Unstable density stratification in binary mixture

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Abstract: Three-dimensional numerical modelling of Soret driven convection in a cubic cell filled with a binary mixture of water (90%) and isopropanol (10%) is performed. The system is heated from above while the Soret coefficient is negative. The concentration and temperature fields are strongly coupled by Soret effect that causes concentration gradients in response to the applied temperature difference. Due to negative Soret effect the heavier liquid is accumulated on the top of the lighter one. At some moment this unstable stratification leads to appearing of motion. The transient behaviour of the velocity, temperature and concentration fields is discussed.

Keywords: Soret effect; buoyancy force; convection; oscillation; instability.


Biographical notes:

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1 Introduction

There are few examples of systems with unstable density stratification which leads to development of instabilities. The most obvious case is the isothermal Rayleigh-Taylor instability when a high density fluid is placed on top of a low density fluid. Even in such situation the hydrostatic equation can be satisfied and hence this is an equilibrium configuration. One might expect such equilibrium to be unstable because the heavier fluid will try to sink below the lighter fluid. The instability causes the two fluids to exchange places.

Another widely considered problem is the Rayleigh-Bénard (RB) instability when a layer of fluid is heated from below or cooled from above. With time the lighter (hotter) liquid will accumulate below the denser (colder) one. The mechanism of instability is well known and it is different from the Rayleigh-Taylor case. At certain value of the temperature difference any perturbation introduced in the system will lead to movements inside the fluid. Periodic rolls, or RB cells, appear due to the coupling between the dynamic and the thermal fields.

In the case of heating from above density stratification is stable in a pure liquid. However in the case of a binary
mixture with negative Soret effect unstable density stratification is established in the system. In comparison with single liquids the mixtures provide richer variety of bifurcation phenomena and convective states with various structural and temporal properties (Platten and Legros, 1984). The threshold condition in mixtures is characterised by solutal Rayleigh number

$$\text{Ra}_s = -\frac{\psi}{\text{Le}} \text{Ra},$$

(1)

where $\text{Le} = D/\alpha$ is the Lewis number. Here $D$ is the molecular diffusion and $\alpha$ is the thermal diffusivity. The strength of Soret effect is described by the separation ratio

$$\psi = C_0(1-C_0) \frac{\beta_T}{\beta_C} S_r,$$

(2)

where

$$\beta_T = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}, \quad \beta_C = \frac{1}{\rho} \frac{\partial \rho}{\partial C}$$

(3)

are the thermal and solutal expansion coefficients. The separation ratio is the ratio of the concentration-induced density gradient to the temperature induced density gradient in the quiescent state. Thus $\psi$ defines the coupling between the temperature and the concentration fields and externally $\psi$ is controlled by varying the mean temperature and the initial concentration of the mixture.

For majority of liquids the density is decreasing with temperature $\partial \rho / \partial T < 0$ and it is the case for water–isopropanol mixture. Thus $\beta_T = -\rho^{-1}(\partial \rho / \partial T) < 0$ is the positive value for our mixture. The sign of $\beta_C$ is not so obvious. Hereafter we consider that $C$ is the concentration of the heavier component, i.e., of water, then $\partial \rho / \partial C < 0$. Thus $\beta_C = \rho^{-1}\partial \rho / \partial C < 0$ is also the positive value. Then the sign of the separation ratio $\psi$ coincides with the sign of Soret coefficient $S_r$. Negative Soret coefficient corresponds to component separation in binary mixtures with the denser component migrating to the hot wall.

The threshold conditions for RB convection in infinite layer (transition from conductive to convective state) is well known $\text{Ra}_0^b = 1708$. In the mixture the critical solutal Rayleigh is associated with $\text{Ra}_s^0$ when concentration boundary layer has no time to develop ($C = C_0$).

$$\text{Ra}_s^0 = \frac{1}{1+\psi} \text{Ra}_0^b.$$

In the opposite case of fully developed conductive profile ($\partial C / \partial z = \text{const}$) the threshold value for a stationary instability is

$$\text{Ra}_s^0 = 720,$$

see for example Ryskin et al. (2003).

