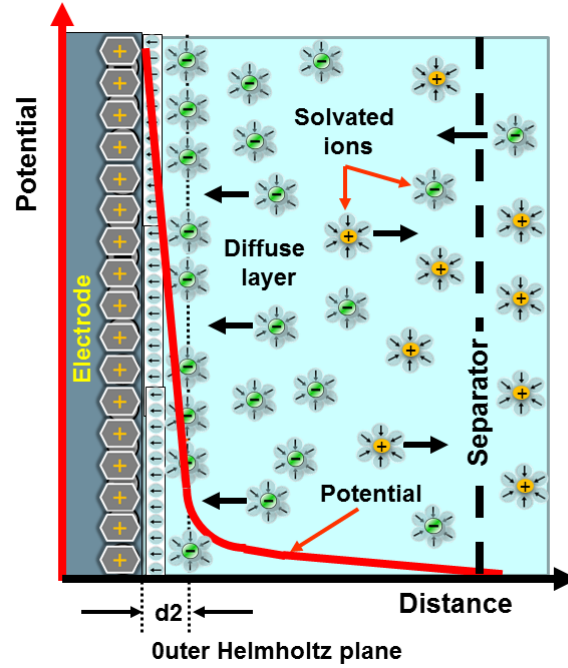


Figure 1: Simplified illustration of the potential development in the area and in the further course of a *Helmholtz double layer*

Keywords: keyword1, keyword2, keyword3

1 Introduction

Our goal in this project is to reproduce the results of a paper by Brown et al[2] that discusses hydration interactions into the Gouy-Chapman model of the electrical double layer. The paper

discusses specific ion effects in aqueous solutions and their impact on the electrical properties of charged interfaces, focusing on the Gouy-Chapman-Stern (GCS) model's success in describing these phenomena. Our study involves reproducing and comprehending the results presented in the paper. Subsequently, we aim to extend this work by investigating additional interactions of the system or making some new assumptions that have not been investigated or understood.

2 Theory

In surface science, a double layer (DL, also called an electrical double layer, EDL) is a structure that appears on the surface of an object when it is exposed to a fluid. The object might be a solid particle, a gas bubble, a liquid droplet, or a porous body. The DL refers to two parallel layers of charge surrounding the object. The first layer, the surface charge (either positive or negative), consists of ions which are adsorbed onto the object due to chemical interactions. The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer. This second layer is loosely associated with the object. It is made of free ions that move in the fluid under the influence of electric attraction and thermal motion rather than being firmly anchored. It is thus called the "diffuse layer."

DLs play a fundamental role in many everyday substances. For instance, homogenized milk exists only because fat droplets are covered with a DL that prevents their coagulation into butter. DLs exist in practically all heterogeneous fluid-based systems, such as blood, paint, ink and ceramic and cement slurry.

Consider a planar surface with a fixed, uniform and sufficiently high negative surface charge density σ_e . The surface is in contact with a solution containing a symmetric 1:1 electrolyte of bulk concentration n_o . The electrostatic potential in the aqueous solution Φ , at a distance x away from the surface fulfills the Poisson equation

$$\epsilon_w \epsilon_o \Phi''(x) = -\rho(x) \quad (1)$$

where the double prime denote the second derivative with respect to the argument, $\epsilon_o = 8.85 \times 10^{-12}$ F/m is the permittivity of free space and $\epsilon_w = 78$ is the dielectric constant of water. The local volume charge density within the electrolyte is

$$\rho(x) = e [n_+(x) - n_-(x)] \quad (2)$$

This reflect the difference of concentration between the mobile electrolyte cations (n_+) and anions (n_-), where $e = 1.6 \times 10^{-19}$ C is the elementary charge. In this regard, it is common to re-express the Poisson equation as

$$\Psi_e''(x) = -4\pi l_e [n_+(x) - n_-(x)] \quad (3)$$

In terms of dimensionless electrostatic potential

$$\Psi_e = \frac{e}{k_B T} \Phi \quad (4)$$

The Bjerrum length in water $l_e = \frac{e^2}{4\pi\epsilon_w\epsilon_o k_B T} = 0.7$, where k_B is the Boltzmann constant, and $T = 300K$ is the absolute temperature. The classical GC model combines the Poisson equation with the Boltzmann distribution for the local ion concentrations

