Electric(al) Double Layer for unsymmetrical electrolytes: Tutorials
非対称電解質による電気二重層：チュートリアル

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A tutorial of the theory of the electrical double layer for unsymmetrical electrolyte is given. The GCS (Gouy-Chapman-Stern) [1, 2, 3] model based on the Grahame’s method [4] is reformulated and the results calculated by the analytical model are compared with the numerical calculation by the use of Poisson-Boltzmann (PB) equation. We also show that the GCS model may be not good approximation for the electrical double layer in multivalent electrolytes solution, because our Monte Carlo (MC) simulation showed the potential inversion region is appeared [5], which can not reproduce by the GCS model.

非対称電解質による電気二重層のGCSモデルによる再定式化をおこない、PBモデルを使った数値計算を比較して、定式化が正しいことを示した。MCシミュレーションの結果により、多価イオンの電解質においては、GCSモデルは良い近似とはならないことが明らかとなった。

1 GCS theory of Electric Double Layer: Unsymmetric electrolytes

In the previous tutorial (TU1) the basics of the electric-double-layer was reviewed [6]. In the present tutorial the electric-double-layer of unsymmetrical electrolyte is given and we will show that the formulation by Grahame [4] and Smagala and Fawcett [7] may be not correct in some equations. Our formulation may be justified by comparing the results obtained by the analytical solution in the present study with the numerical solutions by solving the PB equation directly. We will also show GCS theory does not work in the case of the multi-valent electrolytes by our MC simulation. The MC simulation reproduces the Torrie-Valleau results [5] which showed that the potential inversion region is appeared.

When the valence of the ion is given by \( Z \), for example, in the case of the unsymmetrical electrolytes such as MgCl\(_2\), \( Z(\text{cation}) = +2 \), and \( Z(\text{anion}) = -1 \), and Na\(_2\)SO\(_4\), \( Z(\text{cation}) = +1 \), and \( Z(\text{anion}) = -2 \). If we define the electrolyte by the valence, we will call MgCl\(_2\) is 2:1 electrolyte and Na\(_2\)SO\(_4\) 1:2 electrolyte.

The electric neutrality condition in bulk solution can be written by

\[
\sum_i eZ_i n_i^0 = 0 \quad (1)
\]

Here \( e \) is the elementary charge, \( Z_i \) is the valence of ion species \( i \), \( n_i^0 \) is the bulk number density of species \( i \).

Figure 1: Schematic view of the electric-double-layer of 2:1 unsymmetrical electrolyte solution

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Please note that the definition is occasionally given by the stoichiometric coefficient, in this case MgCl\(_2\) is 1:2 electrolyte and Na\(_2\)SO\(_4\) 2:1 electrolyte.
1.1 2:1 (MgCl₂ type) electrolyte

The charge neutrality condition in 2:1 electrolyte bulk solution can be written by

\[ \sum_i eZ_i n_i^0 = e(Z^+_i n^0_+ + Z^-_i n^0_-) = e(2n^0_+ - n^0_-) = 0 \] (2)

\[ n^-_o = 2n^0_+, \quad n^0_+ = 1000N_A e^* \] (3)

The subscript + and - means cation and anion, respectively. \( N_A \) is the Avogadro number and \( e^*/\text{mol dm}^{-3} \) is the molar concentration of 2:1 electrolyte solution. We use the exact solution of PB equation Eq.(40) in TU1[6]. If we define that potential at the distance \( z \) from the electrode is \( \phi(z) \), \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \epsilon_{GC} \) and \( \epsilon_p \) are the dielectric constant of the GC diffuse layer and the electric permittivity of free space, we have

\[ \frac{d\phi}{dz} = \pm \frac{2k_BT}{\epsilon_0 \epsilon_{GC}} \sum_i n_i^0 \left[ \exp \left( -\frac{Z_i e\phi(z)}{k_BT} \right) - 1 \right] \] (4)

\[ \frac{2k_BT}{\epsilon_0 \epsilon_{GC}} \int \frac{n^0_+}{n^-_o} \left[ \exp \left( -\frac{2e\phi(z)}{k_BT} \right) - 1 \right] + \frac{n^0_-}{n^-_o} \left[ \exp \left( \frac{e\phi(z)}{k_BT} \right) - 1 \right] \] (5)

We will follow Graeme’s formulation[4] and \( y \) is defined as

\[ y = \frac{e\phi(z)}{k_BT}, \quad \frac{dy}{dz} = \frac{e}{k_BT} \frac{d\phi}{dz} \] (6)

\[ \frac{dy}{dz} = \mp \frac{2000k_BT N_A e^* \epsilon_{GC}}{\epsilon_0 \epsilon_{GC}} \sqrt{(e^{-2y} - 1) + 2(e^y - 1)} \] (7)

\[ A \equiv \frac{e}{k_BT} \frac{2000k_BT N_A e^* \epsilon_{GC}}{\epsilon_0 \epsilon_{GC}} \] (8)

\[ \frac{dy}{dz} = \mp A \sqrt{(e^{-2y} - 1) + 2(e^y - 1)} \] (9)

