

Contact during the exam:
Professor Ingve Simonsen
Telephone: 9 34 17 or 470 76 416

Exam in TFY4235/FY8904 Computational Physics
May 07, 2018
09:00

Allowed help: **Alternativ A**

This problem set consists of 6 pages.

This exam is published on Monday, May 7 at 09:00 hours. You can work on your solution till **Thr. May 10, 2018 at 23:00** (“the deadline”). Before the deadline you should submit your final report in the pdf-format and a zip-file containing the documented source code. For the names of the files that you will submit, please use `<lastname>_TFY4235_report.pdf` and `<lastname>_TFY4235_code.zip`; for those of you taking the course using the the FY8904 code, replace the TFY code by this code. The submission of your work you will do via the system “Inspira” that you can find at <https://ntnu.inspera.no/>. You will receive an email at the start of the exam detailing how to log onto this system and how to submit your report via it.

Prior to the deadline you are *also* expected¹, to send the final report to me at email Ingve.Simonsen@ntnu.no with subject TFY4235 or FY8904.²

There are no constraints on the kind of aid you may want to use in connection with this exam, including discussing it with anybody. However, *the report and the computer code you will have to write yourself*. Please attach your computer codes as appendices to the report. Give as a footnote the names of your collaborators during the exam. The report may be written in either Norwegian (either variants) or in English.

Should you run short on time, you are advised to spend the time to do properly what you do instead of following a strategy of doing a little bit here-and-there.

Information posted during the exam, like potential misprints, links to papers, extended deadline etc. will be posted on the web-page of the course at <http://web.phys.ntnu.no/~ingves/Teaching/TFY4235/#Exam> and/or <http://web.phys.ntnu.no/~ingves/Teaching/TFY4235/Exam/>. *It is your responsibility to check this information regularly!*

¹Useful in the unlikely event that something should go wrong with the digital submission via “Inspira” (or you cannot get it to work properly).

²Warning: If your email is too large, the gmail system, to which I also forward my email, may notify you that the message was too large to be delivered to my gmail account. This means that your message was received successfully by the ntnu email system, if you were not informed otherwise.

There are no formal requirements for the format of the report in addition to what was said above. The report should explain what you have been doing, your results, and how you interpret these results. Details should be included to the extent that we as graders can follow your way of reasoning. General background theory that, for instance, can be found in textbooks, is not needed in the report. It is documentation of your work we are interested in! Remember that if you have written an original and clever code for solving the problem, but are not able to explain it well in the report, it is hard to give you full credit.

I plan to have office hours from 13:00-16:00 on Monday May 07 in case you have questions to the problems. Moreover, the teaching assistants (TAs) will also be able to assist you during the exam.

Good luck to all of you!

