

Relaxation of surface tension after a large initial perturbation

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Introduction

For convenience, we restate here the mathematical problem we have to solve (see the problem description in the first part of the booklet).

We have the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad t > 0, \quad x > 0, \quad (1)$$

that describes the diffusion process in a simple one component solution, with initial condition

$$c(x, 0) = c_{eq}, \quad x > 0, \quad (2)$$

right boundary condition

$$\lim_{x \rightarrow \infty} c(x, t) = c_{eq}, \quad t \geq 0, \quad (3)$$

and boundary condition at $x = 0$

$$\lim_{x \rightarrow 0} c(x, t) = c_s(t), \quad t \geq 0, \quad (4)$$

where $c(x, t)$ is the bulk concentration of surfactant, $c_s(t)$ is the subsurface concentration. The latter is defined by a relation with the adsorption $\Gamma(t)$ at the interface, $x = 0$. This relation is called “the adsorption isotherm”. Different surfactants obey different adsorption isotherms. Three of the most common ones are given in Table 1, where K is the so-called adsorption constant, β is the interaction parameter, Γ_∞ is the maximum adsorption, and θ is the surface coverage, given by $\theta(t) \equiv \Gamma(t)/\Gamma_\infty$.

Further, for the adsorption the following holds true:

$$\frac{d\Gamma}{dt} = D \left. \frac{\partial c}{\partial x} \right|_{x=0}, \quad t > 0, \quad (5)$$

$$\Gamma(0) = \Gamma_0. \quad (6)$$

Table 1: Typical adsorption isotherms

	Adsorption isotherm
Frumkin	$Kc_s = \frac{\theta}{1-\theta} \exp(-\beta\theta)$
Van der Waals	$Kc_s = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \beta\theta\right)$
Helfand, Frisch, Lebowitz	$Kc_s = \frac{\theta}{1-\theta} \exp\left(\frac{3\theta - 2\theta^2}{(1-\theta)^2} - \beta\theta\right)$

Table 2: Typical surface equations of state

	Equation of state
Frumkin	$\frac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = -\ln(1-\theta) - \frac{\beta}{2}\theta^2$
Van der Waals	$\frac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = \frac{\theta}{1-\theta} - \frac{\beta}{2}\theta^2$
Helfand, Frisch, Lebowitz	$\frac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = \frac{\theta}{(1-\theta)^2} - \frac{\beta}{2}\theta^2$

The difficulty in solving the problem (1)–(6), however, is in the fact that two of the parameters, namely K and Γ_∞ , cannot be measured and, thus, are not known. So **our task is to find an algorithm for estimating the values of those two parameters**. For doing so, we are given experimental data for the interfacial tension σ (see Fig. 1), which is related to the other variables and parameters by the so-called “equation of state” (see Table 2).

The algorithms used for parametric identification are iterative [2, 3]. We begin with an initial estimate for the unknown parameters and then proceed by obtaining successive estimations that should converge to the real values. Those algorithms **rely on the ability to solve the differential problem efficiently**, if we know an estimate for the parameters. Thus, we begin our study with solving the differential problem. For this purpose, we propose four different numerical methods. Then, we explain how we can estimate the two unknown parameters.

Numerical Methods for Solving the Differential Problem

We suggest several different methods for solving the differential problem (1)–

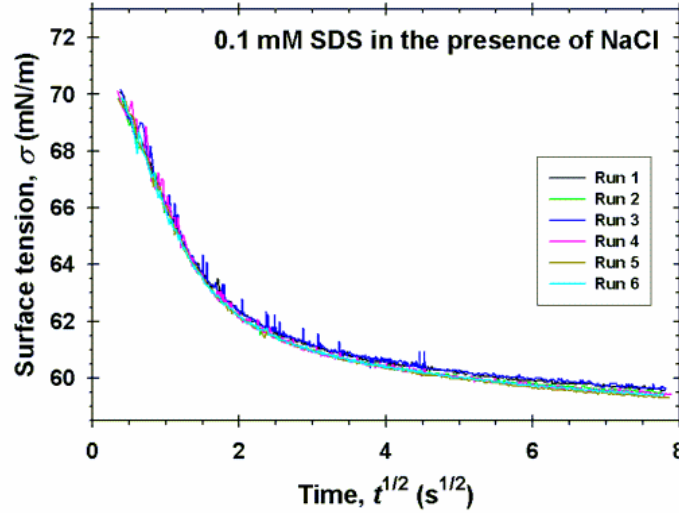


Figure 1: Experimental data for the interfacial tension

(6), that are explained below. Making numerical experiments, we compare them in terms of computational time.

