A test of the boundary doubling method for the numerical solution of diffusion-reaction systems

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Abstract

Numerical methods for solving diffusion-influenced bimolecular reactions in the 1- and 3-dimensional Smoluchowski approach are presented. The finite-difference method is used to solve diffusion-reaction equations for the pair distribution function. The kinetic equation for the concentration is evolved by the Runge–Kutta method with an adaptive time step. The boundary doubling method is introduced to study long-time dynamics where the truncation problem of the infinite boundary is crucial. The results show remarkable accuracy and speed with small number of spatial grid points until long times. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, we presented simple and efficient numerical methods for solving kinetic equations for various diffusion-influenced bimolecular reactions [1]. These methods utilize the finite-difference method to solve diffusion-reaction equations for the pair distribution function and the Runge–Kutta method with an adaptive time step to evolve the kinetic equation for the concentration. As the main difficulty of solving the equations numerically arises from implementing boundary conditions, we introduced the boundary doubling method (BDM) to reduce the truncation error which results from the fact that the outer spatial boundary is truncated at a finite separation, instead of infinity. The BDM is based on the fact that the range covered by diffusive motion is proportional to \( t^{1/2} \) according to the Einstein–Smoluchowski relation and thus the outer boundary can be simply doubled at every quadruple time. In this Letter, we apply the above methods to the classical 1- and 3-dimensional Smoluchowski approach for a diffusion-influenced binary reaction, which can be exactly solved and therefore the numerical accuracy can be easily compared with analytic solutions.

2. Diffusion-reaction equations

Consider a bimolecular reaction represented by \( A + B \rightarrow \text{product} \). The time evolution equation of the bulk concentration of \( A \) is given by:

\[
\frac{\partial}{\partial t} [A] = k(t) [A][B].
\]
where \(k(t)\) is the time-dependent rate coefficient and \([A]\) and \([B]\) are the concentrations of reactants \(A\) and \(B\) at time \(t\), respectively. In the classical Smoluchowski approach, the time-dependent rate coefficient can be calculated from the time-dependent pair distribution function of the reactants \(\rho(r, t)\), which is given in \(d\) spatial dimensions as follows [2]:

\[
k(t) = \frac{2\pi^{d/2}D\sigma^{d-1}e^{-\beta U(r)}}{\Gamma(d/2)} \left\{ \frac{d}{dr}e^{\beta U(r)}\rho(r, t) \right\}_{r=\sigma},
\]

where \(D\) is the relative diffusion constant, \(\Gamma(x)\) the gamma function, \(\sigma\) the reaction distance, \(\beta = (k_BT)^{-1}\) and \(U(r)\) the potential of mean force. \(\rho(r, t)\) is assumed to satisfy the following diffusion equation [2]:

\[
\frac{\partial \rho(r, t)}{\partial t} = D \nabla \cdot e^{-\beta U(r)} \nabla e^{\beta U(r)} \rho(r, t).
\]

This equation requires two boundary conditions at two spatial positions and one initial condition at \(t = 0\) for \(\rho(r, t)\). For the diffusion-influenced reaction system, the above partial differential equation is usually considered to be subject to the random initial and Collins–Kimball boundary conditions which are given by

\[
\rho(r, 0) = e^{-\beta U(r)},
\]

\[
\left\{ \frac{d}{dr}e^{\beta U(r)}\rho(r, t) \right\}_{r=\sigma} = \frac{kqT(d/2)}{2\pi^{d/2}D\sigma^{d-1}} e^{-\beta U(\sigma)} \rho(\sigma, t),
\]

\[
\rho(r \to \infty, t) = 1,
\]

where \(k^0\) is the intrinsic rate constant. The Smoluchowski boundary condition can be obtained as \(k^0 \to \infty\). For simplicity, let us neglect the effects of the detailed short-range structure in the potential of mean force, namely,

\[
U(r) = \begin{cases} 0, & \text{for } r \geq \sigma, \\ \infty, & \text{for } r < \sigma. \end{cases}
\]

### 3. Numerical methods

The Crank–Nicholson finite-difference method is applied to Eq. (3) considering the boundary condition, Eqs. (5) and (6) [1]. Then we can calculate the pair distribution function and the rate coefficient at a given time. The fourth-order Runge–Kutta method with an adaptive step size control by step doubling has an advantage [3] over other algorithms to solve ordinary differential equations since the pair distribution function changes smoothly at long times.