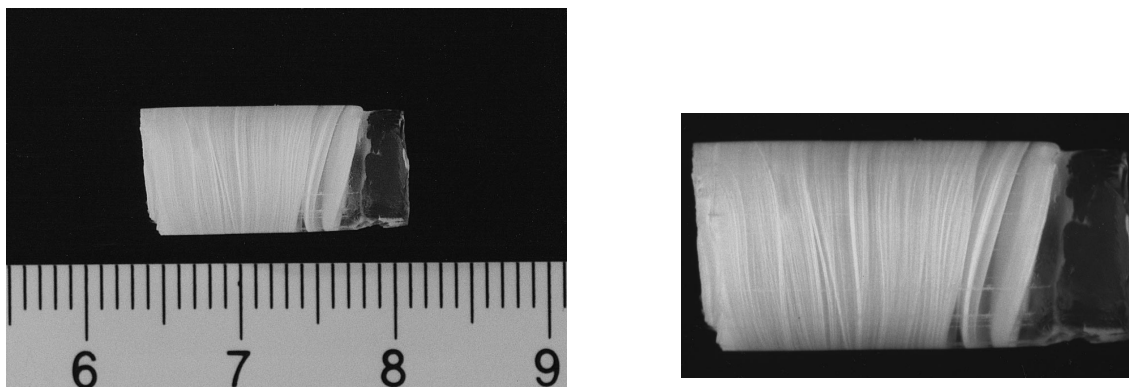


Figure 1: Photographs of the Liesegang pattern obtained experimentally. A 2.1 cm long aerogel rod with diameter 8 mm was wrapped in teflon tape along the long axis. At the left end of the rod a cotton plug soaked in NH_3 was placed (gas a). At the right end, a cotton plug soaked in HCl was placed (gas b). After 5.5 days, the cotton plugs and teflon tape were removed. A precipitate consisting of NH_4Cl (solid s) in the form of a series of clearly defined narrow sheets has been formed. (Adapted after [2, 3]).

Problem 1

Your suggested solution for *Assignment no 2* [1] should be handed in as part of the report. It will count 15% towards the final grade of the course.

Problem 2

This takehome exam is devoted to the study of a particular *reaction-diffusion* system that display the so-called Liesegang phenomenon [2]. To motivate this phenomenon, we cite the the first two paragraphs of the introduction of Ref. [2], which reads:

“A classic high school chemistry experiment consists of placing a cotton plug drenched in ammonia at one end of a long glass tube simultaneously with another one drenched in hydrochloric acid at the other end of the tube. Then one waits, and after some time, a white ring forms on the tube wall. The white ring consists of ammonium chloride, resulting from the gases reacting on contact. From measuring the position of the ring relative to the two ends of the tube, the ratio between the average velocities of the two gases is found. This ratio is then compared to Graham’s law which states that it is equal to the square root of the inverse of the molar masses of the two gases.

What happens if we repeat this experiment substituting a porous medium for the air-filled tube? We have performed such experiments, using a silica aerogel as the porous medium. A large number of closely spaced paper-thin sheets form in the aerogel, spanning it in the radial direction. In Fig. 1, we show a photograph of the precipitate that was formed by exposing the aerogel rod during 5.5 days to the reacting gases.“

We will now try to model the experimental results presented in Fig. 1. To this end, we start by assuming that the system can be described in terms of one spatial coordinate — the

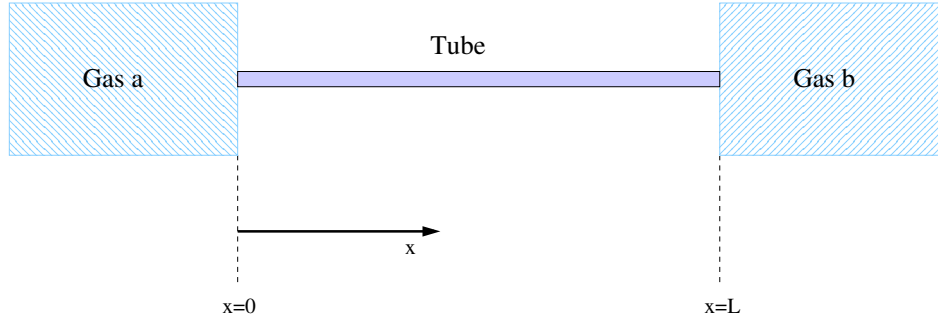


Figure 2: Schematics of the geometry that we consider.

distance x measured along the rod. We choose a coordinate system so that $x = 0$ and $x = L$ correspond to the ends of the tube, respectively (see Fig. 2).

The gases, initially present in the system, we will refer to as gases a and b . They diffuse in the porous medium, meet, and react to produce the (“reaction product”) gas c . This reaction is assumed to be of the form³ $a + b \rightarrow c$ with a *reaction rate* R . Furthermore, when the concentration of the reaction product c satisfies $c(x, t) \geq c_0$ with c_0 a known positive constant, nucleation and precipitation occur resulting in the formation of the solid s which can be observed as white sheets in the photographs in Fig. 1. The constant $c_0 > 0$ is interpreted as the threshold concentration required for the gas c to nucleate into the solid s .

