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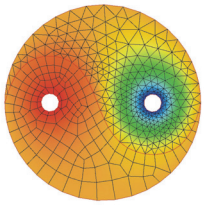

DEVELOPMENT OF ADAPTIVE METHODS FOR REACTION-DIFFUSION AND OTHER TRANSPORT PROBLEMS ARISING IN ELECTROCHEMISTRY

LESŁAW K. BIENIASZ

Institute of Physical Chemistry of the Polish Academy of Sciences,
Department of Complex Systems and Chemical Processing of Information,
ul. Niezapominajek 8, 30-239 Kraków, Poland
Institute of Teleinformatics, Faculty of Electrical and Computer Engineering,
Cracow University of Technology
ul. Warszawska 24, 31-155 Kraków, Poland
E-mail: nbbienia@cyf-kr.edu.pl

Abstract

In the course of over 15 years of work of the author, on the development of adaptive finite-difference methods for reaction-diffusion and other reactive transport phenomena occurring in electrochemistry, much experience has been accumulated, which can also be of interest to modellers in other areas, including materials science. The results of that research are briefly summarized, indicating the advantages and disadvantages of the various methods. It is argued that much more work still has to be done to design satisfactory adaptive methods, even for spatially one-dimensional equations, despite the fact that for such problems the adaptive methodology is currently regarded to be mature.

Key words: computational electrochemistry; reaction-diffusion; finite-difference methods; adaptive grids

1. INTRODUCTION

Computational modelling of reaction-diffusion and other reactive transport phenomena presents a challenging task in many areas of science and technology related to chemistry and biology, materials science not being excluded. The modelling relies on numerically solving relevant governing equations resulting from the continuum theory of matter, such as systems of ordinary differential equations (ODEs) or partial differential equations (PDEs), possibly coupled with algebraic equations (AEs) or differential-algebraic equations (DAEs) as well. Problems of this kind become particularly difficult to solve when the governing equations are singularly perturbed, so that their solutions possess local layers, moving fronts or other highly localised structures. In such cases, adaptive methods that detect such difficult local solution structures, and appropriately concentrate the computational effort on resolving them, are indispensable [15]. Another reason for developing the adaptive methods is the modern trend towards automation of computational procedures: users of the simulation software want to be able to obtain solutions having a guaranteed prescribed accuracy, independently of the location, extension and duration of the local solution structures, which may well not be known *a priori*.

For the past 15 years, the present author has been developing finite-difference adaptive ap-

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proaches to the numerical solution of reaction-diffusion and other reactive transport equations occurring in electrochemistry, as a part of a long-term research programme aimed at creating a new scientific discipline: Computational Electrochemistry [1]. The work concentrated on initial boundary value problems for evolutionary PDEs in one-dimensional space geometry [2-9], boundary value problems for ODEs [10,11], and recently on integral equations [12]. Problems of this kind are often very demanding: the differences of the dimensions of large-scale and small-scale spatial features of the solutions may be of many (let's say 1-13) orders of magnitude. Highly localised temporal features are also encountered.

2. THE ADAPTIVE STRATEGIES STUDIED

Initially, an adaptive moving grid strategy for the solution of systems of evolutionary reaction-diffusion PDEs, based on the state-of-the-art method of Verwer and co-workers (CWI, Holland) was tried [2-5]. The original idea of the method was to decouple every discrete time-stepping operation into two stages. In the first stage, the time stepping on the fixed non-uniform grid, corresponding to the previous time level was performed, in order to obtain tentative solutions for the new time level. The tentative solution was then used to determine the adapted grid for the new time level, by equidistributing a second derivative monitor function. In the second stage the final solution for the new grid was obtained, using the old and the new grids, by a variant of the Crank-Nicolson discretisation scheme. The success was rather moderate. The method was capable of identifying and resolving the local layers and moving fronts. However, severe numerical difficulties were encountered, necessitating considerable modifications of the original strategy. The automatism of the method was also rather debatable, since tuning of the various method parameters was necessary, and it was not clear how to perform the tuning to adjust the method for a large class of examples. A sad observation is that published methods, supposed to be general and automatic, do not necessarily possess such properties, and should be used with much caution.

