A second order scheme for a Robin boundary condition in random walk algorithms

Gianluca Boccardo, Tel Aviv University,
Amir Paster, Tel Aviv University

Key words: Random Walk algorithm, surface reaction, particle tracking

Abstract

Introduction and state of the art When modelling problems involving fluid flow and mass transport, one of the most useful tools is the *advection-diffusion equation* (ADE), due to its flexibility and generality. There are a number of ways to solve the ADE when building a computer model of the considered problem: these can be subdivided mainly in two categories. The first is to use an Eulerian approach, where the equation is directly discretized and solved over the chosen computational domain (usually with a finite-volume or finite-elements approach), obtaining the evolution of the concentration of a certain chemical species. Another choice (and the one we will focus on in this work) is to employ a Lagrangian method, where the motion of the particles is directly solved for: in essence, the particles are tracked solving some form of the Langevin equation describing the stochastic motion of the particles due to diffusion via a random walk (RW).

Random walk schemes are very popular for solving advection-diffusion (or advection-diffusion-*reaction*) problems in a wide variety of setups. There are in fact various benefits to the employment of a RW scheme. First and foremost, in the case of a system characterized by high Péclet numbers, a RW scheme will ensure a minimization of the errors due to numerical diffusion, while an Eulerian code suffers significant numerical diffusion (i.e.: smearing of fronts) when encountering large concentration gradients (unless using a very fine numerical grid). These cases are very common in a wide variety of applications, such as mixing controlled or very fast chemical reactions, or advection-dominated problems. These same issue arises in the cases where there is a necessity of employing non-uniform or "noisy" initial conditions, where a direct description accounting for the position of all the particles (such as in RW) is much more efficient [2].

In the present work we focus on the implementation of boundary conditions in the RW codes. In some simple cases these are straightforward, such as open boundaries of inlet or outflow. Impermeability on domain boundaries (i.e. no flux on walls, $\frac{dC}{dx} = 0$) is also easily translated as a condition of "reflection", where particles impacting the boundaries bounce back with the same velocity magnitude.

A more complicated scenario arises when dealing with heterogeneous reactions. These stand as a middle ground between the no-flux impermeability condition and the "perfect-sink" boundary condition of infinitely fast reaction.

In the current state of the art, the partial first-order reaction on the wall $-D\frac{dC}{dx} = kC$ (i.e.: a Robin boundary condition) is represented in the algorithm by a certain probability for a reflecting particle to be annihilated and removed from the system. Previous works [1] derived this reaction probability as:

$$p = k\sqrt{\frac{\pi\Delta t}{D}} \tag{1}$$

where k is the reaction rate at the boundary, D is the molecular diffusion coefficient, and Δt is the simulation time-step.

Methodology and results In our study we started from the basic statement of the reactive condition, that the diffusive flux into the boundary equals the reaction rate at the boundary. Employing the approximation of a smooth concentration profile at the boundary, it is possible to derive a more general definition for the reaction probability p:

$$p_2 = \frac{p_1}{1 + p_1/2 + \epsilon} \tag{2}$$

where p_1 is the probability given in Eq. 1, and ϵ is the sum of third and higher order terms.

In the second part of our work, we explored two different applications, focusing on the treatment of the reactive boundary condition and the accuracy of our proposed methodology. First, we considered a simple 1D transient, pure diffusion case where we compared our simulation results to a known analytical solution (Fig. 1). Then, we performed a number of random walk simulations in a 2D domain for a steady-state advection-diffusion-reaction problem, spanning a range of Damköhler and Péclet numbers; we compared our results with

grid-converged Eulerian simulations of the same problem, performed with the finite-element model `Comsol` (Fig. 2).

In Fig. 3, we show the normalized error between random walk code and the analytical solution in the 1D case, for a Damköhler number Da=1. As it can be seen, a much greater increase in the accuracy of the simulation can be gained by using the more precise second-order approximation for the estimation of p, with respect to the more immediate (but much costlier) solution of simply decreasing sharply the integration step $\Delta t'$. A similar result can be seen in Fig.4, where it is qualitatively clear that there is an improvement of the random walk algorithm accuracy when using the second order approximation: the average concentration is clearly underestimated when using $p = p_1$.