Here we presents the results of 3D numerical simulations of the non-linear time-dependent Navier-Stokes, heat and mass transfer equations in a system with negative Soret effect. The parameters of the system correspond to a realistic water-isopropanol binary mixture enabling comparison of theoretical predictions with planned experimental studies.

## 2 Problem formulation

### 2.1 Equations and assumptions

Heat and mass transfer in a cubic cell, filled with a binary mixture with initial mass fraction of the heavier component $C_0$, is considered. The top and bottom walls are held respectively at temperatures $T_{\text{hot}}$ and $T_{\text{cold}}$, yielding a temperature difference of $\Delta T = T_{\text{hot}} - T_{\text{cold}} > 0$. All other walls are assumed thermally insulated. The geometry of the problem is shown in Figure 1.

The governing Navier-Stokes, heat and mass transfer equations can be written as:

$$\frac{\partial \mathbf{V}}{\partial t} = -\nabla p + \mathbf{g},$$

(4)

$$\frac{\partial T}{\partial t} = -\nabla \mathbf{V} \cdot \mathbf{g},$$

(5)

$$\frac{\partial C}{\partial t} = -\nabla \mathbf{V} \cdot \mathbf{g},$$

(6)

$$\nabla \cdot \mathbf{V} = 0,$$

(7)

here the momentum, heat and mass fluxes are

$$\mathbf{J}_r = \frac{1}{\rho} [\rho \mathbf{V} \mathbf{V} + P - \mu \nabla \mathbf{V}],$$

$$\mathbf{J}_r = \frac{1}{\rho \mathbf{C}_r} (\mathbf{V} \mathbf{T} - \nu \nabla T),$$

where

$$\mathbf{J}_c = \mathbf{V} \mathbf{C} - D_C \mathbf{D} - S_r C(1-C) \nabla T.$$
The total mass flux $J_c$ comprises a convective transport (first term), a Fickian diffusive flux (second term) and the thermal diffusive flux (last term). Below in the thermal diffusive flux the approximation $C(1 - C) - C_0(1 - C_0)$ will be used. It is common practice for Soret problems if the concentration difference remains small.

In Equations (4)–(7) we have suppressed the Dufour effect (heat transfer driven by a concentration gradient) as it is important only in gas mixtures.

The governing Equations (4)–(7) can be written as

$$\rho \left[ \frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{V} \right] = -\nabla P + \mu \nabla^2 \mathbf{V} + g \rho,$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{V} = 0,$$

$$\frac{\partial C}{\partial t} + \mathbf{V} \cdot \nabla C = D_T \cdot \nabla^2 C + D_S \cdot \nabla[\rho C (1 - C) \nabla T],$$

$$\nabla \cdot \mathbf{V} = 0.$$

The problem (Eqns. 8–11) is solved in Boussinesq approximation. The basis of this approach is that there are little and this variation is neglected everywhere except in the buoyancy term. Thus in Equation (8) the density $\rho$ is replaced by $\rho_0$ everywhere except last gravity-dependent term.

The temperature and he concentration fields deviate from their mean values $T_0$ and $C_0$ so that $T = T_0 + T'$ and $C = C_0 + C'$. Taking into account the density dependence on the temperature and on the concentration, $\rho = \rho_0 + \rho'$, where $\rho_0 = \rho(T_0, C_0)$ and $\rho' \ll \rho_0$, one may write

$$\rho' = \frac{\partial \rho}{\partial T} T' + \frac{\partial \rho}{\partial C} C' = -\rho_0 \beta_T T' + \rho_0 \beta_C C',$$

where $\beta_T$ and $\beta_C$ are defined in Equation (3). Due to the variation of the temperature and of the concentration the pressure will also differ from its equilibrium value ($P_0 = \rho_0 g \mathbf{g} \mathbf{z}$ + const).