For reasons of simplicity, and since it will not cause any confusion, we will in the following let the function $g(x, t)$ denote the concentration at spatial coordinate x and time t for the gas g (of the same name) with $g = a, b, c$. The concentration we will here take as the *number concentration* so that the unit of concentration is meter inverse ($[g(x, t)] = \text{m}^{-1}$). Moreover, the diffusion constant of gas g is $D_g > 0$, and its physical unit is $[D_g] = \text{m}^2/\text{s}$. Similarly, $s(x, t)$ denotes the (number) concentration of “solid” s at spatial-temporal coordinate (x, t) .

The size of the pores in the porous medium is of the order of the mean free path (or less) of the diffusing gas molecules (Knudsen number $\gg 1$); thus the dominating transport mechanism for the gases also inside the porous medium is diffusion. Hence, the relevant equations for concentrations $a(x, t)$, $b(x, t)$, $c(x, t)$, and $s(x, t)$, are [2]

$$\frac{\partial a(x, t)}{\partial t} = D_a \frac{\partial^2 a(x, t)}{\partial x^2} - R a(x, t) b(x, t) \quad (1a)$$

$$\frac{\partial b(x, t)}{\partial t} = D_b \frac{\partial^2 b(x, t)}{\partial x^2} - R a(x, t) b(x, t) \quad (1b)$$

$$\frac{\partial c(x, t)}{\partial t} = D_c \frac{\partial^2 c(x, t)}{\partial x^2} + R a(x, t) b(x, t) - N_1 \theta(c(x, t) - c_0) c^2(x, t) - N_2 c(x, t) s(x, t) \quad (1c)$$

$$\frac{\partial s(x, t)}{\partial t} = N_1 \theta(c(x, t) - c_0) c^2(x, t) + N_2 c(x, t) s(x, t), \quad (1d)$$

where N_1 and N_2 , are known constants and $\theta(\cdot)$ is the Heaviside step function (or unit step function). Equation (1) represents a coupled set of partial differential equations for the

³The reaction of the form $a + b \rightarrow c$ is consistent with the chemicals used in the experiments reported in Ref. [2].

unknown concentrations. The term Rab , appearing several places in Eq. (1), describes the reaction of gasses a and b into c (with R denoting the *reaction rate* of the two former species). The term $N_1\theta(c-c_0)c^2$ describes the nucleation of gas c into its solid form s . Finally, the term N_2cs represents the aggregation of gaseous c onto previously formed aggregates. It should be remarked that the detailed form of Eq. (1) assumes the chemicals used in the study in Ref. [2]; using other chemicals of different stoichiometry will affect numerical values of the model.

In order to be able to solve Eq. (1), initial and boundary conditions have to be introduced. For simplicity, we will here assume that the ends of the tube at $x = 0$ and $x = L$, feeding it with the gases a and b , can be considered as (infinite) reservoirs of constant concentration a_0 and b_0 , respectively; that is, for any time $t \geq 0$ we have $a(0, t) = a_0$ and $b(L, t) = b_0$ [see Fig. 2].

2.1 Exam questions

- a) Rewrite Eq. (1) in *dimensionless form* and use it to discuss a numerical scheme for solving these equations. Specify mathematically the initial and boundary conditions that you will use. In particular, be careful to discuss how you will handle the nonlinear terms that appear on the right-hand side of Eq. (1). Assume that we study the system for sufficiently short times t so that the concentration of gasses a and b at the opposite ends of the tube relative to the respective reservoirs can be approximately set to zero.
- b) Write the code for solving Eq. (1) numerically (remember to comment your code, at least, to some extent).
- c) Test your implementation in order to convince yourself (and everyone else) that your implementation is correct. Can you test your code for some special cases?
- d) Solve the system of partial differential equations (1) for tube length $L = 1$ m; diffusion constants $D_a = 4 \times 10^{-7}$ m²/s, $D_b = (2/3) D_a$, $D_c = (8/15) D_a$; reaction rate $R = 1$ m/s; constants $N_1 = N_2 = R/10$; reservoir concentrations $a_0 = 1$ m⁻¹ and $b_0 = 10 a_0$; and finally a nucleation threshold of $c_0 = 3 \times 10^{-2}$ m⁻¹.

