



Fast arbitrary order moments and arbitrary precision solution of the general rate model of column liquid chromatography with linear isotherm



Samuel Leweke^a, Eric von Lieres^{a,b,*}

^a Forschungszentrum Jülich, IBG-1: Biotechnology, 52425 Jülich, Germany

^b JARA – High-Performance Computing

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ABSTRACT

Algorithms and software are presented for efficiently computing reference solutions of the general rate model with proven error bounds. Moreover, algorithms and software are presented for efficiently computing moments of arbitrary order. The methods are based on numerical inverse Laplace transform, and support both quasi-stationary and dynamic linear binding models. The inlet concentration profiles are treated in a most general way using piecewise cubic polynomials. Algorithmic differentiation obviates manual derivation of the required derivatives. Arbitrary precision arithmetics are applied for minimizing numerical roundoff errors, and several convergence acceleration techniques are evaluated. The implemented software package is freely available as open source on GitHub.

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1. Introduction

In the last decades, dozens if not hundreds of chromatography simulators must have been developed at academic institutions and in industry, applying different mathematical methods and programming languages. The partial differential equations are most often solved using the method of lines, discretizing the spatial coordinate, for example, by finite volumes, or weighted residual methods. Accuracy of the simulation results is usually evaluated by comparing solutions on computational grids with increasing numbers of elements. This way, the approximation order of the mathematical algorithm can be assessed. However, correctness of the simulation code can only be checked by comparing the results with reference solutions that have been computed with a different code, ideally based on a fundamentally different mathematical algorithm for solving the model equations. For this purpose, we present algorithms and software for computing reference solutions of the general rate model (GRM) with arbitrary precision and mathematically proven error bounds. The methods are based on

numerical inverse Laplace transform and, hence, limited to linear binding models. Both quasi-stationary and dynamic binding models are supported. The inlet concentration profiles are treated in a most general way using piecewise cubic polynomials. Arbitrary precision arithmetics are applied for minimizing numerical roundoff errors, and several convergence acceleration techniques are evaluated for speeding up the computations.

Sometimes the full solution of the GRM is not required, but only the first moments of the chromatogram need to be known. In principle, these moments can be calculated from the chromatogram by numerical integration routines. However, once an analytical GRM solution in the Laplace domain is at hand, this can be used for computing the moments much more efficiently.

Based on this approach, we have developed algorithms and software for computing highly accurate moments of arbitrary order. Algorithmic differentiation is applied for obviating the rather tedious and error-prone manual derivation of the required derivatives. In contrast to analytically derived formulas of the first moments, the numerical algorithms can be applied to a much wider class of inlet concentration profiles, namely piecewise cubic polynomials.

All presented algorithms are implemented in the software package *CADET-semi-analytic* which is freely available as open source on GitHub: <https://github.com/modsim/>

* Corresponding author at: Forschungszentrum Jülich, IBG-1: Biotechnology, 52425 Jülich, Germany. Tel.: +49 2461 61 2168.

E-mail address: e.von.lieres@fz-juelich.de (E. von Lieres).

CADET-semi-analytic. The CADET core simulator, which is based on finite volumes, and *CADET-semi-analytic* are validated against each other. Several numerical examples are given that are computationally highly demanding and demonstrate the potential and feasibility of our approach to compute truly arbitrary precision solutions and arbitrary order moments. However, the same methods can of course also be applied with much relaxed error bounds for quickly calculating reference solutions with less correct digits.

2. General rate model

The GRM is the most comprehensive model of mass transfer in column liquid chromatography, when only the axial coordinate in the column and the radial coordinate in the beads are considered (Gu, 1995; Guiochon et al., 2006; Schmidt-Traub et al., 2012; Felinger and Guiochon, 2004). The GRM describes transport of solute molecules through the interstitial column volume by convective flow, band broadening caused by axial dispersion, mass transfer resistance through a stagnant film around the beads, pore (and surface) diffusion in the porous beads (Ma et al., 1996; Schneider and Smith, 1968b; Miyabe, 2007), and adsorption to the inner bead surfaces.

Consider a single chemical component in a column of length $L > 0$ filled with spherical beads of radius $r_p \ll L$. The mass balance in the interstitial column volume is described by

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial z} + D_{ax} \frac{\partial^2 c}{\partial z^2} - \frac{1}{\beta_c} \frac{3}{r_p} k_f [c - c_p(\cdot, \cdot, r_p)]. \quad (1)$$

Here, $c : [0, \infty) \times [0, L] \rightarrow \mathbb{R}^{\geq 0}$ denotes the concentration in the interstitial column volume, $c_p : [0, \infty) \times [0, L] \times [0, r_p] \rightarrow \mathbb{R}^{\geq 0}$ the liquid phase concentration in the beads, k_f the film diffusion coefficient, D_{ax} the dispersion coefficient, u the interstitial velocity, and $\beta_c = \varepsilon_c / (1 - \varepsilon_c)$ the column phase ratio, where ε_c is the column porosity (ratio of interstitial volume to total column volume).

