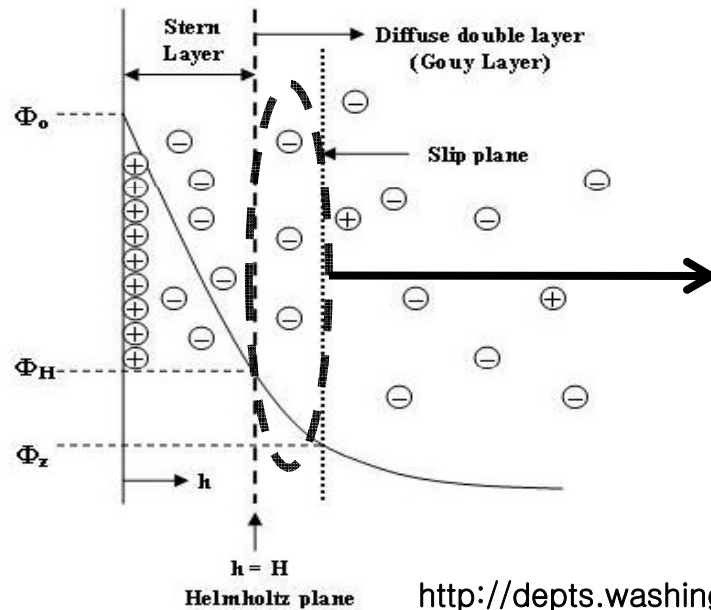


Debye-Hückel theory for interfacial geometries

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The Debye-Hückel theory for bulk electrolyte solutions is generalized to planar interfacial geometries, including screening effects due to mobile salt ions which are confined to the interface and solutions with in general different salt concentrations and dielectric constants on the two sides of the interface. We calculate the general Debye-Hückel interaction between fixed test charges, and analyze a number of relevant special cases as applicable to charged colloids and charged polymers. Salty interfaces, which are experimentally realized by monolayers or bilayers made of cationic and anionic surfactants or lipids, exert a strong attraction on charged particles of either sign at large separations from the interface; at short distances image-charge repulsion sets in. Likewise, the effective interactions between charged particles are strongly modified in the neighborhood of such a salty interface. On the other hand, charged particles which are immersed in a salt solution are repelled from the air (or a substrate) interface, and the interaction between two charges decays algebraically close to such an interface. These general results have experimentally measurable consequences for the adsorption of charged colloids or charged polymers at monolayers, solid substrates, and interfaces.

Introduction – DH theory



PB theory describe the potential distribution of the electrolyte solution near the interface

http://depts.washington.edu/solgel/images/courses/MSE_502/Ch_2/Figure_2.14.JPG

DH potential – Solution of PB equation in linearized case

$$\nabla^2 \psi = -\frac{F}{\epsilon} \sum_{i=1}^n c_{i0} z_i e^{-\frac{z_i e \psi}{kT}} \quad \text{Where, } F \text{ is Faraday constant}$$

For uniform, diluted monovalent ion case: Spherical symmetry

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial^2}{\partial r^2} (r^2 \psi) = -\frac{F c_0}{\epsilon} \left(-e^{\frac{e\psi}{kT}} + e^{-\frac{e\psi}{kT}} \right) \approx \frac{2ce^2}{\epsilon kT} \psi$$

Introduction – DH theory

Solve this inhomogeneous PDE,

$$\rightarrow \psi = \psi_0 \frac{e^{-\kappa r}}{r}, \kappa = \sqrt{\frac{2ce^2}{\epsilon kT}} \quad \lambda_D = \kappa^{-1} = \frac{3.04 \text{ \AA}}{\sqrt{c}}$$

Because DH theory has linear relation, superposition principle is valid.

But with interface,
DH theory should be modified
due to polarization charges
at the interface.

