Mathematical tools

In this appendix we will introduce the key mathematical tools to study the errors and the numerical procedure of the splitting time method combined with the Lattice Boltzmann approach. In particular we show that: i) the splitting procedure introduces an error proportional to Δt^2 if the diffusion coefficients are equal. In other cases the error is only proportional to Δt; ii) NS and RD schemes have different Δt constraints; iii) How to write explicitly the matrices of the numerical schemes, in presence of ligand excess.

(1) Splitting errors: the RD scheme

Following [4], after having rewritten equations (4), (5), (6) and (7) in the compact form $\frac{\partial u}{\partial t} = T_{\mathrm{D}}u + T_{\mathrm{R}}u$, where T_{D} and T_{R} are respectively the diffusion and the reaction operators, the error between the exact solution u_{e} and the splitted solution u_{s} is [4]:

$$\|u_{\mathrm{e}} - u_{\mathrm{s}}\| \leq \frac{\Delta t}{2}[T_{\mathrm{D}}, T_{\mathrm{R}}]u_{\mathrm{e}}(0) + O(\Delta t^2) \tag{57}$$

where $u_e(0)$ is the initial value of the exact solution (at t=0) and the square parenthesis indicates the commutator operation ($[A, B] = AB - BA$). For instance, the commutator for a system in excess of ligand, takes the following value:

$$[T_{\mathrm{D}}, T_{\mathrm{R}}] = \begin{pmatrix} 0 & k_{\mathrm{d}}(D_{\mathrm{M}} - D_{\mathrm{ML}})\nabla^2 \\ k'_{\mathrm{a}}(D_{\mathrm{M}} - D_{\mathrm{ML}})\nabla^2 & 0 \end{pmatrix} \tag{58}$$

from which we can deduce that, if $D_{\mathrm{M}} = D_{\mathrm{ML}}$, the splitting error is proportional to Δt^2 in excess of ligand. If $D_{\mathrm{M}} \neq D_{\mathrm{ML}}$, the splitting error is proportional to Δt.

(2) A concrete example of excess of one ligand

The results shown in the previous sub-appendix, are based on the concrete form of each matrix and of each vector of the problem. Let us consider the reaction-diffusion of the prototype process (1) in the excess of ligand case, in the space domain $\Omega = [0, 1]$ discretized with n_x points. Boundary conditions at x=0, are i) perfect sink for M ($c_{\mathrm{M}}(0, t) = 0$), ii) electroinactivity for ML, i.e. no flux, $\frac{\partial c_{\mathrm{ML}}}{\partial x} = 0$ and iii) at x=1 conditions are those of bulk both for M and ML, $c_{\mathrm{M}}(1, t) = c^*_{\mathrm{M}}$ and $c_{\mathrm{ML}}(1, t) = c^*_{\mathrm{ML}}$. Therefore, we do not need the equations for L and M^0, since we are working in the excess of ligand case and under condition of perfect sink for M. Let us introduce the vector $u^n = (f^n_{1,\mathrm{M}}, f^n_{2,\mathrm{M}}, f^n_{1,\mathrm{ML}}, f^n_{2,\mathrm{ML}})^T$, where $f^n_{1,\mathrm{M}} = (f^n_{1,\mathrm{M},1}, f^n_{1,\mathrm{M},2}, ..., f^n_{1,\mathrm{M},n_x})^T$ and so on for $f^n_{2,\mathrm{M}}$, $f^n_{1,\mathrm{ML}}$ and $f^n_{2,\mathrm{ML}}$. The numerical boundary conditions are the following: $f^n_{1,\mathrm{M},1} = -f^n_{2,\mathrm{M},1}$, $f^n_{1,\mathrm{ML},1} = f^n_{2,\mathrm{ML},1}$, $f^n_{2,\mathrm{M},n_x} = c^*_{\mathrm{M}} - f^n_{1,\mathrm{M},n_x}$ and $f^n_{2,\mathrm{ML},n_x} = c^*_{\mathrm{ML}} - f^n_{1,\mathrm{ML},n_x}$.

In general the numerical scheme will take the following form:

$$\begin{pmatrix} A_{11} & A_{12} & 0 & 0 \\ A_{21} & A_{11} & 0 & 0 \\ 0 & 0 & A_{33} & A_{34} \\ 0 & 0 & A_{43} & A_{33} \end{pmatrix} \begin{pmatrix} f_{1,\mathrm{M}} \\ f_{2,\mathrm{M}} \\ f_{1,\mathrm{ML}} \\ f_{2,\mathrm{ML}} \end{pmatrix}^{n+1} = \begin{pmatrix} B_{11} & B_{12} & B_{13} & B_{13} \\ B_{12}^T & B_{11}^T & B_{13}^T & B_{13}^T \\ B_{31} & B_{31} & B_{33} & B_{34} \\ B_{31}^T & B_{31}^T & B_{34}^T & B_{33}^T \end{pmatrix} \begin{pmatrix} f_{1,\mathrm{M}} \\ f_{2,\mathrm{M}} \\ f_{1,\mathrm{ML}} \\ f_{2,\mathrm{ML}} \end{pmatrix}^{n} + \begin{pmatrix} G_1 \\ G_2 \\ G_3 \\ G_4 \end{pmatrix} \tag{59}$$

The entries of each matrix are represented by sub-matrix A_{ij}, which take different forms depending on the scheme considered. If the space is discretized with n_x points then the dimension of each sub-matrix is $n_x \cdot n_x$.

