A Computation of flux toward a sphere (3D)

In this appendix we give an approximate expression to compute the flux of M across a sphere. As starting point, we consider the expression of the flux:

$$J_{\mathrm{M}} = -D_{\mathrm{M}}\nabla c_{\mathrm{M}} = \left(1 - \frac{\omega_{\mathrm{M}}}{2}\right)\sum_i f_{i,\mathrm{M}}^{neq} v_i = d\frac{\omega_{\mathrm{M}} D_{\mathrm{M}}}{\Delta x}\frac{1}{v}\sum_i f_{i,\mathrm{M}}^{neq} v_i \tag{A-1}$$

which can be simplified in 1D as:

$$J_{\mathrm{M}} = -\frac{\omega_{\mathrm{M}} D_{\mathrm{M}}}{\Delta x}(f_{1,\mathrm{M}} - f_{2,\mathrm{M}}) \tag{A-2}$$

In 1D and in general, for an interface following the grid discretization, i.e. when the points of the grid are located at the interface, the computation of the flux is simply done by using expression (A-1), and no errors arise from the boundary discretization. On the other hand, for instance by considering a spherical electrode and a Cartesian computational grid some problems related to the interface discretization arise. For this problem we have to deal with discretization points which cannot be located exactly at the electrode surface. Indeed, practically all the points lie either outside or inside the electrode. Therefore, the first thing to do is to choose an accurate way to discriminate which points are closer to the electrode and consider these points as surface points. One way is to select as electrode surface points, those points belonging to the electrode and at least surrounded by one solution point. Clearly, the more refined is the grid, the more precise the surface is reproduced. A cube is associated to each point. There are three kinds of cubes:

- cube type A: outside the electrode, within the solution.
- cube type B: located at the electrode surface.
- cube type C: inside the electrode.

The flux at the electrode surface must be computed at the cubes of type B. The procedure consists in counting the total net mass arriving in each cube B and divide by the number of cubes B, i.e.:

$$J_{\mathrm{M}} = \frac{\sum_{i=1}^{n_f}\sum_{\alpha=1}^{3} J_{\alpha,i,\mathrm{M}}\Delta x^2}{\sum_{i=1}^{n_f}\Delta x^2} = \frac{\sum_{i=1}^{n_f}\sum_{\alpha=1}^{3} J_{\alpha,i,\mathrm{M}}}{n_f} \tag{A-3}$$

where the index i labels the cubes B and $\alpha = x, y, z$ runs on the three Cartesian directions. We have introduced the primitive flux along each Cartesian direction, $J_{\alpha,i,\mathrm{M}}$ which denotes the flux of M along the α-direction at the cubes i, which can be computed by using the expression (A-2), where the $f_{i,\mathrm{M}}$ have to be properly chosen. The total number of moles crossing the electrode surface is:

$$n_{\mathrm{M}} = J_{\mathrm{M}} n_f \Delta x^2 t = \sum_{i=1}^{n_f} \sum_{\alpha=1}^{3} J_{\alpha,i,\mathrm{M}} \Delta x^2 t \tag{A-4}$$

Now, if we divide the total net number of moles of M crossing the electrode surface with the real measure of the surface $A = \frac{\pi r_0^2}{2}$ (for the 8th part of the sphere) and the time of integration t, we get:

$$J_{\mathrm{M}} = \frac{\sum_{i=1}^{n_f} \sum_{\alpha=1}^{3} J_{\alpha,i,\mathrm{M}} \Delta x^2 t}{At} = 2 \frac{\sum_{i=1}^{n_f} \sum_{\alpha=1}^{3} J_{\alpha,i,\mathrm{M}} \Delta x^2}{\pi r_0^2} \tag{A-5}$$

Expression (A-5) is the expression we use to compute the flux of M across the sphere.
Another way to compute the flux is to simply consider total net flux of particle leaving from and entering into a site. This quantity can be approximated, in 1D, by:

$$J_{\mathrm{M}} \sim (f'_{2,\mathrm{M}} - f_{1,\mathrm{M}}) \frac{\Delta x}{\Delta t} \tag{A-6}$$

where $f'_{2,\mathrm{M}} = f_{2,\mathrm{M}} + \omega_{\mathrm{M}}(f^{\mathrm{eq}}_{2,\mathrm{M}} - f_{2,})$. (The prime index represents the particle leaving from a site and without prime the particle entering into a site.) If we consider the usual value of the equilibrium function and make some algebra we get:

$$J_{\mathrm{M}} \sim -\frac{(2 - \omega_{\mathrm{M}})\Delta x}{2\Delta t} (f_{1,\mathrm{M}} - f_{2,\mathrm{M}}) \tag{A-7}$$

If we compare the expression (A-7) with the above expression (A-2), we can see that they are exactly the same!