$$n_+ = n_o e^{-\Psi_e} \quad (5)$$

$$n_- = n_o e^{\Psi_e} \quad (6)$$

Which leads to the classical Poisson - Boltzmann equation

$$\Psi_e''(x) = k_e^2 \sinh [\Psi_e(x)] \quad (7)$$

with

$$k_e^2 = 8\pi l_e n_o \quad (8)$$

The length $1/k_e^2$ is known as the the Debye screening length. The Poisson equation expresses interaction through Coulomb potential with electrostatic energies

$$\frac{U_e}{k_B T} = \frac{l_e}{r} \quad \text{and} \quad \frac{U_e}{k_B T} = -\frac{l_e}{r} \quad (9)$$

where r is the separation distance. To model these interactions, we assume that cations produce not only electrostatic but also an additional hydration interaction that we model as a Yukawa potential

$$\frac{U_h}{k_B T} = e^{k(l_h - r)} \frac{l_h}{r} \quad (10)$$

Where $k = 0.3$ is the decay length fo the ordered water layers and r is the distance between two cations. It should be noted here that l_h denotes the ion-ion separation at which the hydrogen is equal to the thermal energy unit $k_B T$. The coice of the Yukawa-like interaction according to the paper we are reviewing is motivated by a phenomenological model of hydrogen forces due to Marcella and Radic and ensure the cation remain fully hydrated near the charged surface. The total cation-cation interaction interaction energy in the model is

$$\frac{U_{tot}}{k_B T} = \frac{U_e}{k_B T} + \frac{U_h}{k_B T} = \frac{l_e}{r} + \frac{l_h}{r} e^{k(l_h - r)} \quad (11)$$

where as the cation-ion interaction remains purely Coulombic ($U_{tot}/k_B T = l_e/r$ for the anion-anion interaction and $U_{tot}/k_B T = -l_e/r$ for the cation-anion interaction). Figure 1 shows the cation-cation interaction energy $U_{tot}(r)/k_B T$ for for different l_h values.

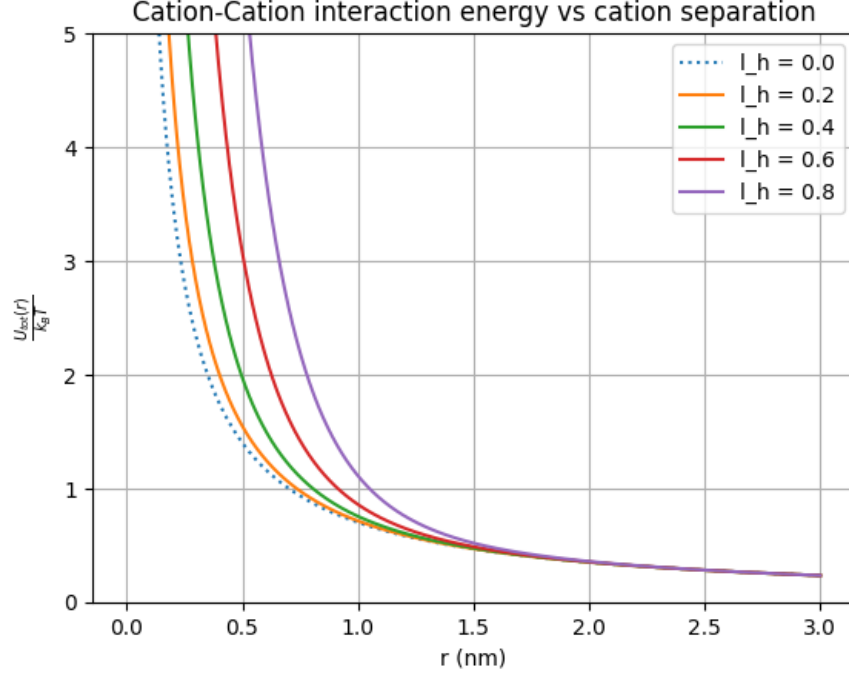


Figure 2: Total cation-cation interaction according to equation 11

Incorporating the hydration interaction into the Poisson equation leads to the inhomogeneous differential Helmholtz equation

$$\Psi''(x) - k^2 \psi_h(x) = -4\pi l_h e^{kl_h} [n_+(x) - n_o] \quad (12)$$

with the local cation and anion concentration fulling the Boltzmann distribution

$$n_+(x) = n_o e^{-(\Psi_e(x) + \Psi_h(x))}, \quad n_- = n_o e^{\Psi_e} \quad (13)$$

