# Spontaneous symmetry breaking of charge-regulated surfaces: Supplementary Material 

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## A. Density functional

Let us consider a single charge-regulated wall placed at $z=0$ in contact with an electrolyte solution of bulk ionic strength $I$ and spanning the space $z>0$. The charge density at the wall is denoted by $\sigma$ and the dimensionless charge density is given by

$$
\begin{equation*}
\sigma^{*}=\frac{a^{2} \sigma}{e}=\eta-\frac{1}{\Theta} \tag{1}
\end{equation*}
$$

Please note that all variables used here and in the remainder have the same meaning as defined in the main text. After subtracting the bulk contribution from the grand potential functional $\Omega$ corresponding to Eq. (2) of the main text and afterwards dividing by the surface area $\mathcal{A}$ of the wall one obtains

$$
\begin{align*}
\frac{\beta \Delta \Omega\left(\sigma^{*}\right)}{\mathcal{A}}= & -\int_{0}^{\infty} d z\left[2 I(\cosh (\psi(z))-1)+\frac{\varepsilon}{2 \beta e^{2}}\left(\psi^{\prime}(z)\right)^{2}\right]+\frac{\sigma^{*} \psi(0)}{a^{2}} \\
& +\frac{1}{a^{2}}\left(-\alpha \eta-\frac{\chi}{2} \eta^{2}+\eta \ln \eta+(1-\eta) \ln (1-\eta)\right) \tag{2}
\end{align*}
$$

where the dimensionless electrostatic potential $\psi$ satisfies the PB equation

$$
\begin{equation*}
\psi^{\prime \prime}(z)=\kappa^{2} \sinh (\psi(z)) \tag{3}
\end{equation*}
$$

subjected to the Dirichlet boundary condition $\psi(\infty)=0$ and to the Neumann boundary condition

$$
\begin{equation*}
\psi^{\prime}(0)=-\frac{\beta e \sigma}{\varepsilon}=-\frac{\beta e^{2}}{\varepsilon a^{2}}\left(\eta-\frac{1}{\Theta}\right)=-\frac{\beta e^{2} \sigma^{*}}{\varepsilon a^{2}} . \tag{4}
\end{equation*}
$$

As usual $\psi^{\prime}$ and $\psi^{\prime \prime}$ denote single and double derivatives with respect to $z$, respectively, and $\eta=\sigma^{*}+\frac{1}{\Theta}$ according to Eq. (1).

## B. Grahame equation

Multiplying both sides of Eq. (3) by $\psi^{\prime}$ one obtains

$$
\psi^{\prime} \psi^{\prime \prime}=\kappa^{2} \sinh (\psi) \psi^{\prime}
$$

which can be rewritten as

$$
\begin{equation*}
\frac{1}{2}\left(\left(\psi^{\prime}\right)^{2}\right)^{\prime}=\kappa^{2}(\cosh (\psi))^{\prime} \tag{5}
\end{equation*}
$$

Integrating Eq. (5) with respect to $z$ and using $\psi(\infty)=\psi^{\prime}(\infty)=0$ gives

$$
\begin{equation*}
\frac{1}{2}\left(\psi^{\prime}\right)^{2}=\kappa^{2}(\cosh (\psi)-1) \tag{6}
\end{equation*}
$$

which leads to

$$
\begin{equation*}
2 I(\cosh (\psi)-1)=\frac{\varepsilon}{2 \beta e^{2}}\left(\psi^{\prime}\right)^{2} \tag{7}
\end{equation*}
$$

For $z=0$, i.e., at the wall, Eq. (6) gives the Grahame equation [1]

$$
\begin{equation*}
\kappa^{2}(\cosh (\psi(0))-1)=\frac{1}{2}\left(\psi^{\prime}(0)\right)^{2}=\frac{\beta^{2} e^{2} \sigma^{2}}{2 \varepsilon^{2}} \tag{8}
\end{equation*}
$$

and therefore,

$$
\begin{equation*}
\psi(0)=\operatorname{sign}(\sigma) \operatorname{arcosh}\left(1+\frac{\beta^{2} e^{2} \sigma^{2}}{2 \varepsilon^{2} \kappa^{2}}\right) . \tag{9}
\end{equation*}
$$