Using the same considerations as above, we extend the validity of expression (A-7) in a 3D geometry, simply by counting the total net number of particles in a cube of type B, and divide by the time interval and the spherical electrode surface:

$$J_{\mathrm{M}} \sim \frac{\sum_{\alpha} J_{\alpha} \Delta x_{\alpha}^2}{A} \tag{A-8}$$

where A is the spherical electrode surface and J_{α} is the flux along a given α-direction computed by using (A-7).

B An exact solution for a 3D spherical electrode in the Laplace domain

In this appendix we report the analytical flux solution at the electrode surface computed with the Laplace transform method for the problem stated in the article, adapted to the spherical geometry (see [1]), with the corresponding initial and boundary conditions, for the case $D_{\mathrm{L}} = D_{\mathrm{ML}}$ and in excess of ligand case. It is based on the Laplace inversion of the following function:

$$F(s) = \frac{1}{s} \frac{(\sqrt{s}+a)(\sqrt{s+B}+a)}{Kc_{\mathrm{L}}^{*}(\sqrt{s}+a) + (\sqrt{s+B}+a)} \tag{B-1}$$

where $a = \frac{\sqrt{D}_{\mathrm{M}}}{r_0}$, $B = k_{\mathrm{d}} + k_{\mathrm{a}} c_{\mathrm{L}}^{*}$. Because the following equality holds:

$$\frac{\sqrt{D}_{\mathrm{M}}}{c_{\mathrm{M,tot}}^{*}} \frac{\partial c_{\mathrm{M}}}{\partial r} = L^{-1}[F(s)] \tag{B-2}$$

the flux of M at the electrode surface is:

$$J_{\mathrm{M}}(t) = c_{\mathrm{M,tot}}^{*} \sqrt{D}_{\mathrm{M}} L^{-1}[F(s)] \tag{B-3}$$

C A detailed description of the GR1 procedure

To be self-contained, we rewrite the interface condition between two adjacent sub-grids (please, see the article for a complete explanation of the symbols):

$$\begin{pmatrix} 1 & -1 \\ -\Delta x_j & -\Delta x_{j+1} \end{pmatrix} \begin{pmatrix} f_{1,\mathrm{X}}^{(j+1)} \\ f_{2,\mathrm{X}}^{(j)} \end{pmatrix} = b_j \tag{C-1}$$

The iterative process in the time domain $[t_1, t_2]$ is defined as follows, (See [2] for the details about the numerical computations of the boundary conditions):

1. Compute the values of $f_{i,\mathrm{X}}^{(k)}$ in the largest subgrid G_k at $t_2 = t_1 + \Delta t_k$, by using the LBGK equation, with the appropriate boundary conditions at $x \to \infty$ and on $\Gamma_{k-1,k}$. The boundary condition on $\Gamma_{k-1,k}$ is numerically solved by eqn (C-1).

2. Compute the values of $f_{i,\mathrm{X}}^{(j)}$ in the subgrid G_j at $t_2 = t_1 + g_j \Delta t_j$, by using the LBGK equation, with the appropriate boundary conditions on $\Gamma_{j,j+1}$ and on $\Gamma_{j-1,j}$ both numerically solved by eqn (C-1), by iterating on j from $k-1$ to 2. In fact, the boundary conditions at each time step, are the coupling conditions between the subgrids.

3. Compute the values of $f_{i,\mathrm{X}}^{(1)}$ in the grid G_1 at $t_2 = t_1 + g_1\Delta t_1$, by using the LBGK equation, with the appropriate boundary conditions on $x = 0$ and on $\Gamma_{1,2}$, the latter numerically solved by eqn (C-1).

