

Continuum representation of the Lennard-Jones potential for the electrical double layer structure

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The Lennard-Jones potential is commonly used to represent hard-sphere repulsion and van der Waals attraction, but it is not easily integrated into continuum mean-field equations for the electrical double layer. Here, a double Yukawa potential is fit to the Lennard-Jones interaction, and the double Yukawa potential is in turn solved in the mean-field limit. The double layer structure is strongly influenced by the presence of the double Yukawa potential, leading to the emergence of a Stern layer and larger contact densities due to van der Waals attraction. The approach is generalized to an arbitrary set of interactions in an electrolyte with multiple constituents.

I. INTRODUCTION

The surface charges of all biological molecules are screened by counterions in equilibrium with a physiological solution, forming an electrical double layer. In general, the interactions between ions in solution extends beyond coulomb forces, such as those given by the finite size of ions (hard-sphere repulsion) or van der Waals attraction. In the small length scale of the electrical double layer (Angstroms to nanometers) these interactions become particularly important, and can change the underlying structure of the double layer. However, these interactions are rarely included in common mean-field models of the electrical double layer, partly because a Green's function of $1/r^n$ in 3D admits an integro-differential linear operator for $n > 1$ which is difficult to simplify in common coordinate systems. To overcome this obstacle, I show that the common Lennard-Jones interaction can be approximated with a double Yukawa interaction and in turn incorporated into 1D ordinary differential equations for the double layer structure.

Some theoretical progress has been made by fitting the Lennard-Jones interaction to a sum of Yukawa interactions, one short range and one longer range potential, to understand the bulk properties of a Lennard-Jones fluid. While this combination is ineffective in capturing the long range behavior of the van der Waals force which decays as $1/r^6$, it is able to capture the important energy well characteristic of the Lennard-Jones interaction. This approach has therefore been successful in finding analytical formulas for thermodynamic properties of bulk solutions[1–4]. One aspect of representing the Lennard-Jones as a double Yukawa potential is also in solving problems in the continuum limit. The continuum limit is a useful approximation in which differential equations can be used to find the average density as a function of the distance from a charged surface. A similar model, with a different purpose and construction, was considered to account for hydration effects in the electrical double layer[5–8]. However, this hydration potential leads to attractive interactions between oppositely charged ions, and does not include an energy well characteristic of the Lennard-Jones interaction.

Here, I derive a double Yukawa construction to model

the behavior of a primitive hard-sphere electrolyte with Lennard-Jones interactions. I show that hard sphere repulsions and attractive van der Waals forces can be represented by this Yukawa construction to give more realistic models of the double layer, including the formation of a Stern layer. I generalize the result to include an arbitrary set of interactions that decay more quickly than $1/r$, and apply this formulation to ions with asymmetric sizes.

II. DOUBLE YUKAWA APPROXIMATION

The Lennard-Jones interaction includes a steric repulsion term and a van der Waals attraction term:

$$U_{LJ} = 4\epsilon \left[\frac{1}{\tilde{r}^{12}} - \frac{1}{\tilde{r}^6} \right] \quad (1)$$

Here, the radial coordinate is normalized by the hard sphere diameter, a , where $\tilde{r} = r/a$. A similar shape of

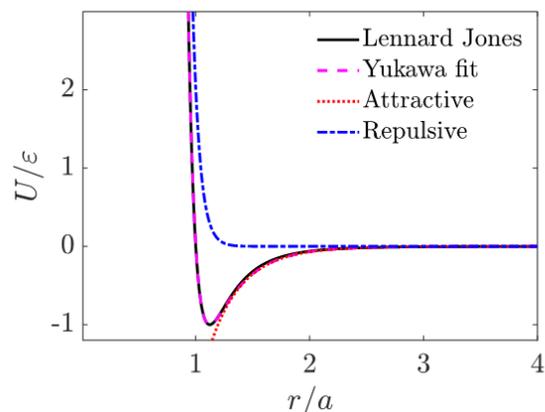


FIG. 1. Fitting of double Yukawa potential to Lennard-Jones interaction[1] with $A = 2.0198$, $\kappa_{\text{rep}}a = 14.735$, and $\kappa_{\text{att}}a = 2.6793$. The double Yukawa is split into two contributions from the repulsive and attractive parts. The overall shape of the interaction is maintained through this fitting procedure, although the long range behavior is not maintained.