The separation of variables can be integrated as

\[ \frac{dy}{\sqrt{(e^{-2y} - 1) + 2(e^y - 1)}} = \mp Adz \] (10)

\[ \frac{dy}{\sqrt{(e^{-2y} - 1)^2(1 + 2e^y)}} = \mp Adz \] (11)

Here we use, \( (e^{-2y} - 1)^2(1 + 2e^y) = (e^{-2y} - 2e^{-y} + 1)(1 + 2e^y) = e^{-2y} - 2e^{-y} + 1 + 2e^y - 4 + 2e^y = e^{-2y} - 3 + 2e^y = (e^{-2y} - 1) + 2(e^y - 1) \)

\[ \frac{dy}{(e^{-y} - 1)\sqrt{1 + 2e^y}} = \mp Adz \] (12)

\[ \frac{dy}{w} = 1 - e^y, \quad \frac{dw}{dy} = -e^y \] (13)

\[ \frac{dy}{(e^{-y} - 1)\sqrt{1 + 2e^y}} = \frac{e^y dy}{(1 - e^y)\sqrt{1 + 2e^y}} = \frac{1 - e^y}{w}\sqrt{1 + 2(1 - w)} \] (14)

\[ \int \frac{dx}{x\sqrt{ax + b}} = 2 \int dt \frac{1}{t^2 - b} \] (15)

Here we use

\[ t = \sqrt{ax + b}, \quad t^2 - b = ax, \quad \frac{dt}{dx} = (ax + b)^{-1/2} \frac{a}{2}, \quad 2 \int dt \frac{1}{t^2 - b} = 2 \int dx \frac{1}{ax\sqrt{ax + b}} \frac{a}{2} \]

\[ 2 \int dt \frac{1}{t^2 - b} = \frac{1}{\sqrt{b}} \int dt \left( \frac{1}{t - \sqrt{b}} - \frac{1}{t + \sqrt{b}} \right) = \frac{1}{\sqrt{b}} \ln \left| \frac{t - \sqrt{b}}{t + \sqrt{b}} \right| \]
y electrolyte ions cannot enter inside OHP and the diffuse layer of double layer extend from OHP to bulk. Please note

Now we integral from \( z = z_{OHP} \) to \( z = z \), i.e., \( y = y_{OHP} \) to \( y = y(z) \). OHP means *Outer Helmholtz Plane* where the electrolyte ions cannot enter inside OHP and the diffuse layer of double layer extend from OHP to bulk. Please note that \( y = e\phi(z)/(k_BT) \).

\[
\mp A \int_{z_{OHP}}^{z} dz = \mp A(z - z_{OHP})
\]

\[
\int_{y_{OHP}}^{y} \frac{dy}{\sqrt{(e^{-2y} - 1) + 2(e^y - 1)}} = -\frac{1}{\sqrt{3}} \ln \left| \frac{\sqrt{1 + 2e^y} - \sqrt{3}}{\sqrt{1 + 2e^y} + \sqrt{3}} \right| + \frac{1}{\sqrt{3}} \ln \left| \frac{\sqrt{1 + 2e^{y_{OHP}}} - \sqrt{3}}{\sqrt{1 + 2e^{y_{OHP}}} + \sqrt{3}} \right|
\]

\[
\pm \sqrt{3} A(z - z_{OHP}) = -\ln \left| \frac{\sqrt{1 + 2e^y} - \sqrt{3}}{\sqrt{1 + 2e^y} + \sqrt{3}} \right| + \ln \left| \frac{\sqrt{1 + 2e^{y_{OHP}}} - \sqrt{3}}{\sqrt{1 + 2e^{y_{OHP}}} + \sqrt{3}} \right|
\]

\[
\exp[\pm \sqrt{3} A(z - z_{OHP})] = \frac{\sqrt{1 + 2e^{y_{OHP}}} - \sqrt{3}}{\sqrt{1 + 2e^{y_{OHP}}} + \sqrt{3}} / \left| \frac{\sqrt{1 + 2e^y} - \sqrt{3}}{\sqrt{1 + 2e^y} + \sqrt{3}} \right|
\]

The potential profile in diffuse layer can be basically determined by Eq.(19).