Explicit Difference Scheme-1. Our first approach is to construct a more or less standard explicit difference scheme. In the set $\bar{\Omega} := [0, X] \times [0, T]$, we introduce a uniform mesh $\bar{\omega}_{h\tau} = \bar{\omega}_h \times \bar{\omega}_\tau$, where $\bar{\omega}_h := \{x_i = ih, i = \overline{0, n}, n = X/h\}$, $\bar{\omega}_\tau := \{t_j = j\tau, j = \overline{0, m}, m = T/\tau\}$.

We construct an explicit difference scheme in the following way. For the diffusion equation (1) we use the finite difference approximations

$$\frac{\partial c}{\partial t} \approx \frac{c(x, t + \tau) - c(x, t)}{\tau} \quad \text{and} \quad \frac{\partial^2 c}{\partial x^2} \approx \frac{c(x + h, t) - 2c(x, t) + c(x - h, t)}{h^2}.$$

We obtain the difference equations

$$\frac{c_i^{j+1} - c_i^j}{\tau} = D \cdot \frac{c_{i+1}^j - 2c_i^j + c_{i-1}^j}{h^2}, \quad i = \overline{1, n-1}, j = \overline{0, m-1}.$$

The initial condition (2) and the right boundary condition (3) are approximated exactly:

$$c_0^0 = 0, \quad c_i^0 = c_{eq}, \quad i = \overline{0, n}.$$

For the left boundary condition (4) we have

$$c_0^{j+1} = c_s(t_j), \quad j = \overline{0, m-1}.$$

Approximating (5), after the rescaling $\theta(t) \equiv \Gamma(t)/\Gamma_\infty$, we straightforwardly obtain

$$\theta^{j+1} = \theta^j + \frac{D\tau}{h\Gamma_\infty}(c_1^{j+1} - c_0^{j+1}), \quad j = \overline{0, m-1}.$$

For the sake of completeness we also include an approximation for the interfacial tension $\sigma(t)$, using the second row of Table 2.

$$\sigma^{j+1} = \sigma_0 - E_B\Gamma_\infty \left[\frac{\theta^{j+1}}{1 - \theta^{j+1}} - \frac{\beta}{2}(\theta^{j+1})^2 \right], \quad j = \overline{0, m-1}.$$

For all other equations of state we proceed analogously.

Explicit Difference Scheme–2. The second finite difference scheme uses nonuniform mesh in space. The spatial step h_i increases as a geometric progression with ratio q :

$\bar{\omega}_h := \{x_{i+1} = x_i + h_i, x_0 = 0, i = \overline{0, n}; h_{i+1} = h_i * q, i = \overline{2, n-3}\}$, with an exception that the first 3 and the last 2 steps are constant ($h_0 = h_1 = h_2$ and $h_{n-1} = h_n$). Thus keeping the ratio q close to 1 the mesh is locally almost uniform. The time step is constant as in the previous scheme.

In the tests performed here $h_0 = 2.5 * 10^{-7}$ and $h_n = 2.5 * 10^{-4}$ for $q = 1.2$, $n = 40$ and the time step is $\tau = 5 * 10^{-5}$.

In Scheme–2 we construct third order finite difference approximation of the spatial terms $\frac{\partial^2 c}{\partial x^2}$:

$$\frac{\partial^2 c}{\partial x^2} \approx a_1^i \cdot c_{i-2}^j + a_2^i \cdot c_{i-1}^j + a_3^i \cdot c_i^j + a_4^i \cdot c_{i+1}^j + a_5^i \cdot c_{i+2}^j.$$