The GR1 scheme can be understood in more detail with the help of figure C-1. Let us focus on the point x_s, the border between G_1 and G_2. The purpose at each time step is to compute the density distribution functions $f_{1,\mathrm{X}}^{(2)}(x_s, t + \Delta t_2)$ and $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_2)$. The procedure outlined in the picture corresponds to a grid refinement factor $g = 2$. At time t every distribution function and concentration is known at each point. For clarity the procedure is split into three steps:

1. At the subgrid G_2 the lattice scheme is applied with a time step Δt_2. By applying the LBGK scheme, all functions $f_{1,\mathrm{X}}^{(2)}$ at the inner points of G_2 are computed at $t + \Delta t_2$. The values of $f_{1,\mathrm{X}}^{(2)}(x_s, t + \Delta t_2)$ cannot be computed by using the above mentioned LBGK scheme, because the point $x_s - \Delta x_2$ is outside the grid G_2. Therefore $f_{1,\mathrm{X}}^{(2)}(x_s, t + \Delta t_2)$ is an unknown boundary condition for the evolution of $f_{1,\mathrm{X}}^{(2)}$ in the subgrid G_2. Its value will be computed by applying the system (C-1) once all entries of b_j will be completely known.

2. At the subgrid G_1 the lattice scheme is applied with a time step Δt_1. For the same considerations given above, all functions are computed at $t + \Delta t_1$, except for $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_1)$, which is an unknown boundary condition for the evolution of $f_{2,\mathrm{X}}^{(1)}$ in the subgrid G_1 because the point $x_s + \Delta x_1$ is outside the grid G_1.

3. At the subgrid G_1 the lattice scheme is applied again, with a time step Δt_1. All functions are computed at $t + \Delta t_2$, except for $f_{2,\mathrm{X}}^{(1)}(x_s - \Delta x_1, t + \Delta t_2)$ and $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_2)$. The first function $f_{2,\mathrm{X}}^{(1)}(x_s - \Delta x_1, t + \Delta t_2)$ is computed by applying the LBGK lattice scheme that requires to know the value of $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_1)$. To know it we perform a time interpolation of $f_{2,\mathrm{X}}^{(2)}(x_s, t)$ and $f_{2,\mathrm{X}}^{(2)}(x_s, t + \Delta t_2)$, e.g. at the first order: $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_1) = \frac{f_{2,\mathrm{X}}^{(2)}(x_s,t) + f_{2,\mathrm{X}}^{(2)}(x_s,t+\Delta t_2)}{2}$. From the geometric point of view, this interpolation is a weighted average of the function $f_{2,\mathrm{X}}^{(2)}(x_s, [t, t + \Delta t_2])$. Finally, $f_{2,\mathrm{X}}^{(1)}(x_s, t + \Delta t_2)$ and $f_{1,\mathrm{X}}^{(2)}(x_s, t + \Delta t_2)$ are computed by applying the system of equations (C-1), where now all entries are known. The procedure is then repeated starting from the new time level $t + \Delta t_2$.

D A detailed description of the GR2 procedure

The complete numerical scheme in the time domain $[t_1, t_2]$ is:

1. Compute the values of $f_{i,\mathrm{X}}^{(k)}$ in the coarser subgrid G_k at $t_2 = t_1 + \Delta t_k$, by using the LBGK equation, with bulk boundary conditions at $x \to \infty$ and the boundary conditions of the problem at the electrode surface.

2. Interpolate the boundary concentration values on $\Gamma_{k-1,k}$: $c_{\mathrm{X}}^{(k-1)} = I(c_{\mathrm{X}}^{(k-1)})$, where I is the interpolation function, in order to supply the boundary conditions for the new computation in the finer subgrid G_{k-1}. For 1D problem the function I is the identity while for 3D problem it is a more complicated function which computes a spatial average of the concentration values.

3. Compute the values of $f_{i,\mathrm{X}}^{(j)}$, (the first time for $j = k-1$) in the finer subgrid G_j at $t_2 = t_1 + g_j \Delta t_j$, by using the LBGK equation g_j times. The boundary conditions at each time step $t_1 + s\Delta t_j$ for $s = 1, \ldots, g_j$ in $\Gamma_{j,j+1}$ are computed by the following formula [2]:

$$f_{i,\mathrm{X}}^{(j)}(x, t_1 + s\Delta t_j) = c_{\mathrm{X}}^{(j)}(x, t_1 + s\Delta t_j) - \sum_{k \neq i} f_{k,\mathrm{X}}^{(j)}(x, t_1 + s\Delta t_j) \qquad \text{(D-1)}$$

   where $c_{\mathrm{X}}^{(j)}(x, t_1 + s\Delta t_j)$ is computed by interpolation from point (2). Equation (D-1) is exact at any order, therefore the accuracy depends only on the interpolation functions used.

4. Repeat point (3) by decreasing j by one unit, until $j = 1$.

References

[1] J. Koutecky and R. Brdicka, *Collect. Czech. Chem. Commun.*, 1947, **12**, 337-355.

