Determination of the stability boundary of a two-layer system of miscible liquids with linear diffusion laws

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Abstract. The authors consider the problem of determining the stability boundary of a two-layer system of miscible liquids placed in a gravity field. Liquids are aqueous solutions of non-reacting substances with different diffusion coefficients, which are linear functions of concentrations. At the very beginning of the evolution, the solutions are separated from each other by an infinitely thin horizontal contact surface. Such a configuration can be easily realized experimentally, although it is more difficult for theoretical analysis since the base state of the system is non-stationary. Once brought into contact, the solutions begin to mix penetrating each other and creating conditions for the development of the double-diffusive instability since the initial configuration of the system is assumed to be statically stable. The problem of the convective instability of a mixture includes the equation of motion written in the Darcy and Boussinesq approximations, the continuity equation, and two transport equations for the concentrations. We apply the linearization method suggested by Wiedeburg (1890) to find a closed-form solution to the non-stationary base state problem including concentration-dependent diffusion laws for species. We derive analytical expressions for neutral stability curves and study corrections introduced by nonlinear diffusion to the stability analysis.

1. Introduction

As it is known, the individual characteristics of each liquid depend on a set of physical constants, the main of which include the coefficients of viscosity, thermal conductivity, surface tension, and diffusion of a solute. In this work, we investigate the effect of the concentration-dependent diffusion (hereafter CDD) in multicomponent aqueous solutions on the convective stability of the mixture. Until recently, almost all literature devoted to the stability of both reacting and non-reacting solutions assumed that the diffusion coefficients of dissolved substances are constant. We can find rare examples where researchers study the CDD effect only in reaction-diffusion problems (for example, [1, 2]). In that works, the medium is considered to be motionless from the very beginning of the evolution. In fact, experts know that the diffusion coefficient of any substance in a solution depends on its concentration. However, researchers prefer to ignore this dependence when solving specific problems, believing that its effect is too weak. In the works [3, 4], for the first time, we have considered the problem of convective stability, in which the...
diffusion coefficients of substances depended on their concentrations. The development of the instability in a two-layer system of miscible reacting liquids placed in a vertical Hele-Shaw cell has been studied experimentally and theoretically. We found that the emergence of macroscopic fluid motion is associated with a new instability mechanism named the CDD convection. This instability is one of the varieties of double-diffusion convection, which includes such classical examples as double-diffusive (DD) instability and diffusive-layer convection (DLC).

In this work, we assume that there are no chemical reactions. We consider the stability problem in the framework of the DD instability [5, 6]. It enables us to simplify the mathematical formulation of the problem and to study the effect of nonlinear diffusion on the stability of a mixture. If the diffusion coefficients of substances are constant, then the base state problem has an exact solution [7]. In the general case of the concentration-dependence of the diffusion coefficients, the stability problem can be solved only numerically [3, 4]. However, in the case of linear diffusion laws, as we found out, it is possible to derive a quasi-analytical solution. In this paper, we use the diffusion equation linearization method proposed by the German physicist Otto Wiedeburg in 1890 [8]. He was not familiar with the concept of hydrodynamic stability and used this technique to calculate the concentration profiles of single aqueous solutions of various substances and compared them with the data of his experiments. Besides, the phenomenon of double-diffusive instability has been discovered only 70 years after his publication. In this work, we apply the Wiedeburg method to study the stability of binary mixtures, find a closed-form solution for the stability problem and investigate the CDD effect on the system stability.

Figure 1. Schematic representation of the two-layer miscible system at the very beginning of the evolution

2. Mathematical formulation
We consider a two-layer system of two miscible solutions, which are located one above the other in a gravity field (Fig. 1). Let us assume that both solutions are aqueous and that the solutes are heavier than pure water. We assume that the concentrations of substances at the very beginning are such that there is a stable density stratification of the medium. It excludes the onset of the Rayleigh-Taylor instability.

The aqueous solutions are spaced apart at the initial time. Let the variables $A$ and $B$ denote, respectively, the concentration of the solution above and below the initial contact surface separating the liquid. Substances dissolved in water are chemically inert, and the entire system as a whole is in isothermal conditions. We assume that the evolution of the system can be described in the framework of a two-dimensional problem. Let the line $x = 0$ defines the position of the initial contact surface between the layers, and the $x$-axis is directed upward against gravity. Let us further assume that the fluid motion is determined by Darcy's law, which means that the inertial terms in the Navier-Stokes equation are neglected. In the experiments, this means that we place the system either in a porous medium with low
permeability or in a Hele-Shaw cell with a narrow gap between the wide sidewalls. The use of Darcy’s law is not essential for further analysis, but it significantly simplifies the formulation of the problem. The description of the behavior of the liquid itself is not essential for this work, in which the focus is on the processes of diffusion of dissolved substances.

