The forgotten effect in liquid thermal diffusion columns

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Abstract. The influence of the density composition dependence on the vertical separation in a liquid thermal diffusion column, the so-called forgotten effect, is analysed. We obtain an exact solution of the basic hydrodynamic equations. The results show that the Horne approximation is valid for small values of the separation parameter. The possibility of steady flow reversions in mixtures with negative Soret coefficients is discussed.

1. Introduction

In the thermal diffusion column proposed by Clusius and Dickel (1938) the elementary thermal diffusion separation is enhanced by coupling it with the convection currents along the column. The phenomenon can be described as follows: a horizontal temperature gradient applied to the initially homogeneous fluid gives rise to a horizontal composition gradient. In the gravitational field convective currents arise and when the steady state is reached a vertical composition gradient is built between the top and the bottom of the apparatus.

The experimental study of the thermal diffusion effect yields the Soret coefficient, a quantity of considerable theoretical and practical importance. In particular it is a good source of information about intermolecular forces and a relevant parameter in the analysis of the hydrodynamic instabilities of two-component fluid layers.

Soret coefficients can be drawn in principle from column steady separation measurements. In this respect a suitable relationship between these quantities has been derived for the case of gaseous mixtures (Saviron *et al* 1969, 1971). In order to obtain a similar relation for liquids it is necessary to do without the pure fluid assumption in the column theoretical description.

In the theory of the column derived by Jones and Furry (1946) the composition dependence of the fluid properties is ignored. However, it seems that in particular the effect of the density composition dependence on the separation—the so-called forgotten effect—could be significant.

Unfortunately the inclusion of this dependence gives rise to the coupling of the basic hydrodynamic equations. Some approximation methods of solution have been used and it appears that for small values of the relevant separation parameter the expression derived by Horne and Bearman (1968) correctly gives the forgotten effect.

The purpose of this paper is to present a simple calculation of the forgotten correction. By assuming the separation parameter and the vertical composition gradient to be constant all over a column cross section, the hydrodynamic equations uncouple and then an exact solution can be found. The first assumption is always

verified because of the small horizontal separations and the second is one of the standard assumptions in column theory.

The solution obtained enables us to check the validity of the approximate expressions and to analyse the possibility of convective flow reversions in mixtures with negative Soret coefficients.

2. Theory

We consider a layer of a two-component liquid mixture between two parallel vertical plates which are placed at $x = \pm L$. The plates are supposed to be maintained at the temperatures T_1 and T_2 $(T_2 > T_1)$. If the temperature difference is not too large the steady motion of the fluid is governed by the fundamental equations in the Boussinesq approximation as follows

$$\nabla \cdot v = 0 \tag{1}$$

$$(v \cdot \nabla)v = -\rho_0^{-1}\nabla p + \rho g/\rho_0 + \nu\nabla^2 v \tag{2}$$

$$(v \cdot \nabla)T = \chi\nabla^2 T \tag{3}$$

$$(v \cdot \nabla)c = -\nabla \cdot J \qquad \text{with} \qquad J = D(sc\bar{c}\nabla T - \nabla c) \tag{4}$$

$$\rho/\rho_0 = 1 - \alpha(T - T_0) - \beta(c - c_0) \tag{5}$$

where v, p and T are the local velocity, pressure and temperature, respectively; c and J are the mass fraction and the diffusive mass flux of the less dense component; g is the gravitational acceleration; s is the Soret coefficient which is considered to be positive when the less dense component diffuses towards the hot region of the fluid; ρ is the density and ν, χ and D are, respectively, the coefficients of kinematic viscosity, thermal diffusivity and ordinary diffusion. α and β in the equation of state (5) are the coefficients of thermal expansion and density variation with composition. Note that $\beta > 0$. Finally, $\bar{c}$ stands for $(1 - c)$ and the subscript indicates that the affected quantities are to be evaluated at the reference state.