The coefficients $a_1^i = u_1, a_2^i = u_2, a_3^i = -(u_1 + u_2 + u_3 + u_4), a_4^i = u_3, a_5^i = u_4 (i = \overline{1, n-1})$, where the vector \mathbf{u} is the solution of the algebraic system:

$$\begin{array}{cccccc} -(h_{i-1} + h_i)u_1 & +(h_{i-1} + h_i)^2u_2 & -(h_{i-1} + h_i)^3u_3 & +(h_{i-1} + h_i)^4u_4 & = 0 \\ -h_i u_1 & +h_i^2 u_2 & -h_i^3 u_3 & +h_i^4 u_4 & = 2 \\ h_{i+1} u_1 & +h_{i+1}^2 u_2 & +h_{i+1}^3 u_3 & +h_{i+1}^4 u_4 & = 0 \\ (h_{i+1} + h_i)u_1 & +(h_{i+1} + h_i)^2u_2 & +(h_{i+1} + h_i)^3u_3 & +(h_{i+1} + h_i)^4u_4 & = 0 \end{array}$$

A third order approximation of (5) (applying the rescaling used in the previous scheme) is:

$$\theta^{j+1} = \theta^j + \frac{D\tau}{h\Gamma_\infty}(11/6c_0^{j+1} - 3c_1^{j+1} + 3/2c_2^{j+1} - 1/3c_3^{j+1}), \quad j = \overline{0, m-1}.$$

The other elements of the scheme are as in the previous Scheme–1.

Ward and Torday Integral Equation. As it is shown in the problem description, the differential problem (1)–(6) is equivalent to the Integral Equation of Ward and Torday. Here we will show this by using a different approach.

Denote now by $c(x, t)$ the bulk concentration minus the equilibrium value c_{eq} . For the time evolution we then have the following problem:

$$\begin{aligned}\partial_t c(x, t) &= D \partial_x^2 c(x, t) \\ c(x, 0) &= 0 \\ c(\infty, t) &= 0 \\ c(0, t) &= c_s(\theta(t)) - c_{eq}\end{aligned}\tag{7}$$

The last equation is in terms of a function f , which is the adsorption isotherm.

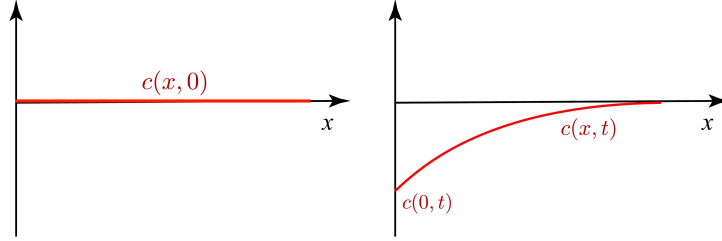


Figure 2: The evolution of the bulk concentration minus its initial value, c_{eq} . The surface adsorption, $\Gamma(t)$ grows in proportion to the diffusion flux from the bulk: $d\Gamma(t)/dt = D \partial_x c(x = 0, t)$

Table 1 lists three separate adsorption isotherms, the Frumkin, the Van der Waals, and the Helfand-Frisch-Lebowitz isotherms.

The adsorption changes with time in proportion to the concentration gradient at the surface:

$$\frac{d\theta}{dt} = \frac{D}{\Gamma_\infty} \partial_x c(x = 0, t)\tag{8}$$

We will write down an expression for the solution to eq. (7), and then subsequently for the solution to eq. (8). We will initially treat $f(\theta(t))$ as a prescribed function, and then find a self consistent solution.

For the problem (7) we apply *Duhamel's Theorem*, which states that if $\Phi(x, t, \tau)$

denotes the solution to the auxiliary problem

$$\begin{aligned}
\partial_t \Phi(x, t, \tau) &= D \partial_x^2 \Phi(x, t, \tau) \\
\Phi(x, 0, \tau) &= 0 \\
\Phi(\infty, t, \tau) &= 0 \\
\Phi(0, t, \tau) &= c_s(\theta(\tau)) - c_{eq}
\end{aligned} \tag{9}$$

where the right hand side in the last equation is taken to be a constant depending on a parameter τ rather than on t , then the solution $c(x, t)$ to the actual problem is given by

$$c(x, t) = \int_{\tau=0}^{\tau=t} \partial_t \Phi(x, t - \tau, \tau) d\tau \tag{10}$$

The solution of the auxiliary problem (9) is given by

$$\Phi(x, t, \tau) = \frac{2(c_s(\theta(\tau)) - c_{eq})}{\sqrt{\pi}} \int_{\frac{x}{\sqrt{4Dt}}}^{\infty} \exp(-\eta^2) d\eta$$