The potential \( \phi_{OHP} \) is determined from the charge density \( \sigma_{GC} \) Eq.(69) in [TU1][6] and Eq.(5).

\[
\sigma_{GC} = e\phi_{GC} \frac{d\phi}{dz}_{OHP} = \mp e\phi_{GC} \left( \frac{2000k_BTNa}{e\phi_{GC}} \right) \sqrt{(e^{-2y_{OHP}} - 1) + 2(e^{y_{OHP}} - 1)}
\]

\[
\bar{B} \equiv \frac{\sigma_{GC}}{\sqrt{2000k_BTNa^2e\phi_{GC}}}
\]

Case I: when \( y_{OHP} > 0 \)

\[
Y \equiv e^{y_{OHP}}, \quad B^2 = Y^{-2} + 2Y - 3
\]

\[
2Y^3 - (3 + B^2)Y^2 + 1 = 0
\]

Case II: when \( y_{OHP} < 0 \)

\[
X \equiv e^{-y_{OHP}}, \quad B^2 = X^2 + 2X^{-1} - 3
\]

\[
X^3 - (3 + B^2)X + 2 = 0
\]

The Eq.(23) and Eq.(25) are the cubic equations and can be solved analytically2, but we prefer to use a numerical solution. In Fig.2 the plot of \( 2Y^3 - (3 + B^2)Y^2 + 1 \) Fig.2(left), \( X^3 - (3 + B^2)X + 2 \) Fig.2(right) are shown and we found that the solution that cross the zero line is unique for \( Y, X \geq 1 \). If there is no specific adsorption \( \sigma_{IHP} = 0 \), \( \sigma_{GC} = -\sigma_M \). Then *we can determine* the \( \phi_{OHP} \) from the given \( \sigma_M \).

From the plot of \( e^{-2y} + 2e^y - 3 \) as shown in Fig.3, there are two solutions for \( y \) which has positive and negative value. From the physical origin, we will take \( y_{OHP} < 0 \) for \( \sigma_{GC} < 0 \) and \( y_{OHP} > 0 \) for \( \sigma_{GC} > 0 \). Please note that \( y = e\phi(z)/(k_BT) \).

The right hand side of Eq.(19) is defined as \( P(z) \), then

\[
P(z) = \left[ \frac{\sqrt{1 + 2e^{y_{OHP}}} - \sqrt{3}}{\sqrt{1 + 2e^{y_{OHP}}} + \sqrt{3}} \right] \exp[\pm \sqrt{3} A(z - z_{OHP})]
\]

2T. G. Smagala and W. R. Fawcett[7] gave the analytical solutions, but their results may be not correct, because the solutions do not converge to 1 when \( B \) becomes zero. Eqs.(14-17) in their paper may be not correct.
Figure 2: plot of $2Y^3 - (3 + B^2)Y^2 + 1, X^3 - (3 + B^2)X + 2$. thick solid line: $B = 0$, solid line: $B = 0.5$, broken line: $B = 1.0$, and dotted line: $B = 1.5$. The solutions $2Y^3 - (3 + B^2)Y^2 + 1 = 0, X^3 - (3 + B^2)X + 2 = 0$ are unique for $Y, X \geq 1$.

Figure 3: plot of $e^{-2y} + 2e^y - 3$

Case (A): for $y > 0$
\[
\sqrt{1 + 2e^y} - \sqrt{3} = (\sqrt{1 + 2e^y} + \sqrt{3})P \\
(1 - P)\sqrt{1 + 2e^y} = \sqrt{3}(1 + P), (1 - P)^2(1 + 2e^y) = 3(1 + P)^2, 1 + 2e^y = 3\frac{(1 + P)^2}{(1 - P)^2} \\
e^y = \frac{1}{2} \left[ \frac{3(1 + P)^2}{(1 - P)^2} - 1 \right] = \frac{1}{2} \frac{13 + 6P + 3P^2 - (1 - 2P + P^2)}{(1 - P)^2} = \frac{1}{2} \frac{1 + 4P + P^2}{(1 - P)^2} = 1 + \frac{6P}{(1 - P)^2} \\
y = \frac{e\phi(z)}{k_B T} = \ln \left[ 1 + \frac{6P}{(1 - P)^2} \right] \\
\phi(z) = \frac{k_B T}{e} \ln \left[ 1 + \frac{6P}{(1 - P)^2} \right] 
\]

Case (B): for $y < 0$
\[
-(\sqrt{1 + 2e^y} - \sqrt{3}) = (\sqrt{1 + 2e^y} + \sqrt{3})P \\
(P + 1)\sqrt{1 + 2e^y} = \sqrt{3}(1 + P), (P + 1)^2(1 + 2e^y) = 3(1 - P)^2 \\
e^y = \frac{1}{2} \left[ \frac{3(1 - P)^2}{(1 + P)^2} - 1 \right] = \frac{1 - 6P + 3P^2 - (1 + 2P + P^2)}{(1 + P)^2} = \frac{1 - 4P + P^2}{(1 + P)^2} = 1 - \frac{6P}{(1 + P)^2} \\
y = \frac{e\phi(z)}{k_B T} = \ln \left[ 1 - \frac{6P}{(1 + P)^2} \right] \\
\phi(z) = \frac{k_B T}{e} \ln \left[ 1 - \frac{6P}{(1 + P)^2} \right] 
\]

