On modelling heat transfer in chemical microsensors

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Abstract

In the present paper heat transfer in a fluid is considered. The Oberbeck-Boussinesq equations for stream function and vorticity are solved by a finite difference method. In the presence of very strong convection puls type solutions occure. The results are applied in the design of microsensors and compared with experimental data.

1 Introduction

In the previous paper [1] numerical solutions to model equations describing heat transfer at very low temperatures have been studied in the case of a rigid heat conductor. The aim of the present paper is to study the effect of convection. The actual application is for a liquid at temperatures in the range between room temperature and the boiling mark of water, hence the classical Fourier law applies. However, there are certain analogies to the previous situation. While in the rigid case at low temperatures a relaxation time, i. e. a certain delay for the appearance of heat flux, was introduced by the internal state variable – semi-empirical temperature, we have here a delay due to the intertia of the fluid. Hence, we observe some quite similar effects, especially for heating pulses.

Such pulses are applied in chemistry inside microsensors where a certain temperature regime is required for the measurement of the concentrations of substances which are chemically unstable in the given temperature range. Consequently, the heating together with the measurement are restricted to very short time intervals.

In the considered electrochemical cell a thin wire working electrode is heated by direct application of a strong alternating current. The resulting thin hot solution layer is used to perform electrolysis at increased temperature without changing the bulk solution properties. This attempt is the basis of a new kind of electrochemical sensors that are capable of oxidizing or reducing inert dissolved substances [2, 3, 4]. Under normal conditions, species of this kind would not present evaluable electrolysis current signals because of their slow reaction rate.

For understanding the processes occurring at a heated electrode surface, different problems have to be solved. Among them, there is the question about temperature outside the metallic electrode body itself, i. e. the temperature profile spreading out from the solid surface toward the bulk of solution. The dimensions of this region do not allow any successful temperature measurement, whereas the electrode body temperature can be determined experimentally.

There have been attempts to describe the temperature field in the solution by the classical heat equation [4]. Convection has been disregarded with the argument, that during the very short pulse times the inertia prevents convective heat transport. However, this turned out to be wrong,

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because the measured temperature in the wire depends on the spatial orientation of the device. Generally, at a vertical wire the temperature is considerably higher [5]. This effect is explained by the convective cooling which is larger for streamlines perpendicular to the heated wire than for parallel ones.

In the present paper we describe the motion of the fluid by the classical Oberbeck-Boussinesq equations, [6]. The system of equations is solved by a finite difference method, [8]. The applied scheme provides a monotone second order approximation of the corresponding differential operators. A procedure suggested by Woods [9] is used for the approximation of boundary conditions for vorticity. Finally, the time-integration of the semi-discretized system is carried out by a half-implicit method.

The paper is organized as follows: in Sec. 2 the set-up of the modelled device is defined, in Sec. 3 we describe the present model, especially the assumptions for the hydrodynamical part and the boundary conditions are discussed. In Sec. 4 we present the numerical method for the solution of the coupled thermo-hydrodynamical model. Finally, in Sec. 5 we present results which are compared with measured data.

2 The experimental set-up

The chemical sensor consists of a metal wire placed along the axis of a glass cylinder which is filled with a solution. The geometry of the sensor is shown in Figure 1.

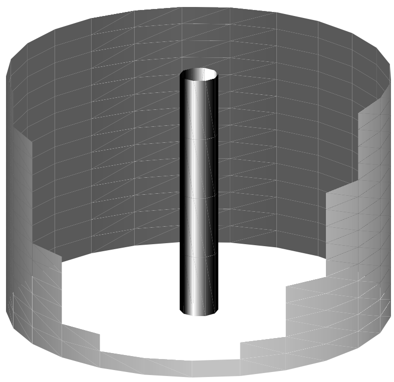

Figure 1: Sensor geometry

The sensor has the following dimensions: $r_1 = 1.25 \times 10^{-5}$ m, $r_2 = 0.025$ m, $h = 0.0191$ m, where r_1 is the radius of the metal wire, r_2 is the radius of the glass cylinder, h is the hight of the sensor. In the present case, a Pt wire and KCl solution were used. Due to an applied voltage alternating current flows through the sensor. The effective value of the current is electronically kept constant for the time interval $[0, T]$. The wire and the surrounding solution are heated that way. Next, the heating current is cut of, and during the time interval $[T_1, T_2]$, $T_1 \geq T$, measurements of the electrolysis are taken.

