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Brute force (or not so brute) digital simulation in electrochemistry revisited

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ABSTRACT

The use of very high order spatial discretisation in digital simulation of electrochemical experiments is assessed, considering up to asymmetric 8-point approximations for the derivatives. A wide range of conditions are examined, including several mechanisms and electrodes and potential-step and potential-sweep experiments. In all cases it is found that asymmetric multi-point approximations in combination with exponentially expanding grids provides very accurate results and with very reduced number of grid points (<15). Consequently, the direct ('brute force') resolution of the finite-difference equation system by standard matrix techniques becomes a competitive and more general alternative to specialised methods like the Thomas algorithm.

1. Introduction

Some years ago, Britz [1] wrote a paper entitled 'Brute Force Digital Simulation in Electrochemistry'. In that work, the direct resolution of the system of equations involved in the finite difference treatment of digital simulation of electrochemical experiments was considered and related to some specialised methods such as the Thomas Algorithm in both its scalar [2,3] and matrix-vector versions [4].

More recently, some papers were published [5–8] where the direct discretisation of the mathematical laws governing the mass transport in electrochemical problems was tackled very efficiently by using multipoint higher-order approximations to the spatial derivatives. A special case was found [7] with an asymmetric four-point formula in an exponentially expanding grid which gives rise to very good results while enabling the use of very high expansion factors in the range 1.41–1.55.

In this paper, the value of other higher-order asymmetric multipoint formulae is assessed. Thus, 5-, 6-, 7- and even 8-point approximations are considered with only one point on the left-hand side of the point of the derivative (the so-called (*N*,2) forms). As will be demonstrated later, with these multi-point approximations very accurate results can be obtained with exceptionally high expansion factors (for example, values close to 2 can be appropriate). Thus, the (*N*,2) formulae show very interesting features:

(1) As above-mentioned, the (*N*,2) forms give rise to accurate results with very high expansions factors in the spatial grid and without numerical oscillations, in contrast with the behaviour of other multi-point formulae.
(2) The (*N*,2) forms are suitable for the application of Thomas-like algorithms. So, all the methodologies developed around the three-point formulae are easily extensible here.
(3) The extremely high expansion factors available under these conditions allow us to cover an extended spatial region with small interval amplitudes near the electrode surface with very, very few points in the grid. For example, a dimensionless distance of 100 (often needed for the simulation of some electrochemical techniques) with a distance of 0.1 for the point nearest to the electrode can be covered with a 12-point grid.
(4) Dealing with such very small grids, the direct resolution of the implicit systems of equations resulting from the application of finite difference methodology by standard procedures is not only possible, but convenient and very competitive in most situations.
(5) The resulting computer programs are very simple to code. In addition, the most tedious to write routines as well as some example programs are given to make it easier for occasional programmers to write their own programs fitting their demands.

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2. Some theoretical considerations

2.1. General

The general expression for the approximation to the spatial first derivatives of the concentration of a given species, j, in a point, i, using the (N,2) forms in an exponentially expanding grid is given by

$$\left(\frac{\partial c^j}{\partial x}\right)_i \approx \frac{1}{h\gamma_e{}^i}\sum_{k=i-1}^{i+N-2}\beta_{k-i}c_k^j \tag{1}$$

whereas the second derivative by

$$\left(\frac{\partial^2 c^j}{\partial x^2}\right)_i \approx \frac{1}{h^2\gamma_e{}^{2i}}\sum_{k=i-1}^{i+N-2}\alpha_{k-i}c_k^j \tag{2}$$

where i denotes the position in the grid ($i = 1, 2, \ldots$), h is the first-interval amplitude, γ_e is the expansion factor, and the coefficients α and β are given by analytical expressions independent of the position in the grid (some of them can be found in [7]). The distance, x, at point i, x_i, is

$$x_i = h\frac{\gamma_e{}^i - 1}{\gamma_e - 1} \tag{3}$$

If we consider Fick's second law, usually addressed in electrochemical problems, for a species, j, in dimensionless form,

$$\frac{\partial C^j}{\partial \tau} = \frac{\partial^2 C^j}{\partial x^2} + \frac{f}{R_0 + x}\frac{\partial C^j}{\partial x} \tag{4}$$

where f is 0, 1 or 2, for planar, cylindrical and spherical electrodes, respectively, and

$$C^j = \frac{c^j}{c^{r*}} \tag{5}$$

$$\tau = \frac{t}{t_r} \tag{6}$$

$$x = \frac{r - r_0}{\sqrt{D_j t_r}} \tag{7}$$

$$R_0 = \frac{r_0}{\sqrt{D_j t_r}} \tag{8}$$

with c^j being the concentration of species j, c^{r^*} the bulk concentration of the reference species, t is time and t_r an appropriate reference time. r is the distance to the centre of the electrode (spherical and cylindrical) and r_0 is the electrode radius. For a planar electrode, x is simply the dimensionless distance from the electrode surface. D_j is the diffusion coefficient of j.