$$P = P_0 + P' = -\rho_0 g \mathbf{g} \mathbf{z} + P' + \text{const}.$$  

Thus, the terms related to the gravity force are

$$-\nabla P + g \rho = -\nabla P' - \rho_0 g \beta_T T' + \rho_0 g \beta_C C'.$$

Finally, in the Boussinesq approximation the momentum Equation (8) takes the form

$$\frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{V} = -\nabla P' - \rho_0 \nabla^2 \mathbf{V} - g \rho \beta_T T' + \rho_0 g \beta_C C'. $$

2.2 Sign of Soret effect

The sign of the Soret coefficient $S_T$ defines the sign of separation, i.e., whether the concentration $C$ is larger near the cold or the hot wall. Consider the case when gravity is absent and thus no convective heat and mass transport are present ($\mathbf{V} = 0$). Impermeability of the solid bounding walls implies that there is no concentration flux through the walls: $J_c = 0$ at the boundaries. In steady state the thermal diffusion flux is constant across the cell and its value is $J_c = 0$. Thus, on the boundaries

$$\nabla C = -S_T C_0 (1 - C_0) \nabla T.$$  

If $S_T < 0$ then $\Delta C/\Delta T > 0$, i.e., the concentration is higher near the hot wall. This is the case of heating from below the product $C_{ch}$ is the denser component ($\beta_C > 0$) then it is the denser component that migrates towards the hot boundary since $\Delta \rho/\Delta T = \beta_T \Delta C/\Delta T > 0$. Thus, the Soret effect is negative when the denser component migrates towards the hot wall.

2.3 Choice of dimensionless variables

Dimensionless variables are used in the numerical calculations. The size of the cell $L$ is the length scale. The velocity, time, pressure and temperature scales are respectively $V_{ch} = \nu L$, $t_s = L^2/\nu$, $P_{st} = \rho_0 V_{ch}^2$, $\Delta T$.

There are a few different types of dimensionless equations depending upon the choice of $C_{ch}$. Let us write dimensionless equations, keeping only one non-identified parameter $C_{ch}$, then the governing non–dimensional equations become:

$$\frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \nabla \mathbf{V} = -\nabla \mathbf{P} + \nabla^2 \mathbf{V}$$

$$\mathbf{V} \cdot \mathbf{V} = 0.$$  

Here $\mathbf{e}$ is the unit vector directed upwards. The formulation of the problem includes Prandtl, Schmidt, Grashof numbers:

$$Pr = \frac{\nu}{\alpha}, \quad Sc = \frac{\nu}{D}, \quad Gr = \frac{g \beta \Delta T L^2}{\nu^2}, \quad Ra = Gr Pr.$$  

The Rayleigh number may be used instead of $Gr$ and the Schmidt number instead of the Lewis number $Sc = Pr/Le$. Here the $\Delta T$ has positive sign as it is used for scaling. In the case of heating from above the product $g \Delta T > 0$ will be negative thus $Ra < 0$ while $g \Delta T > 0$ and $(Ra > 0)$ when heating from below.
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Two versions of Equations (14)–(17), the mostly used in literature, are given below. Depending upon the choice of \( C_{a} \) this characteristic parameter \( \psi \) will enter either in the momentum (Eq. 14) or in the diffusion (Eq. 16) equations.

1st choice: \( C_{a} = -C_{d}(1 - C_{d})\Delta T \)

Choosing this value as the scale for the mass fraction \( C \), the separation ratio \( \psi \) enters into the momentum equation. This type on notation is used by Legros team (Gershuni et al., 1995; Van Vaerenbergh et al., 1990), by Ryskin et al. (2003), etc.

