Linking Aggregation of *Aspergillus niger* Spores to Surface Electrostatics: A Theoretical Approach

(Supporting Information)

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Numerical Calculation of Potential Distributions

In this paper, a method is presented for solving Poisson-Boltzmann equations of model systems where one or several ion-penetrable membranes are considered to be in equilibrium with a symmetrical electrolyte solution. The underlying approach is based on the numerical determination of the concentration profile of an arbitrary ion species, by solving the corresponding electrodiffusion equations instead of directly solving the Poisson-Boltzmann equations. The application of this approach to the given Poisson-Boltzmann model is described in a separate section.

General Approach

Consider a system of parallel-oriented charged ion-penetrable membranes in equilibrium with an electrolyte solution, which is of infinite extent and contains mobile ions of types A and B with respective valences of ν_{A} and $\nu_{\mathrm{B}} = -\nu_{\mathrm{A}}$. Suppose that the membrane charge is continuously distributed throughout the entire volume of each membrane and varies only in the direction perpendicular to the membrane's surfaces, taken here as the z-direction. Further, suppose that the possible diminished solubility of electrolyte ions inside the membranes can be adequately described by z-dependent intrinsic partition coefficients, $b_{\mathrm{A,B}}(z)$. If these coefficients are defined as the quotient of the actual ion concentration profile and the ion concentration profile expected under the assumption of undiminished solubility and Boltzmann distribution of ions, the concentration profiles of the ions A and B along z can be expressed by

$$C_{\mathrm{A,B}}(z) = b_{\mathrm{A,B}}(z) C_{\mathrm{I}}^{\infty}\, \mathrm{e}^{-\frac{\nu_{\mathrm{A,B}} e \Psi(z)}{kT}}, \tag{1}$$

where e is the elementary charge; k, the Boltzmann constant; T, the temperature; $\Psi(z)$, the electric potential at position z; and C_{I}^{∞} the ion concentration in the bulk solution in which Ψ is defined to be zero.
According to the universal definition given above, the functions $b_{\mathrm{A,B}}(z)$ are expected to take values between 0 and 1 inside a membrane and to equal unity outside. By treating these functions as differentiable, equation 1 can be transformed by differentiation with respect to z to give

$$\frac{1}{C_{\mathrm{A}}(z)} \frac{dC_{\mathrm{A}}(z)}{dz} = \frac{1}{b_{\mathrm{A}}(z)} \frac{db_{\mathrm{A}}(z)}{dz} + \frac{\nu_{\mathrm{A}} e E(z)}{kT}. \tag{2}$$

This expression, in which the electric potential distribution has been formally

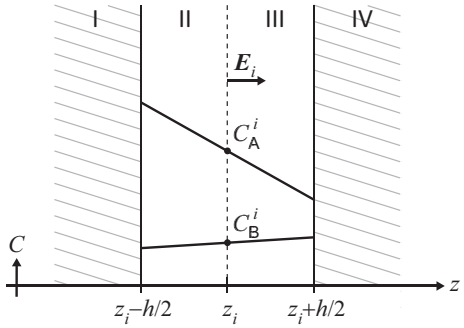

Figure 1: Schematic illustration of the relationship between the electric field $\boldsymbol{E}_i$ and the linearized concentration profiles $C_{\mathrm{A,B}}(z)$ of ions of types A and B in a symmetrical interval around z_i. $\boldsymbol{E}_i$ may be expressed as a superposition of the electric fields arising from the total charge within region I ($-\infty < z < z_i - h/2$), II ($z_i - h/2 < z < z_i$), III ($z_i/2 < z < z_i + h/2$), and IV ($z_i + h/2 < z < \infty$).

replaced by the position-dependent scalar electric field $E(z)$, may be seen as the corresponding electrodiffusion equation at the equilibrium state (note that in this context, the equilibrium state is the state where the total flux of the ions A and B is zero).