By applying (1) and (2) to the right-hand side of (4), one obtains

$$\frac{1}{h^2\gamma_e{}^{2i}}\sum_{k=i-1}^{i+N-2}\alpha_{k-i}C_k^j + \frac{f}{R_0 + x_i}\frac{1}{h\gamma_e{}^i}\sum_{k=i-1}^{i+N-2}\beta_{k-i}C_k^j \tag{9}$$

With a two-point approximation for the left-hand side term in (4), we have

$$\frac{C_i^{j'} - C_i^j}{\delta\tau} \tag{10}$$

where C_i^j represents the (known) concentration of species j at point i at the time τ, whereas $C_i^{j'}$ is the (unknown) concentration of the same species at the same point but at the time $\tau + \delta\tau$.

The combination of (9) and (10) can be given in several ways. Thus, one can take the known values C_i^j in (9) giving rise to the explicit methods (very limited and offering poor results, so, not very interesting), the unknown values $C_i^{j'}$ obtaining the fully implicit method, the average of C_i^j and $C_i^{j'}$ (the Crank-Nicolson method), a combination of smaller fully implicit time steps (the extrapolation methods) or a multipoint approximation for (10) obtaining, for example the BDF (backward differentiation formula). In any case, the most interesting question for our 'brute force' approximation is to deal with implicit methods. So, in this section the procedure will be illustrated for the case of the fully implicit (FI) method.

In the context of the FI method, the combination of (9) and (10) leads to

$$-C_i^j = -C_i^{j'} + \frac{\lambda}{\gamma_e{}^{2i}}\sum_{k=i-1}^{i+N-2}\left(\alpha_{k-i} + \frac{fh\gamma_e{}^i}{R_0 + x_i}\beta_{k-i}\right)C_k^{j'} \tag{11}$$

with

$$\lambda = \frac{\delta\tau}{h^2} \tag{12}$$

For example, with the (6,2) forms Eq. (11) can be re-written in the most convenient way

$$a_{-1,i}C_{i-1}^{j'} + a_{0,i}C_i^{j'} + a_{1,i}C_{i+1}^{j'} + a_{2,i}C_{i+2}^{j'} + a_{3,i}C_{i+3}^{j'} + a_{4,i}C_{i+4}^{j'} = b_i^j \tag{13}$$

with

$$\begin{aligned}
a_{-1,i} &= \alpha_{-1} + \frac{fh\gamma_e{}^i}{R_0 + x_i}\beta_{-1}\\
a_{0,i} &= \alpha_0 + \frac{fh\gamma_e{}^i}{R_0 + x_i}\beta_0 - \frac{\gamma_e{}^{2i}}{\lambda}\\
a_{1,i} &= \alpha_1 + \frac{fh\gamma_e{}^i}{R_0 + x_i}\beta_1\\
&\ldots\\
a_{4,i} &= \alpha_4 + \frac{fh\gamma_e{}^i}{R_0 + x_i}\beta_4\\
b_i^j &= -\frac{\gamma_e{}^{2i}}{\lambda}C_i^j
\end{aligned} \tag{14}$$

For each participating species in a given process, an equation equivalent to (13) can be written (exactly the same if all diffusion coefficients are equal and slightly different otherwise [2]) at each node, i, except for $i = 0$. The resulting equations, together with the surface conditions for $i = 0$ and the assumption that $C_i^{j'} = C^{j*} = c^{j*}/c^{r*}$ for $i \geq i_{\mathrm{MAX}}$ (with i_{MAX} being the last node of the grid placed at a distance x_{MAX} from the electrode surface), gives rise to a complete system of equations (linear in this case) that can be solved in different ways.

2.2. The Thomas algorithm

With the standard three-point approximation for the space derivatives, the Thomas algorithm has been largely used when semi-infinite conditions hold. Provided that the last point is far enough from the electrode surface for being unaffected by the perturbation at the electrode surface (*i.e.*, $C_{i_{\mathrm{MAX}}}^{j'} = C^{j*}$), the backward substitution in the linear system of equations, the combination with the surface conditions and the subsequent forward substitution gives rise to an efficient method to find all the values of $C_i^{j'}$. In the scalar version, this algorithm is only applicable if the profiles of all the participant species are uncoupled. This is to say, they are all independent of each other.

The Thomas algorithm has been extended to asymmetric four-points approximation (4,2) by Britz and Strutwolf [9], by taking a 'post-infinite' point at $i_{\mathrm{MAX}} + 1$ where the concentration is also