Thus the governing non-dimensional equations become:

\[
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \nabla^2 \mathbf{v} - \text{Gr}(\Theta + \psi/c)e, \quad (18)
\]

\[
\frac{\partial \Theta}{\partial t} + \mathbf{v} \cdot \nabla \Theta = \frac{1}{Pr} \nabla^2 \Theta, \quad (19)
\]

\[
\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \frac{1}{Sc} (\nabla^2 c - \nabla^2 \Theta), \quad (20)
\]

\[
\nabla \cdot \mathbf{v} = 0. \quad (21)
\]

2nd choice: \( C_{a} = (\beta_{r}/\beta_{c})\Delta T \)

In this case the separation ratio enters into the diffusion equation. This kind of representation is used by Lücke team (Fütterer and Lücke, 2002). It allows to solve the full solutal-convective problem, when \( \psi = 0 \), without essential changes in the numerical code.

Thus the governing non-dimensional equations become:

\[
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \nabla^2 \mathbf{v} - \text{Gr}(\Theta - c)e, \quad (22)
\]

\[
\frac{\partial \Theta}{\partial t} + \mathbf{v} \cdot \nabla \Theta = \frac{1}{Pr} \nabla^2 \Theta, \quad (23)
\]

\[
\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \frac{1}{Sc} (\nabla^2 c + \psi \nabla^2 \Theta), \quad (24)
\]

\[
\nabla \cdot \mathbf{v} = 0. \quad (25)
\]

Boundary conditions

No slip condition for the velocity at the rigid walls \( \mathbf{v} = 0 \), constant temperatures at the top and bottom while heating from above \( \Theta(z = 0) = 0 \), \( \Theta(z = 1) = 1 \); lateral walls are thermally insulated: \( \partial \Theta/\partial n = 0 \) at \( x = 0;1 \).

Absence of mass flux \( J_c = 0 \) at the impermeable rigid walls gives:

1st choice \( \partial \psi/c - \Theta = 0 \)

2nd choice \( \partial \psi/c + \psi \Theta = 0 \).

The considered system has several very different time scales according to the physical properties of the liquid: the viscous time

\[
\tau_v = L^2/\nu = 70 \text{ s},
\]

the thermal time

\[
\tau_h = L^2/\alpha = 770 \text{ s},
\]

the diffusion time

\[
\tau_D = L^2/D = 1.15 \times 10^5 \text{ s}.
\]

2.4 Numerical technique

Present results are obtained using the presentation of equations according to the 1st choice, Equations (18)–(21). We use a finite-volume formulation in its cell-centres representation based on an explicit single time step marching method. Convergence and grid independence studies were performed by comparing with benchmark solutions in the case of a pure liquid (see Shevtsova et al., 2003). The presence of three very different time scales impose additional conditions on numerical procedure.

To properly resolve the transport phenomena one should perform calculations with a time step smaller then any of the characteristic physical times, i.e., \( \tau < \tau_c \). Nevertheless the calculations should cover a long period of physical time, at least by the order of magnitude the final time should be comparable with diffusion time, \( \tau_{\text{final}} \leq \tau_D \). Since the geometry and test liquid are chosen the heat and mass transfer are controlled by two parameters: \( \psi < 0 \) and \( Ra_s(\text{GR}) \).

3 Results and discussion

The 3D numerical simulations were performed in a cubic cell with \( Pr = 10.85 \), \( Le = 6.7 \times 10^{-3} \) and \( \psi = -0.4 \), hence, \( |\psi/Le| = 60 \). To understand the development of convective instability with time here we present the results only for one value of applied temperature difference which gives \( Ra_s = 6.5 \times 10^5 \).

The existence of several different time scales leads to very fascinating phenomena in liquid mixtures. Finite amplitude convective oscillations in binary mixture with Soret effect were theoretically predicted by Shliomis and Souhar (2000). They claimed that in colloidal mixtures, where diffusion time is much larger than thermal time, the concentration gradients establish so slowly that Soret convection starts before this gradient reaches its stationary value, i.e., for \( Ra < Ra_s^0 \) but \( Ra_s > Ra_s^0 \) (for positive \( \psi \) and heating from below or negative \( \psi \) and heating from above). The increasing fluid velocity mixes up the concentration field, eliminating thereby the driving force of the Soret convection. Thus fluid motion kills itself and the concentration profile returns to the conductive state since the applied Rayleigh number \( Ra_s < Ra_s^0 \). Then the concentration gradient is formed again and the process is repeated. The authors stated that magnetic colloids, with \( |\psi/Le| \) very large (see Eq. 1), perfectly fit these...
requirements. Recently Ryskin et al. (2003) pointed out that convective perturbations do not decay although \(|\psi/Le| > 1\) hence there is no mechanism that drives the system back to the conductive state. The present numerical study shows that the convective oscillations arise in the system as predicted by Shliomis and Souhar (2000) and decay after a few cycle in agreement with Ryskin et al. (2003).