3 Model assumptions

Unsteady heat transport in liquid can be described by the Oberbeck-Boussinesq system of equations [6]:

$$\frac{\partial \vec{v}}{\partial t} = -(\vec{v}\,\nabla)\vec{v} - \frac{1}{\rho}\nabla p + \nu\Delta\vec{v} + (1 - \beta(\theta - \theta_0))\vec{g}\,, \tag{1}$$

$$
\begin{aligned}
\mathrm{div}\vec{v} &= 0\,, && (2)\\
\frac{\partial\theta}{\partial t} &= -\vec{v}\,\nabla\theta + a\,\Delta\theta + f && (3)
\end{aligned}
$$

where

$$a = \frac{\lambda}{c\,\rho}\,, \quad \nu = \frac{\eta}{\rho}\,, \quad f = \frac{q}{c\,\rho}\,,$$

$\vec{v}$ is the velocity, t is the time, ρ is the density, p is the pressure, ν is the kinematic viscosity, β is the coefficient of expansion, θ is the temperature, $\vec{g}$ is the acceleration of gravity, a is the thermal conductivity, λ is the heat conductivity, c is the specific heat, q is the power of heat source per unit volume, η is the dynamic viscosity. This model is based on the following physical assumptions:

1. the liquid is incompressible and viscous,
2. heat conductivity, specific heat capacity, coefficient of expansion and viscosity of the liquid do not depend on temperature and pressure,
3. the dependence of the density on temperature is taken into account only for the term in the general Navier-Stokes equation that describes presence of the gravity field.

Introducing new variables – vector potential $\vec{\psi}$ and vorticity $\vec{\omega}$ ($\vec{v} = \nabla\times(\xi\vec{\psi})$, $\vec{\omega} = \xi\nabla\times\vec{v}$, $\xi = 1/r$) for 2D cylindrical coordinates this system can be rewritten [7]:

$$
\begin{aligned}
\frac{\partial}{\partial r}\left(ar\frac{\partial\theta}{\partial r} - \frac{\partial\psi}{\partial z}\theta\right) + \frac{\partial}{\partial z}\left(ar\frac{\partial\theta}{\partial z} + \frac{\partial\psi}{\partial r}\theta\right) &= r\frac{\partial\theta}{\partial t} - f\,r\,, && (4)\\
\frac{\partial}{\partial r}\left(\nu r\frac{\partial\omega}{\partial r} - \frac{\partial(\psi - 2\nu z)}{\partial z}\omega\right) + \frac{\partial}{\partial z}\left(\nu r\frac{\partial\omega}{\partial z} + \frac{\partial\psi}{\partial r}\omega\right) &= r\frac{\partial\omega}{\partial t} - \beta g\frac{\partial\theta}{\partial r}\,, && (5)\\
\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right) + \frac{\partial}{\partial z}\left(\frac{1}{r}\frac{\partial\psi}{\partial z}\right) &= -r\omega\,, && (6)
\end{aligned}
$$

In the 2D case the vector potential is called stream function.
Equation (4) transforms to the classical heat conduction equation in the portion of the domain corresponding to the metal wire ($\psi = const = 0$).
The power of heat source per unit volume in the wire was calculated according to the formulas:

$$q = \frac{I^2 R}{\pi r_1^2 h}\,\chi_{[0,T]}(t)\,\chi_{[0,r_1]}(r)\,, \quad R = \rho^*\frac{h}{\pi r_1^2}\,, \tag{7}$$

where R is the resistance of the wire, I is the current and ρ^* is the specific resistance of the wire material.
At the initial moment $t = 0$, the temperature field is assumed to be homogeneous and equal to θ_0, vorticity and stream function vanish.
The boundary conditions for the temperature are the following:

at $r = 0$

$$\frac{\partial\theta}{\partial r} = 0\,, \tag{8}$$

at $z = 0$ and $z = h$

$$
\begin{aligned}
\frac{\partial\theta}{\partial z} &= 0 && \text{for } 0 \le r \le r_1\,, && (9)\\
\theta &= \theta_0 && \text{for } r_1 < r \le r_2\,, && (10)
\end{aligned}
$$

at $r = r_2$

$$\theta = \theta_0\,, \tag{11}$$

at $r = r_1$

$$\theta^- = \theta^+ , \quad \lambda^- \left(\frac{\partial \theta}{\partial r}\right)^- = \lambda^+ \left(\frac{\partial \theta}{\partial r}\right)^+ , \quad \left(\frac{\partial \theta}{\partial z}\right)^- = \left(\frac{\partial \theta}{\partial z}\right)^+ , \tag{12}$$

where superscripts − and + denote the corresponding one-sided limits.
The following boundary conditions were considered for the stream function:

$$\psi = 0 , \quad \frac{\partial \psi}{\partial \vec{n}} = 0 , \tag{13}$$

where $\vec{n}$ is the external normal vector.