Subsequently, the investigations were redirected [6-8] towards an alternative state-of-the art approach, also originating from the Verwer group and known as the LUGR method (Local Uniform Grid Refinement), but similar to the plethora of methods developed by other authors. The original idea of the method, hereafter termed the patch-adaptive strategy (PAS), was to repeat the time-stepping (at every discrete time level) on a number of gradually refined uniform spatial grids and grid patches (cf. figure 1a). A uniform grid covering the entire space interval was taken first. Then, the solution was repeated on an analogous grid but with a halved step size. The solutions on the grids were compared, and in areas where the solutions differed by more than the prescribed error tolerance, further refined uniform grid patches were overlaid, and the time-stepping was again redone on these patches, taking the known solutions from previous grids as boundary values. Solutions corresponding to other areas were accepted as sufficiently accurate, and were not recalculated any more. The new solutions on the patches were compared with those on the former grids or patches, and the patch addition process was repeated recursively until the solutions were sufficiently accurate everywhere in space. A temporal error was also controlled, allowing time step adjustments, by using error estimators inherent in the time integrators utilised (3^{rd} order Rosenbrock ROWDA3 scheme and 2^{nd} order extrapolated BDF scheme). This simple approach proved much more successful than the formerly tried moving grid, allowing a nearly automatic solution of a large selection of electrochemical evolutionary governing equations in one-dimensional space geometry [6-8]. Table 1 and figures 2-4 present an example of an electrochemical reaction-diffusion problem, and its solution by the PAS. The PAS has been found useful for: (a) problems defined on single and multiple space

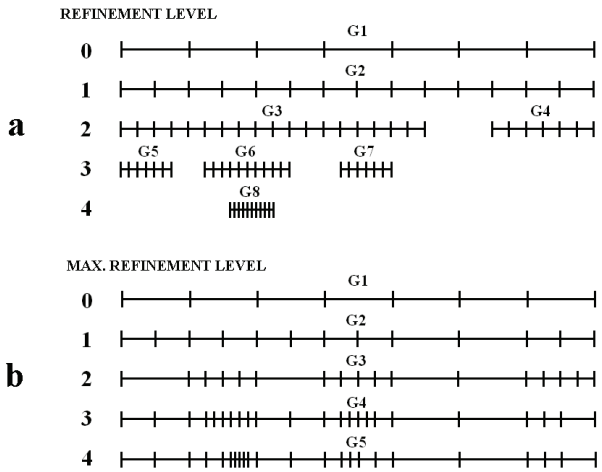

Fig. 1. *Examples of sequences of grids G1, G2, G3, ..., on which a given problem is re-solved in the course of spatial grid adaptation process, in the case of the PAS (a), and the strategy with individual grid node addition/removal (b).*

intervals; (b) transport conditions determined by diffusion, reaction-diffusion, convection-diffusion, and migration-diffusion (Nernst-Planck-electroneutrality and Nernst-Planck-Poisson equations); (c) governing equations for distributed unknowns, optionally accompanied by additional DAEs in time variable, for the unknowns localised at the boundaries (typical e.g. for adsorption); (d) local and non-local (e.g. periodic) boundary conditions. However, in some cases the PAS proved computationally over-expensive, requiring very large numbers of spatial grid nodes or discrete time levels.

An attempt to reduce the cost of the PAS was undertaken in [9], by replacing the formerly used conventional, low-order spatial discretisation, by a compact scheme resulting from modifications of the classical Numerov discretisation [13,14]. The scheme cannot be applied to all kinds of problems listed above, but in cases when it can be applied, it brings a visible improvement in terms of accuracy, efficiency, and resistance to certain numerical difficulties. However, the reasons for the inefficacies of the PAS are more complicated.