In Fig.4 the plots of $\sqrt{1 + 2e^y} - \sqrt{3}, -(\sqrt{1 + 2e^y} - \sqrt{3})$ and $\sqrt{1 + 2e^y} + \sqrt{3}$ are shown. $P(z)$ should be positive, then the solutions are different for $y > 0$ and $y < 0$. The final results of Eq.(27-28) may differ from Grahame’s results\(^3\)

**Analytical solution:** when there is no specific adsorption, the $\phi_{\text{OH}}$ is obtained by Eq.(23) and Eq.(25). From this value the potential at the metal electrode $\phi_M$ can be determined using the potential slope at the inner layer

\(^3\)Eq.(13a) in Grahame’s paper may be not correct.
Change in the inner layer and the metal potential \( \sigma \). (3) Apply the boundary condition \( \sigma_M = -\varepsilon_0 \varepsilon_W d\phi/dz\mid_{M+} = -\varepsilon_0 \varepsilon_W d\phi/dz\mid_{OHP+} \). For diffuse layer the potential profile can be evaluated from Eqs. (27)-(28).

**Numerical Solution:** numerical solution can be obtained by the use of Eq.(5). When there is no specific adsorption (1) Set \( \sigma_M \), dielectric constant, thickness of the inner layer, (2) Use the value of \( \phi_{OHP} \) determined by Eq.(23-25). (3) Apply the boundary condition \( \sigma_M = -\varepsilon_0 \varepsilon_W d\phi/dz\mid_{M+} = -\varepsilon_0 \varepsilon_W d\phi/dz\mid_{OHP+} \), calculate the linear potential change in the inner layer and the metal potential \( \phi_M \). (4) Make the uniform mesh of the potential profile calculation (5) Using Eq.(5) and \( \phi(z + dz) \simeq \phi(z) + (d\phi/dz) dz \), the potential profile can be obtained. (6) If \( \phi(z = +\infty) \neq 0 \), change \( \phi_{OHP} \) and do the steps (3)-(5) again.

![Figure 4: plot of \( \sqrt{1 + 2e^y} - \sqrt{3}(\text{dotted line}), - (\sqrt{1 + 2e^y} - \sqrt{3})(\text{broken line}) \) and \( \sqrt{1 + 2e^y} + \sqrt{3} \) (solid line)](image)

**Concentration:** the separation of cation and anion density profile from the charge density \( \rho(z) \) is

\[
\rho(z) = e \sum_i Z_i n_i^0 \exp \left( -\frac{Z_i e\phi(z)}{k_B T} \right)
\]

(29)

\[
= e Z_+ n_+^0 \exp \left( -\frac{Z_+ e\phi(z)}{k_B T} \right) + e Z_- n_-^0 \exp \left( -\frac{Z_- e\phi(z)}{k_B T} \right)
\]

(30)

\[
z \to +\infty, \quad \rho(+\infty) \to 0, \quad \phi(+\infty) \to 0
\]

(31)

\[
\rho(+\infty) = e Z_+ n_+^0 + e Z_- n_-^0 = 0
\]

(32)

\[
2n_+^0 = n_-^0, \quad \text{for 2:1 unsymmetric electrolyte} \quad n_+^0 = 1000N_A c^*
\]

(33)

\[
c_+(z) = c^* \exp \left( -\frac{2\varepsilon_0 \phi(z)}{k_B T} \right)
\]

(34)

\[
c_-(z) = 2c^* \exp \left( \frac{\varepsilon_0 \phi(z)}{k_B T} \right)
\]

(35)

**1.1.1 Results: 2:1 electrolytes**

In Fig.5 the calculation results by analytical solution (solid line) and numerical solution (dotted line) for the 0.5 M 2:1 electrolyte solution on the positively and negatively electrified electrode are shown. It has been found that these are completely the same, then our reformulation may be justified. The potential profile is not symmetric about the sign of the surface charge density of the electrode, i.e., the absolute value of potential for the positively electrified electrode is greater than that for the negatively electrified one. The physical origin can be understood from Fig.6. In Fig.6 the concentration profiles of divalent cation (solid line) and the monovalent anion (dashed line) are shown. The effective thickness of the double layer for the positively electrified electrode (Fig.6 right, monovalent anion distribution) is longer than that for the negatively electrified electrode (Fig.6 left, divalent cation), because the cations with +2e charge have high screening ability. Then the magnitude of the potential for the negatively electrified is greater than that for positively charged electrode.

In the last part of this tutorial we will show that the GCS model is not good approximation to describe the electric-double-layer for multivalent electrolyte solution.