Inserting the Boltzmann distribution into equation into equation 7 and equation 12 yields two second order coupled differential equations for the two fields.

$$\Psi_e''(x) = \frac{k_e^2}{2} \left[e^{\Psi_e(x)} - e^{-(\Psi_e(x) + \Psi_h(x))} \right] \quad (14)$$

$$\Psi_h''(x) - k^2 \Psi_h(x) = \frac{k_h^2}{2} \left[1 - e^{-(\Psi_e(x) + \Psi_h(x))} \right] \quad (15)$$

Where k_e (the inverse Debye screening length) is defined in equation 8, and

$$k_h^2 = 8\pi l_h e^{kl_h} n_o \quad (16)$$

To solve the two coupled differential equations in equations 14, and 15, we need 4 boundary conditions. Two of them are

$$\Psi_e'(x) = -4\pi l_e \frac{\sigma_e}{e}, \quad \Psi_h'(x) = 4\pi l_h e^{kl_h} \sigma_h \quad (17)$$

They reflect the surface charge density σ_e and the density of sources for the hydration interaction for the cation with the surface. The other two boundary conditions are

$$\Psi_e(x \rightarrow \infty) = \Psi_h(x \rightarrow \infty) = 0 \quad (18)$$

This boundary condition renders the surface to be isolated. The parameters $k^{-1} = 0.3$ and $\sigma = 5(nm^2)$ are fixed constants but they can be adjusted to fit the experimental results. The two coupled differential equations were and will be analyzed in the discussion section.

3 Methods

- Solving coupled nonlinear differential equations can be quite a feat, yet Python, with its libraries like SciPy, along with numerical methods such as boundary value problem (BVP) solvers and Newton-Raphson iteration, presents a potent solution. First, with a BVP solver like `scipy.integrate.solve_bvp`, one can discretize the domain, converting the problem into a set of algebraic equations. This solver then iteratively adjusts boundary conditions until a solution meeting both the boundary conditions and differential equations is attained[4]. This approach suits boundary value problems where both initial and final states are known.
- On the other hand, the Newton-Raphson method offers an alternative route. As reference we followed Brown et al [2] for Newton Raphson method[3]. By iteratively refining the solution based on the linearization of equations around an initial guess, convergence to the solution is pursued. Though it converges rapidly for well-behaved systems, it demands the computation of Jacobian matrices, which can be computationally taxing for larger systems. Nonetheless, with meticulous implementation and efficient coding practices, both BVP solvers and Newton-Raphson iteration offer robust solutions to coupled nonlinear differential equations, accommodating various problem complexities and computational resources.