For a layer with a large aspect ratio we can neglect end effects, searching for a steady field in the form

$$v = \{0, 0, w(x)\} \qquad T = T(x) \qquad c = c(x, z) \tag{6}$$

where z is the coordinate along the layer and w the corresponding component of v. If, as usual in column theory, we further neglect vertical diffusion, equations (1)–(4) are reduced to

$$\nu\frac{d^2 w}{dx^2} = \frac{1}{\rho_0}\frac{dp}{dz} + \frac{\rho}{\rho_0}g \tag{7}$$

$$\frac{d^2 T}{dx^2} = 0 \tag{8}$$

$$w\frac{\partial c}{\partial z} = D\frac{\partial}{\partial x}\left(\frac{\partial c}{\partial x} - sc\bar{c}\frac{dT}{dx}\right). \tag{9}$$

These equations are to be solved subject to the boundary conditions at the walls

$$w(L) = w(-L) = 0 \tag{10}$$

$$T(-L) = T_1 \qquad T(L) = T_2 \tag{11}$$

$$J_x(L) = J_x(-L) = 0 \tag{12}$$

also taking into account the conditions indicating that the stream is closed:

$$\int_{-L}^{L} w \, dx = 0 \tag{13}$$

$$\int_{-L}^{L} wc \, dx = 0. \tag{14}$$

Before going on we shall introduce the scale factors L and $g\alpha(T_2 - T_1)L^2/2\nu$ for length and velocity, respectively, denoting with starred symbols the corresponding dimensionless variables. Furthermore it is convenient to introduce, as customary in separation problems, the auxiliary function

$$G(x^*) = \frac{1}{S+1} \int_{-1}^{x^*} w^* \, dx^* \tag{15}$$

where S is the so-called separation parameter (Schechter *et al* 1972) defined by

$$S = \beta s c \bar{c}/\alpha. \tag{16}$$

As the horizontal separations are of the order of $c\bar{c}(T_2 - T_1)/T_0$ and therefore very small, we shall assume the separation parameter to be constant all over a column section. Note that $S > 0$ for positive Soret coefficients.

Differentiating (7) with respect to x, taking into account equations (5), (8), (9), (11) and (12) and assuming the vertical composition gradient to be independent of x, we find for the function $G(x^*)$ the fourth-order differential equation

$$d^4 G/dx^{*4} = -RG - 1. \tag{17}$$

The quantity R is a Rayleigh number based upon the vertical composition gradient

$$R = \beta \delta g L^4/\nu D \tag{18}$$

where δ stands for $\partial c/\partial z$. Note that $R > 0$ for $\delta > 0$, that is, when as usual the less dense component migrates to the top of the layer.

Equation (17) is to be solved subject to the boundary conditions (10) and (13) which, in terms of the function $G(x^*)$, are

$$G(1) = G(-1) = G'(1) = G'(-1) = 0 \tag{19}$$

where G' stands for the x^* derivative of $G(x^*)$. The solution of (17) and (19) yields the convective motion.

In order to determine the composition gradient δ, we shall integrate (9) with respect to x using conditions (13) and (14). We find

$$-S\Psi(R) = 1 + S \tag{20}$$

where

$$\Psi(R) = \frac{\int_{-1}^{1} G(x^*) \, dx^*}{R \int_{-1}^{1} G^2(x^*) \, dx^*}. \tag{21}$$

Once the function $G(x^*)$ has been calculated, these equations allow us to determine R and therefore the vertical composition gradient.

For the case in which the density composition dependence is ignored, i.e. $\beta = R = S = 0$, the above equations lead to the following known expression for the corresponding vertical composition gradient

$$\delta_0 = \frac{504}{(2L)^4} \frac{\nu s D c \bar{c}}{\alpha g}. \tag{22}$$

In the general case, taking into account that R can be written in terms of δ_0 as

$$R = \frac{63}{2} \frac{\delta}{\delta_0} S \tag{23}$$

equation (20) gives the ratio δ/δ_0 as a function of the separation parameter. This ratio represents the correction to δ_0 due to the forgotten effect.

