Short Communication

Consistency Proof of the Sequential Algorithm for the Digital Simulation of Systems Involving First-Order Homogeneous Kinetics

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In electrochemical digital simulations[1,2] involving, along with diffusional transport, homogeneous chemical reactions, there is a small problem of tactics in the discretisation of the dynamic equation when using the simple explicit method which, while not being very efficient, is frequently used because of the ease of its implementation.

For clarity, take the simple Reinert–Berg experiment,[3] in which in effect a diffusion-limiting potential jump is applied to a species in solution, undergoing first-order chemical decay (reactions (1) and (2)], where A is the electroactive

$$A + ne^- \rightarrow B \tag{1}$$

$$A \xrightarrow{k} P \tag{2}$$

and decaying substance, B its reduced form and P the decay product, of no further interest here. In a one-dimensional cell arrangement, the dimensionless dynamic equation is eqn. (3) in which C is the concentration of A normalised

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} - KC \tag{3}$$

by its initial bulk value, T is the time normalised by the abitrary observation time τ, X is the distance normal to the electrode normalised by the characteristic diffusion length $\sqrt{(D\tau)}$ and $K = k\tau$ is the dimensionless homogeneous rate constant (see Ref. 2 for details). Boundary conditions are given by eqn. (4). The system has an analytical solution,[2,3]

$$\begin{aligned} &T = 0, \text{ all } X\text{: } C = 1 \\ &T > 0, X = 0\text{: } C = 0 \\ &T > 0, X >> 1\text{: } C = e^{-KT} \end{aligned} \tag{4}$$

so it is easy to check a given simulation technique.

In digital simulations of systems such as this one, C is represented by a number of sample points C_i ($i = 0, 1, \ldots n$) at the (dimensionless) distances 0, H, $2H$, ... nH from the electrode. Given computed values of C at time T, a new array C' at time $T + \delta T$ is to be computed. Eqn. (3) must be discretised, and the small problem enters here. One can perform the calculation for, say, point C_i in what we call 'parallel' or 'sequential' mode.[2] In parallel mode, old values of C are used for both diffusional and chemical changes, and the discrete expression is given by eqn. (5), where

$$C_i' = C_i + \lambda(C_{i-1} - 2C_i + C_{i+1}) - K\delta T C_i \tag{5}$$

$\lambda = \delta T/H^2$ (again, see Ref. 2 for details). This strategy implies a total separation of diffusional and chemical changes, although we know that they are in fact coupled. A crude attempt at coupling, the sequential method, has been common practice.[1,4,5] Here, one allows first for diffusional changed, then uses the resulting intermediate C-values to compute the chemical changes as well: if C_i'' is the intermediate diffusion-augmented value, we have eqns. (6) and (7). This device has been discussed in some detail by Nielsen *et al.*,[5] who provide a non-rigorous justification for it by means of a counter-example. It does appear to give somewhat better results than the parallel method, but so far no consistency proof has been shown for it. This communication provides such a proof.

$$C_i'' = C_i + \lambda(C_{i-1} - 2C_i + C_{i+1}) \tag{6}$$

$$C_i' = C_i'' - K\delta T C_i'' \tag{7}$$

We shall now describe a third, hypothetical, method, the transformational algorithm, employed previously.[6] It is hypothetical because it is not expected to be used, but does

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provide the desired consistency proof of the sequential algorithm. Both sides of eqn. (3) are multiplied by e^{KT} to give eqn. (8), and noting that eqn. (9) holds, eqn. (8) can

$$\frac{\partial C}{\partial T} e^{KT} = \frac{\partial^2 C}{\partial X^2} e^{KT} - KCe^{KT} \tag{8}$$

$$\frac{\partial}{\partial T}\left(Ce^{KT}\right) = \frac{\partial C}{\partial T} e^{KT} + KCe^{KT} \tag{9}$$

then be rewritten as eqn. (10). Discretising the left-hand

$$\frac{\partial}{\partial T}\left(Ce^{KT}\right) = e^{KT} \frac{\partial^2 C}{\partial X^2} \tag{10}$$

term for the interval δT for C_i as eqn. (11), and the right-

$$\frac{\partial}{\partial T}\left(C_i e^{KT}\right) \simeq \frac{C_i' e^{K(T+\delta T)} - C_i e^{KT}}{\delta T} \tag{11}$$

hand side as usual, the discrete expression of eqn. (10) for C_i' becomes eqn. (12). Dividing throughout by e^{KT} finally

$$C_i' e^{K(T+\delta T)} = C_i e^{KT} + e^{KT}\lambda(C_{i-1} - 2C_i + C_{i+1}) \tag{12}$$

yields eqn. (13). Combining eqns. (6) and (7) for the se-

$$C_i' = e^{-K\delta T}\left[C_i + \lambda(C_{i-1} - 2C_i + C_{i+1})\right] \tag{13}$$

quential algorithm, we obtain eqn. (14), which, for small

$$\begin{aligned} C_i' &= (1-K\delta T)C_i'' \\ &= (1-K\delta T)\left[C_i + \lambda(C_{i-1} - 2C_i + C_{i+1})\right] \end{aligned} \tag{14}$$