Let us now consider a single point at any position z_i centered in an interval of dimension h (see Figure 1). The electric field at this point (E_i) may be decomposed into four contributions: (i) E_i^{I}, the electric field contribution arising from the charge between $z \to -\infty$ and $z = z_i - h/2$; (ii) E_i^{II}, the contribution from the charge between $z = z_i - h/2$ and $z = z_i$; (iii) E_i^{III}, the contribution from the charge between $z = z_i$ and $z = z_i + h/2$; and (iv) E_i^{IV}, the contribution from the charge between $z = z_i + h/2$ and $z \to \infty$. However, as $E_i^{\mathrm{I}} + E_i^{\mathrm{II}} = E_i^{\mathrm{III}} + E_i^{\mathrm{IV}}$ for electroneutrality, it can be simply noted that

$$E_i = 2E_i^{\mathrm{I}} + 2E_i^{\mathrm{II}}. \tag{3}$$

Next, by choosing further h to be so small that the gradients $\frac{dC_{\mathrm{A,B}}(z)}{dz}$ and the space charge density of fixed membrane charges $\rho_{\mathrm{fix}}(z)$ can be assumed to be approximately constant for $z_i - h/2 < z < z_i + h/2$, we can rewrite equation 2 as

$$\frac{1}{h} - \frac{C_{\mathrm{A}}(z_i - h/2)}{hC_{\mathrm{A}}^i} \approx \frac{1}{2b_{\mathrm{A}}^i}\frac{db_{\mathrm{A}}(z)}{dz}\Big|_{z=z_i} + \frac{\nu_{\mathrm{A}} e}{kT}\left(E_i^{\mathrm{I}} + E_i^{\mathrm{II}}\right), \tag{4}$$

where it follows from Gauss' law that

$$
\begin{aligned}
E_i^{\mathrm{II}} &= \frac{1}{2\epsilon_0\epsilon_\mathrm{r}} \int_{z_i-h/2}^{z_i} \rho(z)\, dz \\
&\approx \frac{h}{8\epsilon_0\epsilon_\mathrm{r}} \left(2\rho_{\mathrm{fix}}^i + \rho_{\mathrm{A+B}}^i + \rho_{\mathrm{A+B}}(z_i - h/2)\right)
\end{aligned}
\tag{5}
$$

with

$$
\rho_{\mathrm{A+B}}^i = \nu_\mathrm{A} F C_\mathrm{A}^i + \nu_\mathrm{B} F C_\mathrm{B}^i = \nu_\mathrm{A} F \left(C_\mathrm{A}^i - \frac{b_\mathrm{A}^i b_\mathrm{B}^i {C_\mathrm{I}^\infty}^2}{C_\mathrm{A}^i} \right) \tag{6}
$$

and

$$
\begin{aligned}
\rho_{\mathrm{A+B}}(z_i - h/2) &= \nu_\mathrm{A} F C_\mathrm{A}(z_i - h/2) + \nu_\mathrm{B} F C_\mathrm{B}(z_i - h/2) \\
&= \nu_\mathrm{A} F \Bigg(C_\mathrm{A}(z_i - h/2) \\
&\quad - \frac{b_\mathrm{A}(z_i - h/2) b_\mathrm{B}(z_i - h/2) {C_\mathrm{I}^\infty}^2}{C_\mathrm{A}(z_i - h/2)} \Bigg).
\end{aligned}
\tag{7}
$$

The physically relevant solution of equation 4 with respect to the concentration profile of ion species A thus reads

$$
C_\mathrm{A}^i = \frac{p}{2} - \left(\frac{p^2}{4} - q \right)^{\frac{1}{2}} \tag{8}
$$

with

$$
\begin{aligned}
p = {} & \frac{2\rho_{\mathrm{fix}}^i}{\nu_\mathrm{A} F} - \frac{8\epsilon_0\epsilon_\mathrm{r} kT}{h^2 \nu_\mathrm{A}^2 eF} + \frac{8\epsilon_0\epsilon_\mathrm{r} E_i^\mathrm{I}}{h\nu_\mathrm{A} F} + \frac{4\epsilon_0\epsilon_\mathrm{r} kT}{h\nu_\mathrm{A}^2 eF} \frac{1}{b_\mathrm{A}^i} \frac{db_\mathrm{A}(z)}{dz}\Big|_{z=z_i} \\
& - \frac{b_\mathrm{A}(z_i - h/2) b_\mathrm{B}(z_i - h/2) {C_\mathrm{I}^\infty}^2}{C_\mathrm{A}(z_i - h/2)} + C_\mathrm{A}(z_i - h/2)
\end{aligned}
\tag{9}
$$