4 Numerical method

We solve the system (4)–(6) by a finite difference method. The equations for temperature (4) and vorticity (5) are approximated by Samarskii's difference scheme for non self-conjugated elliptic operators [8]. This scheme provides a monotone second order approximation of the corresponding partial differential operators.
The central-difference approximation was used for the discretization of the stream function equation (6). A procedure suggested by Woods [9] was applied for approximating the boundary conditions to ω. According to this procedure, vorticity values on the boundary are found numerically from equation (6) taking into account relations (13). It provides a second order approximation of boundary conditions for vorticity.
Now, the time integration of the system is carried out by the following half-implicit difference scheme:

$$\Lambda_\theta(\psi^l)T^{l+1} = \frac{\theta^{l+1} - \theta^l}{\tau} - q , \tag{14}$$

$$\Lambda_\omega(\psi^l)\omega^{l+1} = \frac{\omega^{l+1} - \omega^l}{\tau} - \beta g(\nabla^r \theta^{l+1}) , \tag{15}$$

$$\Lambda_\psi \psi^{l+1} = -\omega^{l+1} , \tag{16}$$

where the difference operators Λ approximate the left-hand sides of equations (4)–(6), ∇^r is the difference operator that approximates derivative in r-direction, the superscripts denote time level, and τ is the time step.
Each of the linear algebraic systems (14)–(16) is solved by the method suggested in [10, 11].

5 Results

We use a nonuniform spatial grid with 90×20 knots in all calculations. It has to be mentioned that the half-implicit difference scheme (14)–(16) is not absolutely stable. In fact, it has a restriction on the time discretization step in order to guarantee convergence. Calculations are carried out with automatic time step selection and local error control, the time step varies in the range $10^{-6} - 10^{-3}$ s. Numerical values of platinum and water parameters are taken from [12].
The initial temperature θ_0 is equal to $20^o C$.
We perform experiments with current values from 0.1 (0.1) to 0.6 A. The heating time is $T = \infty$. Figure 2 presents the stationary temperature distribution in the sensor for $I = 0.5$ A. Note that the temperature distribution has a strongly pronounced gradient in r-direction in the region close to the wire. As it is seen, there is a remarkable temperature gradient in z-direction in the wire. From the results for other current values we can conclude that the temperature difference between the ends of the wire increases with increasing current. So, for $I = 0.1$ A and $I = 0.5$ A the differences

are equal to 2.3^oC and 12^oC, respectively.

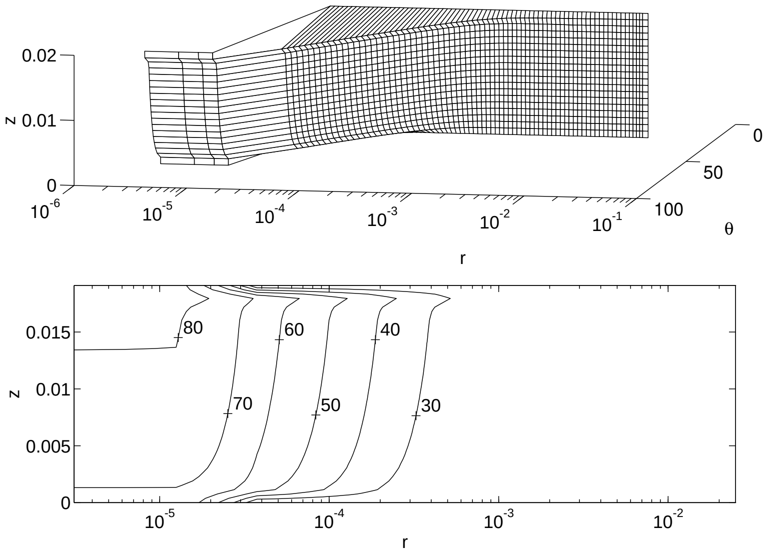

Figure 2: Temperature distribution in the sensor

Figure 3 presents the average wire temperature versus time. Dashed lines show calculated temperature. For $I = 0.6$ A the calculation was stopped at the moment when the temperature in the wire had reached the boiling mark. The solid lines show the results of wire temperature measurements. The results were obtained by the method described in [5]. As it is seen, there is a good agreement with the numerical results.