**1.2 1:2 (Na₂SO₄ type) electrolyte**

The formulation is the same as 2:1 electrolyte. The charge neutrality condition gives

\[
\sum_i e Z_i n_i^0 = e (Z_+ n_+^0 + Z_- n_-^0) = e (n_+^0 - 2n_-^0) = 0
\]

(36)

\[
n_+^0 = 2n_-^0, \quad n_-^0 = 1000N_A c^*
\]

(37)
Figure 5: Potential profiles of the GCS electric-double-layer of 0.5 M 2:1 electrolyte solution. The outer Helmholtz plane (OHP) is located at 2.125 Å from the electrode and is shown as vertical bar. The solid line is calculated from Eqs.(27)-(28) and the dotted line is calculated numerically by the use of PB equation. The solid and dotted lines are overlapped completely. The zero line of potential is also shown for the guide of reader’s eye.

Figure 6: Concentration profiles of the counter and co-ions of the GCS electric-double-layer of 0.5 M 2:1 electrolyte solution. The outer Helmholtz plane (OHP) is located at 2.125 Å from the electrode and shown as vertical bar. The charge density of the electrode in the left figure is \( \sigma = -0.185 \text{ C m}^{-2} \), and that in the right figure is \( \sigma = +0.185 \text{ C m}^{-2} \).
The exact solution of PB equation Eq.(40) in TUI[6] gives

\[
\frac{\partial \phi}{\partial z} = \pm 2k_BT \sum \frac{1}{e_{\text{GC}}} \int_0^\infty \left[ \exp \left( -\frac{Z_i e\phi(z)}{k_BT} \right) - 1 \right] \nu_i^n - \frac{\partial}{\partial z} \left( \frac{2 e\phi(z)}{k_BT} \right) - 1 
\]

(38)

\[
\frac{\partial \phi}{\partial z} = \pm 2k_BT \sum \frac{1}{e_{\text{GC}}} \int_0^\infty \frac{2 e\phi(z)}{k_BT} - 1 + \frac{2 e\phi(z)}{k_BT} - 1 \nu_i^n
\]

(39)

\[
\frac{\partial \phi}{\partial z} = \pm 2k_BT \sum \frac{1}{e_{\text{GC}}} \int_0^\infty \frac{2 e\phi(z)}{k_BT} - 1 + \frac{2 e\phi(z)}{k_BT} - 1 \nu_i^n
\]

(40)

\[
(e^y - 1)^2 (1 + 2e^{-y}) - (e^{2y} - 2e^y + 1) (1 + 2e^{-y}) = e^{2y} - 2e^y + 1 + 2e^y - 4 + 2e^{-y} = e^{2y} + 2e^{-y} - 3
\]

(41)

\[
\frac{dy}{e^y - 1} = A dz, \quad A = e^{k_BT} \sum \frac{1}{e_{\text{GC}}} = e^{k_BT} \frac{200k_BT N \alpha e^y}{e_{\text{GC}}}
\]

(42)

\[
w = 1 - e^{-y}, \quad \frac{dw}{dy} = e^{-y} = 1 - w
\]

(43)

\[
\frac{dy}{e^y (1 - e^{-y}) \sqrt{1 + 2e^{-y}}} = \frac{w}{1 + 2(1 - w)} = \frac{dw}{w \sqrt{-2w + 3}}
\]

(44)

Now we integral from \(z = z_{\text{OHPP}}\) to \(z = z, y = y_{\text{OHPP}}\) to \(y = y(z)\). Please note that \(y = e\phi(z)/(k_BT)\).

\[
\int_{z_{\text{OHPP}}}^y dy (1 - e^{-y}) \sqrt{1 + 2e^{-y}} = +A \int_{z_{\text{OHPP}}}^z dz = +A(z - z_{\text{OHPP}})
\]

(45)

\[
\int_{z_{\text{OHPP}}}^y dy (1 - e^{-y}) \sqrt{1 + 2e^{-y}} = \frac{1}{\sqrt{3}} \ln \frac{\sqrt{1 + 2e^{-y} - \sqrt{3}}}{\sqrt{1 + 2e^{-y} + \sqrt{3}}} - \frac{1}{\sqrt{3}} \ln \frac{\sqrt{1 + 2e^{-y_{\text{OHPP}}} - \sqrt{3}}}{\sqrt{1 + 2e^{-y_{\text{OHPP}}} + \sqrt{3}}}
\]

(46)

\[
\sqrt{1 + 2e^{-y_{\text{OHPP}}} - \sqrt{3}} = \sqrt{1 + 2e^{-y_{\text{OHPP}}} + \sqrt{3}} \exp[\pm \sqrt{3}A(z - z_{\text{OHPP}})]
\]

(47)

The potential profile in diffuse layer can be determined by Eq.(47).