One reason is related to the spatial error control. The PAS works efficiently when the spatial error does not propagate to large distances, i.e. when the so-called pollution effects are not significant. If this is not the case, the PAS creates very large grid patches, sometimes even covering the entire space interval, which results in grid over-refinement. The remedy can be to use a different grid enrichment method, by adding individual grid nodes rather than grid patches, and by allowing the node removal as well (see figure 1b). This is a substantial modification of the method, since instead of the uniform grid patches one must use non-uniform grids. As a result, the overall spatial accuracy may deteriorate. Furthermore, the individual node addition/removal requires that the solution be repeated on the entire grids, and not only on local grid patches, which may increase the computational cost in another way. Experiments with the individual node addition/removal, performed in [10,11] (so far only for ODEs, not yet for evolutionary PDEs) reveal, however, that the net cost may be competitive to that of the PAS, especially in the case of examples when the PAS was expensive. It should be noted that a number of the contemporary adaptive methods, especially those based on the idea of multi-grids, involves the solution recalculation on the entire grids, with seemingly satisfactory results. On the other hand, the results of the comparisons of various known error estimators, grid refinement indicators, and grid refinement strategies, performed in [10,11], suggest that none of them is ideal. The spatial errors are inherently non-local, and should not be used as indicators for grid refinement. The indicators should be local.

Table 1. *An example of a reaction-diffusion PDE system possessing a solution with a moving front (model of a double potential step experiment for a simple electrochemical reaction mechanism of electrochemically generated luminescence:* $A \rightleftharpoons B + e^-$, $A + e^- \rightleftharpoons C$, $B + C \rightarrow 2\,A + \text{light}$*). All variables are in dimensionless form. The larger* κ*, the more localised the reaction front is.*

parameters:	κ = dimensionless rate constant of the homogeneous reaction τ = dimensionless duration of the forward potential pulse
governing equations:	$\partial c_A(x,t) / \partial t = \partial^2 c_A(x,t) / \partial x^2 + 2\, r(x,t)$, $\partial c_B(x,t) / \partial t = \partial^2 c_B(x,t) / \partial x^2 - r(x,t)$, $\partial c_C(x,t) / \partial t = \partial^2 c_C(x,t) / \partial x^2 - r(x,t)$, where $r(x,t) = \kappa\ c_B(x,t)\, c_C(x,t)$ is the homogeneous reaction rate
initial conditions:	$c_A(x,0) = \mathrm{erf}(\ 0.5\, x\, \tau^{\ -1/2}\ )$, $c_B(x,0) = \mathrm{erfc}(\ 0.5\, x\, \tau^{\ -1/2}\ )$, $c_C(x,0) = 0$
boundary conditions:	$c_A(0,t) = 0$, $c_B(0,t) = 0$, $c_C(0,t) = 1$, $c_A(x_{max},t) = 1$, $c_B(x_{max},t) = 0$, $c_C(x_{max},t) = 0$
analytical concentrations for $\kappa \rightarrow \infty$:	$c_{A,\,anal}(x,t) = 1 - \left\| \mathrm{erfc}\left[\ 0.5\, x\, (t+\tau)^{-1/2}\ \right] - 2\ \mathrm{erfc}(\ 0.5\, x\, t^{-1/2}\ ) \right\|$, $c_{B,\,anal}(x,t) = \max\left\{ 0,\ \mathrm{erfc}\left[\ 0.5\, x\, (t+\tau)^{-1/2}\ \right] - 2\ \mathrm{erfc}(\ 0.5\, x\, t^{-1/2}\ )\ \right\}$, $c_{C,\,anal}(x,t) = \max\left\{ 0,\ 2\ \mathrm{erfc}(\ 0.5\, x\, t^{-1/2}\ ) - \mathrm{erfc}\left[\ 0.5\, x\, (t+\tau)^{-1/2}\ \right]\right\}$