To follow the evolution of heat and mass transport in cubical volume all quantities were recorded at points \(P_1 = \{x = 0.55, y = 0.5, z = 0.84\}\) (near the hot wall) and at \(P_2 = \{x = 0.55, y = 0.5, z = 0.12\}\) (near the cold one), see locations in Figure 1. Evolution with time of vertical velocity, temperature and concentration \((C - C_0)\) scaled by factor \(10^{-4}\) are shown in Figure 2 for \(Ra = 6.5 \times 10^5\) at point \(P_1\) by solid line and at point \(P_2\) by dotted line.

**Figure 2** Time dependence of velocity, temperature and concentration at point \(P_1\) (solid line) and \(P_2\) (dotted line); \(\psi = -0.4, Ra = 6.5 \times 10^5, Pr = 10.85, Le = 6.7 \times 10^{-3}\).

The linear temperature field is established quickly after imposition of a temperature difference \(\Delta T\). Due to negative Soret effect the heavier liquid slowly rises up to the hot wall, see lower plot in Figure 2. Induction period, during which the system remains motionless, \(V_z = 0\) at upper plot, is significantly smaller than diffusion time \(\tau_D\) (by 26 times), although it lasts six thermal times \(\tau_{th}\). At some moment strong motion arises and faded, velocity rises up from zero to a sharp peak at \(t = 109\) min. Note, that motion starts at upper part (at \(P_1\)) earlier than near the bottom (at \(P_2\)). The positive sign of the velocity along the centreline and the fact that the velocity is larger at \(P_1\) indicate that the heavier hot liquid starts to move down along the wall and the cold liquid is drawn up in the central part. Thus, the columnar vertical structure of the flow is formed. The heavier liquid is washed away from the hot wall and it will never achieve the same level later in time. The first splash is followed by a few more pulses of convection, but not so powerful. Note, that the concentration at point \(P_1\) achieve maximum at time moment, when the velocity starts to grow. During the following oscillations the component separation will lead to other temporal concentration maxima, but they never exceed 40% of this first maximum.

The concentration and temperature profiles along \(z\)-axis at different time moments are shown in Figure 3 in the middle of the cell along the line \(l_1 = \{y = 0.5, x = 0.3\}\) (solid line) and along the line \(l_2 = \{y = 0.5, x = 0.3\}\) (dashed line), (see locations of \(l_1\) and \(l_2\) in Fig. 1). The vertical dashed lines in Figure 2 show the moments at which the snapshots of flow fields have been done. The temperature field visibly changes only during the first oscillation, so to amplify the effect the deviations of the temperature profile from linear in Kelvin (K) are shown in Figure 3 (on the left side). They are determined as

\[
\delta T = (T - T_0) + \Delta T(z/L).
\]

The first snapshot (Fig. 3(a)) at the appearance of the motion (first vertical line in Fig. 2 at \(t = 75\) min) demonstrates that both the temperature and concentration are only functions of \(z\), i.e., solid and dashes lines are identical. However if the temperature is a linear function of \(z\) \((\delta T = 0)\) the concentration exhibits non-linear distribution along \(z\)-axis. According to the theory (Shliomis and Souhar, 2000) the diffusion skin-layer depth

\[
\delta = 4\sqrt{\frac{\Delta T(z/L)}{\pi}}
\]