We choose the following quantities as the units of measurement for length, time, velocity, pressure, and concentration

\[ \lim_{0}^{A} gK_{A}^{\beta A}, \quad \frac{D_{A0} v}{gK_{A}^{\beta A} A_{\text{lim}}^{2}}, \quad \frac{gK_{A}^{\beta A} A_{\text{lim}}^{2}}{\nu}, \quad \frac{\eta D_{A0}}{K}, \quad A_{\text{lim}}, \quad B_{\text{lim}}, \]

respectively. Here, we use the standard notation for quantities [3, 4]. Thus, the dimensionless equations of convection of an incompressible fluid, written in the Darcy approximation, for the problem under consideration have the form:

\[ \nabla \cdot \mathbf{v} = 0, \quad \mathbf{v} = -\nabla p - (A + RB) \mathbf{n} = 0, \quad \frac{\partial A}{\partial t} + \mathbf{v} \cdot \nabla A = \nabla \cdot ((1 + \alpha A) \nabla A), \quad \frac{\partial B}{\partial t} + \mathbf{v} \cdot \nabla B = \delta \nabla \cdot ((1 + \beta B) \nabla B), \]

\[ x > 0: \quad A(0, x, y) = A_0, \quad B(0, x, y) = 0, \quad \mathbf{v} = 0; \quad x \leq 0: \quad A(0, x, y) = 0, \quad B(0, x, y) = B_0, \quad \mathbf{v} = 0, \]

where \( \mathbf{v} \) is the fluid velocity, \( p \) is the pressure, \( \mathbf{n} \) is the unit vector in the direction of the \( x \)-axis. In problem (1-6), we obtain several dimensionless parameters that determine the evolution of the system

\[ R = \frac{\beta B_{\text{lim}}}{\beta A_{\text{lim}}}, \quad \delta = \frac{D_{A0}}{D_{B0}}, \quad \alpha = \frac{\alpha A_{\text{lim}}}{A_{\text{lim}}}, \quad \beta = \frac{\beta B_{\text{lim}}}{B_{\text{lim}}}, \quad A_0 = \frac{A_0}{A_{\text{lim}}}, \quad B_0 = \frac{B_0}{B_{\text{lim}}}, \]

which are, respectively, the Rayleigh number ratio, the diffusion coefficient ratio, the linear corrections to the diffusion coefficients of species, the initial concentrations of species.

3. Base state solution

The problem (1-6) has an unsteady solution, which describes the diffusion processes. The elements of the fluid are not involved in macroscopic motion. We will call this state a base state solution. Let us assume further that the fluid velocity equals zero in Eq. (2) and that the concentration fields depend only on \( x \)-coordinate and time: \( A_0(x,t), B_0(x,t) \). The resulting time-dependent nonlinear equations are

\[ \frac{\partial A_0}{\partial t} = \frac{\partial^2 A_0}{\partial x^2} + \frac{\alpha}{2} \frac{\partial^2 A_0}{\partial x^2}, \quad \frac{\partial B_0}{\partial t} = \frac{\partial^2 B_0}{\partial x^2} + \frac{\beta}{2} \frac{\partial^2 B_0}{\partial x^2}, \]

should be complemented with the boundary and initial conditions.

In the case \( \alpha = 0, \beta = 0 \), Eqs. (8,9) become linear, and the solution to the problem is well known [7]:
A(t, x) = \frac{1}{2} A_0 \left[ 1 + \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\xi^2} d\xi \right] \left[ 1 - \frac{2}{\sqrt{\pi}} \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) \right] = \frac{1}{2} A_0 \text{erfc} \left( \frac{x}{2\sqrt{t}} \right),

(10)

where the solution is presented for one substance.

To solve problem equations (8,9) for the general case, Wiedeburg has proposed the following technique [8]: the solution (10) is substituted into the last term (8) as an approximation of the partial differential problem that can be solved exactly (the only solution for the concentration A is shown):

\[
A(t, x) = \frac{1}{2} A_0 \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) + \alpha A_0 \left[ 1 - \frac{1}{4} \alpha A_0 \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) \right] + \frac{1}{4} \alpha A_0^2 \left[ \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) - \frac{2}{\sqrt{\pi t}} e^{\frac{x^2}{4t}} \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) \right] + \frac{1}{8} \alpha A_0^3 \left[ 1 + \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) \right],
\]

(11)

We define the following dimensionless quantity

\[
\Delta \rho(t, x, y) = A(t, x, y) + RB(t, x, y),
\]

(12)

to characterize the distribution of species at any moment. Analysis of the density (12) along the vertical coordinate is key to the stability analysis. By using the solution (11), we obtain:

\[
\Delta \rho(t, x) = \frac{A_0}{2} \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) + \frac{R B_0}{2} \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) + \frac{\alpha A_0^2}{8} \left[ \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) - \frac{2}{\sqrt{\pi t}} e^{\frac{x^2}{4t}} \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) \right] + \frac{R B_0}{8} \beta \left[ \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) - \frac{2}{\sqrt{\pi t}} e^{\frac{x^2}{4t}} \right].
\]

(13)

where the part of the expression that does not depend on the corrections of the diffusion coefficients is represented by the first two terms.

