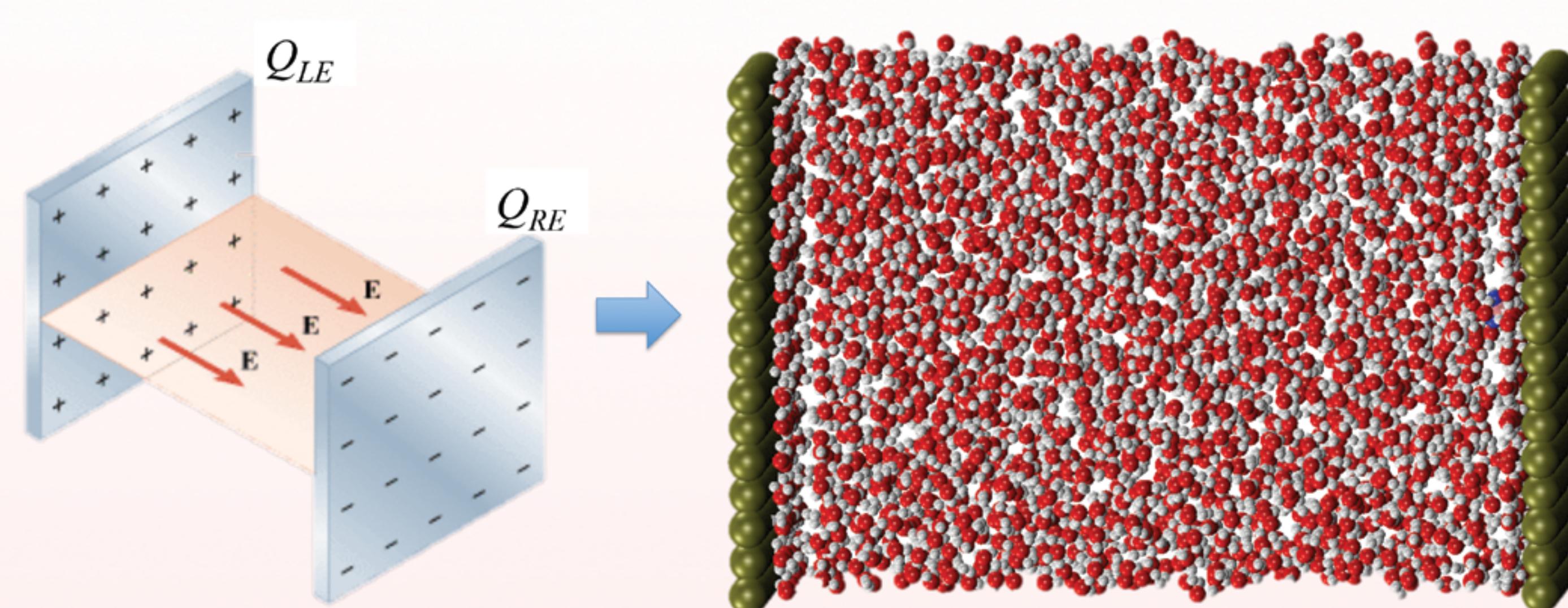


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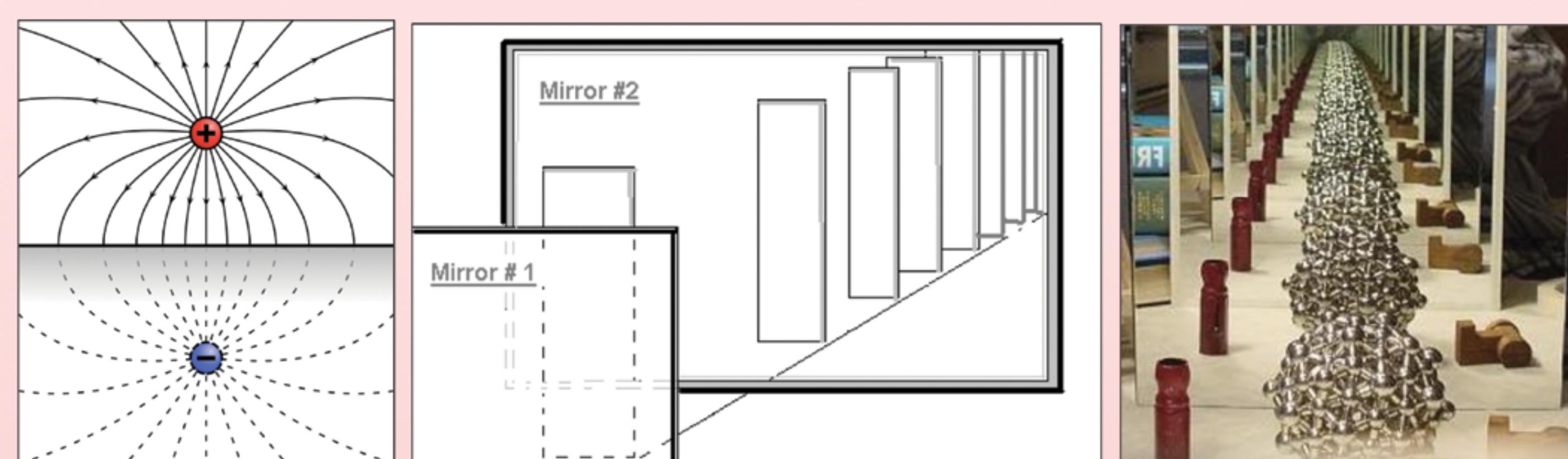
## Introduction

Understanding of the mechanisms in electrochemical cells can provide meaningful insights to improve the battery efficiency. Building computational models for electrochemical cells is non-trivial task. A computationally efficient method is presented here for the treatment of complicated interactions between the polarizable metallic electrodes holding constant potentials and the electrolyte layer separating them. The method combines a fluctuating uniform electrode charge with explicit image charges to account for the polarization effect of the electrode, and a constant uniform charge can be added to account for the constant applied voltages.