The error resulting from restricting the outer boundary will be significant at long times since the physical value of the pair distribution function at the truncated boundary changes with time. The outer truncated boundary should be large enough to satisfy Eq. (6), while \(\Delta r\) needs to be small enough in order to obtain converged results, with the number of grid points as small as possible. This causes crucial problem for a long-time dynamics. Using the fact that the range of region covered by diffusive motion is proportional to \(t^{1/2}\) (the Einstein–Smoluchowski relation), the BDM with a growing outer boundary which evolves with time is introduced. The outer boundary can be simply doubled at every quadruple time without expensive interpolations due to the finite number of discrete grids. The detailed BDM scheme was introduced in our previous paper [1].

One possible drawback of the method is that the error may increase abruptly right after the outer boundary and \(\Delta r\) are doubled. However, the adaptive size Runge–Kutta method can minimize such error by reducing the time step size around the doubling time as will be shown below.

For \(d = 1\) and \(d = 3\), the diffusion equation with the Smoluchowski boundary condition \((k^0 \to \infty)\) for a random initial condition when \([A]_0 = [B]_0\) can be solved exactly to give [4]

\[
[A]_1d = \left( \sqrt{\frac{16D\Delta t}{\pi}} + \frac{1}{[A]_0} \right)^{-1}.
\]

\[
[A]_k = \left( 4\pi^2 D\Delta t + 8\pi^2 \sqrt{\frac{\pi}{D\Delta t}} \right)^{-1}.
\]

Therefore, we can examine the numerical accuracy by comparing with the above exact results.
4. Results and discussions

In Fig. 1, we plot the survival probability curves \( P(t) \equiv [A]/[A]_0 \) in log–log scale for several values of \( N \) in 1-dimension. The values for the parameters are: \( D = 2.0 \times 10^{-9} \text{ m}^2 \text{s}^{-1}, \sigma = 1.0 \times 10^{-10} \text{ m}, [A]_0 = 1.0 \times 10^9 \text{ m}^{-1} \) and initial \( \Delta t = 1.0 \times 10^{-16} \text{ s} \). In order to realize the Smoluchowski boundary condition numerically, we take a large value for \( k^0(=10^4 \times D/\sigma) \). A nearly indistinguishable result compared with the exact one is obtained for only \( N = 32 \) and the calculation is done fast (< 1 s). All the calculations are performed on a SGI R10000 workstation. The adaptive size Runge–Kutta method is shown to be useful. With a fixed time-step size algorithm, one should calculate \( 1.0 \times 10^{15} \) steps until \( 0.1 \text{ s} \). Interestingly, all the curves show the same correct slope (\(-1/2\)) even for \( N > 2 \). This results from the fact that in 1-dimension, the pair distribution function becomes linear with respect to \( r \) in the long-time limit as 

\[
\rho(r,t) = \text{erf} \left( \frac{r - \sigma}{2 \sqrt{D t}} \right) \equiv \frac{r - \sigma}{\sqrt{\pi D t}} \quad (d = 1),
\]

where \( \text{erf}(x) \) denotes the error function.

Let us define the relative error of the numerical calculation as

\[
\varepsilon(t) = \left| 1 - \frac{P_{\text{calc}}(t)}{P_{\text{exact}}(t)} \right|.
\]

We plot the error as a function of time on a log–log scale for the same values of \( N \) as above within Fig. 1. It is noted that the error is found to remain constant in the long time, which suggests that the truncation error is reduced efficiently. The ripples in the curves represent the variation of the truncation error due to the boundary doubling. We note that the adaptive size Runge–Kutta method suppresses the error resulting from change of \( \Delta \tau \) effectively, by reducing \( \Delta t \) by about 1/100 times right after the boundary doubling.