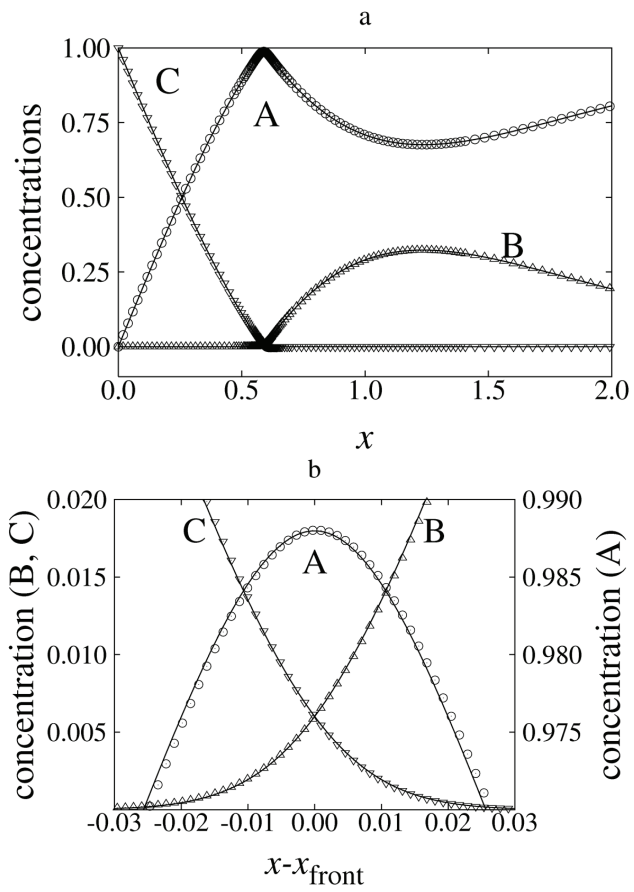

Fig. 2. Typical solutions for concentration profiles of species A, B and C at $\tau = 1$ and $\kappa = 10^6$ in the example from table 1, obtained by the PAS at $t = 0.2$ (points), shown in the large scale (a) and within the moving reaction front located at x_{front} (b). Solid lines represent either analytical solutions for $\kappa \to \infty$ (a), or local-steady-state solutions (b).

A second reason for the inefficacy of the PAS (and similar static regridding methods) is the increase of the temporal error in the cases when the spatial solution features become more and more localised. This problem causes that the number of discrete time levels needed increases and may become excessively large (cf. the example results in figures 3 and 4). The problem does not occur with moving grids, but in view of the aforementioned difficulties with the moving grid methods, the present author would be reluctant to combine the static regridding with moving grids, despite the recent attempts to do so, seen in the literature.

3. UNSOLVED PROBLEMS

In view of the above results, the crucial, and in the opinion of the present author, still unsolved problem, is how to design local refinement indicators that would produce, as cheaply as possible, grids possessing minimum numbers of nodes needed to force all errors below a prescribed error tolerance.