interaction can be given by a double Yukawa potential:

$$U_{DY} = \frac{A\varepsilon}{\tilde{r}} \left[e^{-\kappa_{\text{rep}}a(\tilde{r}-1)} - e^{-\kappa_{\text{att}}a(\tilde{r}-1)} \right] \quad (2)$$

The fitting parameters of the double Yukawa are A , κ_{rep} , and κ_{att} . Figure 1 shows the fit of the double Yukawa potential to the Lennard-Jones potential, using the parameters from [1]. Evidently, this approximation is adequate to capture the important features of the short range LJ potential. However, it cannot capture the longer range $1/r^6$ attraction. Also, a perfect hard sphere repulsion is

only strictly enforced as $\kappa_{\text{rep}}a \rightarrow \infty$.

Based on numerical difficulties of solving the resulting boundary value problems in the mean-field limit, A , κ_{rep} , and κ_{att} are chosen to provide reasonable fits of the Lennard-Jones interaction without perfectly conforming to the interaction potential shape. These choices allow for the equations to be solved numerically using MATLAB's `bvp4c` function, but future work with greater numerical accuracy will include the solutions to the properly fit equations. Here, we choose $\varepsilon = 1$ kJ/mol or $\tilde{\varepsilon} = \varepsilon/(k_bT) = 0.4$ at room temperature, as a typical depth of the energy well.

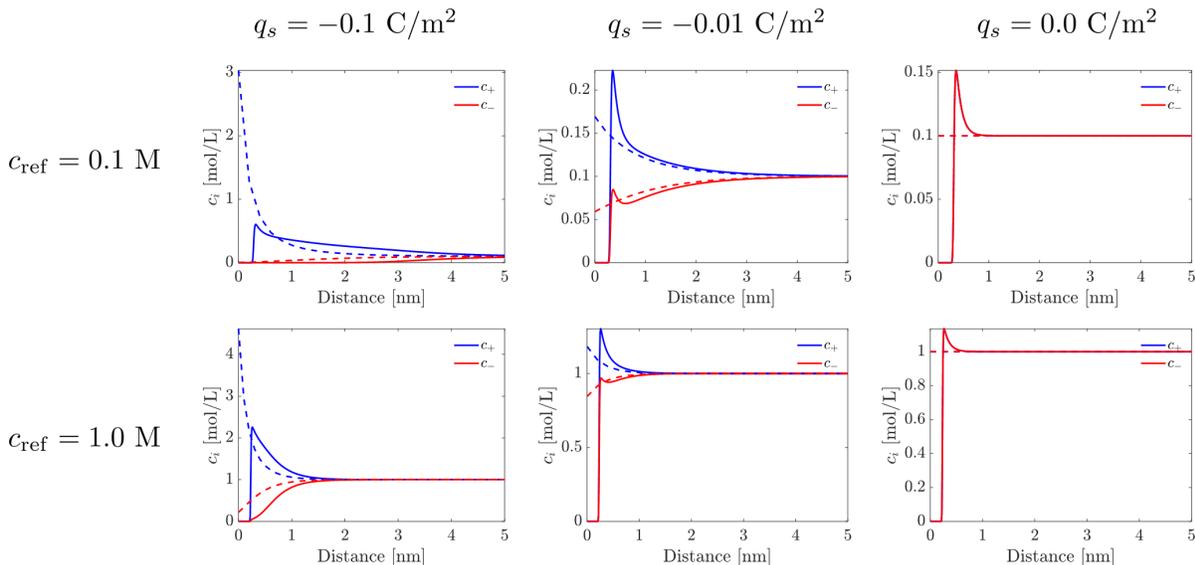


FIG. 2. The solution of equation 7 at different bulk ion concentrations. For each case, the diameter of ions is assumed to be $a = 0.4$ nm. The solid lines are for $A = 5$, $\tilde{\varepsilon} = 0.4$, $\kappa_{\text{rep}}a = 7.5$, and $\kappa_{\text{att}}a = 4$. The dotted lines represent the Poisson-Boltzmann solution to the equation, with $A = 0$.