Fig. 2 shows survival probability curves for several values of \( N \) in 3-dimensions and the time dependence of the relative error is also shown. The parameters are the same as those in Fig. 1, except \([A]_0 = 1.0 \times 10^{-9} \text{ m}^{-3}\) and \(k^0 = 10^4 \times 4 \pi D \sigma\). When \( N = 10^3 \), the numerical result is indistinguishable from the exact one until about \( 1.0 \times 10^{-16} \text{ s} \). For \( N = 10^4 \), it gives correct results up to about \( 1.0 \times 10^{-8} \text{ s} \) and takes about 1 min for calculation. For \( N = 10^5 \), it shows a similar behavior up to \( 1.0 \times 10^{-7} \text{ s} \) within about 12 min. As mentioned...
in the previous work [1], the most time-consuming part is the inversion routine of the tridiagonal matrix and, therefore, the computing time is roughly proportional to $N$.

For the same values of $N$, the deviations from the exact results are larger than those in 1-dimension, which can be attributed to the nonlinearity of the pair distribution function at long times. The pair distribution function in 3-dimensions in the long time limit is given by [4]

$$\rho(r, t) = 1 - \frac{\sigma}{r} \text{erfc} \left( \frac{r - \sigma}{2\sqrt{Dr}} \right) \approx 1 - \frac{\sigma}{r}$$

($d = 3$),

where $\text{erfc}(x)$ is the complementary error function. We notice that the slope of each of the survival probability curves tends to change from the exact value of $-3/2$ to the value of $-1/2$ in the long time limit, which reflects the fact that the pair distribution function is treated, in this time region, linearly due to the insufficient number of grid points, $N$ (see Fig. 1).

Here one could think that the present method can be improved by adopting an appropriate nonlinear transform scheme, which makes the pair distribution function linear as that in 1-dimension. Indeed, the results are greatly improved using the transformation relation, $l(r, t) \equiv r \rho(r, t)$, as shown below. One can make the transformed pair distribution function linear in the long time limit, namely, $l(r, t \to \infty) \equiv r - \sigma$. If this relation and Eq. (7) are applied to the above Eqs. (2)–(6) in 3-dimensions, they become

$$k(t) = 4\pi D\sigma^2 \left[ \frac{d}{dr} l(r, t) \right]_{r=\sigma},$$

$$\frac{d}{dt} l(r, t) = D \frac{d^2 l(r, t)}{dr^2},$$

$$l(r, 0) = r,$$

$$\left[ \frac{d}{dr} l(r, t) \right]_{r=\sigma} = \frac{1}{\sigma} + \frac{k^0}{4\pi D\sigma^2} l(\sigma, t),$$

$$l(r \to \infty, t) = \infty.$$

These equations can be solved by the same numerical method as above.

As a result, we plot survival probability curves for several values of $N$ in 3-dimensions and the time dependence of the relative error in Fig. 3. All the parameters are the same as those in Fig. 2. Note that even $N = 2$ gives highly accurate results in the long time limit and only $N = 16$ is enough to give an indistinguishable result at all times. This is a more accurate result than that in 1-dimension for same value of $N$. The relative error rather decreases as time goes, which results from the linear behavior of the transformed pair distribution function at long times. The transformed pair distribution function in 3-dimensions is closer to the linear function asymptotically than that in 1-dimension.

5. Concluding remarks

We have applied our previously developed methods to the classical 1- and 3-dimensional Smoluchowski approach and have compared the results with the exact analytical results. The truncation error which results from restricting the infinite outer boundary is avoided by introducing the BDM. And the methods are suitable for the long-time dynamics. The present method shows remarkable accuracy and speed with only a small number of spatial grid points until long times due to the linear behavior of pair distribution function in 1-dimension. In 3-dimensions we have made the asymptotic pair distribution function linear by the nonlinear transformation. The re-
sults are also accurate for a small number of grid points. It takes less than 1 s to give indistinguishable results in both dimensions. Even when the number of the grid points is only 2, the present method predicts the correct slope of the survival probability curve at long times in both dimensions.

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