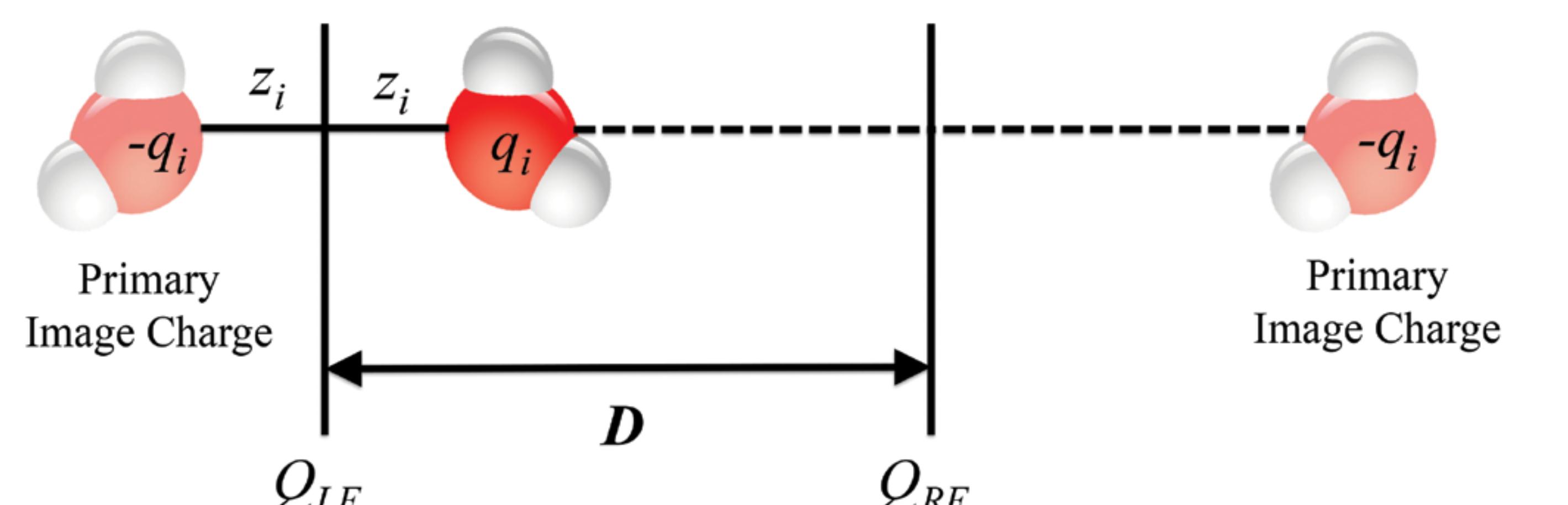


## Theoretical Background

According to electrodynamics, when a point charge is placed near a metal plane, the free electrons in the metal will respond to the electrostatic field induced by this charge, which results in an induced field back to the point charge. The simplest representation of such interaction is the image-charge model, which can be solved by employing the Poisson's equation into this system. The induced field is equivalent to a mirror image charge (carrying same charge but with the opposite sign) to the surface of the metal plane.