The potential \(\phi_{\text{OHPP}}\) is determined from the charge density \(\sigma_{\text{GC}}\) and Eq.(41).

\[
\sigma_{\text{GC}} = e_{\text{GC}} \frac{d\phi}{dz}_{\text{OHPP+}} = \pm e_{\text{GC}} \frac{200k_BT N \alpha e^y}{e_{\text{GC}}} \sqrt{e^{2y_{\text{OHPP}}} + 2e^{-y_{\text{OHPP}}} - 3}
\]

(48)

Case I: when \(y_{\text{OHPP}} > 0\)

\[
Y \equiv e^{y_{\text{OHPP}}}, \quad B^2 = Y^2 - 3 + 2Y^{-1}
\]

(49)

\[
Y^3 - (3 + B^2)Y + 2 = 0
\]

(50)

Case II: when \(y_{\text{OHPP}} < 0\)

\[
X \equiv e^{-y_{\text{OHPP}}}, \quad B^2 = X^{-2} - 3 + 2X
\]

(51)

\[
2X^3 - (3 + B^2)X^2 + 1 = 0
\]

(52)
The Eq.(50) and Eq.(52) are the cubic equations and can be solved analytically, but we prefer to use a numerical solution. In Fig.2 the plot of $Y^3 - (3 + B^2)Y + 2(3 + B^2)X^2 + 1(3 + B^2)$ are shown and we found that the solution that cross the zero line is unique for $Y, X \geq 1$.

If there is no specific adsorption $\sigma_{OHP} = 0$, $\sigma_{GC} = -\sigma_M$. Then we cat determine the $\phi_{OHP}$ from the given $\sigma_M$.

From the plot of $e^{2y} + 2e^{-y} - 3$ as shown in Fig.7, there are two solutions for $y$ which has positive and negative value. From the physical origin, we will take $y_{OHP} < 0$ for $\sigma_{GC} < 0$ and $y_{OHP} > 0$ for $\sigma_{GC} > 0$. Please note that $y = \phi(z)/(k_BT)$.

![Figure 7: plot of $e^{2y} + 2e^{-y} - 3$](image)

\[
Q(z) \equiv \frac{\sqrt[3]{1 + 2e^{-y} - \sqrt[3]{3}}}{\sqrt[3]{1 + 2e^{-y} + \sqrt[3]{3}}} \exp[\mp \sqrt[3]{3}(z - z_{OHP})]
\]

**Case (A):** for $y > 0$

\[
-(\sqrt[3]{1 + 2e^{-y} - \sqrt[3]{3}}) = (\sqrt[3]{1 + 2e^{-y} + \sqrt[3]{3}}) Q
\]

\[
(1 + Q)\sqrt[3]{1 + 2e^{-y}} = \sqrt[3]{3}(1 - Q), (1 + Q)^2(1 + 2e^{-y}) = 3(1 - Q)^2, 1 + 2e^{-y} = 3(1 - Q)^2/(1 + Q)^2
\]

\[
e^{-y} = \frac{1}{2} \left[ (1 - Q)z - 1 \right] = \frac{3 - 6Q + 3Q^2 - (1 + 2Q + Q^2)}{(1 + Q)^2} = \frac{1 - 4Q + Q^2}{(1 + Q)^2} = 1 - \frac{6Q}{(1 + Q)^2}
\]

\[
y = -\frac{\phi(z)}{k_BT} = \ln \left[ 1 - \frac{6Q}{(1 + Q)^2} \right]
\]

\[
\phi(z) = -\frac{k_BT}{e} \ln \left[ 1 - \frac{6Q}{(1 + Q)^2} \right]
\]

**Case (B):** for $y < 0$

\[
\sqrt[3]{1 + 2e^{-y} - \sqrt[3]{3}} = (\sqrt[3]{1 + 2e^{-y} + \sqrt[3]{3}}) Q
\]

\[
(1 - Q)\sqrt[3]{1 + 2e^{-y}} = (1 + Q)^3, (1 - Q)^2(1 + 2e^{-y}) = 3(1 + Q)^2
\]

\[
e^{-y} = \frac{1}{2} \left[ (1 + Q)z - 1 \right] = \frac{3 + 6Q + 3Q^2 - (1 - 2Q + Q^2)}{(1 - Q)^2} = \frac{1 + 4Q + Q^2}{(1 - Q)^2} = 1 + \frac{6Q}{(1 - Q)^2}
\]

\[
y = \frac{\phi(z)}{k_BT} = \ln \left[ 1 + \frac{6Q}{(1 - Q)^2} \right]
\]

\[
\phi(z) = -\frac{k_BT}{e} \ln \left[ 1 + \frac{6Q}{(1 - Q)^2} \right]
\]

**Analytical solution:** When there is no specific adsorption, the $\phi_{OHP}$ is obtained by Eq.(50) and Eq.(52). From this value the potential at the metal electrode $\phi_M$ can be determined using the potential slope at the inner layer $\sigma_M = -\varepsilon_0\varepsilon_W\phi_z/dz|_{\text{M}} = -\varepsilon_0\varepsilon_W\phi_z/dz|_{\text{OHP}}$. For diffuse layer the potential profile can be evaluated from Eqs.(54)-(55).