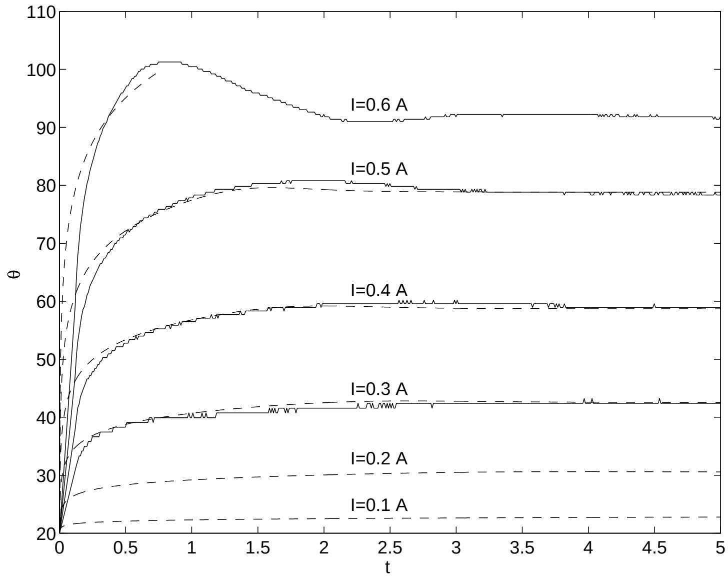

Figure 3: Wire temperature versus time

Figure 4 shows the stationary velocity field in the device for $I = 0.5$ A. It is seen that the liquid motion has relatively large velocity values in the region close to the wire.

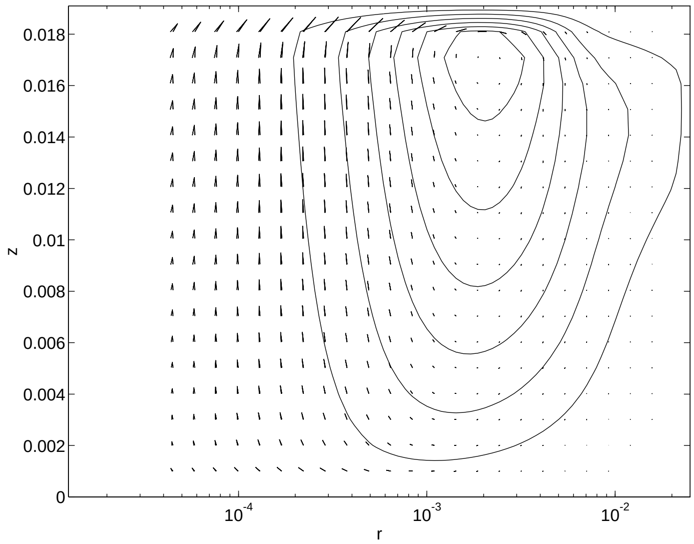

Figure 4: Velocity field in the sensor

For the case when the heating time T is finite in the upper part of the sensor puls type solutions are observable. Figure 5 presents a contour plot of the temperature distribution on the line $z = 0.017$ m versus time for $T = 1$ s. It has to be mentioned that amplitude of this puls is just 0.05^0C.