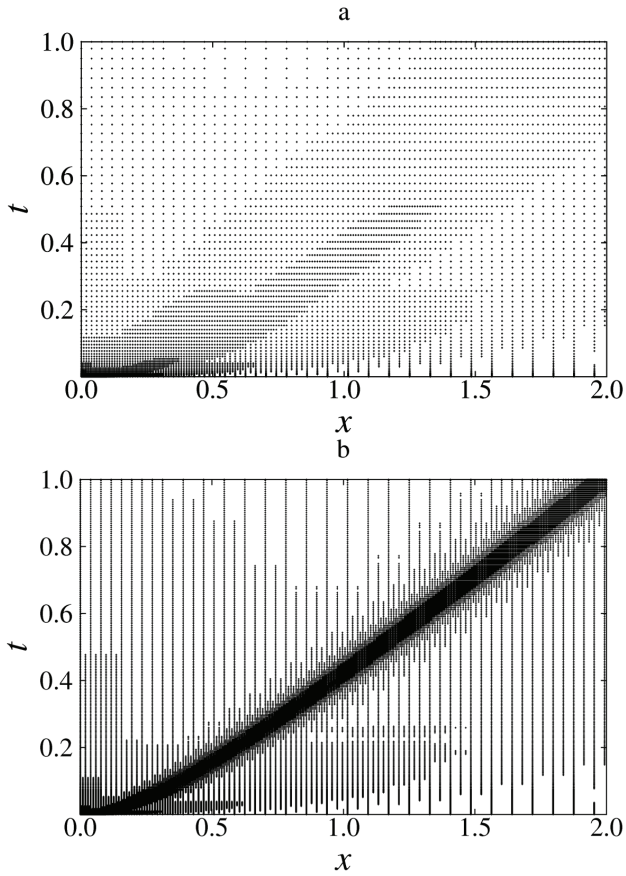

Fig. 3. Fragments of typical spatio-temporal grids resulting from the PAS calculations for the example from table 1, for $\tau = 1$ and $\kappa = 10^3$ (a) and $\kappa = 10^6$ (b). Note the increase of the number of discrete time levels with increasing κ.

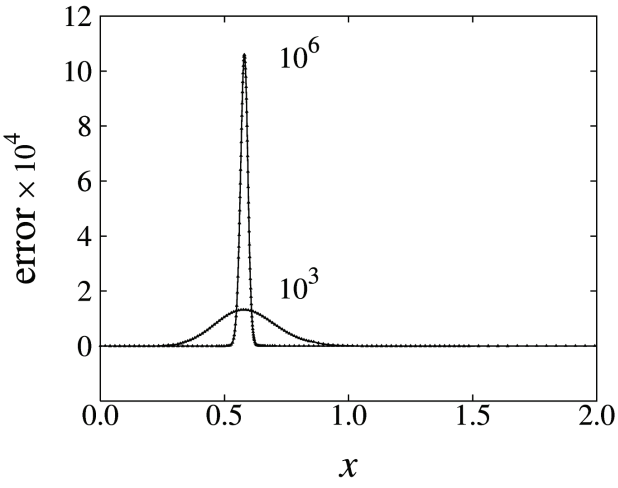

Fig. 4. Estimated temporal errors of the concentration of species A at $t = 0.2$, obtained by the PAS (ROWDA3 time integrator) for the example from table 1, for $\tau = 1$ and $\kappa = 10^3$ and $\kappa = 10^6$ (the curves are labelled with the respective κ values), in the calculations that produced the results depicted in figure 3. Note the increase of the errors with increasing κ, within the region of the reaction front.

Another unsolved problem is how to reduce the temporal error observed in static regridding methods in the case of narrow moving fronts. Finally, it should be realised, the all of the above (if not all of

the existing) adaptive methods are not able to detect spatial or temporal features that have a character of a highly localised spatial peak or spike, if the dimensions of the spike are much smaller than any of the currently used grid step size. Spatial spikes may not be present in the case of reaction-diffusion problems, where layers and moving fronts are more characteristic, but in general this is one more unsolved problem for adaptive methods.

4. CONCLUSIONS

Summing up, it has been possible to achieve a significant progress on the way towards a fully automatic finite-difference solution of reaction-diffusion and other transport equations occurring in electrochemistry. However, much more work still has to be done to design satisfactory adaptive methods, even for spatially one-dimensional equations, despite the fact that for such problems the adaptive methodology is currently regarded to be mature.

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ROZWÓJ METOD ADAPTACYJNYCH DLA ZAGADNIEŃ REAKCJI-DYFUZJI I INNYCH PROBLEMÓW TRANSPORTU WYSTĘPUJĄCYCH W ELEKTROCHEMII

Streszczenie

W ciągu ponad 15 lat pracy autora nad rozwojem adaptacyjnych metod różnic skończonych dla zagadnień reakcji-dyfuzji oraz innych zjawisk transportu reakcyjnego występujących

w elektrochemii, nagromadziło się wiele doświadczeń, które mogą być interesujące dla badaczy zajmujących się modelowaniem w innych dziedzinach, łącznie z nauką o materiałach. Wyniki tych badań zostaną krótko przedstawione, ze wskazaniem na wady i zalety różnych metod. Przedstawione zostaną argumenty na rzecz tezy, że potrzeba znacznie więcej pracy aby zaprojektować zadowalające metody adaptacyjne, nawet dla równań w przestrzeni jednowymiarowej, mimo iż obecnie uważa się, że metodologia adaptacyjna dla takich problemów osiągnęła stan dojrzały.

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