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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:

$$E_{in} = \frac{k_e Q^2 \lambda_D^2}{2\varepsilon_r R^2} e^{-2R/\lambda_D} \int_0^R \left[-\frac{\sinh\left(\frac{Z}{\lambda_D}\right)}{Z^2} + \frac{\cosh\left(\frac{Z}{\lambda_D}\right)}{Z\lambda_D} \right]^2 Z^2 dZ \qquad \text{(A1)}$$

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

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

$$\int_0^R \frac{\sinh^2\left(\frac{Z}{\lambda_D}\right) + 1}{\lambda_D^2} dZ \qquad \text{(A2)}$$

The first term in Eq.A2 is:

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

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

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

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

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

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

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

and

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

The second term in Eq.A2 is:

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

The third term in Eq.A2 is:

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

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

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

$$\frac{k_e Q^2 \lambda_D^2}{2\varepsilon_r R^2} e^{-\frac{2R}{\lambda_D}} \left\{ \frac{1}{2\lambda_D} \sinh\left(\frac{R}{\lambda_D}\right) \cosh\left(\frac{R}{\lambda_D}\right) + \frac{R}{2\lambda_D^2} - \frac{1}{R} \sinh^2\left(\frac{R}{\lambda_D}\right) \right\} \quad \text{(A8)}$$

Appendix 2

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

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

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

After substituting $2Z/\lambda_D$ by ω in Eq.A9 we get:

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

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

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

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

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

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

$$\frac{k_e Q^2}{2\varepsilon_r R} \quad \text{(A11)}$$

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

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

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

$$\frac{k_e Q^2}{2\varepsilon_r R^2} \left[\frac{R}{2} + \frac{R}{2} - R \right] = 0 \qquad \text{(A12)}$$

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

$$\frac{k_e Q^2}{\varepsilon_r R^2} \lim_{\lambda_D \to \infty} \left\{ e^{-2R/\lambda_D} \left\{ \frac{R^2}{\lambda_D^2} + \frac{2R}{3!\,\lambda_D}\left(\frac{R}{\lambda_D}\right)^3 + \cdots \right\} \left[\frac{\lambda_D^2}{2R} + \frac{\lambda_D}{4} \right] \right\} =$$

$$\frac{k_e Q^2}{2\varepsilon_r R} \qquad (A13)$$

Appendix 4

Here we calculate the energies, E_{CC}, E_{in} and E_{out}, when λ_D approaches zero.

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

$$\frac{k_e Q^2}{2\varepsilon_r R^2} \cdot \lim_{\lambda_D \to 0} \lambda_D \frac{1 - e^{-\frac{2 \cdot R}{\lambda_D}}}{2} = 0 \qquad \text{(A14)}$$

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

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

$$\frac{k_e Q^2}{2\varepsilon_r R^2} \lim_{\lambda_D \to 0} \left[\frac{\lambda_D}{2} \frac{1 - e^{-\frac{4 \cdot R}{\lambda_D}}}{4} + \frac{R}{2} e^{-\frac{2R}{\lambda_D}} - \frac{\lambda_D^2}{R} \frac{1 - 2e^{-\frac{2R}{\lambda_D}} + e^{-\frac{4 \cdot R}{\lambda_D}}}{4} \right] = 0 \qquad \text{(A15)}$$

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

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

References

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