III. DERIVATION OF MEAN-FIELD EQUATIONS

Now we turn to deriving mean-field equations for the double Yukawa interactions. For the simplest case, we assume a primitive model of an electrolyte, with symmetrically sized ions interacting with a smeared out surface charge density, q_s . We assume that the atoms of the charged surface are arranged in a 2D hexagonal close-packed lattice, and that the surface atoms have the same diameter as the ions in solution. We first neglect any of the discrete effects of the solvent, including the short-range LJ interactions with the solvent molecules.

For a single Yukawa potential, the total internal energy of the interaction is given by a double integral of an interaction between the total number densities of ions at

each point:

$$U = \frac{1}{2} \int_V dr \int_V dr' \left[\left(\sum_i c_i(r) \right) G(r-r') \left(\sum_j c_j(r') \right) \right] \quad (3)$$

Here, G is the Green's function which is $G(r) = \frac{A\tilde{\varepsilon}a}{r} \exp(-\kappa(r-a))$. In the case of each of the interactions constituting the double Yukawa potential. The Yukawa potential admits a linear operator L such that $LG(r-r') = \delta(r-r')$, where $L = \frac{-1}{4\pi A\tilde{\varepsilon}a \exp(\kappa a)} (\nabla^2 - \kappa^2)$. We define a potential Ψ as:

$$\Psi = \int_V dr' \left[G(r-r') \left(\sum_j c_j(r') \right) \right] \quad (4)$$

Which allows us to write down an ordinary differential equation in the mean-field limit:

$$\nabla^2 \Psi - \kappa^2 \Psi = -4\pi A\tilde{\varepsilon}a e^{\kappa a} \sum_j c_j \quad (5)$$

However, we are only interested in the difference of the non-electrostatic potential from a reference potential set by a reservoir, Ψ_{ref} . We therefore make a convenient change of variables to $\psi = \Psi - \Psi_{\text{ref}}$ [5].

$$\nabla^2 \psi - \kappa^2 \psi = -4\pi A \tilde{\epsilon} a e^{\kappa a} \sum_j c_j - c_{j,\text{ref}} \quad (6)$$

We can treat the two Yukawa potentials equivalently to introduce two new potentials, ψ_{rep} and ψ_{att} . The set of differential equations becomes:

$$\begin{aligned} \nabla^2 \phi &= -4\pi \ell_b (c_+ - c_-) \\ \nabla^2 \psi_{\text{rep}} - \kappa_{\text{rep}}^2 \psi_{\text{rep}} &= -4\pi A \tilde{\epsilon} a e^{\kappa_{\text{rep}} a} \sum_i (c_i - c_{i,\text{ref}}) \\ \nabla^2 \psi_{\text{att}} - \kappa_{\text{att}}^2 \psi_{\text{att}} &= 4\pi A \tilde{\epsilon} a e^{\kappa_{\text{att}} a} \sum_i (c_i - c_{i,\text{ref}}) \end{aligned} \quad (7)$$

Here, ℓ_b is the Bjerrum length ($\ell_b = 0.7$ nm) and ϕ is the electric potential (normalized by the thermal voltage). The source of the non-electrostatic fields $\nabla \psi_{\text{rep}}$ and $\nabla \psi_{\text{att}}$ is the surface density of atoms on the surface, which interact with an identical Lennard-Jones potential with electrolyte. Therefore, the density of ions interact with each other and the surface with Lennard-Jones interactions. The boundary condition for a planar electrical double layer are:

$$\begin{aligned} \hat{n} \cdot \nabla \phi(0) &= -4\pi \ell_b q_s & \nabla \phi(\infty) &= 0 \\ \hat{n} \cdot \nabla \psi_{\text{rep}}(0) &= -4\pi A \tilde{\epsilon} a e^{\kappa_{\text{rep}} a} \sigma_s & \nabla \psi_{\text{rep}}(\infty) &= 0 \\ \hat{n} \cdot \nabla \psi_{\text{att}}(0) &= 4\pi A \tilde{\epsilon} a e^{\kappa_{\text{att}} a} \sigma_s & \nabla \psi_{\text{att}}(\infty) &= 0 \end{aligned} \quad (8)$$