In the liquid phase of the porous beads the mass balance is given by

$$\frac{\partial c_p}{\partial t} = D_p \left(\frac{\partial^2 c_p}{\partial r^2} + \frac{2}{r} \frac{\partial c_p}{\partial r} \right) + \frac{D_s}{\beta_p} \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) - \frac{1}{\beta_p} \frac{\partial q}{\partial t}, \quad (2)$$

where $q : [0, \infty) \times [0, L] \times [0, r_p] \rightarrow \mathbb{R}^{\geq 0}$ denotes the solid phase concentration in the beads, D_p the effective diffusion coefficient in the beads, D_s the surface diffusion coefficient, and $\beta_p = \varepsilon_p / (1 - \varepsilon_p)$ the particle phase ratio, where ε_p is the particle porosity (ratio of pore volume to total bead volume). The GRM is used with both quasi-stationary (Eq. (3)) and dynamic (Eq. (4)) linear binding models. Nonlinear binding models, such as the Langmuir model (Langmuir, 1916), are not applicable in this study, as they lead to convolution integrals or other analytically non-solvable equations in the Laplace transformed equations.

$$0 = k_a c_p - k_d q, \quad (3)$$

$$\frac{\partial q}{\partial t} = k_a c_p - k_d q. \quad (4)$$

The following boundary conditions are imposed for all $t \in (0, \infty)$ and $z \in [0, L]$:

$$u c_{in}(t) = u c(t, 0) - D_{ax} \frac{\partial c}{\partial z}(t, 0) \quad (5)$$

$$\frac{\partial c}{\partial z}(t, L) = 0, \quad (6)$$

$$k_f [c - c_p(\cdot, \cdot, r_p)] = \varepsilon_p D_p \frac{\partial c_p}{\partial r}(\cdot, \cdot, r_p) + (1 - \varepsilon_p) D_s \frac{\partial q}{\partial r}(\cdot, \cdot, r_p), \quad (7)$$

$$\frac{\partial c_p}{\partial r}(\cdot, \cdot, 0) = 0. \quad (8)$$

Here, $c_{in} : [0, \infty) \rightarrow \mathbb{R}^{\geq 0}$ denotes the inlet concentration profile. Eqs. (5) and (6) are referred to as the Danckwerts boundary conditions (Danckwerts, 1953). The following initial conditions are applied for all $z \in [0, L]$ and $r \in [0, r_p]$:

$$c(0, z) = 0, \quad c_p(0, z, r) = 0, \quad q(0, z, r) = 0. \quad (9)$$

3. Laplace domain solutions

Recently, analytical solutions of the GRM with Danckwerts boundary conditions and quasi-stationary (Qamar et al., 2014) as well as dynamic (Miyabe, 2014) linear binding models have been obtained in Laplace domain. In the following, we present a unified derivation which is valid for both the quasi-stationary and the dynamic case, along the lines of Qamar et al. (2014).

3.1. Common parts

First, those parts of the analytical solution in the Laplace domain are derived, that are common to the quasi-stationary and dynamic binding models. We start by taking the Laplace transform in time t of all state variables c , c_p , and q to obtain \bar{c} , \bar{c}_p , and \bar{q} , respectively. For the interstitial concentration c , the transformed variable $\bar{c} : [0, \infty) \times [0, L]$ is defined by Eq. (10) (Davies, 2002):

$$\bar{c}(s, z) := \int_0^\infty e^{-st} c(t, z) dt, \quad s \geq 0. \quad (10)$$

Using the initial conditions Eq. (9) the Laplace transform of the model equations Eqs. (1) and (2) for $s \geq 0$ reads

$$s\bar{c}(s, \cdot) = -u \frac{\partial \bar{c}}{\partial z} + D_{ax} \frac{\partial^2 \bar{c}}{\partial z^2} - \frac{3}{r_p} \frac{k_f}{\beta_c} [\bar{c}(s, \cdot) - \bar{c}_p(s, \cdot, r_p)], \quad (11)$$

$$s\bar{c}_p(s, \cdot, \cdot) = D_p \left(\frac{\partial^2 \bar{c}_p}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{c}_p}{\partial r} \right) + \frac{D_s}{\beta_p} \left(\frac{\partial^2 \bar{q}}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{q}}{\partial r} \right) - \frac{1}{\beta_p} s\bar{q}(s, \cdot, \cdot). \quad (12)$$

We presume that the solution of the general rate model Eqs. (1)–(9) is continuously differentiable with bounded derivative and solution, which allows to differentiate under the integral sign and justifies the Laplace transforms above. The boundary condition at the bead center Eq. (8) has the Laplace transform

$$\frac{\partial \bar{c}_p}{\partial r}(\cdot, \cdot, 0) = 0 \quad (13)$$

and for the boundary condition between porous beads and interstitial column volume Eq. (7) we get

$$k_f [\bar{c} - \bar{c}_p(\cdot, \cdot, r_p)] = \varepsilon_p D_p \frac{\partial \bar{c}_p}{\partial r}(\cdot, \cdot, r_p) + (1 - \varepsilon_p) D_s \frac{\partial \bar{q}}{\partial r}(\cdot, \cdot, r_p). \quad (14)$$

From here on, the solution of the two cases differs slightly.

3.2. Quasi-stationary case

Applying the Laplace transform to the quasi-stationary binding model Eq. (3) results in

$$0 = k_a \bar{c}_p - k_d \bar{q}. \quad (15)$$

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