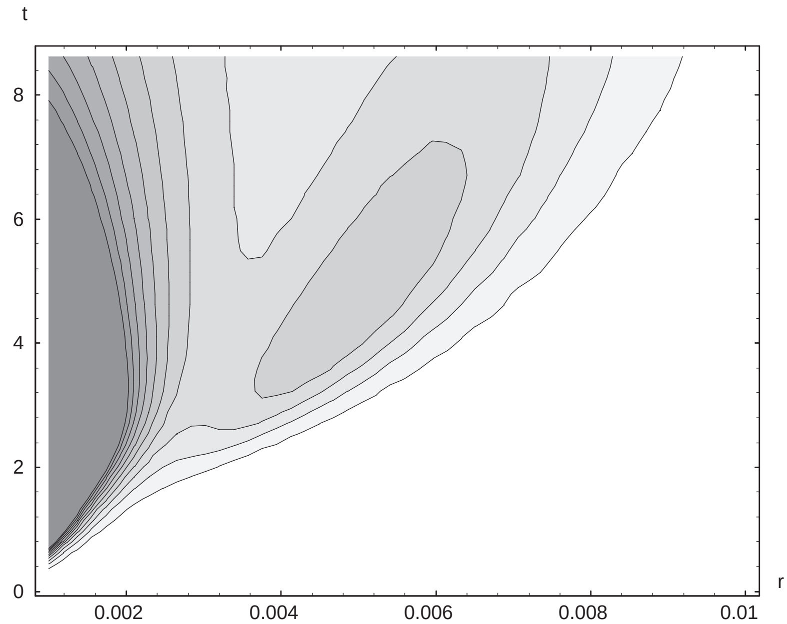

Figure 5: Contour plot of temperature distribution on line $z = 0.017$ m versus time

The influence of the boundary conditions for the temperature at the ends of the sensor on the results was investigated, too. Calculations were carried out for the case when, instead of boundary condition (10), the following one was used:

$$\frac{\partial \theta}{\partial z} = 0\,. \tag{17}$$

Figure 6 shows a contour plot of the temperature for this case. The results show that this change of boundary conditions influences the temperature distribution in very small regions close to the ends of the sensor. The same can be mentioned about the velocity field. This change does not influence the average wire temperature.

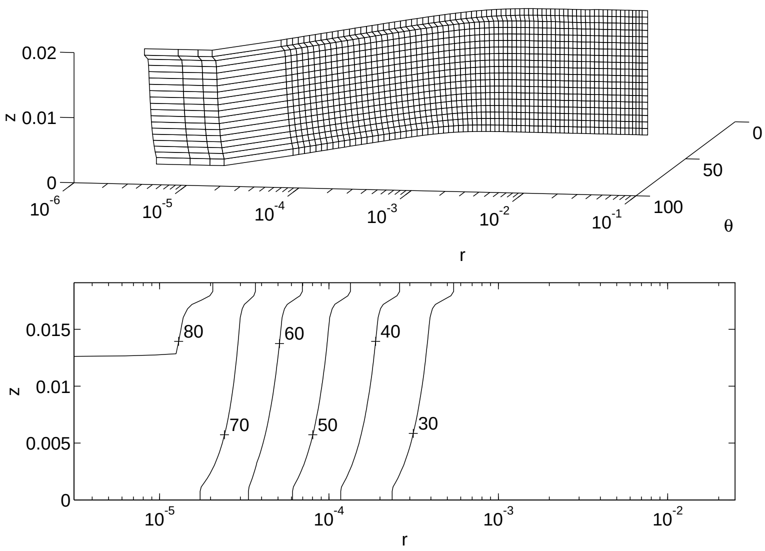

Figure 6: Temperature distribution in the sensor (boundary conditions (17) at the ends of the sensor)

It is interesting to note that there is a very small dependence of the wire temperature on the sensor height h. Thus, for $I = 0.5$ A numerical experiments predicted a wire temperature equal to 81.5^oC for $h = 0.04$ m and 83^oC for $h = 0.06$ m.
The same has to be mentioned about an increase of the sensor radius r_2. For $r_2 = 0.05$ m ($h = 0.0191$ m) the final wire temperature was equal to 76^oC.

6 Concluding remarks

The considered problem leads to large Rayleigh numbers ($10^6 - 10^7$). The resulting numerical problems can be handled by the proposed algorithm. There is good agreement between numerical and experimental results.
Some effects have been consciously neglected in the present model, such as the dependence of the liquid parameters on the temperature and pressure and power density dependence on temperature. Moreover, in the present paper we do not discuss the possible dissipation of current from the wire into the solution. It was proven by numerical experiments [13] that for the sensor at hand this effect can be ignored. In general, it is determined by a presence of a specific double layer between wire and solution with a capacity per wire surface unit equal to about 0.2 F/m^2, [14]. For an AC frequency of 1 kHz and the given dimensions of the wire (the electrical properties of the solution are irrelevant) the double layer works as an electrical isolator.

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