For an interface composed of hard spheres closely packed into a hexagonal lattice, the surface density of the hard spheres, σ_s is:

$$\sigma_s = \frac{1}{a^2 \sqrt{3}} \quad (9)$$

The electrochemical potential of the ions will include contributions from the new non-electrostatic potentials.

$$\frac{\mu_i}{k_b T} = \ln(c_i) + z_i \phi + \psi_{\text{rep}} + \psi_{\text{att}} \quad (10)$$

Therefore, at equilibrium, the ion concentration will be determined by a Boltzmann distribution:

$$c_i = c_{i,\text{ref}} \exp(-z_i \phi - \psi_{\text{rep}} - \psi_{\text{att}}) \quad (11)$$

The full set of equations is solved for a 1:1 electrolyte at different concentrations and surface charge densities for ions with $a = 0.4$ nm. The resulting profiles are given in Figure 2. The double layer structure when including the Lennard-Jones interaction is significantly different from the predictions of Poisson-Boltzmann, which only includes the electrostatic interactions. The two most noticeable features are the formation of a Stern layer, a

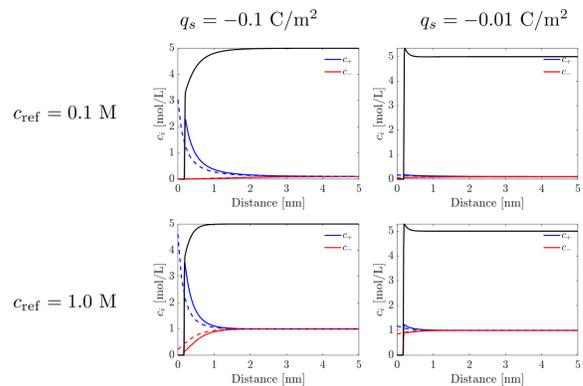


FIG. 3. The solution of equation 7 in a 1 M salt solution with 5 M solvent bulk concentration. For each case, the diameter of ions and solvent molecules is assumed to be $a = 0.4$ nm. The solid lines are for $A = 5$, $\tilde{\epsilon} = 0.4$, $\kappa_{\text{rep}} a = 7.5$, and $\kappa_{\text{att}} a = 4$. The solid black line is the solvent concentration. The dotted lines represent the Poisson-Boltzmann solution to the equation, with $A = 0$.

layer the size of an ionic radius at which the ion concentration cannot exceed zero, and also the localization of ions near the surface due to attractive van der Waals forces.

We can next add in some uncharged solvent molecules of the same size with identical non-electrostatic interactions. Here, for numerical convenience, we choose to add a solvent at a concentration of 5 M. This gives a total bulk packing fraction of 14 %. For bulk water, this value is typically around 40 %. However, in this concentrated regime, the equations become more difficult to solve, and the hardness of the spheres $\kappa_{\text{rep}} a \gg 1$ is necessary to properly account for steric interactions. Therefore, we restrict ourselves to less concentrated bulk solutions with a solvent concentration of 5 M. Interestingly, the presence of uncharged solvent leads to better agreement with the PB theory. However, the concentration profile of the solvent is strongly affected by the presence of the LJ interactions. At low charge densities, the solvent is localized at the surface, and at high charge densities, the solvent is displaced by the high concentration of cations which screen the surface charge density. The solvent has a similar sharp Stern layer which prevents the solvent from approaching closer than one radius towards the surface.