**Numerical solution:** Numerical solution can be obtained by the use of Eq.(41). When there is no specific adsorption (1) Set $\sigma_M$, dielectric constant, thickness of the inner layer, (2) Use the value of $\phi_{OHP}$ determined by Eq.(50) and Eq.(52). (3) apply the boundary condition $\sigma_M = -\varepsilon_0\varepsilon_W\phi_z/dz|_{\text{M}} = -\varepsilon_0\varepsilon_W\phi_z/dz|_{\text{OHP}}$, calculate the linear potential change in the inner layer and the metal potential $\phi_M$. (4) make the uniform mesh of the potential profile calculation (5) Using Eq.(41) and $\phi(z + dz) \approx \phi(z) + (d\phi/dz)_z dz$ the potential profile can be obtained. (6) If $\phi(z = +\infty) \neq 0$, change $\phi_{OHP}$ and do the steps (3)-(5) again.
Concentrations: the separation of cation and anion density profile from the charge density $\rho(z)$ is

$$\rho(+\infty) = eZ_+ n_+^0 + eZ_- n_-^0 = 0$$

$$n_+^0 = 2n_-^0, \quad \text{for } 1:2 \text{ unsymmetric electrolyte} \quad n_-^0 = 1000N_A e^*$$

$$c_+(z) = 2c^* \exp \left( \frac{-e\phi(z)}{k_B T} \right)$$

$$c_-(z) = c^* \exp \left( \frac{2e\phi(z)}{k_B T} \right)$$

1.2.1 Results: 1:2 electrolytes

In Fig.8 the calculation results by analytical solution(solid line) and numerical solution (dotted line) for the 0.5 M 1:2 electrolyte solution on the positively and negatively electrified electrode are shown. Again these calculation results are completely the same, then our reformulation may be justified. If the sign of the charge of electrode, counter-ion and co-ion of 1:2 electrolytes are carried out inversion, the potential profile and concentration profiles (Fig.9) are the same as those for 2:1 electrolyte solutions.

![Figure 8: Potential profiles of the GCS electric-double-layer of 0.5 M 1:2 electrolyte solution. The outer Helmholtz plane (OHP) is located at 2.125 Å from the electrode and is shown as vertical bar. The solid line is calculated from Eqs.(54)-(55) and the dotted line is calculated numerically by the use of PB equation. The solid and dotted lines are overlapped completely. The zero line of potential is also shown for the guide of reader’s eye.](image)

![Figure 9: Concentration profiles of the counter and co-ions of of the GCS electric-double-layer of 0.5 M 1:2 electrolyte solution. The outer Helmholtz plane (OHP) is located at 2.125 Å from the electrode. The charge density of the SAM terminal of the left figure is $\sigma = -0.185 \text{ C m}^{-2}$, and that of the right figure is $\sigma = +0.185 \text{ C m}^{-2}$.](image)
2 Monte Carlo simulation of 2:1, 1:2, 2:2 electrolytes

By the use of Monte Carlo simulation based on primitive model (ions: hard sphere + point charge, solvent: dielectric medium without structure), Torrie and Valleau showed the potential-inversion region for the potential profile of the double-layer for 1:2, 2:1, 2:2 electrolyte solution[5]. This potential inversion cannot reproduced by the GCS (or Poisson-Boltzmann) model. This may be due to the correlation between the electrolyte ions and that between the electrode an ions should be considered.

The detail of our MC simulation will be reported elsewhere, then we describe the method briefly. The canonical Monte Carlo simulation has been done with the primitive model. The diameter of the hard sphere for cation and anion is 4.25 Å, then OHP is located at 2.15 Å from the electrode. The surface charge of the electrode is not uniformly distributed but the elementary charge $\pm e$ is located in a regular array on $(\sqrt{3} \times \sqrt{3})$-R30° mesh points of the terminal dissociated group of self-assembled monolayer(SAM) of thiol on Au(111) is simulated. The size of the two-dimensionally periodic unit cell is $20 \times 17.3 \times 66.6$ Å used. The dielectric constant of the structureless electrolyte solution is 78.5 and the temperature of the system is 300 K. The charge neutrality condition is kept for the surface charge and those of electrolyte in the unit cell. To consider the long-range electrostatic interaction in 2D unit cell accurately Lekner method[8] is used.