When a point charge is place between two parallel metal planes, it creates the image charges in both electrode "mirrors". What's more, the first-order image charge (or primary image charge) on one of the electrodes will continue to create its image to the other electrode, and recursively, to form an infinite number of images (higher-order image charges).



Schematic view for image charge method to simulate the electrochemical cells

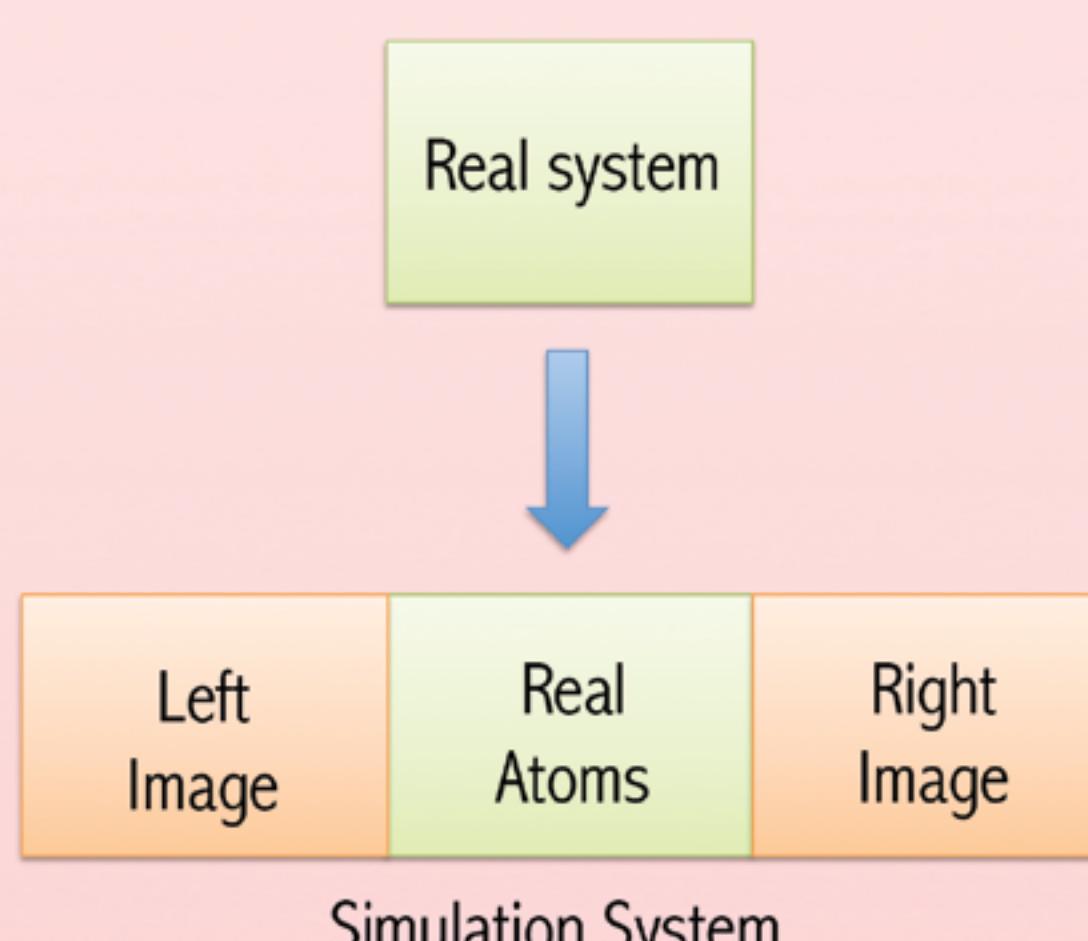
The total columbic interactive potential is divided into two parts. The first part includes the interactions between the real charges and the **primary image charges**. This part contributes to the dominant forces acting on real charges, and can be described by using the conventional Columbic interactions.

