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**Research** article

## Density of electric field energy around two surface-charged spheres surrounded by electrolyte II. The smaller sphere is inside the larger one

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## Appendix 1

The Poisson equation is [8]:

$$\nabla^2 V(\underline{r}) = -\frac{\rho(\underline{r})}{\varepsilon_0 \varepsilon_r} \tag{A1}$$

where  $\rho(\underline{r})$  is the charge density,  $\varepsilon_0$  is the vaacum permittivity and  $\varepsilon_r$  is the relative static permittivity.

The solution of the above Poisson equation is [8]:

$$V(\underline{r}) = \iiint d^3 \underline{r}' \frac{\rho(\underline{r}')}{4\pi\varepsilon_0 \varepsilon_r |\underline{r}-\underline{r}'|}$$
(A2)

In the case of the Poisson-Boltzmann equation [8, 9]  $-\frac{\rho(\underline{r})}{\varepsilon_0 \varepsilon_r}$  (in Eq A1) is equal with

$$-\frac{\rho(\underline{r})}{\varepsilon_0\varepsilon} = \sum_i \frac{z_i q n_i^0}{\varepsilon_0\varepsilon_r} e^{-\frac{z_i q V(\underline{r})}{k_B T}}$$
(A3)

where q is the elementary charge (positive or negative depending on the charge of the i-th type of ion),  $z_i$  is the charge number of the i-th type of ion,  $k_B$  is the Boltzmann constant, T is the absolute temperature,  $\rho(\underline{r})$  is the charge density of the ions in the electrolyte and  $\varepsilon_r$  is the relative static permittivity of the electrolyte.

The Screened Poisson equation is [8]:

$$\nabla^2 V(\underline{r}) - \lambda_D^{-2} V(\underline{r}) = -\frac{\rho_{ex}(\underline{r})}{\varepsilon_0 \varepsilon_r}$$
(A4)

where  $\rho_{ex}(\underline{r})$  is the density of the external charge at position  $\underline{r}$ ,  $\varepsilon_0$  is the electric constant and  $\varepsilon_r$  is the relative static permittivity of the electrolyte,  $\lambda_D$  is the Debye length. Note, that Eq A4 is valid if the electrolyte itself is electrically neutral. The solution of this equation is [8]:

$$V(\underline{r}) = \iiint d^3 \underline{r}' \frac{\rho_{ex}(\underline{r}')}{4\pi\varepsilon_0\varepsilon_r} \frac{e^{-|\underline{r}-\underline{r}'|/\lambda_D}}{|\underline{r}-\underline{r}'|}$$
(A5)

i.e. the potential is the superposition of the so called screened Coulomb potential of the external charges.

*Appendix 2* The electric field energy density of N+1 charged spheres surrounded by electrolyte where N small spheres located within a large sphere

The coordinates of the center of the larger sphere are  $(x_L, y_L) = (0, 0)$ 

$$u_F(x_P, y_P, z_P) = \frac{\varepsilon_r \varepsilon_0}{2} \underline{E} \cdot \underline{E} = \frac{\varepsilon_r \varepsilon_0}{2} \left( \{ E_{Lx} + \sum_{i=1}^N E_{ix} \}^2 + \{ E_{Ly} + \sum_{i=1}^N E_{iy} \}^2 + \{ E_{Lz} + \sum_{i=1}^N E_{iz} \}^2 \right) (A6)$$

where the electric field created by the i-th sphere at point  $P_1$  is:

$$\underline{E}_{i} = \left(E_{ix}, E_{iy}, E_{iz}\right) = -\frac{dV_{i}}{dD_{i}} \left(\frac{x_{P} - x_{i}}{D_{i}}, \frac{y_{P} - y_{i}}{D_{i}}, \frac{z_{P} - z_{i}}{D_{i}}\right)$$
(A7)

where  $D_i = \sqrt{(x_P - x_i)^2 + (y_P - y_i)^2 + (z_P - z_i)^2}$  is the distance between point P<sub>1</sub> and the center of the i-th charged sphere and

$$\frac{dV_{i}}{dD_{i}} = \begin{cases} \frac{k_{e}Q_{i}\lambda_{D}}{\varepsilon_{r}R_{i}}\sinh(R_{i}/\lambda_{D})\left[-\frac{e^{-\frac{D_{i}}{\lambda_{D}}}}{D_{i}^{2}}-\frac{e^{-\frac{D_{i}}{\lambda_{D}}}}{D_{i}\lambda_{D}}\right] & \text{if } D_{i} > R_{i}\\ \frac{k_{e}Q_{i}\lambda_{D}}{\varepsilon_{r}R_{i}}e^{-\frac{R_{i}}{\lambda_{D}}}\left[-\frac{\sinh\left(\frac{D_{i}}{\lambda_{D}}\right)}{D_{i}^{2}}+\frac{\cosh\left(\frac{D_{i}}{\lambda_{D}}\right)}{D_{i}\lambda_{D}}\right] & \text{if } D_{i} < R_{i}\end{cases}$$

where  $0 < \sqrt{x_i^2 + y_i^2} < R_L - R_i$  and  $\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} > R_i + R_j$  where  $i \neq j$ .  $Q_i$  is the total surface charge of the i-th small sphere of radius  $R_i$ .



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