Relaxation of Surface Tension After a Large Initial Perturbation

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Mathematical Formulation of the Problem

We have the diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \;\; t > 0, \;\; x > 0 \tag{1}$$

with initial condition

$$c(0, x) = c_{\text{eq}}, \;\; x > 0, \tag{2}$$

right boundary condition

$$\lim_{x\to\infty} c(t, x) = c_{\text{eq}}, \;\; t \geq 0, \tag{3}$$

and boundary condition at $x = 0$

$$\lim_{x\to 0} c(t, x) = c_s(t), \;\; t \geq 0. \tag{4}$$

The Left Boundary Condition

At $x = 0$, we have

$$\lim_{x \to 0} c(t, x) = c_s(t), \;\; t \geq 0, \tag{5}$$

where

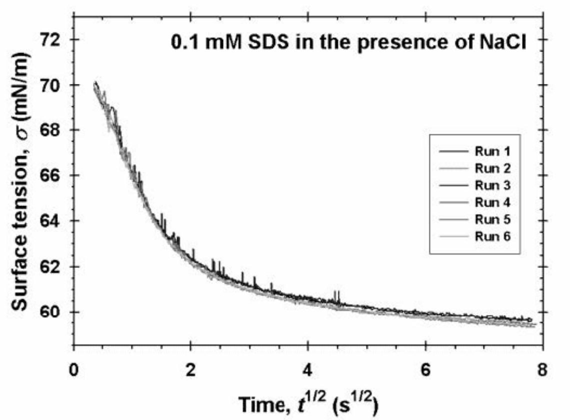
$$K c_s(t) = \frac{\theta(t)}{1 - \theta(t)} \exp\left(\frac{\theta(t)}{1 - \theta(t)} - \beta\theta(t) \right) \quad \text{(Van der Waals)}, \tag{6}$$

$$\theta(t) := \frac{\Gamma(t)}{\Gamma_\infty}, \tag{7}$$

$$\frac{d\Gamma}{dt} = D\frac{\partial c}{\partial x}, \;\; t > 0, \;\; x = 0, \quad \Gamma(0) = \Gamma_0. \tag{8}$$

Problems to Be Solved

- How to solve the differential problem (1)–(8), if we know the parameters' values?
- How to estimate the parameters Γ_∞ and K, given some experimental data for $\sigma(t)$?



Parametric Identification

- The main idea of the parametric identification lies in the following. We define

$$\varepsilon(\Gamma_\infty, K) = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{\sigma_i - \bar{\sigma}_i}{\sigma_i}\right)^2$$

- We want to minimize $\varepsilon(\Gamma_\infty, K)$.
- Schittkowski, K.: Numerical Data Fitting in Dynamical Systems. A Practical Introduction with Applications and Software. Springer. 2002.
- Englezos, P., Kalogerakis, N.: Applied Parameter Estimation for Chemical Engineers. Marcel Dekker, Inc. 2001.
- Gauss–Newton method

- MATLAB procedure
- Modified gradient method
  - We begin with some initial values for the parameters:
  $$\bar{p}_0 = (\Gamma_\infty^{(0)}, K^{(0)}).$$
  - Having found $\bar{p}_k$, we obtain
  $$\bar{p}_{k+1} = \bar{p}_k - \left(\mu_k \frac{\partial \varepsilon}{\partial \Gamma_\infty}, \nu_k \frac{\partial \varepsilon}{\partial K} \right) \Bigg|_{\bar{p}=\bar{p}_k},$$
  where μ_k and ν_k are adaptively determined, such that the error decreases.
  - $$\frac{\partial \varepsilon}{\partial \Gamma_\infty} \Bigg|_{\bar{p}=\bar{p}_k} \approx \frac{\varepsilon(\Gamma_\infty^{(k)} + \delta, K^{(k)}) - \varepsilon(\Gamma_\infty^{(k)} - \delta, K^{(k)})}{2\delta}$$

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

$$\beta\Theta^3 - \beta\Theta^2 + (2 + 2A)\Theta - 2A = 0, \qquad (9)$$

where

$$A = \frac{\sigma_0 - \sigma(64)}{E_b \Gamma_\infty^{(0)}}.$$

Let us denote the real root of Θ as Θ_1. Substituting Θ_1 in the Van der Waals equation for adsorption isotherms we obtain an initial value for K.

$$K^{(0)} = \frac{1}{c_{eq}} \frac{\Theta_1}{1 - \Theta_1} exp\left(\frac{\Theta_1}{1 - \Theta_1} - \beta\Theta_1\right) \qquad (10)$$

Solving the Differential Problem

- Difference scheme
- It can be shown that our problem is equivalent to the so called Ward and Torday integral equation:

$$\Gamma(t) = \Gamma_0 - \left(\frac{D}{\pi}\right)^{1/2} \int_0^t \frac{c_s(\tau) - c_{eq}}{(t-\tau)^{1/2}} d\tau$$

$$= \Gamma_0 - \left(\frac{1}{\pi}\right)^{1/2} \int_0^t \frac{F(\Gamma(t))}{(t-\tau)^{1/2}} d\tau$$

