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Open Questions on Reliable Measurements of Soret Coefficients

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Abstract This study was motivated by experimental problems arising in the design of optical digital interferometry for measurements of Soret coefficients in laboratory conditions. Our attention is mainly focused on thermal design of the set-up. The goal is to establish a linear temperature profile inside the experimental cell while heating from above. The measures for preventing deleterious convection inside the working liquid and outside the experimental cell (in the surrounding gas) are carefully examined. It is pointed out that both convection in the liquid and in the surrounding gas have a strong negative effect on the quality of optical measurements.

Keywords Convection · Soret coefficient · Measurements

Introduction

Diffusion is an important transport mechanism in nature. A mixture at equilibrium is homogeneous and molecular motion has no directional preference. When a mixture is subjected to thermal or compositional gradient, the mass fluxes of the individual components appear. This process is referred to as molecular or thermal diffusion depending on the gradient that induces the fluxes.

Diffusion plays an important role in many industrial processes, such as fluid separation, distillation, drying and coating, crystal growth, material processing, and oil extraction. The prediction of mass transfer in multicomponent systems greatly relies on the knowledge of diffusion and thermal diffusion coefficients. However, data coming from different experiments are widely scattered. The theories used to predict the molecular diffusion coefficients in liquids are not always in a good agreement with the experimental data. One of the explanations of this disagreement is the existence of buoyancy-induced flows. This is especially important for measurements of thermodiffusion (Soret) coefficients in terrestrial conditions, since experimental techniques require establishing a temperature gradient in the fluid in gravity field (Platten 2006; Wiegand 2004). Roughly, the experimental methods can be divided into two classes: (1) methods that employ the presence of buoyancy convection in the measurements; (2) methods, in which buoyancy convection plays deleterious role. Here our attention is focused on the second class, which is mainly represented by optical methods. All these methods may face a problem of parasitic convection in the experimental cell. In a controlled microgravity environment, its influence is greatly reduced allowing one to approach a true diffusion limit.

Unlike the other techniques developed for measurement of thermodiffusion coefficients, the optical digital interferometry allows measuring the concentration and temperature not only at fixed points (e.g. at the hot and cold plates), but also their distributions along the diffusion path (Mialdun and Shevtsova 2008). Knowledge of the spatial temperature and concentration fields

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enables one to examine the presence of convective flows and study their influence on the measured values of Soret and diffusion coefficients. To the best of our knowledge, such studies have not been reported.

Experiment Design

A new experimental set-up was designed to study heat and mass transfer in liquids with Soret effect (Mialdun and Shevtsova 2008). The suggested instrument consists of two principal parts: the optical Soret cell (in some way similar to that used earlier (Zhang et al. 1996)) and an interferometric system in combination with equipment for digital recording and processing the phase information.

The experiments were performed in a transparent cubic cell filled initially by a homogenous mixture. The thermal gradient is imposed by heating and cooling the top and bottom walls of the cell, respectively. The spatial temperature variation induces mass transfer through the Soret effect. Both temperature and composition variations contribute to the spatial distribution of the refractive index. The local gradients of composition and temperature inside the fluid are calculated from refractive index gradients both for steady state and dynamic regimes.

Soret Cell

The primary idea of the experimental cell design was to have a linear temperature distribution inside liquid when heating from above. The cell geometry is shown in Fig. 1. An optical cubic cell of internal size $L =$ 10 mm with initial thickness of lateral walls 5 mm was made of quartz. First experiments with binary mixture (water and isopropanol) revealed a serious problem: we were unable to see the concentration variations due to thermodiffusion process after processing the digital images.

The most obvious explanation is the presence of the convection in the experimental cell. The levels of top and bottom copper plates were checked by cathetometer WILD Heerbrugg (Switzerland), model KM 345. With this procedure the plates were leveled to a maximal inclination of 2.5 ± 0.2 mrad. After all technical points were inspected, we proceeded to the analysis of temperature field inside the cell.