For these parameters, plot the concentrations $a(x, t)$, $b(x, t)$, $c(x, t)$ and $s(x, t)$ as function of $0 < x/L < 1$ for a few values of the time t . In particular, demonstrate that the function $s(x, t)$ displays “sheets” of well-defined high concentration consistent with what is seen in Fig. 1. Does the calculated sheet structure depend on your choices for Δx and Δt ?

In your report, remember to specify all the numerical parameters (like Δx and Δt) that you assume in performing the numerical calculations.

- e) Let x_n denote the position of sheet $n = 1, 2, \dots$ defined so that $x_n < x_{n+1}$. Use your simulation results, assuming the parameters of the previous sub-problem, to calculate the sheet-sheet distance $\Delta\xi_n = x_{n+1} - x_n$. Does $\Delta\xi_n$ depend on time and/or on n ? What happens to the sheet-sheet distance when the nucleation threshold c_0 is changed?
- f) Based on your simulation results, identify the physical mechanism that is responsible for the formation of the sheet structure [seen in $s(x, t)$]. Will such sheet structure always be formed independent of the values of the diffusion constant of the gases $D_g \geq 0$?

So far we have assumed D_g ($g = a, b, c$) to be constants. However, one can imagine that the precipitate (solid s) may clog up the pores of the porous medium resulting in a reduced diffusivity for the gases in regions where the concentration of s is high. Hence, we will now study what happens when the diffusion constants D_g are decreasing with increasing value of the function $s(x, t)$. To this end, we will introduce modified diffusion “constants” (or functionals) defined by

$$\bar{D}_g[s(x, t)] = \frac{D_g}{1 + \frac{s(x, t)}{s_0}}, \quad g = a, b, c. \quad (2)$$

Here s_0 is a constant threshold concentration for solid s for which $s(x, t) = s_0$ represents the onset of significant dependence of the diffusivity of the gases on the precipitation concentration $s(x, t)$.

It should be remarked that when D_g is replaced by $\bar{D}_g[s(x, t)]$ in Eq. (1), one should make the following replacement

$$D_g \frac{\partial^2 g(x, t)}{\partial x^2} \rightarrow \frac{\partial}{\partial x} \left(\bar{D}_g[s(x, t)] \frac{\partial g(x, t)}{\partial x} \right), \quad (3)$$

due to how the diffusion equation is derived.

- g) Implement the use of the diffusion functional $\bar{D}_g[s(x, t)]$ in conjunction with Eq. (1). Run the simulations for different values of the threshold s_0 and discuss how these values affect the formation of the sheet structure.

The coupled set of equations (1) was derived under the assumption that the reaction that takes place is of the form $a + b \rightarrow c$.

- h) Modify Eq. (1) so that it describes the situation for which the reaction is of the form $2a + b \rightarrow c$. Run the simulations for this new reaction form and compare your results to those obtained previously when the reaction was of the form $a + b \rightarrow c$. What has changed (if anything)?

References

- [1] Assignment 02 can be found at http://web.phys.ntnu.no/~ingves/Teaching/TFY4235/Assignments/TFY4235_Assignment_02.pdf
- [2] M. A. Einarsrud, F. A. Maaø, A. Hansen, M. Kirkedelen, and J. Samseth, *Band formation during gaseous diffusion in aerogels*, Phys. Rev. E **57**, 6767–6773 (1998).
- [3] J. Samseth, M.B. Kirkedelen, F.A. Maaø, A. Hansen, and M.-A Einarsrud, *Liesegang pattern formation by gas diffusion in silica aerogels*, J. Non-Cryst. Solids **225**, 298–302 (1998).