Conclusions The main result of this work is to provide a simple and robust way of improving the predictive capabilites of Lagrangian random walk algorithms in the case of reacting boundary conditions. Such a reactive boundary is a very common physical setup and of great interest in the modelling of a diverse range of applications both in reaction engineering and environmental science. This kind of improvement should afford practitioners a greater reach when dealing with the trade-off between simulation accuracy and computational cost.

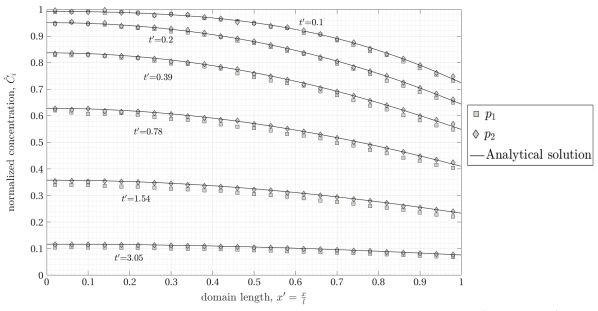

Figure 1: Average concentration over time in the 1D problem. The b.c. at x'=0 is of no flux, while at x'=1 a Robin b.c is set.

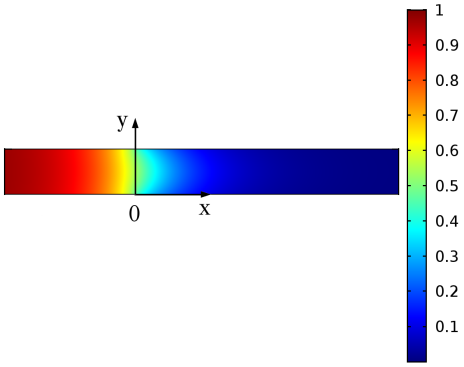

Figure 2: Contour plot of the steady state normalized concentration in the 2D problem. The reactive wall boundary conditions are set on $x > 0$ and a constant $C = 1$ for $x \to -\infty$.

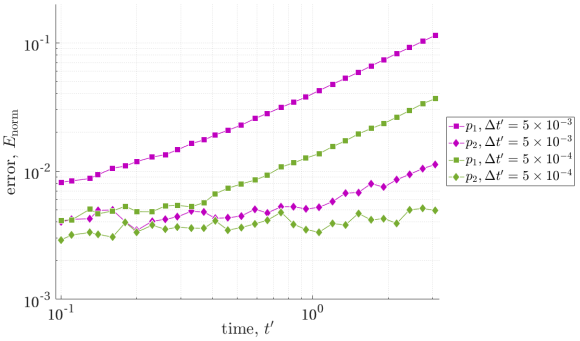

Figure 3: Normalized error over time: values for simulations with Da=1, $\Delta t' = 5 \times 10^{-3}$ and $\Delta t' = 5 \times 10^{-4}$ (purple and green datasets, respectively) are shown. Different approximations for the boundary reaction probability p are employed: $p = p_1$ (squares), $p = p_2$ (diamonds).

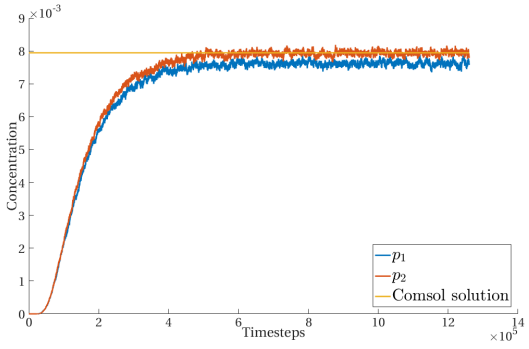

Figure 4: Time evolution of average particle concentration for the 2D problem (for Pe=1 and Da=100), comparing first order (blue) with second order approximation (red) for reaction probability p. Steady state result of the Comsol simulations are shown for comparison, represented as a straight line. Here $p_1 = 1$ and $p_2 = 0.667$.

References

[1] Agmon, Noam. *Journal of Chemical Physics*, **81**, 6, 2811–2817, 1984.

[2] Paster, Amir and Bolster, Diogo and Benson, David A. *Journal of Computational Physics*, **263**, 91–112, 2014.