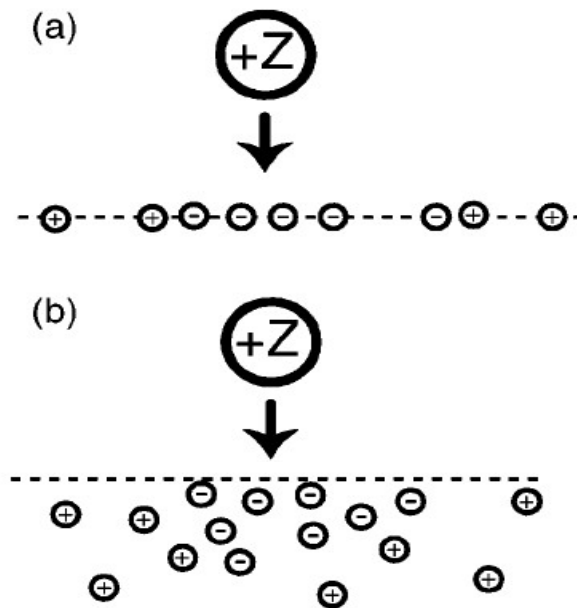
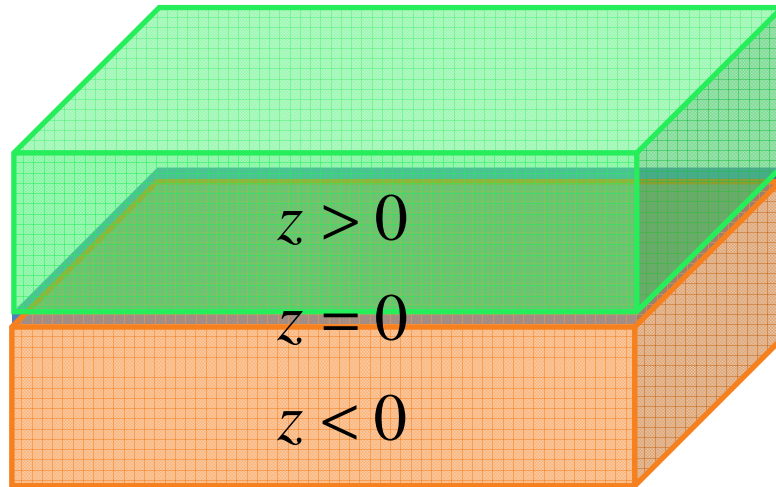


FIG. 1. Charged colloidal particle interacting with (a) a salty plane, and (b) a salty half-space. In both cases, polarization charges of opposite sign gather near the colloidal particle and lead to a strong attraction to the interface.

Modification

Mobile salt ion distributions at the upper, lower, interface are given as,



$M_>$ different type of $n_j^>$ ions with charge $q_j^>$ ($j=1,2,\dots,M_>$)

$M_=>$ different type of $n_j^=>$ ions with charge $q_j^=>$ ($j=1,2,\dots,M_=>$)

$M_<$ different type of $n_j^<$ ions with charge $q_j^<$ ($j=1,2,\dots,M_<$)

And satisfy the Electroneutrality condition in each region

And locate test charges at R_i carry Q_i

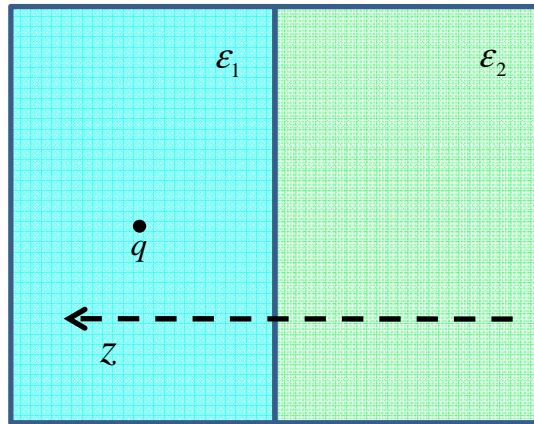
Partition function of system produced by electrostatic potential is,