3. Results and conclusions

According to the previous equations, to determine δ/δ_0 we must first calculate the function $\Psi(R)$. Since the differential equation (17) has two solutions depending on the sign of R, we find for $R > 0$, i.e. $\delta > 0$

$$\Psi(R) = \frac{4\alpha_2(\alpha_2\mu - \alpha_1)}{5\alpha_1\alpha_2 - 4\mu(\alpha_2^2 + \alpha_3)} \tag{24}$$

where

$$\mu^4 = \tfrac{1}{4}R$$

$$\alpha_1 = \cosh 2\mu - \cos 2\mu \qquad \alpha_2 = \sinh 2\mu + \sin 2\mu \qquad \alpha_3 = \sinh 2\mu \sin 2\mu$$

and for $R < 0$, i.e. $\delta < 0$

$$\Psi(R) = \frac{2\beta_1(\beta_1\gamma - 2\beta_3)}{5\beta_1\beta_3 - \gamma(\beta_2 + 2\beta_1^2)} \tag{25}$$

where

$$\gamma^4 = -R$$

$$\beta_1 = \sinh \gamma \cos \gamma + \cosh \gamma \sin \gamma \qquad \beta_2 = \sinh^2 \gamma + \sin^2 \gamma \qquad \beta_3 = \sinh \gamma \sin \gamma.$$

By using (24) and (25), from (19) we can figure out numerically δ/δ_0 as a function of S. Then some interesting results are obtained. In the first case, $\delta > 0$, (19) has solutions only for $S > 0$. Thus, for positive Soret coefficients the less dense component migrates to the top of the column. On the other hand for $\delta < 0$, (19) has solutions only when $S < 0$ and hence for negative Soret coefficients the less dense component sinks towards the bottom.

From these results we may conclude that there are no solutions with $S < 0$, $\delta > 0$. These solutions would obviously correspond to a reversion of the convective flow. Although some earlier experiments conducted in a column connected with reservoirs at the ends showed such a reversion it seems that it was due to density changes in the reservoirs (Tyrrell 1961). More recent experiments (Johnson and Beyerlein 1978) performed in a carefully constructed column closed at both ends do not exhibit any steady reversion in agreement with our theoretical predictions.

The full curve in figure 1 shows the obtained values of δ/δ_0 as a function of S. As can be seen, the forgotten contribution to the vertical separation is always small.
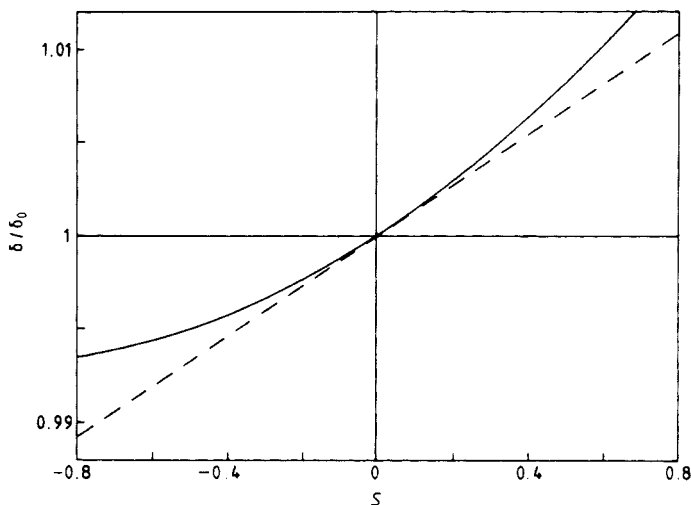

Figure 1. The forgotten correction δ/δ_0 as a function of the separation parameter $S = \beta sc\bar{c}/\alpha$.

A simple relation between δ/δ_0 and S can be derived by expanding the function $\Psi(R)$ in powers of R. Then after tedious but straightforward calculations we obtain from (19) the following linear approximation

$$\frac{\delta}{\delta_0} = 1 + \frac{19}{2 \times 13 \times 55} S. \tag{26}$$

This expression coincides with the one given by Horne and Bearman (1968) and is represented as the broken curve in figure 1. As can be appreciated, (26) can be confidently used without restrictions in practice on S for the determination of the Soret coefficient of a liquid mixture from column steady separation measurements.

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