The integral equation

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

is equivalent to the initial problem for the fractional order ODE

$$D_*^\alpha y(t) = f(t, y(t))$$

$$y^{(k)}(0) = y_0^{(k)}, \qquad k = 0, 1, ..., [\alpha] - 1.$$

For our problem $\alpha = 1/2$ and the integral equation reads:

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

and the differential problem is

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

$$y^{(k)}(0) = y_0^{(k)}.$$

Explicit Difference Scheme

We construct an explicit difference scheme on the mesh $\omega_{h\tau} = \omega_h x \omega_\tau$, where $\omega_h := \{x_i = ih, i = \overline{0,n}, n = X/h\}$, $\omega_\tau := \{t_j = j\tau, j = \overline{0,m}, m = T/\tau\}$:

$$\frac{c_i^{j+1} - c_i^j}{\tau} = D.\frac{c_{i+1}^j - 2c_i^j + c_{i-1}^j}{h^2}, \; i = \overline{1, n-1}, j = \overline{0, m-1}, \tag{11}$$

$$c_0^0 = 0, \quad c_i^0 = c_{eq}, \quad i = \overline{0,n}, \tag{12}$$

$$c_0^{j+1} = c_s(t_j), \; j = \overline{0, m-1}, \tag{13}$$

$$\theta^{j+1} = \theta^j + \frac{D\tau}{h\Gamma_\infty}(c_1^{j+1} - c_0^{j+1}), \; j = \overline{0, m-1}, \tag{14}$$

$$\sigma^{j+1} = \sigma_0 - E_B\Gamma_\infty \left[\frac{\theta^{j+1}}{1-\theta^{j+1}} - \frac{\beta}{2}(\theta^{j+1})^2\right], \; j = \overline{0, m-1}. \tag{15}$$

Numerical Method for Solving the Ward and Torday Integral Equation

We propose the following iterative scheme for solving the Ward and Torday integral equation (1)

$$\Theta(t) = \frac{\Gamma_0}{\Gamma_\infty} - \frac{1}{\Gamma_\infty}\sqrt{\frac{D}{\pi}}\int_0^t \frac{c_s(\tau) - c_{eq}}{(t-\tau)^{1/2}} d\tau \qquad (16)$$

$$\Theta(nh) = \frac{\Gamma_0}{\Gamma_\infty} - \frac{1}{\Gamma_\infty}\sqrt{\frac{Dh}{\pi}}\left(\sum_{i=0}^{n-2} \frac{c_s(ih) - c_{eq}}{\sqrt{n-i}} + 2(c_s((n-1)h) - c_{eq})\right) \qquad (17)$$

$$c_s(ih) = \frac{1}{K}\frac{\Theta(ih)}{1-\Theta(ih)} exp\left(\frac{\Theta(ih)}{1-\Theta(ih)} - \beta\Theta(ih)\right), 0 \le i \le n{-}1, n \ge 1 \qquad (18)$$

Modification of Adams method for fractional order ODE

predictor scheme:

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

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

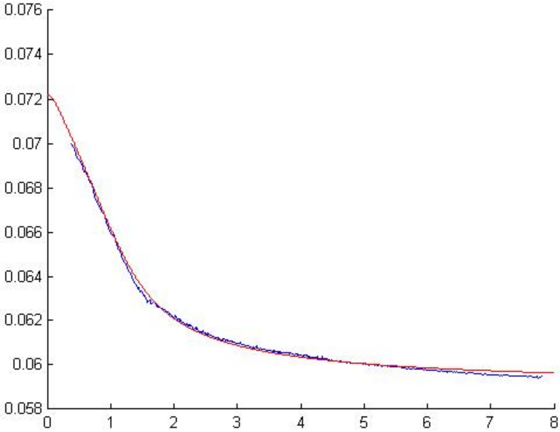
corrector scheme:

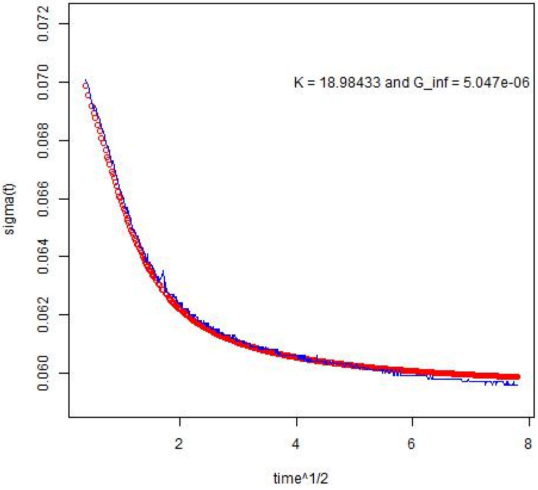
$$y_{k+1} = \frac{1}{\Gamma(\alpha)} \left(\sum_{j=0}^{k} a_{j,k+1} f(t_j, y_j) + a_{k+1,k+1} f(t_{k+1}, y^P_{k+1}) \right),$$

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

Numerical Experiments

Using the aforementioned algorithm, we obtain the following values for the model parameters: $\Gamma_\infty = 5.0741x10^{-6}$, $K = 19.3733$.




K = 18.98433 and G_inf = 5.047e-06
sigma(t)
0.060
0.062
0.064
0.066
0.068
0.070
0.072
2
4
6
8
time^1/2

THANK YOU FOR YOUR ATTENTION!