The sign of $\sigma$ and $\sigma^{*}$ are the same according to Eq. (1) and for brevity we define the dimensionless parameter $\lambda=\frac{\beta e^{2}}{4 \varepsilon \kappa a^{2}}$. With these, Eq. (9) can be rewritten as

$$
\begin{equation*}
\psi(0)=\operatorname{sign}\left(\sigma^{*}\right) \operatorname{arcosh}\left(1+8 \lambda^{2}\left(\sigma^{*}\right)^{2}\right) . \tag{10}
\end{equation*}
$$

## C. Electrostatic potential

The PB equation for our setup is analytically solvable and its solution is well know [2, 3]:

$$
\begin{equation*}
\psi(z)=4 \operatorname{artanh}(\gamma \exp (-\kappa z)) ; \quad \gamma=\tanh \left(\frac{\psi(0)}{4}\right) . \tag{11}
\end{equation*}
$$

Taking the derivative with respect to $z$, one obtains

$$
\begin{equation*}
\psi^{\prime}(z)=-4 \kappa \gamma \frac{\exp (-\kappa z)}{1-\gamma^{2} \exp (-2 \kappa z)} \tag{12}
\end{equation*}
$$

Therefore,

$$
\begin{align*}
\int_{0}^{\infty} d z\left(\psi^{\prime}(z)\right)^{2} & =16 \kappa^{2} \gamma^{2} \int_{0}^{\infty} d z \frac{\exp (-2 \kappa z)}{\left(1-\gamma^{2} \exp (-2 \kappa z)\right)^{2}} \\
& =8 \kappa \int_{0}^{\infty} d z \frac{2 \kappa \gamma^{2} \exp (-2 \kappa z)}{\left(1-\gamma^{2} \exp (-2 \kappa z)\right)^{2}} \\
& =8 \kappa \int_{0}^{\infty} d z\left(\frac{d}{d z} \frac{-1}{1-\gamma^{2} \exp (-2 \kappa z)}\right) \\
& =8 \kappa\left|\frac{-1}{1-\gamma^{2} \exp (-2 \kappa z)}\right|_{z=0}^{\infty} \\
& =8 \kappa\left(-1+\frac{1}{1-\gamma^{2}}\right) \\
& =\frac{8 \kappa \gamma^{2}}{1-\gamma^{2}} \tag{13}
\end{align*}
$$

The parameter $\gamma$ is determined by using the boundary condition relating the electric displacement vector to the charge density at the wall. Combining Eqs. (4) and (12), one obtains

$$
\begin{equation*}
\psi^{\prime}(0)=-4 \kappa \frac{\gamma}{1-\gamma^{2}}=-\frac{\beta e \sigma}{\varepsilon} \tag{14}
\end{equation*}
$$

which leads to

$$
\begin{equation*}
\frac{\gamma}{1-\gamma^{2}}=\frac{\beta e^{2} \sigma^{*}}{4 \kappa \varepsilon a^{2}}=\lambda \sigma^{*} \tag{15}
\end{equation*}
$$

Solving Eq. (15) for $\gamma$ and inserting it in Eq. (13), one finally arrives at

$$
\begin{equation*}
\int_{0}^{\infty} d z\left(\psi^{\prime}(z)\right)^{2}=4 \kappa\left(-1+\sqrt{1+4 \lambda^{2}\left(\sigma^{*}\right)^{2}}\right) \tag{16}
\end{equation*}
$$

## D. Grand potential

Using Eqs. (7) and (10) in Eq. (2), one can write

$$
\begin{align*}
\frac{\beta \Delta \Omega\left(\sigma^{*}\right)}{\mathcal{A}}= & -\int_{0}^{\infty} d z \frac{\varepsilon}{\beta e^{2}}\left(\psi^{\prime}\right)^{2}+\frac{\sigma^{*}}{a^{2}} \operatorname{sign}\left(\sigma^{*}\right) \operatorname{arcosh}\left(1+8 \lambda^{2}\left(\sigma^{*}\right)^{2}\right) \\
& +\frac{1}{a^{2}}\left(-\alpha \eta-\frac{\chi}{2} \eta^{2}+\eta \ln \eta+(1-\eta) \ln (1-\eta)\right) \tag{17}
\end{align*}
$$