4 Results

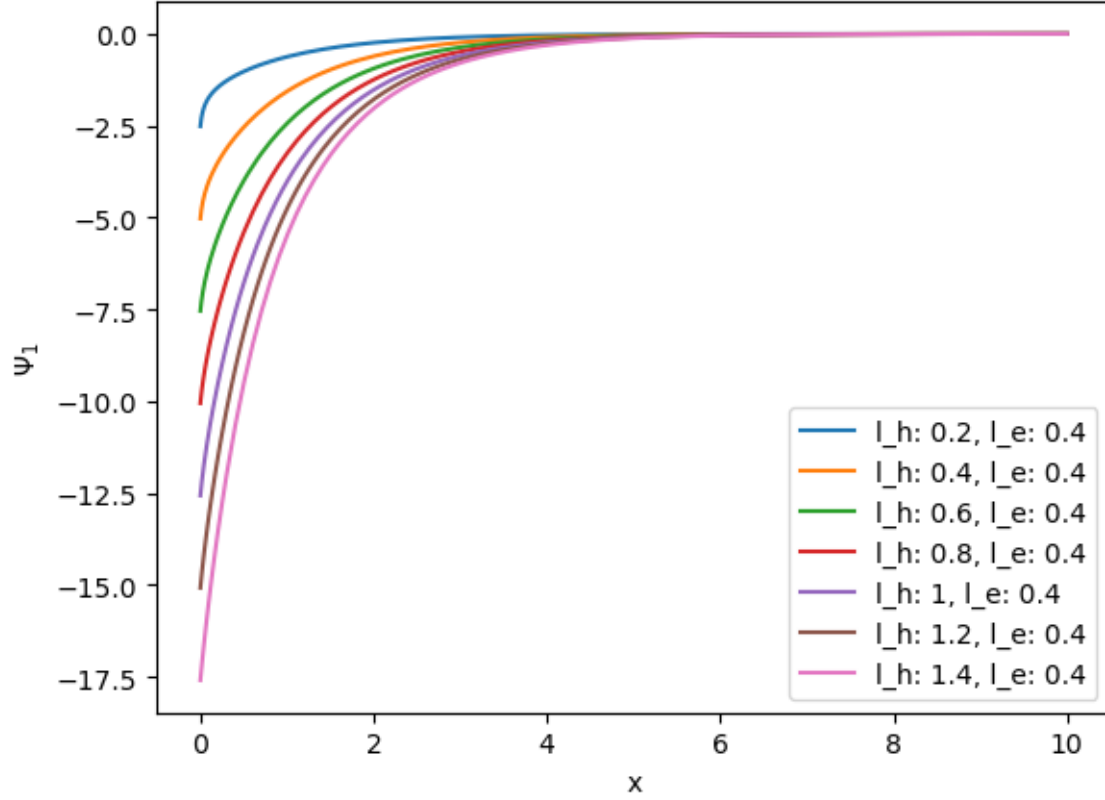


Figure 3: The figure displays the dimensionless electrostatic potential, $\Psi_e(x)$, for a surface charge density of $\sigma_{e/e} = -1/\text{nm}^2$. The solid lines depict the results for uniform dielectric constant, $\epsilon_{\text{rel}}(x) \equiv 1$, as shown in the diagram of Figure 3, cell size $a = 2 l_h = 0.2 - 1.4$ nm. All results are obtained for fixed parameters: $\kappa^{-1} = 0.3$ nm, $\sigma_{e/e} = -1/\text{nm}^2$, $\sigma_h = 5/\text{nm}^2$, and $\kappa_e^{-1} = 1$ nm. The Debye screening length $\kappa_e^{-1} = 1$ nm corresponds to a bulk salt concentration of $n_0 = 0.1$ M = $0.057/\text{nm}^3$; for large x , all curves in the diagram converges to this value.