at the setting of the convection should remain thinner than a half of the fluid depth. Although the authors pointed out that this condition might not be valid for molecular solution, in our water-isopropanol system this condition is suitable, i.e., \(\delta = 0.44L\). The second snapshot (Fig. 3(b)) at \(t = 90\) min shows that \(C\) and \(\delta T\) profiles along \(l_1\) and \(l_2\) start to diverge first near the hot wall. There are no horizontal gradients near the cold wall. So, it one more indication that convection starts near the hot wall where the heavy liquid has accumulated. If a dense viscous layer stays on top of a less dense viscous layer, the lower layer will become unstable and form a Rayleigh Taylor instability in isothermal case. Here in non-isothermal case the mechanism of instability is more complex although there are some similarities.

Figure 3(c) corresponds to the peak of velocity at \(t = 109\) min when the convective motion occupies entire cell. The maximal value of vertical velocity depends on the value of \(Ra\), but can be roughly estimated in following way: the growth of the velocity lasts until non-linear term \(\nabla \cdot \mathbf{v}\) becomes comparable with viscous term \(\nu \nabla^2 \mathbf{v}\) in Equation (18).
In this consideration only vertical component $V_z$ can be taken into account, and it results in $V_z^* \sim \nu L = 140 \times 10^{-6}$ m/s. The calculated value for $Ra_s = 6.5 \times 10^5$ is in reasonable agreement with $V_z^*$ by the order of magnitude as $V_z = 35 \times 10^{-6}$ m/s (see Fig. 2). They differ only by factor four. Figure 3(d) shows $C$ and $\delta T$ fields at the time when the velocity arrives to the minimal value after the flash ($t = 127$ min). At this time contrary to Figure 3(b) the largest horizontal gradients of the physical quantities occur near the cold wall.
The oscillations decay with time, but the system never arrives to the initial motionless state even on long time scale. The dependencies, shown in Figure 2, were calculating much longer in time. The profiles of $C$ and $\delta T$ are shown in Figure 3(e) at $t = 6.81$ h, where the velocity is quite small. Along with developed concentration boundary layer near the hot and cold walls the horizontal gradients of $C$ and $\delta T$ do exist in the cell, which are absent at the conductive state.

The isolines of concentrations in $xz$-plane are given in Figures 4–6 for $Ra_s = 6.5 \times 10^5$ at some of described time instants. This cross section is shown by shadow in Figure 1. The solid lines correspond to the $C$ levels above initial value, $C_0 = 0.9$, and the dotted lines shows regions with $C \leq C_0$. The levels of concentration were chosen exactly the same in all Figures 4–6. Figure 4, being in agreement with Figure 3(b), underlines that in the upper part of the cell the heavy liquid starts to move and points of inflection of isolines are appeared somewhat at $x \approx 0.18$ and $x \approx 0.82$. The convective motion did not yet develop at the lower part of the cell. This delay in time is clearly seen in velocity plots at Figure 2.

Figure 4 Isolines of concentration at $t = 90$ min

![Figure 4](image1)

Figure 5 Isolines of concentration at $t = 109$ min

![Figure 5](image2)

The concentration field in Figure 5 corresponding to the peak time ($\tau_p = 109$ min) shows that the flow pattern has a finger (or columnar) type when cold and lighter liquid is drawn up (inside limited horizontal extension) to the hot wall. By the time, when velocity after the first flash arrives to the minimum, the binary mixture is well mixed, see Figure 6. The concentration field is almost uniform in comparison with the previous snapshot.

We have found a remarkable feature in the evolution of the flow pattern with time. The temperature and concentration fields in Figures 4–8 are symmetrical with respect to the centreline $l_1$ until the observation time is less than 25% of the diffusion time, i.e., $t = 7$ h $= \tau_p/4$. Later in time the symmetry gets broken, but the system maintains stochastic oscillations. The isolines of the concentration and the temperature fields just before breaking the symmetry are shown in Figures 7 and 8. In the central part of the cell the concentration has almost the same value as at initial point, $C = C_0$. Closer to the hot and cold walls the small accumulation of heavier and lighter components take place. The non-uniformity of temperature is extremely small, as the levels of isolines are $\delta T \approx 7.0 \times 10^{-3}$ K while $\Delta T = 10$ K and $\delta T < 0$.