The partial derivative in (10) evaluates to

$$\partial_t \Phi(x, t, \tau) = (c_s(\theta(\tau)) - c_{eq}) \frac{x}{\sqrt{4\pi D}(t - \tau)^{3/2}} \exp\left[-\frac{x^2}{4D(t - \tau)}\right]$$

Substituting this into (10), we get

$$c(x, t) = \frac{x}{\sqrt{4\pi D}} \int_{\tau=0}^{\tau=t} \frac{(c_s(\theta(\tau)) - c_{eq})}{(t - \tau)^{3/2}} \exp\left[-\frac{x^2}{4D(t - \tau)}\right] d\tau$$

We thus have

$$\partial_x c(x=0, t) = \frac{1}{\sqrt{4\pi D}} \int_{\tau=0}^{\tau=t} \frac{(c_s(\theta(\tau)) - c_{eq})}{(t - \tau)^{3/2}} d\tau$$

The change in adsorption is given by:

$$\frac{d\theta(t)}{dt} = \frac{D}{\Gamma_\infty} \partial_x c(x=0, t) = \frac{1}{2\Gamma_\infty} \left(\frac{D}{\pi}\right)^{1/2} \int_{\tau=0}^{\tau=t} \frac{(c_s(\theta(\tau)) - c_{eq})}{(t - \tau)^{3/2}} d\tau$$

Integrating with respect to t , we arrive at the Ward and Torday integral equation

$$\theta(t) = \theta_0 - \frac{1}{\Gamma_\infty} \left(\frac{D}{\pi}\right)^{1/2} \int_0^t \frac{(c_s(\theta(\tau)) - c_{eq})}{(t - \tau)^{1/2}} d\tau$$

which is equation (13) in the problem description.

As a first option for solving numerically the Ward and Torday integral equation for $t = t_j = j\tau, j = 0, 1, \dots$ we applied **the method of quadratures by using a modification of the Left Rectangle Rule**:

$$\theta(t_{j+1}) = \frac{\Gamma_0}{\Gamma_\infty} - \frac{1}{\Gamma_\infty} \sqrt{\frac{D\tau}{\pi}} \left(\sum_{i=0}^{j-1} \frac{c_s(t_i) - c_{eq}}{\sqrt{j+1-i}} + 2(c_s(t_j) - c_{eq}) \right),$$

where

$$c_s(t_i) = \frac{1}{K} \frac{\theta(t_i)}{1 - \theta(t_i)} \exp\left(\frac{\theta(t_i)}{1 - \theta(t_i)} - \beta\theta(t_i)\right), \quad 0 \leq i \leq j, \quad j \geq 0.$$

is expressed by using the Van der Waals equation for the adsorption isotherm.

Equivalent Fractional Order ODE. It is well known [1], that the integral equation

$$y(t) = \sum_{\nu=0}^{[\alpha]-1} y^{(\nu)} \frac{t^\nu}{\nu!} + \frac{1}{\Gamma(\alpha)} \int_0^t (t-u)^{\alpha-1} f(u, y(u)) du \quad (11)$$

is equivalent to the initial value problem for the fractional order ODE

$$\begin{aligned} D_*^\alpha y(t) &= f(t, y(t)) \\ y^{(k)}(0) &= y_0^{(k)}, \quad k = 0, 1, \dots, [\alpha] - 1, \end{aligned}$$

where $[\alpha]$ is the smallest integer $\geq \alpha$.

For the Ward and Torday integral equation we have $\alpha = 1/2$, $[\alpha] = 1$ and the integral equation (11) reads:

$$y(t) = y_0 + \frac{1}{\sqrt{\pi}} \int_0^t \frac{f(u, y(u))}{\sqrt{t-u}} du, \quad (12)$$

where

$$f(u, y(u)) = \frac{\sqrt{D}}{\Gamma_\infty} (c_{eq} - c_s(u)).$$

The equivalent differential problem is

$$D_*^{1/2} y(t) = f(t, y(t)) \quad (13)$$

$$y(0) = y_0. \quad (14)$$

To solve the problem (13)–(14) we use a **modification of the Adams method for fractional order ODEs**, proposed and investigated in [1]. The method is of predictor-corrector type. Applied to the problem (13), (14), it reads:

Predictor scheme:

$$y_{k+1}^P = y_0 + \frac{1}{\Gamma(\alpha)} \sum_{j=0}^k b_{j,k+1} f(t_j, y_j),$$

where the coefficients $b_{j,k+1}$ are given by

$$b_{j,k+1} = \frac{h^\alpha}{\alpha} ((k+1-j)^\alpha - (k-j)^\alpha).$$

Corrector scheme:

$$y_{k+1} = y_0 + \frac{1}{\Gamma(\alpha)} \left(\sum_{j=0}^k a_{j,k+1} f(t_j, y_j) + a_{k+1,k+1} f(t_{k+1}, y_{k+1}^P) \right),$$

where

$$a_{j,k+1} = \frac{h^\alpha}{\alpha(\alpha+1)} \begin{cases} (k^{\alpha+1} - (k-\alpha)(k+1)^\alpha) & j = 0, \\ ((k-j+2)^{\alpha+1} - (k-j)^{\alpha+1}) & 1 \leq j \leq k, \\ 1, & j = k+1 \end{cases}$$

Parametric Identification

In the section “Numerical Experiments”, we give examples of using two implemented in MATLAB and R functions for numerical optimization. Here we propose a basic iterative algorithm that explains how we can obtain an estimation for the two parameters.

Let us denote

$$\varepsilon(\Gamma_\infty, K) = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{\hat{\sigma}^i - \sigma^i}{\hat{\sigma}^i} \right)^2}.$$

where $\hat{\sigma}^i$ are the values of the numerical solution while σ^i are the experimental data.

The algorithm is the following:

1. Begin with an initial estimation for the parameters— $\Gamma_\infty^{(0)}, K^{(0)}$.
2. Let us have $(\Gamma_\infty^{(k)}, K^{(k)})$. We solve the differential problem with those values for the parameters to obtain $\varepsilon(\Gamma_\infty^{(k)}, K^{(k)})$.
3. Solve the differential problem with values for the parameters, consecutively, $(\Gamma_\infty^{(k)} + \delta, K^{(k)})$, $(\Gamma_\infty^{(k)} - \delta, K^{(k)})$, $(\Gamma_\infty^{(k)}, K^{(k)} + \delta)$, and $(\Gamma_\infty^{(k)}, K^{(k)} - \delta)$ to obtain an approximation of $\frac{\partial \varepsilon}{\partial \Gamma_\infty}(\Gamma_\infty^{(k)}, K^{(k)})$ and $\frac{\partial \varepsilon}{\partial K}(\Gamma_\infty^{(k)}, K^{(k)})$.
4. Obtain the next estimation as

$$(\Gamma_\infty^{(k+1)}, K^{(k+1)}) = (\Gamma_\infty^{(k)}, K^{(k)}) - \left(\mu \frac{\partial \varepsilon}{\partial \Gamma_\infty}, \nu \frac{\partial \varepsilon}{\partial K} \right),$$

where μ and ν are determined adaptively, so that the error decreases.

Remark: For the initial estimation of the parameters Γ_∞ and K we propose the following approach.

Starting with an initial value for Γ_∞ and using the surface tension σ at $t = 64$ from the experimental data, we derive the following cubic equation for θ :

$$\beta\theta^3 - \beta\theta^2 + (2 + 2A)\theta - 2A = 0,$$

where

$$A = \frac{\sigma_0 - \sigma(64)}{E_B \Gamma_\infty}.$$

Let us denote the real root of the above equation as θ_1 . Substituting θ_1 in the Van der Waals equation for the adsorption isotherm we obtain an initial value for K :

$$K_0 = \frac{1}{c_{eq}} \frac{\theta_1}{1 - \theta_1} \exp \left(\frac{\theta_1}{1 - \theta_1} - \beta\theta_1 \right) \quad (15)$$

Numerical Experiments

First, we compare the computational times for solving the differential problem (1)–(6) and its equivalent formulations by using the different numerical methods. In Table 3, we present computational times for the aforementioned numerical methods. The programs, used for the tests, were implemented in the FORTRAN programming language.