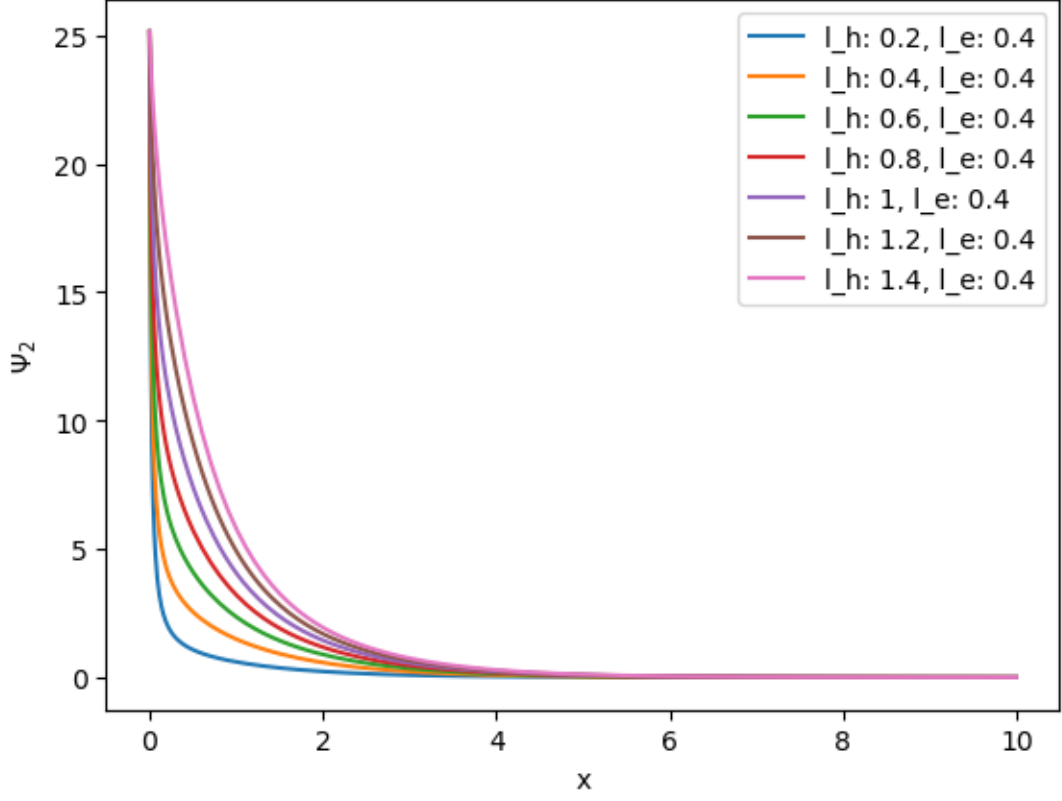


Figure 4: The figure displays the dimensionless hydration potential, $\Psi_h(x)$, for a surface charge density of $\sigma_{e/e} = -1/\text{nm}^2$. The solid lines depict the results for uniform dielectric constant, $\epsilon_{\text{rel}}(x) \equiv 1$, as shown in the diagram of Figure 3, cell size $a = 2 l_h = 0.2 - 1.4$ nm. All results are obtained for fixed parameters: $\kappa^{-1} = 0.3$ nm, $\sigma_{e/e} = -1/\text{nm}^2$, $\sigma_h = 5/\text{nm}^2$, and $\kappa_e^{-1} = 1$ nm. The Debye screening length $\kappa_e^{-1} = 1$ nm corresponds to a bulk salt concentration of $n_0 = 0.1$ M = $0.057/\text{nm}^3$; for large x , all curves in the diagram converges to this value.

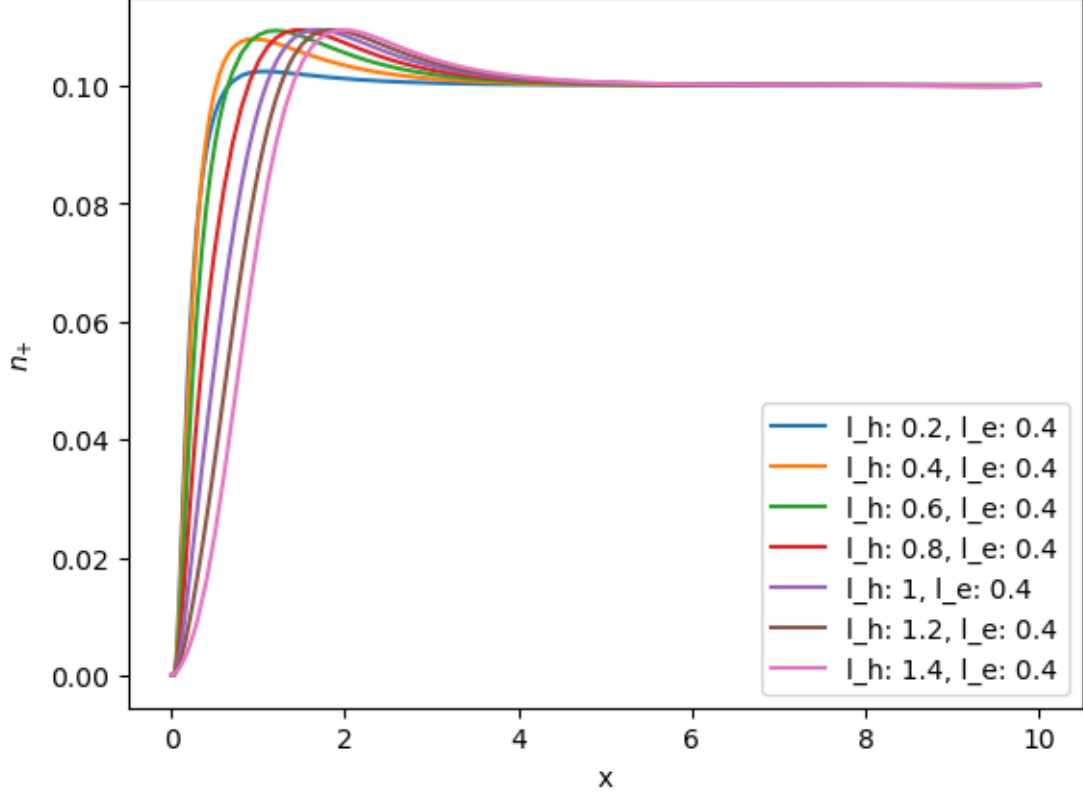


Figure 5: The figure illustrates the counterion concentration profile, $n_+(x)$, for various salt concentrations in the bulk, characterized by different values of n_0 , and specific parameters: $\kappa^{-1} = 0.3$ nm, $\sigma_{e/e} = -1/\text{nm}^2$, $\sigma_h = 5/\text{nm}^2$, and $l_e = 0.4$ nm. The curves depict different salt concentrations. In the inset, predictions of the lattice gas Gouy-Chapman (GC) model are presented with a cell size of $a = 2$ $l_h = 0.2 - 1.4$ nm, calculated using equation 05, for the same range of salt concentrations as depicted in the diagram.