$$Q_{LE} = \sum_i \frac{q_i z_i}{D} + \frac{\Delta V \epsilon_0 A}{D}$$

Higher Order Image Charges      Effective Charges for Applied Voltages

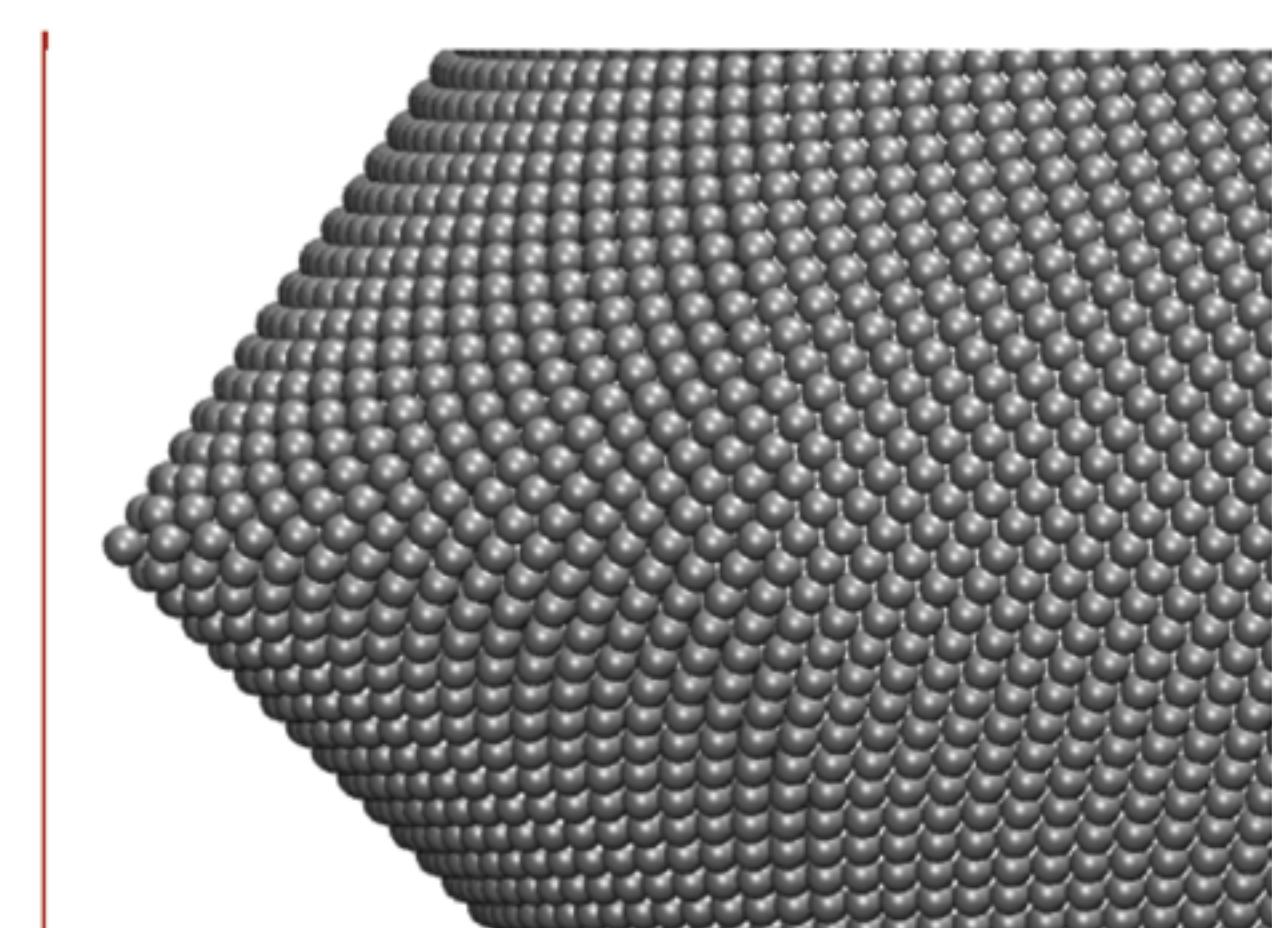
The second part includes the electric potential created from the higher-order image charges as well as the effective charges accounting for the applied voltages. The electric field originated from this potential can be approximated as interactions between the uniformly distributed plane charges and those real charges on electrolyte atoms. In total, the model constructed in this way can be seen as a framework for prototypical electrochemical cell simulations. Implementation of this method as an in-house code attached to LAMMPS provides a powerful tool for the study of the detailed mechanisms in the ultra-thin electrolyte under a range of applied voltages.