$$\begin{aligned} \longrightarrow Z[\{\mathbf{R}_N\}] = \int \tilde{\mathcal{D}} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}_c(\mathbf{r}) v(\mathbf{r}, \mathbf{r}') \hat{\rho}_c(\mathbf{r}') \right\}. \quad (1) \\ \int \tilde{\mathcal{D}} \equiv \prod_{j=1}^{M_>} \left[\frac{1}{n_j^>!} \prod_{k=1}^{n_j^>} \int \frac{d\mathbf{r}_{k,j}^>}{\lambda^3} \Theta[z_{k,j}^>] \right] \\ \times \prod_{j=1}^{M_<} \left[\frac{1}{n_j^<!} \prod_{k=1}^{n_j^<} \int \frac{d\mathbf{r}_{k,j}^<}{\lambda^3} \Theta[-z_{k,j}^<] \right] \\ \times \prod_{j=1}^{M_=} \left[\frac{1}{n_j^=!} \prod_{k=1}^{n_j^=} \int \frac{d\mathbf{r}_{k,j}^=}{\lambda^2} \delta[z_{k,j}^=] \right], \quad (2) \end{aligned}$$

Modification

In equation, coulomb operator $v(r,r')$ is,

'Classical electrodynamics, John David Jackson Chapter4'



$$\epsilon_1 \vec{\nabla} \cdot \vec{E} = \rho(z > 0)$$

$$\epsilon_2 \vec{\nabla} \cdot \vec{E} = 0(z < 0)$$

$$\vec{\nabla} \times \vec{E} = 0(\text{everywhere})$$

$$\rightarrow \lim_{z \rightarrow 0^+} \begin{Bmatrix} \epsilon_1 E_z \\ E_x \\ E_y \end{Bmatrix} = \lim_{z \rightarrow 0^-} \begin{Bmatrix} \epsilon_1 E_z \\ E_x \\ E_y \end{Bmatrix}$$

<Boundary condition>

By using image charge method,(in cylindrical coordinates)

$$\Phi = \frac{1}{4\pi\epsilon_1} \left(\frac{q}{R_1} + \frac{q'}{R_2} \right) \text{for}(z > 0)$$

$$\vec{E} = -\vec{\nabla} \Phi \propto \left(\frac{\partial}{\partial \rho} \hat{\rho} + \frac{1}{\rho} \frac{\partial}{\partial \phi} \hat{\phi} + \frac{\partial}{\partial z} \hat{z} \right) \Phi$$



$$\Phi = \frac{1}{4\pi\epsilon_2} \left(\frac{q''}{R_2} \right) \text{for}(z < 0)$$



Takes the limit and compare component by component in B.C

Modification

→ $q - q' = q'', \frac{1}{\epsilon_1}(q + q') = \frac{1}{\epsilon_2} q''$

→ $v(\mathbf{r}, \mathbf{r}')$

$$= \begin{cases} \frac{l_B}{|\mathbf{r} - \mathbf{r}'|} + \frac{\epsilon - \epsilon'}{\epsilon + \epsilon'} \frac{l_B}{\sqrt{(\mathbf{r} - \mathbf{r}')^2 + 4zz'}} & \text{for } z, z' \geq 0 \\ \frac{2l_B \epsilon}{(\epsilon + \epsilon')|\mathbf{r} - \mathbf{r}'|} & \text{for } z \geq 0 \geq z', \end{cases} \quad (3)$$

$$l_B = \frac{e^2}{4\pi\epsilon kT} : \text{ Bjerrum length}$$

And charge density operator $\hat{\rho}(\mathbf{r})$ is given by,

→
$$\hat{\rho}_c(\mathbf{r}) \equiv \sum_{i=1}^N Q_i \delta(\mathbf{r} - \mathbf{R}_i) + \sum_{j=1}^{M_{>}} \sum_{k=1}^{n_j^{>}} q_j^{>} \delta(\mathbf{r} - \mathbf{r}_{k,j}^{>})$$

$$+ \sum_{j=1}^{M_{<}} \sum_{k=1}^{n_j^{<}} q_j^{<} \delta(\mathbf{r} - \mathbf{r}_{k,j}^{<}) + \sum_{j=1}^{M_{=}} \sum_{k=1}^{n_j^{=}} q_j^{=} \delta(\mathbf{r} - \mathbf{r}_{k,j}^{=})$$

(4)