and

$$
q = \frac{8\epsilon_0\epsilon_\mathrm{r} C_\mathrm{A}(z_i - h/2)}{h^2 \nu_\mathrm{A}^2 eF} - b_\mathrm{A}^i b_\mathrm{B}^i {C_\mathrm{I}^\infty}^2. \tag{10}
$$

Equations 8–10 provide the basis for the numerical calculation of non-linear ion concentration and potential profiles (i.e., within a region of dimension much greater than h). For instance, if at a certain position z_0, the electric field, i.e., $E(z_0)$, and the ion concentration of any ion species, i.e., $C_{\mathrm{A}}(z_0)$, are known, the profiles among z_0 and $z_{\mathrm{e}} > z_0$ may be solved by the following scheme:

1. Divide the region between z_0 and z_{e} into N intervals of thickness $h = \frac{z_{\mathrm{e}} - z_0}{N}$

2. For $i = 1, 2, ..., N$, calculate

   i) $E_i^{\mathrm{I}} = \begin{cases} E(z_0) & : \quad i = 1 \\ E_{i-1}^{\mathrm{I}} + E_{i-1}^{\mathrm{II}} + E_{i-1}^{\mathrm{III}} & : \quad i > 1 \end{cases}$,

   where $E_{i-1}^{\mathrm{II}} + E_{i-1}^{\mathrm{III}} = \frac{h}{2\epsilon_0 \epsilon_{\mathrm{r}}} \left(\rho_{\mathrm{fix}}^{i-1} + \rho_{\mathrm{A+B}}^{i-1} \right)$ with respect to Gauss' law

   ii) $C_{\mathrm{A}}(z_i - h/2) = \begin{cases} C_{\mathrm{A}}(z_0) & : \quad i = 1 \\ 2C_{\mathrm{A}}^{i-1} - C_{\mathrm{A}}(z_{i-1} - h/2) & : \quad i > 1 \end{cases}$

   iii) C_{A}^i via equations 8–10

3. For $i = 1, 2, ..., N$, calculate $\Psi(z_i)$ via equation 1.

Solutions to the Spore Interface Model

Potential profiles as solutions of the model equations defined in the main text were essentially obtained by the scheme given above. For that, we set $z_0 = 0$, $z_e = d/2$, $E(z_0) = \frac{d\Psi(z)}{dz}\big|_{z=0} = \frac{\sigma}{\epsilon_0 \epsilon_{\mathrm{r}}}$; estimated first $C_{\mathrm{A}}(z_0)$; and then optimized this quantity iteratively with respect to $|E(z_e)|$ in order to find a potential distribution that approximately satisfies the given electroneutrality condition $\frac{d\Psi(z)}{dz}\big|_{z=d/2} = 0$. It is to be noted, however, that this procedure alone does not apply to the general case of potential-dependent ionization of fixed groups. To account for this, a second iterative cycle was used, in which, according to equation 5 of the main text, each ρ_{fix}^i was independently determined by

$$\rho_{\mathrm{fix}}^i = \frac{\rho_{\mathrm{fix},0}}{\frac{C_{\mathrm{H_3O^+}}^{\infty}}{K_{\mathrm{a}}} \mathrm{e}^{-\frac{e\Psi(z_i)}{kT}} + 1}. \tag{11}$$

To reach convergence with this approach, the set of ρ_{fix}^i of the first iteration was calculated from the latter equation with the respective potential values $\Psi(z_i)$ set to zero. In the subsequent iterations, these values were obtained from the solution to the given set of ρ_{fix}^i of the preceding iteration.