The temperatures inside liquid (pure water) and glass wall were measured optically. The results of this test are shown in Fig. 2. The dashed and solid lines display vertical temperature profiles inside the liquid and inside the quartz glass which were measured 0.5 mm away from the contact line (along the vertical solid lines shown on the left side of Fig. 1). The expected linear profile is given by dashed-dotted line. Indeed, the measured temperatures do not coincide with the expected linear profile. However, both experimental profiles have common behavior along the major part of the plot. The disagreement is observed near the top and bottom parts of the cell: at the top, liquid is hotter than the glass, while at the bottom the situation is opposite. These tests reveal the presence of lateral heat fluxes, which are localized at the top and bottom parts of the side walls. There are a few possible reasons:

1. Different heat conductivities of contact materials;
2. The thermal distribution imposed by the entire geometry of set-up.
3. Heat transfer through the external side of lateral walls, i.e. glass-air side.

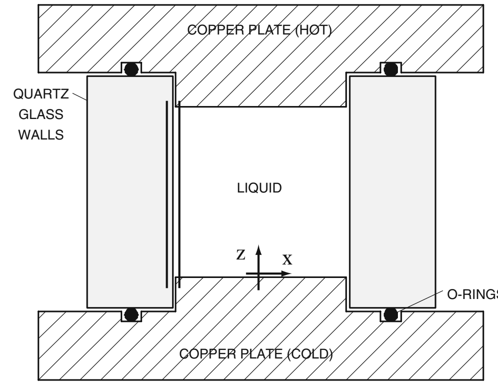

Fig. 1 Experimental cell

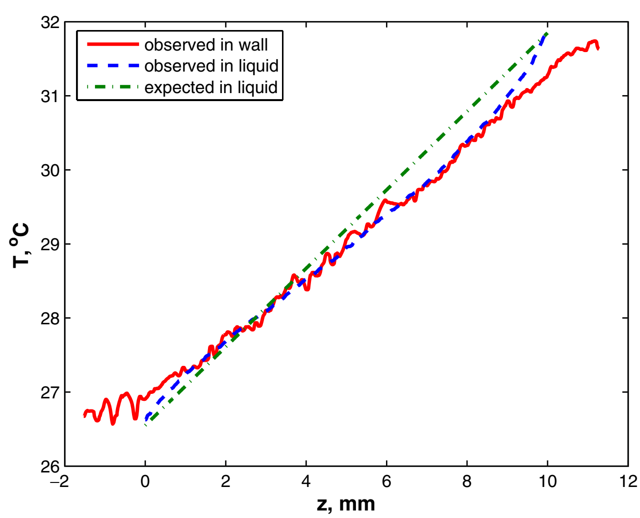

Fig. 2 The vertical temperature profiles: inside glass wall, inside liquid (water) and expected linear behaviour

Thermal Design

The thermo-physical properties of contact materials are very different. The thermal conductivities λ are listed in Table 1. To clarify the effect of different materials in contact on the thermal field in the liquid, the temperature distribution was numerically examined.

Let us introduce the Cartesian coordinate system with the origin at the center of the cold wall, see Fig. 1. First the 2D problem was solved in simplified geometry: square cell, half of which occupied by liquid ($0.0 \leq x \leq 0.5$) and other half by quartz glass ($0.5 \leq x \leq 1$). The heat transfer inside each substance is described by equation

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial z^2} = 0, \qquad (1)$$

while the heat fluxes are equal along the contact line:

$$\lambda_l \partial_x T_l = \lambda_w \partial_x T_w \quad \text{at} \quad x = 0.5.$$

Here subscripts "l" and "w" stand for liquid and wall. The remote lateral walls (quartz/air) are taken either thermally insulating or perfectly conducting. The upper wall is hot and the lower is cold. The solution did not reveal *large* difference either we take the real values of thermal diffusivities λ_l/λ_w from the Table 1 or values equal to each other, i.e. $\lambda_l/\lambda_w = 1$. Thus, the different heat conductivities of contact materials are not responsible for the measured non-uniformity of the temperature.