Modification

After **Hubbard–Stratonovich transformation**, the partition function is up to second order fluctuating field ϕ is given as,

$$\begin{aligned} \longrightarrow Z[\{\mathbf{R}_N\}] = \int \frac{D\phi}{Z_0} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) v_{\text{DH}}^{-1}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') \right. \\ \left. - i \sum_{i=1}^N Q_i \phi(\mathbf{R}_i) + S \right\}, \end{aligned} \quad (5)$$

$$\begin{aligned} v_{\text{DH}}^{-1}(\mathbf{r}, \mathbf{r}') \equiv v^{-1}(\mathbf{r}, \mathbf{r}') + [\kappa_{>}^2 \Theta(z) + \kappa_{<}^2 \Theta(-z) \\ + \kappa_{=} \delta(z)] \delta(\mathbf{r} - \mathbf{r}') / 4\pi \ell_B. \end{aligned} \quad (6)$$

where Z_0 is the partition function of inverse coulomb operator,

$Z_0 \propto \sqrt{\det(v)}$, S is ideal entropy mixing

$\kappa_{>}, \kappa_{<}, \kappa_{=}$: screening length about upper, lower, in plane

$$\kappa_{>}^2 = 4\pi l_B \sum_j (q_j^>)^2 c_j^>, \kappa_{<}^2 = 4\pi l_B \frac{\epsilon}{\epsilon'} \sum_j (q_j^<)^2 c_j^<, \kappa_{=}^2 = 4\pi l_B \sum_j (q_j^=)^2 c_j^<$$

After shifting the fluctuating field ϕ , linear terms of ϕ in (6) is removed and the effective free energy term of n test particle can be separated.

Modification

$$\begin{aligned} \rightarrow Z[\{\mathbf{R}_N\}] &= e^{-\mathcal{F}[\{\mathbf{R}_N\}]} \int \frac{\mathcal{D}\phi}{Z_0} \\ &\times \exp\left\{-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}) v_{\text{DH}}^{-1}(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') + \mathcal{S}\right\}. \end{aligned} \quad (7)$$

$$\mathcal{F}[\{\mathbf{R}_N\}] = \frac{1}{2} \sum_i Q_i^2 v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_i) + \sum_{i>j} Q_i Q_j v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_j). \quad (8)$$

effective free energy of test particle

After Fourier transformation of $v_{\text{DH}}(r, r')$ in plane direction and adjust the canonical relation between $v_{\text{DH}}(r, r')$ and it's inverse we can set the differential equation and solve it for each regions.


$$v_{\text{DH}}(\mathbf{r}, \mathbf{r}') = \int \frac{d\mathbf{p}}{(2\pi)^2} e^{i\mathbf{p} \cdot (\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel})} v_{\text{DH}}(z, z', \mathbf{p}), \quad (10) \quad \int_{-\infty}^{\infty} d\tilde{z} v_{\text{DH}}(z, \tilde{z}, \mathbf{p}) v_{\text{DH}}^{-1}(\tilde{z}, z', \mathbf{p}) = \delta(z - z'), \quad (11)$$

$$\rightarrow -4\pi \ell_B \delta(z - z') = \left[\frac{\partial^2}{\partial z^2} - \kappa_{>}^2 - p^2 \right] v_{\text{DH}}(z, z', \mathbf{p}), \quad (12)$$

$$-4\pi \frac{\ell_B}{\eta} \delta(z - z') = \left[\frac{\partial^2}{\partial z^2} - \kappa_{<}^2 - p^2 \right] v_{\text{DH}}(z, z', \mathbf{p}), \quad (13)$$

After transformation the equation is 2nd order partial Differential equations contain source term


Modification Result



$$v_{\text{DH}}(z, z', \mathbf{p}) = \frac{4\pi\ell_B}{\sqrt{\kappa_{>}^2 + p^2} + \eta\sqrt{\kappa_{<}^2 + p^2} + \kappa_{=}} \times e^{-z\sqrt{\kappa_{>}^2 + p^2} + z'\sqrt{\kappa_{<}^2 + p^2}} \quad (14) \quad \text{For } z \geq 0 \geq z'$$

$$v_{\text{DH}}(z, z', \mathbf{p}) = \frac{2\pi\ell_B}{\sqrt{\kappa_{>}^2 + p^2}} \left[e^{-|z-z'|\sqrt{\kappa_{>}^2 + p^2}} + \frac{\sqrt{\kappa_{>}^2 + p^2} - \eta\sqrt{\kappa_{<}^2 + p^2} - \kappa_{=}}{\sqrt{\kappa_{>}^2 + p^2} + \eta\sqrt{\kappa_{<}^2 + p^2} + \kappa_{=}} \right] \times e^{-(z+z')\sqrt{\kappa_{>}^2 + p^2}} \quad (15)$$