(2.1) Complete scheme: matrices A and B

$$A_{11} = [1]_{n_x \cdot n_x} \quad A_{12} = diag(1, 0, ..., 0)_{n_x \cdot n_x} \quad A_{33} = A_{11} \quad A_{34} = -A_{12}$$

$$A_{21} = diag(0, ..., 0, 1)_{n_x \cdot n_x} \quad A_{43} = A_{21}$$

$$B_{11} = \begin{pmatrix} 0 & . & . & 0 \\ 1 - \frac{\omega_{\mathrm{M}} + k_{\mathrm{a}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & 1 - \frac{\omega_{\mathrm{M}} + k_{\mathrm{a}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$B_{12} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{\omega_{\mathrm{M}} - k_{\mathrm{a}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{\omega_{\mathrm{M}} - k_{\mathrm{a}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$B_{13} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{k_{\mathrm{d}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{k_{\mathrm{d}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x} \quad B_{31} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{k_{\mathrm{a}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{k_{\mathrm{a}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$B_{33} = \begin{pmatrix} 0 & . & . & 0 \\ 1 - \frac{\omega_{\mathrm{ML}} + k_{\mathrm{d}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & 1 - \frac{\omega_{\mathrm{ML}} + k_{\mathrm{d}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$B_{34} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{\omega_{\mathrm{ML}} - k_{\mathrm{d}} \Delta t}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{\omega_{\mathrm{ML}} - k_{\mathrm{d}} \Delta t}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$G_1 = \begin{bmatrix} c_{\mathrm{M}}^0 \\ 0 \\ . \\ 0 \end{bmatrix}_{n_x}^{k+1} \quad G_2 = \begin{bmatrix} 0 \\ . \\ 0 \\ c_{\mathrm{M}}^* \end{bmatrix}_{n_x}^{k+1} \quad G_3 = \begin{bmatrix} 0 \\ . \\ . \\ 0 \end{bmatrix}_{n_x}^{k+1} \quad G_4 = \begin{bmatrix} 0 \\ . \\ 0 \\ c_{\mathrm{ML}}^* \end{bmatrix}_{n_x}^{k+1}$$

(2.2) Diffusive scheme: matrices $A_{\mathbf{D}}$ and $B_{\mathbf{D}}$

Keeping the same notations as for the complete scheme, the only sub-matrices that change are:

$$B_{13} = B_{31} = 0$$

$$B_{11} = \begin{pmatrix} 0 & . & . & 0 \\ 1-\frac{\omega_{\mathrm{M}}}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & 1-\frac{\omega_{\mathrm{M}}}{2} & 0 \end{pmatrix}_{n_x \cdot n_x} \quad B_{12} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{\omega_{\mathrm{M}}}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{\omega_{\mathrm{M}}}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

$$B_{33} = \begin{pmatrix} 0 & . & . & 0 \\ 1-\frac{\omega_{\mathrm{ML}}}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & 1-\frac{\omega_{\mathrm{ML}}}{2} & 0 \end{pmatrix}_{n_x \cdot n_x} \quad B_{34} = \begin{pmatrix} 0 & . & . & 0 \\ \frac{\omega_{\mathrm{ML}}}{2} & 0 & . & . \\ 0 & . & 0 & . \\ 0 & 0 & \frac{\omega_{\mathrm{ML}}}{2} & 0 \end{pmatrix}_{n_x \cdot n_x}$$

(2.3) Reactive scheme: matrices $A_{\mathbf{R}}$ and $B_{\mathbf{R}}$

For the reactive scheme it is interesting to see the form of the matrices for the implicit scheme, because we are going to use the splitting only for fast chemical processes not convergent with the NS scheme. The new matrices take the following form:

$$A_{\mathrm{R}} = 1 + \begin{pmatrix} A'_{11} & A'_{12} & A'_{13} & A'_{13} \\ A'_{21} & A'_{22} & A'_{13} & A'_{13} \\ A'_{31} & A'_{31} & A'_{33} & A'_{34} \\ A'_{31} & A'_{31} & A'_{43} & A'_{44} \end{pmatrix}$$

$$A'_{11} = \tfrac{k_{\mathrm{a}}\Delta t}{2} \cdot diag(0,1,...,1)_{n_x \cdot n_x} \quad A'_{12} = diag(1, \tfrac{k_{\mathrm{a}}\Delta t}{2}, ..., \tfrac{k_{\mathrm{a}}\Delta t}{2})_{n_x \cdot n_x}$$