At the next step, calculations of Eq. 1 were performed in complex and absolutely realistic geometry shown in Fig. 1 (using FEMLAB). Simulations were performed in a quarter of the cell and the computed temperature field is presented in Fig. 3. The behavior of the isotherms indicates that the most dangerous thermal constraints are hidden at the corners of the system. A rubber O-ring of about 1 mm thick is used to prevent leakage of the liquid. The initial thickness of the glass wall was 5 mm and rubber O-ring was placed in the middle of the wall. The thermal contact between quartz glass and copper at the top (bottom) of the cell can be described as a piecewise function. From the internal side of the O-rings the small gap between copper and quartz is filled by working liquid (region 1 in Fig. 3); from external side the gap is filled by surrounding gas (region 3). Apparently, air is very bad heat conductor and isotherms approach to the region 3 almost vertically (i.e. $dT/dz \to 0$). The thermal conductivity of rubber is higher than that of air, but still much less than that of liquid, and isotherms approach to the region 2 with larger inclinations. Integrally, this temperature field creates significant heat fluxes, which cause a lateral heat flux inside the liquid near the corners. Numerical modeling has been revealed that diminishing the height of the protrusion of copper plates into the cell has also a positive effect for reducing lateral heat fluxes.

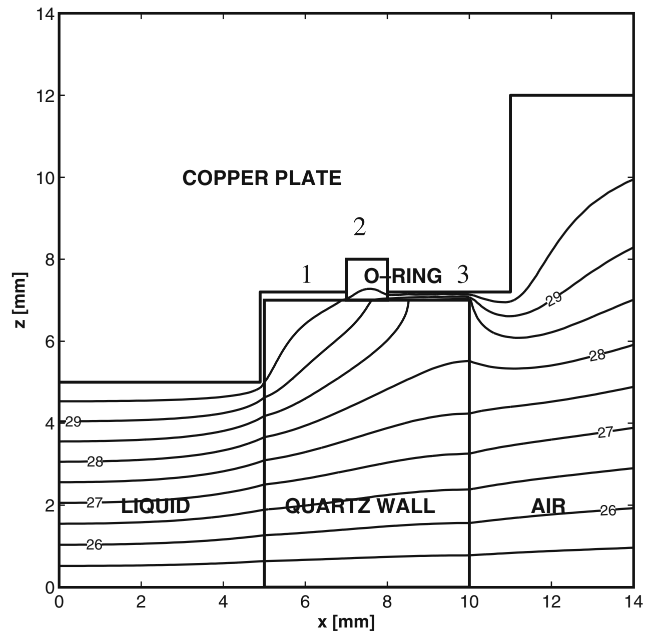

Fig. 3 Temperature field in the system with thick quartz walls. O-ring is located in the top of the glass in the middle (z-axis origin is shifted to the cell center)

Table 1 Thermal conductivities of used materials

	Air	Rubber	Water	Quartz glass	Copper
λ $W/(m \cdot K)$	0.02	0.16	0.6	1.4	400.

Having this knowledge in hands, the proper idea is to avoid contact with air (cut off the lateral wall below the region 3). We have chosen a new cell, which wall thickness is equal to the length of the region 1 ($\sim 1.3mm$) and contact line on the top is completely covered by rubber O-ring. Curves 1 and 2 in Fig. 4 show horizontal temperature gradients inside liquid along the contact line in the case of the thin and thick walls (numerical results).

The comparison of curves 1 and 2 pointed out that in the case of new design, the values of horizontal temperature gradients near the corners are strongly reduced although they are not completely eliminated.

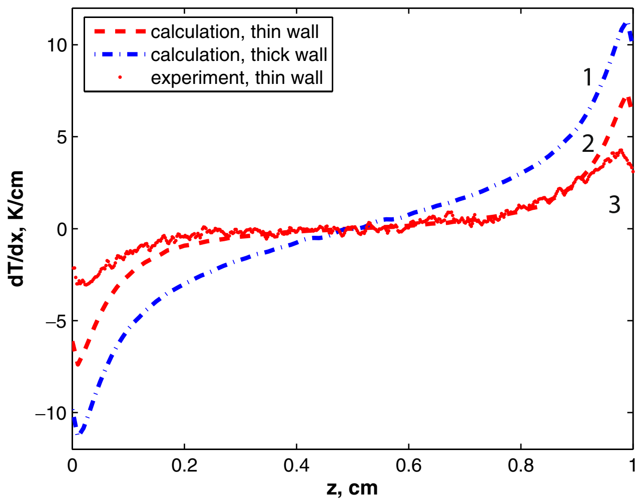

Fig. 4 The horizontal temperature gradient inside liquid close to the wall. Dashed curves 1 and 2 show numerical results in the case of thick and thin walls respectively; the curve 3 shows experimental measurements for the thin walls

