Research article

Electric energies of a charged sphere surrounded by electrolyte

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Appendix 1

In order to calculate $E_{in}$ let us substitute the derivative of Eq.2 into Eq.3:

$$
E_{in} = \frac{k_e Q^2 \lambda_D^2}{2 \varepsilon_c R^2} e^{-2R/\lambda_D} \int_0^R \left[ \frac{\sinh \left( \frac{Z}{\lambda_D} \right)}{Z^2} + \frac{\cosh \left( \frac{Z}{\lambda_D} \right)}{Z \lambda_D} \right]^2 Z^2 dZ
$$

(A1)

The integral in Eq.A1 can be separated to three terms:

$$
\int_0^R \left[ \frac{\sinh \left( \frac{Z}{\lambda_D} \right)}{Z^2} + \frac{\cosh \left( \frac{Z}{\lambda_D} \right)}{Z \lambda_D} \right]^2 Z^2 dZ = \int_0^R \frac{\sinh^2 \left( \frac{Z}{\lambda_D} \right)}{Z^2} dZ - \int_0^R \frac{\sinh \left( \frac{2Z}{\lambda_D} \right)}{Z \lambda_D} dZ + \int_0^R \frac{\sinh^2 \left( \frac{Z}{\lambda_D} \right) + 1}{\lambda_D^2} dZ
$$

(A2)

The first term in Eq.A2 is:

$$
\int_0^R \frac{e^{2Z/\lambda_D} - 2 + e^{-2Z/\lambda_D}}{4Z^2} dZ = \left[ -\frac{e^{2Z/\lambda_D}}{4Z} \right]_0^R + \frac{1}{2\lambda_D} \int_0^R \frac{e^{2Z/\lambda_D}}{Z} dZ + \left[ \frac{1}{2Z} \right]_0^R
$$
\[
\left[ -\frac{e^{-2Z/\lambda_D}}{4Z} \right]_0^R - \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} = \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} - \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} + \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} = \left[ 1 - \frac{e^{2Z/\lambda_D}}{4Z} \right]_0^R + \left[ 1 - \frac{e^{2Z/\lambda_D}}{4Z} \right]_0^R = \]

\[
\frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} - \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} + \frac{1}{2R} \left[ 1 - \cosh \left( \frac{2R}{\lambda_D} \right) \right] \]  
(A3)

Note that above we used \([1]: \int e^{ax} x^{-z} dx = \left( -\frac{e^{ax}}{x^z} + a \int e^{ax} x^{-z} dx \right)\).

Calculating the last term in Eq. A3 we used the following two limits:

\[
\lim_{Z \to 0} \left[ 1 - \frac{e^{2Z/\lambda_D}}{Z} \right] = \lim_{Z \to 0} \frac{1 - \left[ 1 + 1 \frac{2Z}{\lambda_D} \right] + \frac{1}{2!} \left( \frac{2Z}{\lambda_D} \right)^2 + \frac{1}{3!} \left( \frac{2Z}{\lambda_D} \right)^3 + \cdots }{Z} = -\frac{2}{\lambda_D} \]  
(A4)

and

\[
\lim_{Z \to 0} \left[ 1 - \frac{e^{2Z/\lambda_D}}{Z} \right] = \lim_{Z \to 0} \frac{1 - \left[ 1 - 1 \frac{2Z}{\lambda_D} \right] + \frac{1}{2!} \left( \frac{2Z}{\lambda_D} \right)^2 - \frac{1}{3!} \left( \frac{2Z}{\lambda_D} \right)^3 + \cdots }{Z} = \frac{2}{\lambda_D} \]  
(A5)

The second term in Eq. A2 is:

\[
- \int_0^R \frac{\sinh \left( \frac{2Z}{\lambda_D} \right)}{2\lambda_D} \frac{dZ}{Z} = \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} - \frac{1}{2\lambda_D} \int_0^R e^{\frac{2Z}{\lambda_D}} \frac{dZ}{Z} = \]  
(A6)

The third term in Eq. A2 is:

\[
\int_0^R \frac{\sinh^2 \left( \frac{Z}{\lambda_D} \right)}{\lambda_D^2} \frac{dZ}{Z} + \int_0^R \frac{1}{\lambda_D^2} dZ = \frac{1}{\lambda_D^2} \left[ \frac{\lambda_D}{2} \sinh \left( \frac{Z}{\lambda_D} \right) \cosh \left( \frac{Z}{\lambda_D} \right) + \frac{Z}{2} \right]_0^R \]  
(A7)

After summarizing the three terms (Eqs. A3, A6, A7) of the integral in Eq. A1 we get \( E_{in} \):

\[
E_{in} = \frac{k_e Q^2}{2\varepsilon_R R^2} e^{-\frac{2R}{\lambda_D}} \left\{ \frac{1}{2\lambda_D} \sinh \left( \frac{R}{\lambda_D} \right) \cosh \left( \frac{R}{\lambda_D} \right) + \frac{R}{2\lambda_D} + \frac{1}{2R} \left[ 1 - \cosh \left( \frac{2R}{\lambda_D} \right) \right] \right\} =
\]
\[
\frac{k_e Q^2 \lambda_D^2}{2 \varepsilon_r R^2} e^{-\frac{2R}{\lambda_D}} \left( \frac{1}{2 \lambda_D} \sinh \left( \frac{R}{\lambda_D} \right) \cosh \left( \frac{R}{\lambda_D} \right) + \frac{R}{2 \lambda_D^2} - \frac{1}{R} \sinh \left( \frac{R}{\lambda_D} \right) \right) \]  

(A8)