$$A'_{13} = -\tfrac{k_{\mathrm{d}}\Delta t}{2} \cdot diag(0,1,...,1)_{n_x \cdot n_x} \quad A'_{21} = diag(\tfrac{k_{\mathrm{a}}\Delta t}{2}, ..., \tfrac{k_{\mathrm{a}}\Delta t}{2}, 1)_{n_x \cdot n_x}$$

$$A'_{22} = \tfrac{k_{\mathrm{a}}\Delta t}{2} \cdot diag(1,...,1,0)_{n_x \cdot n_x} \quad A'_{31} = -\tfrac{k_{\mathrm{a}}\Delta t}{2} \cdot diag(0,1,...,1)_{n_x \cdot n_x}$$

$$A'_{33} = diag(1, \tfrac{k_{\mathrm{d}}\Delta t}{2}, ..., \tfrac{k_{\mathrm{d}}\Delta t}{2})_{n_x \cdot n_x} \quad A'_{34} = diag(-1, \tfrac{k_{\mathrm{d}}\Delta t}{2}, ..., \tfrac{k_{\mathrm{d}}\Delta t}{2})_{n_x \cdot n_x}$$

$$A'_{43} = diag(\tfrac{k_{\mathrm{d}}\Delta t}{2}, ..., \tfrac{k_{\mathrm{d}}\Delta t}{2}, 1)_{n_x \cdot n_x} \quad A'_{44} = \tfrac{k_{\mathrm{d}}\Delta t}{2} \cdot diag(1,...,1,0)_{n_x \cdot n_x}$$

$$B_{\mathrm{R}} = diag(0,1,...,1,0,0,1,...,1,0)_{16 \cdot n_x^2}$$

(3) Numerical errors

In general, the numerical scheme, whatever methods we have chosen, takes the following form:

$$Au^{n+1} = Bu^n + G \tag{60}$$

where u^n is the vector of the density distribution functions, discretized in space and time, n is the time step level $t_n = n\Delta t$, G is a vector taking into account the boundary conditions and possibly, the non linearity of the problem, A and B are operators depending on the boundary conditions and specifically on the numerical method of integration. For instance, considering the particular problem introduced in appendix A.2, for the NS scheme A and B take the form defined in sub-appendix A.2.1, for the D process $A = A_{\mathrm{D}}$ and $B = B_{\mathrm{D}}$ (see sub-appendix A.2.2) and for the R process $A = A_{\mathrm{R}}$ and $B = B_{\mathrm{R}}$ (see sub-appendix A.2.3).
When G does not contain any non linearity, the scheme (60) is convergent if the spectral radius of iteration matrix $A^{-1}B$ is less than one [19]:

$$\rho(A^{-1}B) < 1 \tag{61}$$

for $t \in [n\Delta t, (n+1)\Delta t]$. We will use inequality (61) to study the convergence conditions of the different schemes.
We consider only complexes for which $K' > 1$. The complete linear scheme, i.e. the case of excess of ligand solved with the complete scheme (20) gives the following convergence condition:

$$\Delta t < \frac{2}{k_{\mathrm{a}} c_{\mathrm{L}}^*} \tag{62}$$

Indeed, the spectral radius of the iteration matrix is equal to the maximum value of all its eigenvalues and one of the important properties is that $\rho(A^{-1}B) \leq \|A^{-1}B\|$. Then the proof of condition (62) reduces to study the norm $\|A^{-1}B\|$. Considering the explicit form of the matrices A and B given in sub-appendix A.2.1, we have $\|A\| \leq 2$, so $1/\|A^{-1}\| \leq \|A\| \leq 2$, and $\|B\| \leq k'_{\mathrm{a}}\Delta t$. Therefore, $\|A^{-1}B\| \leq \|A^{-1}\|\|B\| \leq \|A^{-1}\|k'_{\mathrm{a}}\Delta t$ and by applying the convergent condition (61) we get inequality (62).
The application of the splitting time procedure to the same problem is possible numerically for any values of k_{a}, because inequality (61) is always satisfied. So the complete scheme is conditionally convergent while the split scheme is always convergent.
The convergence of the non linear scheme has to be investigated by applying the fixed point theorem [19], also known as the Banach theorem. Roughly speaking, the theorem says that a numerical scheme $u^{n+1} = Tu^n$, where T is a (non linear) operator, is convergent to a unique solution if T is a contraction, i.e.

$$\forall u, v \quad \exists 0 \leq L < 1 \text{ such that} \quad \|Tu - Tv\| \leq L\|u - v\| \tag{63}$$

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By using the Banach theorem to the reactive part of the time split procedure solved with the implicit Euler method, equation (35), we obtain that the numerical scheme is always convergent. Indeed, the numerical reactive scheme takes the form $u^{n+1} = u^n + Fu^{n+1}$, where F is a non linear operator, and it can be put in the form $u^{n+1} = Tu^n$, where $T = \bar{F}^{-1}$ and $\bar{F}u = u - Fu$. Therefore, $\|Tu - Tv\| \leq \|(1-F)^{-1}\|\|u - v\|$, and, because of $\|(1-F)^{-1}\| < 1$ for each F, the Banach theorem holds.