$K\delta T$ approaches eqn. (13). Since no weakening assumptions or approximations were made in deriving eqn. (10) and the discretisation eqn. (11) is consistent, this constitutes a mathematical consistency proof of the sequential algorithm.

Fig. 1 shows simulation errors for the parallel, sequential and transformational algorithms, as well as for the third-order Runge–Kutta technique[7] for comparison. It is seen that the sequential algorithm is a little superior to the parallel one, but for larger K values, where the approximation $(1-K\delta T) \simeq e^{-K\delta T}$ no longer holds, the two methods are equally poor and converge towards each other. The transformational method can clearly cope with any K value: not surprisingly, since in this case, for large K, when the chemical reaction dominates diffusional changes, eqn. (13) in fact approaches identity with the analytical solution.

Now we do not need to simulate the Reinert–Berg system, since we have the solution. In simulation practice, however, we meet systems of dynamic equations for several species. A simple example is the catalytic system of reaction (15), for which the dynamic equations are eqns. (16) and (17).

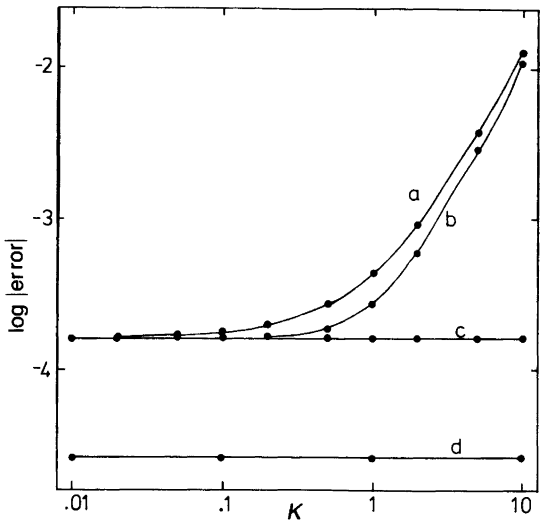

Fig. 1. Logarithm of the magnitude of the relative error in computed current for the Reinert–Berg system for a range of K-values, for the methods (a) parallel algorithm, (b) sequential algorithm, (c) transformational algorithm and (d) Runge–Kutta integration.[7] The six-point current approximation was used to compute the currents.[2]

$$A + ne^- \rightarrow B \text{ (reversible)} \tag{15}$$

$$B \xrightarrow{k} A$$

$$\frac{\partial C_A}{\partial T} = \frac{\partial^2 C_A}{\partial X^2} + KC_B \tag{16}$$

$$\frac{\partial C_B}{\partial T} = \frac{\partial^2 C_B}{\partial X^2} - KC_B \tag{17}$$

More complex systems are, in fact, the rule. (See, for example, Refs. 2 and 8.) In these cases, the transformational algorithm can be applied to at most one species' equation, but the sequential method can be used for all: in the above catalytic case, eqns. (16) and (17), one would compute $C_{B,i}''$ by eqn. (6), then derive the homogeneous kinetic term in eqn. (7) from this and use it for both species A and B as in eqns. (18)–(20).

$$C_{B,i}'' = C_{B,i} + \lambda(C_{B,i-1} - 2C_{B,i} + C_{B,i+1}) \tag{18}$$

$$C_{B,i}' = C''_{B,i} - K\delta TC_{B,i}'' \tag{19}$$

$$C_{A,i}' = C_{A,i} + \lambda(C_{A,i-1} - 2C_{A,i} + C_{A,i+1}) + K\delta TC_{B,i}'' \tag{20}$$

Thus, diffusional and chemical changes are approximately coupled with a technique shown above to be consistent with the model for small $K\delta T$. As seen in Fig. 1 [for the Reinert–Berg system, eqns. (1) and (2)], the method constitutes a modest improvement for K values up to about unity. Above this, better metods, such as whole-equation Runge–Kutta[2,7] or Crank–Nicolson,[2] should be used, or, in

extreme cases, the heterogeneous equivalent method of eliminating the homogenous terms from the dynamic equations.[6,9,10]

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