Figure 6 Isolines of concentration at $t = 127$ min

![Figure 6](image3)

Figure 7 Isolines of concentration at $t = 6.81$ h

![Figure 7](image4)
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Figure 8 Isolines of $\delta T$ in K at $t = 6.81$ h. All drawn isolines are negative

The snapshot of the velocity field at this time moment is shown by arrows in Figure 9 at the same $xz$-plane. The concentration is represented by colours. Obviously, that the flow pattern has a 3D structure, consisting from a few vorticities. At $xz$-plane the liquid is preferably moving up, so at other planes it will move downward.

Figure 9 (Colour online). The snapshot of the velocity field at $t = 6.81$ h. The colours show the variation of the concentration

Let us look insight the mechanism of instability. Heating from above, the imposed temperature gradient contributes a stabilising density gradient and Soret effect generates a destabilising concentration gradient. Let us estimate the gravity dependent terms in the momentum Equation (12), which are responsible for convection. Taking also into account (Eq. 2) one may write

$$\begin{align*}
-\bar{g}\beta_r T' + \bar{g}\beta_C C' &= -\bar{g}\beta_r T' \left[ 1 - \frac{\beta_C}{\beta_r} \frac{C'}{T'} \right] \\
&= -\bar{g}\beta_r T' \left[ 1 + S_r C_0 \left( 1 - C_0 \right) \frac{\beta_C}{\beta_r} \right] \\
&= -\bar{g}\beta_r T'[1 + \psi].
\end{align*}$$

(26)

Although $\psi$ is negative, $\psi = -0.4$, the expression (Eq. 26) for the buoyancy force maintains the same sign as $[1 + \psi]>0$. Thus it is not the temperature dependence of the density which is responsible for driving convection like in the classical case.

The reason is that the concentration fluctuations in liquids are much more dangerous for the instability of the system than thermal fluctuations because of their relatively long life time, $\tau_0 >> \tau_0$. Suppose that a fluid particle is perturbed upward from a cooler region (heating from above). This element is denser (because of the lower temperature) and lighter (because of lower concentration) than the nearby fluid. Its temperature will rapidly becomes equal to that of the surrounding fluid. The concentration is not yet equalised to that of the surrounding. Thus this less dense element will rise further. This convective instability occurs even though the overall density is not adverse as in the usual Benard problem.

4 Conclusions

We have studied an instability which occurs when a mixture with negative Soret effect is heated from above. 3D numerical simulations were performed in a cubic cell filled with a mixture of water (90%) and isopropanol (10%). This instability has a number of exciting features. The motion arises after a certain latency time, which is much smaller than diffusion time but much larger than the thermal time. The first splash is followed by a few more pulses of convection, but not so powerful. The amplitude of convection decays in time. For very long times, the flow pattern exhibits incessant stochastic motion.

Certain characteristic of this instability were theoretically predicted for colloidal suspension (Shliomis and Souhar, 2000). The present results demonstrate that some results of linear stability analysis are valid for wider class of liquids, than it was foreseen by authors. At the early stage of time history many aspect of the theory are supported by our calculations in water based mixture, e.g., the time of spreading of the concentration boundary layer, the evaluation for the velocity peak at first oscillation.

Recently the similar problem was intensively investigated in experiments with colloidal solutions (Cerbino et al., 2002; Mazzoni et al., 2004). Although our study is performed in finite size system and for water solution the many features of Soret driven instability are similar to those observed in extended layers with colloidal and polymer solutions (Cerbino et al., 2002; Mazzoni et al., 2004; Sakurai et al., 2001; La Porta and Surko, 1998).
Thus the mechanism of instability appears to be similar and close to mechanism of salt fingering. Due to the large differences between viscous, thermal and diffusion times the system has a tendency to fingering buoyant instabilities.

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