Further, using Eq. (16), Eq. (17) can be rewritten as

$$
\begin{align*}
\frac{\beta \Delta \Omega\left(\sigma^{*}\right)}{\mathcal{A}}=\frac{1}{a^{2}}[ & \frac{1}{\lambda}\left(1-\sqrt{1+4 \lambda^{2}\left(\sigma^{*}\right)^{2}}\right)+\left|\sigma^{*}\right| \operatorname{arcosh}\left(1+8 \lambda^{2}\left(\sigma^{*}\right)^{2}\right) \\
& \left.-\alpha \eta-\frac{\chi}{2} \eta^{2}+\eta \ln \eta+(1-\eta) \ln (1-\eta)\right] \tag{18}
\end{align*}
$$

where the relation $\frac{4 \kappa \varepsilon a^{2}}{\beta e^{2}}=\frac{1}{\lambda}$ is used.

## E. Symmetric charge interval $(\Theta=2)$

As mentioned in the main text, $\Theta=2$ corresponds to a symmetric charge interval. For this case, $\eta=\sigma^{*}+\frac{1}{2}$ according to Eq. (1) and using this, Eq. (18) can be written as:

$$
\begin{align*}
\beta \Delta \widetilde{\Omega}\left(\sigma^{*}\right)=\frac{1}{a^{2}}[ & \frac{1}{\lambda}\left(1-\sqrt{1+4 \lambda^{2}\left(\sigma^{*}\right)^{2}}\right)+\left|\sigma^{*}\right| \operatorname{arcosh}\left(1+8 \lambda^{2}\left(\sigma^{*}\right)^{2}\right) \\
& -\alpha\left(\frac{1}{2}+\sigma^{*}\right)-\frac{\chi}{2}\left(\frac{1}{2}+\sigma^{*}\right)^{2} \\
& \left.+\left(\frac{1}{2}+\sigma^{*}\right) \ln \left(\frac{1}{2}+\sigma^{*}\right)+\left(\frac{1}{2}-\sigma^{*}\right) \ln \left(\frac{1}{2}-\sigma^{*}\right)\right] \tag{19}
\end{align*}
$$

where $\Delta \widetilde{\Omega}\left(\sigma^{*}\right)=\frac{\Delta \Omega\left(\sigma^{*}\right)}{\mathcal{A}}$ is the free energy per unit surface area. Clearly, $\beta \Delta \widetilde{\Omega}\left(\sigma^{*}\right)$ in Eq. (19) is symmetric about $\sigma^{*}=0$, i.e., $\beta \Delta \widetilde{\Omega}\left(-\sigma^{*}\right)=\beta \Delta \widetilde{\Omega}\left(\sigma^{*}\right)$, provided the condition

$$
\begin{equation*}
(2 \alpha+\chi) \sigma^{*}=0 \tag{20}
\end{equation*}
$$

is fulfilled. According to this condition, on the line $\chi=-2 \alpha$ two states with $\sigma_{1}^{*}$ and $\sigma_{2}^{*}=-\sigma_{1}^{*}$ correspond to the same value of $\beta \Delta \widetilde{\Omega}\left(\sigma^{*}\right)$. Therefore, if a state with $\sigma_{1}^{*}$ corresponds to the global minimum of $\beta \Delta \widetilde{\Omega}\left(\sigma^{*}\right)$, there will be another state with $\sigma_{2}^{*}=-\sigma_{1}^{*}$ with the same minimum, i.e., the two states with $\sigma_{1}^{*}$ and $\sigma_{2}^{*}$ coexist. As shown in Fig. 3 of the main text, for $\alpha \gtrsim-14$ and $\chi=-2 \alpha$ the global minimum corresponds to $\sigma^{*}=-\sigma^{*}=0$ (see Fig. 3(a)) whereas for $\alpha \lesssim-14$, it shifts to $\sigma_{1}^{*} \gtrsim-\frac{1}{2}$ and $\sigma_{2}^{*}=-\sigma_{1}^{*} \lesssim \frac{1}{2}$ (see Fig. 3(b)).
[1] D. C. Grahame, Chem. Rev. 41, 441 (1947).
[2] R. J. Hunter, Foundations of colloid science (Clarendon Press, Oxford, 1989).
[3] W. B. Russel, D. A. Saville, W. R. Schowalter, Colloidal dispersions (Cambridge University Press, 1989).


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