And for $z \geq 0, z' \geq 0$
 where $\eta = \frac{\epsilon'}{\epsilon}$


 These results are can be applied in various situation
 Ex) metallic half plane, air water interface, lipid bilayer immersed in salt solution...

Application (limit case)

⊙ First check the conversion to the classical DH theory (bulk solution)

($\kappa_{>} = \kappa_{<}, \kappa_{=} = 0$, and no dielectric jump, $\epsilon = \epsilon'$)

$$\rightarrow V_{\text{DH}}(z, z', p) = \frac{2\pi l_B}{\sqrt{\kappa^2 + p^2}} e^{-|z-z'|\sqrt{\kappa^2 + p^2}}$$

$$V_{\text{DH}}(\mathbf{r}, \mathbf{r}') = \int \frac{d\vec{p}}{(2\pi)^2} e^{i(\vec{r}_{\parallel} - \mathbf{r}'_{\parallel}) \cdot \vec{p}} V_{\text{DH}}(z, z', p)$$

$$\rightarrow v_{\text{DH}}(\mathbf{r}, \mathbf{r}') = \ell_B \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}. \quad (16)$$

→ It converge to classical result

⊙ In metallic half space, $\eta \rightarrow \infty$

$$\rightarrow V_{\text{DH}}(z, z', p) = \frac{2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left\{ e^{-|z-z'|\sqrt{\kappa_{>}^2 + p^2}} - e^{-(z+z')\sqrt{\kappa_{>}^2 + p^2}} \right\}$$

From here we can define the self energy of test charge

$$\rightarrow v_{\text{DH}}(\mathbf{r}, \mathbf{r}') = \ell_B \frac{e^{-\kappa_{>}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} - \ell_B \frac{e^{-\kappa_{>}\sqrt{(\mathbf{r}-\mathbf{r}')^2 + 4zz'}}}{\sqrt{(\mathbf{r}-\mathbf{r}')^2 + 4zz'}}. \quad (17)$$

Application (Self energy)

→ $V_{DH}^{self}(z) = \int \frac{d\mathbf{p}}{(2\pi)^2} [V_{DH}(z, z, p) - V_{DH}(\infty, \infty, p)] \quad (18)$

$$= \int \frac{d\vec{p}}{(2\pi)^2} \left[\frac{-2\pi l_B}{\sqrt{\kappa^2 + p^2}} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right] = -l_B \frac{e^{-2z\kappa}}{2z}$$

So, interface strongly attracts any kind of charges

$$\mathcal{F}[\{\mathbf{R}_N\}] \propto \frac{1}{2} \sum_i Q_i^2 V_{DH}(\mathbf{R}_i, \mathbf{R}_i) + \sum_{i>j} Q_i Q_j V_{DH}(\mathbf{R}_i, \mathbf{R}_j). \quad (8)$$

⊙ In low dielectric half space, $\eta \rightarrow \infty$

→ $V_{DH}(z, z', p) = \frac{2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left\{ e^{-|z-z'|\sqrt{\kappa^2 + p^2}} + e^{-(z+z')\sqrt{\kappa^2 + p^2}} \right\}$

$$V_{DH}(\mathbf{r}, \mathbf{r}') = \ell_B \frac{e^{-\kappa > |\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} + \ell_B \frac{e^{-\kappa > \sqrt{(\mathbf{r}-\mathbf{r}')^2 + 4zz'}}}{\sqrt{(\mathbf{r}-\mathbf{r}')^2 + 4zz'}}, \quad (20)$$