The experimental curve 3 (thin walls) being in agreement with calculations (curve 2) indicates that the horizontal temperature gradients are negligibly small at the central part of the cell. Note that the real heat fluxes near the corners are smaller than numerical ones and they are not symmetrical with respect to the mid-height. The lateral heat fluxes could be diminished by using innovative sealing materials with higher thermal conductivity. However, the tested sealing materials with better thermal conductivity have higher hardness in comparison with normal rubber. Extreme care has to be taken when clamping glass part of the cell between copper plates and this kind of seal. And even with that, probability of glass crack is quite high. Thus, one should find a way to perform the measurements taking into account small heat fluxes. Due to them, the small corner regions in the liquid are affected by convection which mixes up the binary liquid. As it was mentioned above, the optical digital interferometry method (see Mialdun and Shevtsova 2008) enables measuring the concentration and temperature differences between two arbitrary points along the diffusion path. It allows one to perform the measurements of Soret and diffusion coefficients using information only from the central part of the cell, i.e. in convection free zone. Moreover, it appears that on the boundaries of the convection-free zone the condition of zero mass flux is well satisfied during the whole diffusion process and not only in steady state. This condition is important to the companion theoretical approach and its fulfillment was proven by the measurements of the diffusion coefficients. The Soret coefficient can be determined from the steady state condition while the diffusion coefficients can only be obtained from records within the time dependent process.

The target of the experiments is to measure the evolution of the concentration difference with time $\Delta C(t) = C(z_1, t) - C(z_2, t)$ at the horizontal boundaries of convection-free zone and determine the Soret coefficient S_T and the relaxation time τ_r using an equation

$$\Delta C(t) = -S_T C_0(1 - C_0)\Delta T \times \left\{ \frac{\Delta z}{L} - \frac{4}{\pi^2} \sum_{n,\mathrm{odd}}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \frac{t}{\tau_r}\right) \times \left[\cos\left(\frac{n\pi z_1}{L}\right) - \cos\left(\frac{n\pi z_2}{L}\right) \right] \right\}$$

The diffusion coefficient D is determined from the relaxation time $\tau_r = L^2/\pi^2 D$.

One may argue that the problem of convection could be easily overcome using cell with a larger aspect ratio, i.e. ratio of width/height. Recently a set of experiments was performed in the cell of 6 mm height and 18 mm side walls, i.e. aspect ratio is equal 3. Although the area, affected by convection, is smaller but it exists. To obtain reliable results the "convection-free" central zone should be again cropped out. In addition, increasing the length of side wall leads to the increase of the optical path trough the cell.

Heat Exchange with Surrounding Gas

The new design with thinner walls allowed us to establish the temperature in the cell close to the linear profile, but imposed an additional problem: rather strong sensitivity of the temperature field inside the cell to the thermal conditions in surrounding gas (due to the thin walls). The diffusion experiments are long: it takes a few days to reach steady state. It appeared that the experimental points $\Delta C(t)$ perform periodic oscillations around the fitting curves with the period of about 24 h. To avoid the influence of daily oscillations of the surrounding gas temperature, the entire set-up was enclosed in a thermostabilized box made of heat insulating material. The box was supplied with active thermostabilizing system based on air-to-air cooling/heating assembly and precise PID controller (both of *Supercool*).

Thermostabilizing completely eliminated daily oscillations but a new problem has raised. The experimental points $\Delta C(t)$ were widely scattered. Strong motion in gas phase around the cell, which is caused by inner fan of box thermostabilizing system, disturb the interferometry and leads to the large scattering of the results. Large plate, interrupting the gas flow, were inserted in the box to prevent disturbance in gas phase over optical path. The final design of the experimental set-up with the implementation of Max–Zehnder interferometer is shown in Fig. 5. The light beam of He-Ne laser is expanded by the spatial filter and then passes through the beam splitter ($BS1$) where it is splitted into two beams of equal intensity. One (object beam) passes through the Soret cell perpendicular to the temperature gradient (in z-direction in Fig. 1) and another one (reference beam) bypasses it. After passing mirrors both parallel beams are combined ($BS2$), and resulting interference patterns are recorded by CCD camera.

Note that the temperature profile in the gas phase explains non-equal heat fluxes near the top and bottom inside liquid, curve 3 in Fig. 4. The heat fluxes would be equal if the temperature profile in gas was symmetrical with respect to mid-height of the cell.