5 Discussion

- **Refined Theoretical Frameworks:** One promising avenue lies in developing refined theoretical frameworks that capture the nuances of hydration at charged surfaces. This demands incorporating factors like:
 - **Ion Size Asymmetry:** Electrostatic interactions in the EDL are not uniform. Accounting for the varying sizes of cations and anions will lead to a more accurate description of ion distribution and potential profiles.
 - **Surface Roughness:** Idealized smooth surfaces don't reflect reality. Incorporating surface roughness into the model will provide insights into how surface topography influences the ordering and dynamics of hydrated ions.[1]
 - **Solvent Polarization Effects:** Water molecules, the primary solvent, are not passive bystanders. Their response to the electric field plays a crucial role in determining the EDL structure. Advanced models that account for solvent polarization will lead to a more complete picture.
- **Bridging Theory and Experiment:** Bridging the gap between theory and experiment is another exciting research frontier. Techniques like:
 - **Surface-Sensitive Spectroscopy:** These methods provide direct, nanoscale probes

of the EDL, allowing researchers to measure the solvation structure and dynamics of ions at the interface.

- **Atomic Force Microscopy (AFM):** AFM offers unparalleled spatial resolution, enabling the direct visualization of hydration layers and their interaction with the charged surface.
 - **Electrochemical Impedance Spectroscopy (EIS):** By measuring the impedance of the interface, EIS provides insights into the dynamics of ions and the influence of hydration on charge transfer processes.
 - **Computational Physics:** The power of computational physics cannot be overstated. Techniques like:
 - **Molecular Dynamics (MD) Simulations:** MD allows researchers to simulate the behavior of ions and solvent molecules at the atomic level, providing a dynamic picture of the EDL with solvation effects explicitly included.
 - **Density Functional Theory (DFT) Calculations:** DFT offers a powerful tool to study the electronic structure of the interface and how it interacts with hydrated ions, revealing the underlying forces governing ion adsorption and solvation phenomena.
 - **Colloid and Interface Science:** A deeper understanding of hydration effects can lead to the design of novel materials with tailored stability and rheological properties, impacting areas like drug delivery and microfluidics.
 - **Electrochemical Energy Storage:** Optimizing electrolytes for batteries and supercapacitors hinges on understanding how hydration influences ion transport and electrode interactions. Research in this area can pave the way for next-generation energy storage devices.
 - **Biophysics:** Hydration plays a critical role in biological systems, influencing protein interactions, cell membrane function, and numerous physiological processes. By unraveling the dance of hydration at biological interfaces, researchers can gain insights into disease mechanisms and develop targeted therapies.
- Investigating hydration interactions within the EDL offers a rich tapestry for physics research. By fostering collaboration between theoretical, experimental, and computational disciplines, this field holds immense potential to not only deepen our fundamental understanding of electrochemistry but also drive innovation and address societal challenges across a vast array of disciplines. Unveiling the intricate interplay of ions and their hydration shells promises to be a transformative journey for physics research with far reaching consequences.

6 Conclusion

Our study closely aligns with the referenced paper’s results, showcasing a solid grasp of the subject and technical skills. Looking ahead, we aim to go beyond meeting course requirements and aspire to make a valuable contribution worthy of publication. Leveraging our newfound knowledge and skills, we are poised to advance the field of electromagnetism and contribute meaningfully to scientific discourse. Our goal is to find the hydration interaction for two polarizable spheres of extremely different diameter. Using the Gouy-Chapman model we are going to understand how factors like surface curvature, ion size effects, and electrostatic interactions influence hydration phenomena. Through comparative analysis and experimental validation, the research seeks to enhance our understanding of hydration effects in various systems, including colloidal suspensions and biological interfaces, with potential implications for material design and biomedical applications.

Acknowledgments

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