→ $V_{DH}^{self}(z, z, p) = \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[\frac{-\kappa}{2\sqrt{\kappa^2 + p^2} + \kappa} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right]$

Interface strongly repel any kind of charges

Application (salty interface)

a) Thin lipid bilayer immersed in solution, $\eta = 1$ and $\kappa_+ = \kappa_- = \kappa$

$$\rightarrow V_{DH}^{self}(z, z, p) = \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[\frac{-\kappa}{2\sqrt{\kappa^2 + p^2} + \kappa} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right]$$

$$V_{DH}^{self}(z) = \int \frac{d\vec{p}}{(2\pi)^2} V_{DH}^{self}(z, z, p) = \int \frac{2\pi p dp}{(2\pi)^2} \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[\frac{-\kappa}{2\sqrt{\kappa^2 + p^2} + \kappa} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right]$$

✳ By definition of incomplete Gamma function,

$$" \Gamma(0, x) = \int_x^\infty t^{-1} e^{-t} dt ", \text{ set } (t - \kappa_- = 2z\sqrt{\kappa^2 + p^2}, x = z(\kappa_- + 2\kappa))$$

$$\rightarrow V_{DH}^{self}(z) = - \frac{\ell_{BK=}}{2} e^{z\kappa} = \Gamma[0, z(\kappa_- + 2\kappa)], \quad (24)$$

for $z \ll (\kappa_- + 2\kappa)^{-1}$

$$V_{DH}^{self}(z) \simeq - \frac{\ell_{BK=} e^{-2z\kappa}}{2z(\kappa_- + 2\kappa)}$$

for $z \gg (\kappa_- + 2\kappa)^{-1}$

$$V_{DH}^{self}(z) \simeq - \frac{\ell_{BK=}}{2} \ln[z(\kappa_- + 2\kappa)]$$

\rightarrow Always attractive

Application (salty interface)

b) Monolayer at air / water interface , $\eta = 0$

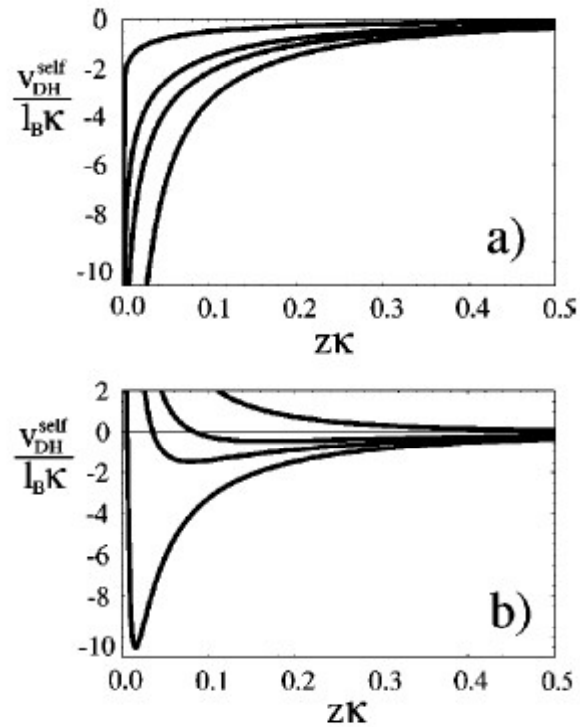
$$\rightarrow V_{DH}^{self}(z, z, p) = \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[1 + \frac{\sqrt{\kappa^2 + p^2} - \kappa_{\equiv}}{\sqrt{\kappa^2 + p^2} + \kappa_{\equiv}} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right]$$

$$\begin{aligned} V_{DH}^{self}(z) &= \int \frac{d p}{(2\pi)^2} V_{DH}^{self}(z, z, p) = \int \frac{2\pi p dp}{(2\pi)^2} \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[1 + \frac{\sqrt{\kappa^2 + p^2} - \kappa_{\equiv}}{\sqrt{\kappa^2 + p^2} + \kappa_{\equiv}} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right] \\ &= \int \frac{2\pi p dp}{(2\pi)^2} \frac{+2\pi l_B}{\sqrt{\kappa^2 + p^2}} \left[1 + \frac{\sqrt{\kappa^2 + p^2} - \kappa_{\equiv}}{\sqrt{\kappa^2 + p^2} + \kappa_{\equiv}} e^{-(2z)\sqrt{\kappa^2 + p^2}} \right] = \frac{l_B}{2z} e^{-(2z)\kappa} - 2l_B \kappa_{\equiv} e^{(2z)\kappa_{\equiv}} \Gamma(0, 2z(\kappa_{\equiv} + \kappa)) \end{aligned}$$