4. Neutral curve for convective instability

In this paper, we assume that the initial configuration of the system is statically stable: \( A_0 < RB_0 \). Double-diffusive instability requires a finite amount of energy to maintain the growth of disturbances. If the base state implies that the liquid in the mechanical equilibrium, the instability can be caused by the potential energy of one of the components. This potential energy strongly depends on how different the diffusion coefficients of the substances. Immediately after the start of mixing, the center of gravity of the mixture tends to be lower, leading to the release of kinetic energy, which results in the onset of the convection. If the layer with the fast component is initially at the bottom, then the DD instability develops:

\[ \varphi R > 1, \quad \delta > 1, \]

(14)

where \( \varphi = B_0/A_0 \). Thus, \( \varphi R \) and \( \delta \) are the governing parameters for the stability problem.

At the very beginning of evolution, the density profile \( \Delta \rho \) has no extrema, and the derivative of \( \Delta \rho \) along the coordinate \( x \) is everywhere negative. Consequently, the onset of the instability can be detected.
by the occurrence of an extremum on the density profile (13). If the CDD effect is not taken into account,
then we obtain the following expression:

\[
\frac{\partial \Delta \rho}{\partial x} \bigg|_{x=0, \beta=0} = \frac{A_0 e^{-\alpha x^2/4\pi t}}{2/\sqrt{\pi t}} - R \frac{B_0 e^{-\beta x^2/4\pi t}}{2/\sqrt{\pi t}},
\]

which we equate to zero, and after simple transformations, we get:

\[
x^2 = \frac{4\delta t}{1-\delta} \ln \frac{\phi R}{\sqrt{\delta}}.
\]

Taking into account that the left side of (16) is always positive, we obtain the following conditions for
the onset of instability (provided that (14) is fulfilled):

\[
\delta > \phi^2 R^2.
\]

This result is well-known in the literature on the instability of the DD instability in a two-layer system
(see, for example, [9]). The neutral stability curve for this case is shown in Fig. 2 with a solid line.

Let us now consider the influence of the CDD effect on the convective stability. We take the total
derivative of the density (13) with respect to the coordinate \(x\) and collect terms with the same powers in
time:

\[
\frac{\partial \Delta \rho}{\partial x} = \frac{1}{\sqrt{\pi t}} \left[ \frac{A_0}{2} + \frac{\alpha A_0^2}{4} - \frac{3\alpha A_0^2}{8} \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) e^{-\alpha x^2/4\pi t} - R \left( \frac{B_0}{2} + \frac{\beta B_0^2}{4} + \frac{3\beta B_0^2}{8} \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) e^{-\beta x^2/4\pi t} \right) \right] +
\]

\[
+ \frac{1}{\pi t} \left[ \frac{\alpha A_0^2}{8} x e^{-\alpha x^2/8} - \frac{\beta B_0^2}{8} x e^{-\beta x^2/8} \right]
\]

\[
+ \frac{1}{\pi t/\sqrt{\pi t}} \left[ \frac{\pi \alpha A_0^2}{16} x^2 \text{erfc} \left( -\frac{x}{2\sqrt{t}} \right) e^{-\alpha x^2/4\pi t} - \frac{\beta B_0^2}{16} x^2 \text{erfc} \left( \frac{x}{2\sqrt{t}} \right) e^{-\beta x^2/4\pi t} \right].
\]

To find the condition of the neutral stability, we must equate (18) to zero. Let us assume that the
instability develops over long observation times. This assumption is quite justified since the characteristic
diffusion processes are one of the slowest among the processes of heat and mass transfer. It means that we
must take into account in (18) only terms proportional to \(t^{1/2}\). Then instead of (16), we get

\[
x^2 = \frac{4\delta t}{1-\delta} \ln \left[ \frac{\phi R}{\sqrt{\delta}} \left( \frac{1}{4} \beta B_0 \right) \right].
\]
Taking into account that the left-hand side of (19) is always positive, we obtain the following condition for the instability onset of instability:

\[\delta > \phi^2 R^2 \left( 1 + \frac{1}{4} (\alpha A_0 - \beta B_0) \right)^2.\]  

(20)

The formula (20) gives the correction to the neutral curve (17) in the main order. One can see that the CDD effect gives the maximum effect if the components of the binary mixture depend on the concentration in different ways, i.e. the correction factors \(\alpha\) and \(\beta\) have different signs (Fig. 2).

5. Conclusion

Generally, the problems with nonlinear diffusion of matter are hard to consider since they can be solved only numerically, even for the simple diffusion laws. Additional complicating factor is the assumption that the initial state of the system includes a two-layer system, where the solutions are separated in space by a contact surface. In the course of the evolution of the system, a non-stationary process of mixing of solutions begins. Thus, the base state of the system is an irreversibly changing state of the medium. In this paper, we apply Otto Wiedeburg’s linearization method to obtain time-dependent expressions for the concentration of substances and the density of the medium. We use these expressions to investigate the onset of double diffusion instability. As a result, we obtain analytical formulas for neutral curves of double diffusion instability and study the effect of the concentration-dependent diffusion on the convective stability of the mixture.

Acknowledgments

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