In Fig. 10 the potential profiles of the double-layer for 0.5 M 2:1 electrolyte solution is shown. The solid line is obtained by the averaged potential over the plane parallel to the electrode and broken line is from the 1D GCS theory. At $z = 15.6$ Å (= SAM thickness) from the electrode the regular array of the dissociated terminal is located and then OHP is at $z = 17.725$ Å. The left side in Fig.10 is the hard-wall electrified and the right side is the neutral hard wall at $z = 66.6$ Å. The potential profile is completely different from that of GCS results. The GCS results showed that the potential is increased monotonously, however in MC simulation the region where the potential is positive is appeared, even though the electrified electrode is negatively charged. In 1982 Torrie and Valleau reported MC simulation and modified PB equation showed this potential inversion region for 0.5 M 2:1 electrolytes and the peak value of the potential is $+7.7$ mV for $-0.15$ C m$^{-2}$ electrified electrode[5]. In this sense our simulation can reproduce Torrie-Valleau results. The physical origin for the appearance of the potential inverted region could be understood from the concentration profiles of the electrolytes as shown in Fig.11. The divalent cations and the negatively charged electrode interact strongly, and divalent cations are localized at the region very close to OHP. Total charge screened by those cations is more than that of surface charge, i.e. overcompensated, then there is a peak of anion distribution at $z = OHP +$ diameter of the hard-sphere.

![Figure 10: MC calculation results of the potential profiles of the electric double layer for 0.5 M 2:1 unsymmetrical electrolyte solution. MC simulation (solid line) and GCS model (broken line). The quarter of the terminal of SAM is dissociated and the regular array of those has the surface charge density of $-0.185$ C m$^{-2}$ (left side of the figure). The vertical dotted line is the position of OHP. In the right side of the figure there is a hard wall that has no chrage.](image-url)

In Fig. 12 the potential profiles for the EDL of 0.5 M 2:1 electrolyte with positively charged interface is shown. Again MC simulation result differ significantly from GCS result. In this case the counter is monovalent anion and the EDL may be expected to be almost the same as GCS results. The potential has a small inverted region but the potential has minus few mV. These results may be due to the high correlation of ion interaction. The effective thickness is increased than that for negatively charged interface, then the potential at SAM terminal is ca. 100 mV, which is greater than that $-60$ mV for the negatively charged interface.

In Fig. 13 the potential profile for the EDL of 0.5 M 1:2 electrolyte with positively charged ($+0.185$ C m$^{-2}$) interface
Figure 11: MC calculation results of the concentration profiles of the 0.5 M 2:1 unsymmetrical electrolyte. The solid line is divalent cation distribution and broken line is anion distribution. The electrified interface of SAM terminal \((\sigma = -0.185 \text{ C m}^{-2})\) is located at \(z = 15.6 \text{ Å}\) and neutral hard wall at 66.6 Å.

Figure 12: MC calculation results of the potential profiles of the electric double layer for 0.5 M 2:1 unsymmetrical electrolyte solution. MC simulation (solid line) and GCS model (broken line). The regular array of SAM terminal has the surface charge density of +0.185 C m\(^{-2}\) (left side of the figure). The vertical dotted line is the position of OHP. In the right side of the figure there is a hard wall that has no charge.
is shown. In this case the potential profile is just the inversion of that for 0.5 M 2:1 electrolyte with negatively charged (-0.185 C m\(^{-2}\)) interface.

![Figure 13: MC calculation results of the potential profiles of the electric double layer for 0.5 M 1:2 unsymmetrical electrolyte solution. MC simulation (solid line) and GCS model (broken line). The quarter of the terminal of SAM is dissociated and the regular array of those has the surface charge density of +0.185 C m\(^{-2}\) (left side of the figure). The vertical dotted line is the position of OHP. In the right side of the figure there is a hard wall that has no charge.](image-url)

In Fig. 14 the EDL for 0.5 M 2:2 symmetric electrolyte is shown. The GCS result differ significantly from the results obtained by MC simulation. As reported by Torrie-Valleau\[5\] even in symmetric electrolyte the inverted potential region can be found. From Fig. 15 the cation (anion) distribution has a peak around \(z = \text{hardwall} + \text{diameter of hard sphere}\). This show the overcompensation of divalent counter-ion (cation), which is found for multivalent unsymmetric electrolyte solutions as shown above.

We are now investigating that this kind of potential-inversion can induce a double layer effect of redox reaction on the electrode and have been found some evidence for it.

![Figure 14: MC calculation results of the potential profiles of the electric double layer for 0.5 M 2:2 symmetrical electrolyte solution. MC simulation (solid line) and GCS model (broken line). The regular array of SAM terminal has the surface charge density of -0.185 C m\(^{-2}\) (left side of the figure). The vertical dotted line is the position of OHP. In the right side of the figure there is a hard wall that has no charge.](image-url)
Figure 15: MC calculation results of the concentration profiles of the 0.5 M 2:2 symmetrical electrolyte. The solid line is divalent cation distribution and broken line is anion distribution. The electrified interface of SAM terminal ($\sigma = -0.185 \ \text{C m}^{-2}$) is located at $z = 15.6 \ \text{Å}$ and neutral hard wall at 66.6 Å.

References