$$\rightarrow V_{DH}^{self}(z) = \frac{l_B e^{-2\kappa z}}{2z} - 2l_B \kappa_{\equiv} e^{2z\kappa_{\equiv}} \Gamma[0, 2z(\kappa_{\equiv} + \kappa)]. \quad (25)$$

It has some different behavior with ratio between κ_{\equiv}, κ

Application (salty interface)



a) Bilayer case : always attractive

b) Monolayer, air/water interface : have some minima if $\kappa_{\perp} > \kappa$

FIG. 2. Rescaled self-energy of a charged particle as a function of the rescaled distance from the salty interface. κ is the inverse screening length in the bulk, and κ_{\perp} is the in-plane screening length. Shown are results for (a) matching dielectric constants on both sides of the interface, $\epsilon = \epsilon'$, and (b) vanishing dielectric constant on the other side of the interface, $\epsilon' = 0$. The screening length ratios are $\kappa_{\perp} / \kappa = 1, 5, 10,$ and 50 , from top to bottom.

Application (polymer)

Polyelectrolyte polymer can be regarded as line charge

$$\text{Recall } \mathcal{F}\{\mathbf{R}_N\} = \frac{1}{2} \sum_i Q_i^2 v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_i) + \sum_{i>j} Q_i Q_j v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_j). \quad (8)$$

Make continuous distribution and do transformation, then self energy for polymer is given as,

$$f_{\text{DH}}^{\text{self}}(z) = \frac{\tau^2}{2} \int_{-\infty}^{\infty} \frac{dp}{2\pi} [v_{\text{DH}}(z, z, p) - v_{\text{DH}}(\infty, \infty, p)] \quad (32)$$

For large and small separation from wall, self energy is asymptotically,

$$f_{\text{DH}}^{\text{self}}(z) \simeq \frac{\ell_B \tau^2}{2} \left(\frac{\kappa_{>} - \kappa_{=}}{\kappa_{>} + \kappa_{=}} \right) \sqrt{\frac{\pi}{\kappa_{>} z}} e^{-2z\kappa_{>}}. \quad (33) \quad \text{for } z \gg \kappa_{>}^{-1} \quad \longrightarrow \quad \text{Attraction and repulsion rely on the charge density ratio}$$

$$f_{\text{DH}}^{\text{self}}(z) \simeq \ell_B \tau^2 \frac{1-\eta}{1+\eta} \ln(1/\kappa_{>} z). \quad (34) \quad \text{for } z \ll \kappa_{>}^{-1} \quad \longrightarrow \quad \text{Attraction and repulsion rely on the dielectric constant ratio}$$

Conclusion

- ① Debye-Hückel theory can be modified if we consider screening effect at the boundary
- ① Separate partition function with test charge and system by field theoretical approach, define the self energy of test charge
- ① For high dielectric constant ratio, in the case of metallic half space, there is attractive interaction with interface and test charge
- ① For low dielectric constant ratio, in the case of air / water interface, attraction and repulsion depend on salt concentration ratio between interface and bulk

Limitation

- ⦿ Debye-Hückel theory fit well in low concentration of salt.
It means that higher correction PB equation should be considered.
- ⦿ The system was restricted that summation of charge in each region is zero and the salt ions are confined.
- ⦿ Mutual interaction between test charges should be considered carefully if the interface strongly attract them

$$\mathcal{A}[\{\mathbf{R}_N\}] = \frac{1}{2} \sum_i Q_i^2 v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_i) + \left(\sum_{i>j} Q_i Q_j v_{\text{DH}}(\mathbf{R}_i, \mathbf{R}_j) \right) \quad (8)$$