Set of experiments on measurement of Soret coefficients has been performed for extensive scientific validation of the developed technique against recent published data for water/ethanol mixtures. The measured and literature data (Zhang et al. 1996; Dutrieux et al. 2002) for Soret coefficients are summarized in Fig. 6. The results of our experiments using a cubic cell with 10 mm side (see Fig. 1) are shown by open squares. The filled squares correspond to our results in another cell with aspect ratio 3 (6 × 18 × 18 mm). The results for different cells are slightly diverged, although they follow general trend. The difference can not be attributed only to the aspect ratio. Protrusions in horizontal copper plates, indicated in Fig. 1, were absent in the flattened cell with aspect ratio 3. Besides the rubber sealing was used in cubic cell, while PTFE sealing was used in flattened cell. The quantitative comparison of Soret coefficients reveals excellent agreement with the published data.

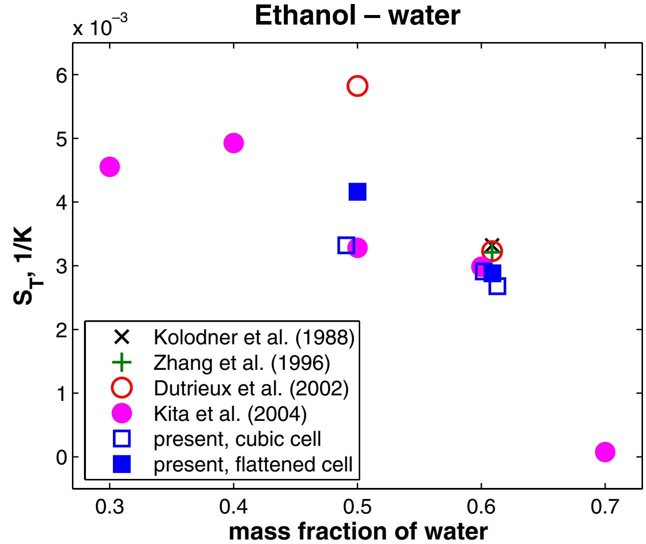

Fig. 6 Soret coefficient of water/ethanol as a function of mass fraction of water in present work (open squares correspond to the experiments in cubic cell; the filled squares correspond to the experiments in a cell with aspect ratio—three) and literature data (Zhang et al. 1996; Kolodner et al. 1988; Kita et al. 2004; Dutrieux et al. 2002)

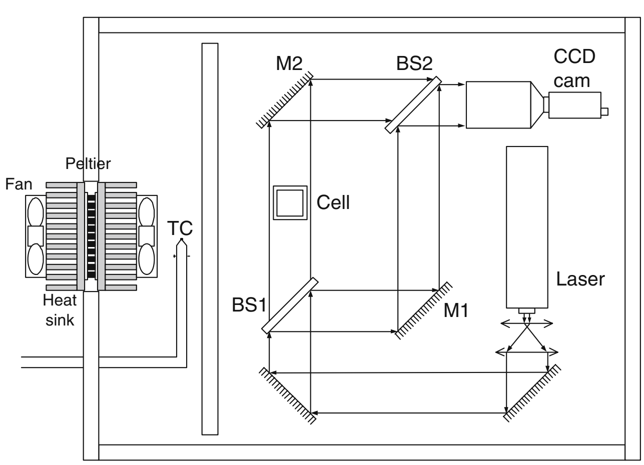

Fig. 5 Scheme of experimental set-up

Conclusions

Recently, we have developed a novel experimental technique based on optical digital interferometry for investigating the thermodiffusion process in liquids and measuring mass transport coefficients (Mialdun and Shevtsova 2008). Certainly, optical methods have a lot of positive features such as non-intrusiveness and high sensitivity. The use of these methods in microgravity environment is very beneficial. However, when working with temperature gradients in gravity field, all these techniques are affected by convection to some extent. Here we examine the appearance of convective flows, identify their location, and find the ways to minimize them. Convection inside the working liquid might be intuitively expected. We have pointed out that the quality of results is also affected by convection in the gas phase around the cell. Convection in the gas phase disturbs the optical path and leads to a large scattering of experimental points. So, for optical methods, convection in the surrounding gas is as undesirable as convection inside the diffusion cell.

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