Appendix 2

In order to calculate \( E_{out} \) let us substitute the derivative of Eq.1 into Eq.3:

\[
E_{out} = \frac{k_e Q^2 \lambda_D^2}{2 \varepsilon_r R^2} \sinh \left( \frac{R}{\lambda_D} \right) \int_R^\infty e^{-2Z/\lambda_D} \left[ \frac{1}{Z} + \frac{1}{\lambda_D} \right]^2 dZ =
\]

\[
\frac{2k_e Q^2}{\varepsilon_r R^2} \sinh \left( \frac{R}{\lambda_D} \right) \int_R^\infty e^{-\frac{2Z}{\lambda_D}} \left[ \frac{\lambda_D^2}{4Z^2} + \frac{\lambda_D}{2Z} + \frac{1}{4} \right] dZ \quad \text{(A9)}
\]

After substituting \( 2Z/\lambda_D \) by \( \omega \) in Eq.A9 we get:

\[
E_{out} = \frac{\lambda_D^2}{\varepsilon_r R^2} k_e Q^2 \sinh \left( \frac{R}{\lambda_D} \right) \left\{ \int_0^\infty \frac{e^{-\omega}}{\omega} d\omega + \int_0^\infty \frac{e^{-\omega}}{\omega} d\omega + \int_0^\infty \frac{e^{-\omega}}{4} d\omega \right\}
\]

\[
\frac{\lambda_D^2 k_e Q^2}{\varepsilon_r R^2} \sinh \left( \frac{R}{\lambda_D} \right) \left\{ - \int_0^\infty \frac{e^{-\omega}}{\omega} d\omega + \int_0^\infty \frac{e^{-\omega}}{\omega} d\omega + \int_0^\infty \frac{e^{-\omega}}{4} d\omega \right\} =
\]

\[
\frac{\lambda_D^2 k_e Q^2}{\varepsilon_r R^2} e^{-\frac{2R}{\lambda_D}} \left[ \frac{\lambda_D}{2R} + \frac{1}{4} \right] \sinh \left( \frac{R}{\lambda_D} \right) \quad \text{(A10)}
\]

Note that above we used [1]: \( \int \frac{e^{ax}}{x^2} dx = \left( -\frac{e^{ax}}{x} + a \int \frac{e^{ax}}{x} dx \right) \).

Appendix 3

\[
E_{CC} = \frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to \infty} \lambda_D e^{-\frac{R}{\lambda_D}} \sinh \left( \frac{R}{\lambda_D} \right) =
\]

\[
\frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to \infty} \lambda_D e^{-\frac{R}{\lambda_D}} \left[ \frac{R}{\lambda_D} + \frac{1}{3!} \left( \frac{R}{\lambda_D} \right)^3 + \frac{1}{5!} \left( \frac{R}{\lambda_D} \right)^5 + \cdots \right] =
\]

\[
\frac{k_e Q^2}{2 \varepsilon_r R} \quad \text{(A11)}
\]
Here we calculate the energies, $E_{CC}$, $E_{in}$ and $E_{out}$, when $\lambda_D$ approaches zero.

$$E_{CC} = \frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to 0} \lambda_D e^{\frac{-R}{\lambda_D}} \left( \frac{R}{\lambda_D} \right) =$$

$$\frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to 0} \lambda_D \left( \frac{1 - e^{\frac{-2R}{\lambda_D}}}{2} \right) = 0 \quad (A14)$$

$$E_{in} = \frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to 0} \left\{ e^{\frac{-2R}{\lambda_D}} \left( \frac{\lambda_D}{2} \sinh \left( \frac{R}{\lambda_D} \right) \cosh \left( \frac{R}{\lambda_D} \right) + \frac{R}{2} - \frac{\lambda_D^2}{R} \sinh^2 \left( \frac{R}{\lambda_D} \right) \right) \right\} =$$

$$\frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to 0} e^{\frac{-2R}{\lambda_D}} \left[ \frac{2 R}{4} - \frac{2 R}{4} \frac{e^{\lambda_D} - e^{-\lambda_D}}{4} + \frac{R}{2} - \frac{\lambda_D^2}{R} \frac{2 R}{4} e^{\lambda_D} - 2 + e^{\lambda_D} \right] =$$

$$\frac{k_e Q^2}{2 \varepsilon_r R^2} \lim_{\lambda_D \to 0} \left[ \frac{\lambda_D}{2} \left( 1 - e^{\frac{-4R}{\lambda_D}} \right) + \frac{R}{2} e^{\frac{-2R}{\lambda_D}} - \lambda_D^2 \frac{1 - 2 e^{\frac{-2R}{\lambda_D}} + e^{\frac{-4R}{\lambda_D}}}{4} \right] = 0 \quad (A15)$$
\[ E_{\text{out}} = \frac{k_e Q^2}{\varepsilon R^2} \lim_{\lambda_D \to 0} \left\{ \sinh^2 \left( \frac{R}{\lambda_D} \right) \left[ \frac{\lambda_D^2}{2R} + \frac{\lambda_D}{4} \right] \right\} e^{-2R/\lambda_D} = \]

\[ \frac{k_e Q^2}{\varepsilon R^2} \lim_{\lambda_D \to 0} \left\{ 1 - 2e^{-\frac{2R}{\lambda_D}} + e^{-\frac{4R}{\lambda_D}} \left[ \frac{\lambda_D^2}{2R} + \frac{\lambda_D}{4} \right] \right\} = 0 \] (A16)

References

1. Moll VH (2015) Special Integrals of Gradshteyn and Ryzhik: the Proofs–Volume II. Series: Monographs and Research Notes in Mathematics, CRC Press.