[2] D. Alemani, B. Chopard, J. Galceran and J. Buffle, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3331-3341.

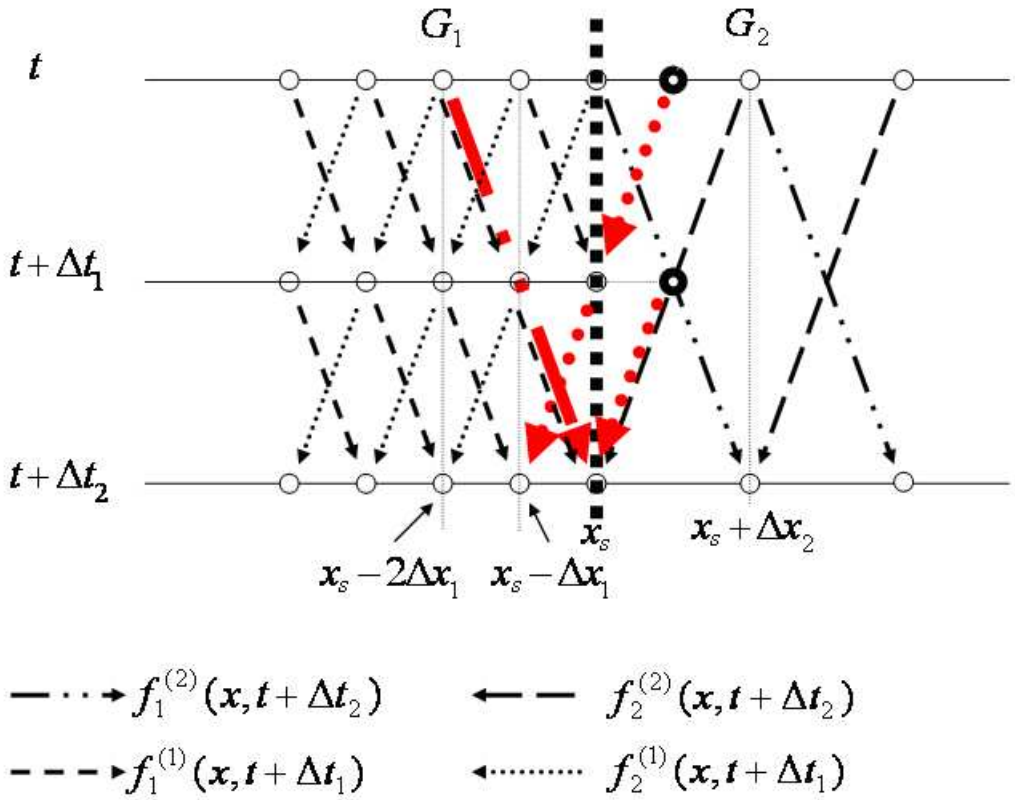

Figure C-1: The GR1 scheme for a planar electrode (1D). The arrows represent the evolution of the corresponding density distribution functions in the subgrid G_1 along a time step Δt_1 and in the subgrid G_2 along a time step Δt_2. The horizontal lines are the time level t, $t+\Delta t_1$ and $t+\Delta t_2$. The unknown density distribution functions, needed for boundary conditions, are marked with a bolder line. For the subgrid G_2 the unknown is $f^{(2)}_{1,\mathrm{X}}(x_s, t+\Delta t_2)$. For the subgrid G_1 the unknowns are: $f^{(1)}_{2,\mathrm{X}}(x_s, t+\Delta t_1)$, $f^{(1)}_{2,\mathrm{X}}(x_s-\Delta x_1, t+\Delta t_2)$, $f^{(1)}_{2,\mathrm{X}}(x_s, t+\Delta t_1)$. From time interpolation of $f^{(2)}_{2,\mathrm{X}}(x_s, t)$ and $f^{(2)}_{2,\mathrm{X}}(x_s, t+\Delta t_2)$ we can compute $f^{(1)}_{2,\mathrm{X}}(x_s, t+\Delta t_1)$. Then, we can compute $f^{(1)}_{2,\mathrm{X}}(x_s-\Delta x_1, t+\Delta t_2)$ by applying the lattice scheme and, finally, $f^{(1)}_{2,\mathrm{X}}(x_s, t+\Delta t_2)$ and $f^{(2)}_{1,\mathrm{X}}(x_s, t+\Delta t_2)$ are computed by applying the system of equations (C-1).