Table 3: Computational times for solving the differential problem with different numerical methods

Numerical method	Computational time
Explicit difference scheme-1	5.48433s
Explicit difference scheme-2	2.04687s
Ward and Torday integral equation-1	1.92554s
Fractional order ODE	1.59375s

Second, we compare the accuracy of the methods for solving the Ward and Torday integral equation on a particular case of this equation:

$$u(t) = 1 - \frac{1}{\sqrt{\pi}} \int_0^t \frac{u(\tau)}{\sqrt{t-\tau}} d\tau,$$

whose exact solution is known:

$$u(t) = \exp(t)\operatorname{erfc}(\sqrt{t}),$$

erfc being the Complimentary Error Function. As expected, the Adams method for fractional order ODE is more accurate than the modification of the Left Rectangle Rule.

Now, we give some results for the estimated model parameters Γ_∞ and K . Using the explicit difference scheme-1 and the MATLAB procedure “lsqnonlin”, we obtain the following values— $\Gamma_\infty = 5.0741 \times 10^{-6}$ and $K = 19.3733$. For those values we obtain the result for σ , that is shown on Figure 3.

Using the algorithm described in the section “Paramametric Identification” and again the explicit difference scheme-1, we obtain similar results— $\Gamma_\infty = 4.9728 \times 10^{-6}$, $K = 20.0028$.

We have used also the modification of the Left Rectangle Rule for the integral equation and a general-purpose optimization R function ‘optim’ [4] with default options to find the two unknown parameters K and Γ_∞ . From previous experiments it is known that Γ_∞ is approximately of order 10^{-6} . We set initial value of $\Gamma_\infty = 0.5 \times 10^{-6}$ and derive K_0 from equation (15). These are our starting values in the optimization procedure. We minimize the relative error equal to $\varepsilon(\Gamma_\infty, K)$, defined above, where $\hat{\sigma}^i$ are the values of the numerical solution while σ^i are the experimental data.

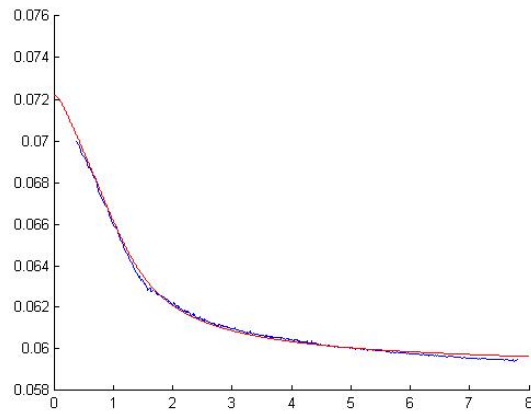


Figure 3: Numerical solution $\sigma(t)$ for model parameters $\Gamma_\infty = 5.0741 \times 10^{-6}$ and $K = 19.3733$

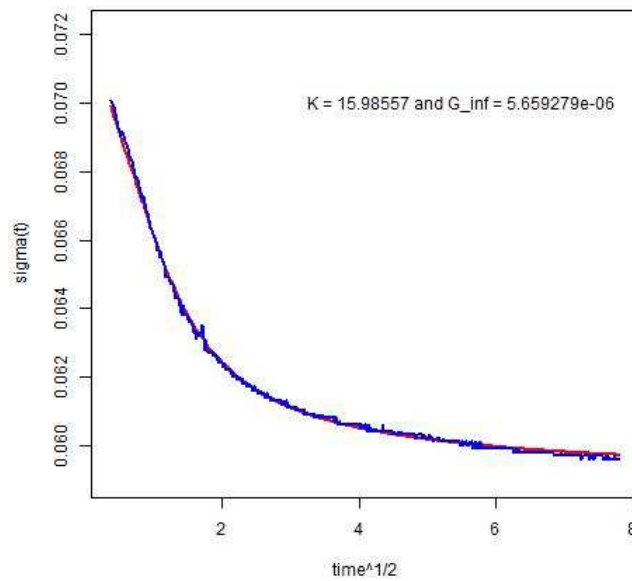


Figure 4: Numerical solution $\sigma(t)$ for model parameters $\Gamma_\infty = 5.659 \times 10^{-6}$ and $K = 15.659$

Conclusion

As a result of the work of our group we present different ways for solving the differential problem (1)–(6) and its equivalent formulations. All of them give similar results, but the Adams method for solving the equivalent fractional order ODE is the fastest one. In addition, this method has better accuracy than the modification of the Left Rectangle Rule for solving the equivalent integral equation.

We also propose different ways for estimating the two unknown parameters—by means of already implemented in MATLAB and R functions, as well as by an algorithm we have implemented.

References

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