## Computationally Efficient Algorithm



In the first generation of implementation, the image point charges are represented by dummy atoms. However, the system size (number of particles) increase from  $N$  to  $3N$ . Such implementation also limit the performance of the domain-decomposition, by restricting that the decomposed factor can only be 3.

In the new implementation. The model is achieved as a new potential function of the force field. Several strategies, such as the newly designed neighbor-list algorithm, reduced FFT transform, are applied to improve the performance.

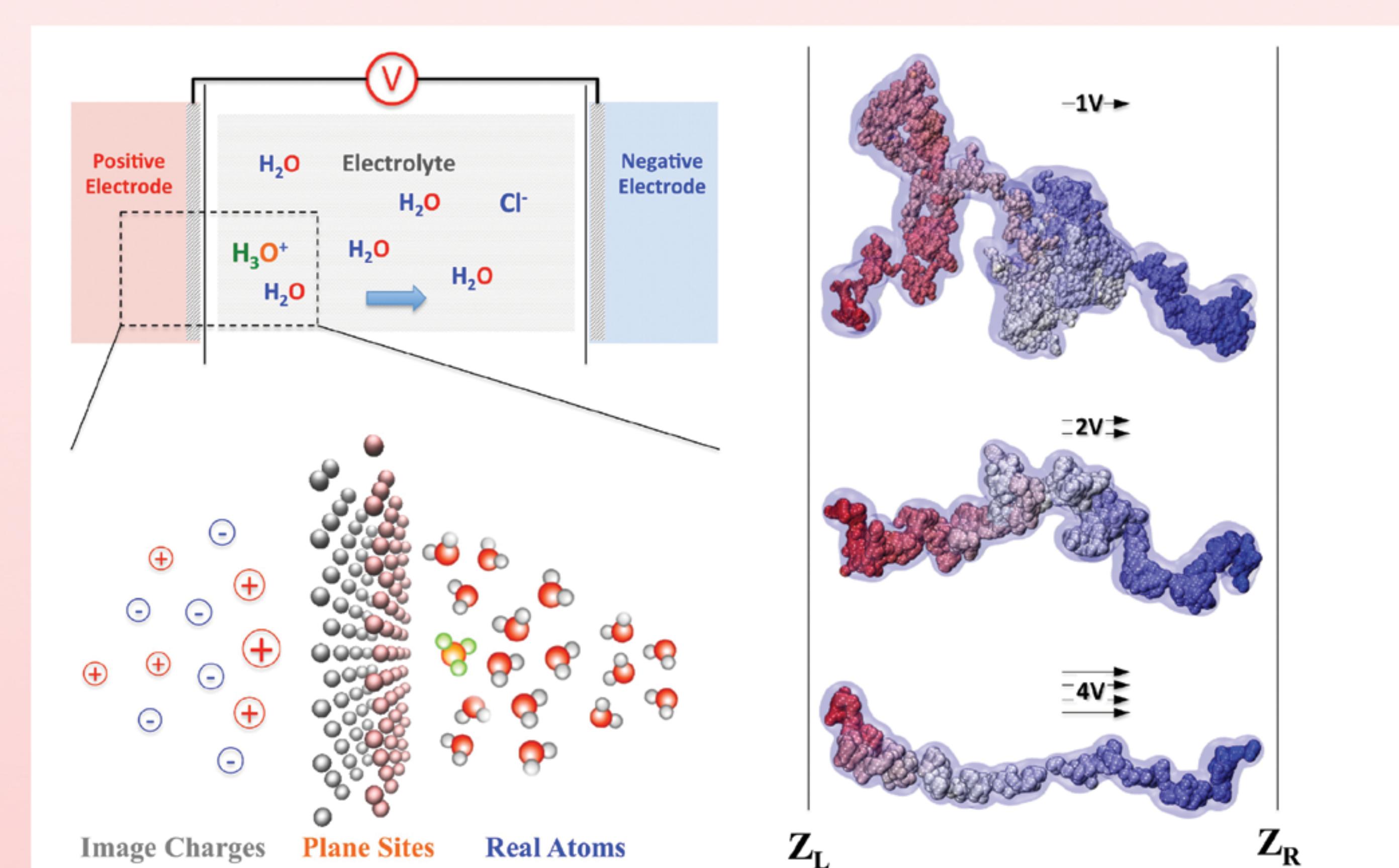


The atoms in the electrode planes show high symmetry in the x-y plane. Therefore, the distance between electrolytes and the electrode atoms can be simplified to only calculate the z component of the distances, and the x, y components can be read from the list as the offset of the unit cells. The computational cost can be largely reduced in this case.

In sum, the code employ the symmetry properties of the system to improve the simulation efficiency. Originally, the code can produce **~5 ps/day** while it can produce **~170 ps/day** under the optimal settings of the simulations.

## Application in Proton Transport

Proton transport through an ultra-thin electrolyte layer between platinum electrodes under a range of applied voltages is explored using reactive molecular dynamics simulation. The proton transport process is decomposed into vehicular and Grotthuss hopping components, and the two mechanisms and their correlations are investigated as a function of applied voltage. At higher applied voltages, the effect of the hopping mechanism is much larger as compared with the vehicular mechanism. As the voltage is increased, the net correlation between these two mechanisms goes from negative to positive, and both the hopping frequency as well as the number of consecutive forward hops increases. This behavior results in a larger total diffusion constant at higher values of the voltage. The behavior of the hydrated excess proton is therefore substantially different under an applied external voltage than in the normal bulk water environment.



This research was partially supported by the Office of Naval Research (ONR Grant N0014-12-1-1021). This work was partially completed with resources provided by the University of Chicago Research Computing Center (RCC).