IV. GENERALIZATION TO AN ARBITRARY NUMBER OF INTERACTIONS

The approach presented for the double Yukawa construction is applicable to an arbitrary set of interaction potentials between ions or solvent molecules i and j . Here, I derive the generalized set of ordinary differential equations for this set of interactions, and I apply the result to understanding the interactions in a primitive electrolyte with asymmetric ion sizes. Following the pre-

vious derivation, we define a linear operator L_{ij} which corresponds to the Green's function for the interaction between species i and species j , G_{ij} .

$$L_{ij}G_{ij}(r-r') = \delta(r-r') \quad (12)$$

The internal energy can be defined for each of the interactions:

$$U_{ij} = \frac{1}{2} \int_V dr \int_V dr' [\alpha_i \alpha_j c_i(r) G_{ij}(r-r') c_j(r')] \quad (13)$$

The total energy from the interaction is $U = \sum_i \sum_j U_{ij}$.

The choice of α_i is determined by what is the source of the field (number density or charge). Let us define a set of potentials which are again mathematically convenient:

$$\Psi_{ij} = \int_V dr' [\alpha_j G_{ij}(r-r') c_j(r')] \quad (14)$$

Applying the linear operator L_{ij} to this equation, we arrive at a useful mean-field formula for the non-electrostatic interaction.

$$L_{ij}\Psi_{ij} = \alpha_j c_j(r) \quad (15)$$

We are interested in the difference in the constructed potential between the solution and the bulk. Therefore, we substitute in $\psi = \Psi - \Psi_{\text{ref}}$.

$$L_{ij}\psi = \alpha_j (c_j - c_{j,\text{ref}}) \quad (16)$$

Each ion's concentration is governed by a Boltzmann distribution of the potentials it experiences.

$$c_i(r) = c_{i,\text{ref}} \exp\left(-\sum_j \alpha_j \psi_{ij}\right) \quad (17)$$

The source of the fields will again be the surface density of molecules at an interface. The result is sufficiently generalizable such that the interactions with surface species can be unique from the interactions with other species in the bulk.

With this construction, I apply the concept to asymmetric hard sphere electrolytes. The solution to the set of equations is given in Figure 4 for a cation of diameter $a_+ = 0.4$ nm and an anion of diameter $a_- = 0.2$

nm. The difference in size causes charge separation even at zero surface charge density, since the thickness of the Stern layer is different for each ion. Even with a slightly negative surface charge density, the smaller anion is the ion closest to the surface.

V. CONCLUSION

The double Yukawa construction is a useful approximation to include common Lennard-Jones interactions into continuum models for the electrical double layer. The finite size of the ions leads to the formation of a Stern layer at an interface, and van der Waals attraction leads to an increased contact density at the edge of the Stern layer. The model allows for the inclusion of solvent, which has Lennard-Jones interactions itself. The approach is very general, and ion specificity such as ion size and ion-ion interaction energy-well depth can be tuned independently.

This approach can be extended to any form of two-body interactions that decay more quickly than $1/r$. Also, linearization of the equations may lead to useful analytical results for electrokinetic problems and colloidal stability. Finally, the pressure between surfaces can be altered significantly by the non-electrostatic field when a pore size becomes smaller than 1 nm. This approach does not take into account fluctuations or correlation effects arising from the discreteness of ions. Further work is required to integrate these results into more accurate representations of the double layer.

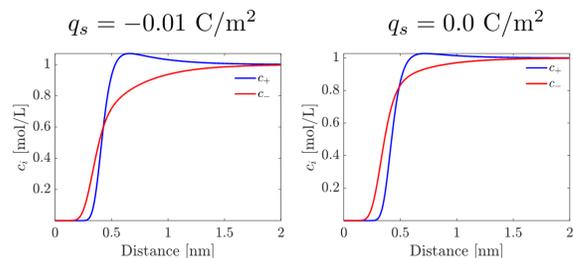


FIG. 4. The solution of equation 16 in a 1 M salt solution with implicit solvent at different charge densities. For each case, the diameter of anions is $a_- = 0.2$ nm and the diameter of the cation is $a_+ = 0.4$ nm. The profiles are given for all $\kappa_{ij} = 10/\text{nm}$.

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