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# Technical Note

# Marangoni instability of a layer of binary liquid in the presence of nonlinear Soret effect

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## 1. Introduction

Although the Soret effect induces only small chemical separations, its influence on the variations of physical parameters may be larger than the influence of the thermal gradient from which it results. The effect has been recognized and extensively studied in the Rayleigh–Bénard problem for instabilities generated by density fluctuations [1–4]. In the same way that for the mixture density, the Soret effect may influence significantly the surface tension variations in the presence of a temperature gradient. The interaction between thermocapillary and concentration-capillary mechanisms for promoting motion in binary mixture fluids has motivated many authors to study the Marangoni–Bénard instability in the presence of the Soret effect and important similarities with the Rayleigh–Bénard convection have been evidenced [5].

In this paper we aim to study the influence of the nonlinear Soret effect on the stationary Marangoni–Bénard stability conditions in a binary mixture layer with a flat free surface. The reason for our analysis is the recently recognized important effect of the nonlinear Soret diffusion on morphological stability [6].

From the non-equilibrium thermodynamics [7], the flux of solute in the presence of concentration and temperature gradients can be written as

$$\mathbf{J}_{\mathrm{C}} = -\rho D_{\mathrm{c}}(\nabla c + \tilde{S}_{\mathrm{T}}\nabla T), \tag{1}$$

where $c$ is the concentration of one component of the mixture, $T$ the temperature, $\rho$ the mixture mass density, $D_{\mathrm{c}}$ the isothermal diffusion coefficient. The parameter $\tilde{S}_{\mathrm{T}}$ is a coefficient that quantifies the Soret effect. For the latter several expressions are used in the literature. The most used assumption is that $\tilde{S}_{\mathrm{T}}$ does not depend on concentration and this corresponds to linear Soret effect. For dilute solutions however the thermodiffusive contribution to the mass flux is usually considered to be proportional to the concentration. This dependence is observed also in concentrated mixtures where significant variations with composition of the Soret effect are observed in the measurements, including a sign change at intermediate concentrations [5].

To face most situations that can be encountered in metallic and semi-conductor melts as well as in organic liquid solutions, the term $\tilde{S}_{\mathrm{T}}$ should be considered as a function of $c$. In terms of the thermodynamics of irreversible processes, the dependence of the thermodiffusion flux on the concentration makes expression (1) nonlinear. To investigate the possible effects of such a nonlinear dependence, here it is assumed, after [6], $\tilde{S}_{\mathrm{T}}$ to be approximated by

$$\tilde{S}_{\mathrm{T}} = S_{\mathrm{T}}(\beta_0 + \beta_1 c), \tag{2}$$

where $S_{\mathrm{T}} = D_{\mathrm{T}}/D_{\mathrm{c}}$ is the Soret coefficient, $D_{\mathrm{T}}$ is the thermodiffusion coefficient, and $\beta_0$ and $\beta_1$ are constant. The usual linear approximation of the total solute flux in a mixture of mean concentration $c_0$ is recovered by putting $\beta_0 = c_0(1-c_0)$ and $\beta_1 = 0$ into (2) and (1). For dilute solutions, $\beta_0 = 0$ and $\beta_1 = 1$. In the present study the coefficient $\beta_0$ is taken to be positive and $\beta_1$ assumes both signs. The Soret coefficient may have either positive or negative values.

Neglecting the small contribution of the Dufour effect [7], the traditional Fourier law $\mathbf{J}_{\mathrm{Q}} = -k\nabla T$ holds for the heat flux, $k$ being thermal conductivity. When a binary fluid layer bounded by a rigid wall and a free surface with a non-uniform surface tension is subjected to a constant

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temperature gradient across it, an equilibrium solute concentration gradient will be established. By increasing gradually the temperature difference between the layer boundaries, the equilibrium state will breakdown at some critical value of the temperature gradient and convective motion will start. If the mixture density is approximately constant, which holds for some dilute solutions, or if the layer is under reduced gravity, the mechanism of onset of convection is that of Marangoni instability related to the dependence of the surface tension $\sigma$ on the temperature and the solute concentration.

$$\sigma(T,c) = \sigma_0 - \alpha_T(T-T_0) + \alpha_c(c-c_0);$$
$$\alpha_T = \left(-\frac{\partial\sigma}{\partial T}\right)_0, \quad \alpha_c = \left(\frac{\partial\sigma}{\partial c}\right)_0, \tag{3}$$

where $\sigma_0$, $T_0$ and $c_0$ are some reference values. The constants $\alpha_T$ and $\alpha_c$ are the rates of change of the surface tension with temperature and concentration. If the solute is a surfactant, $\alpha_c$ is positive. As for $\alpha_T$, it is usually positive, but in some systems may be negative on a small range of composition.

In the present paper the linear stability analysis of a binary mixture liquid layer bounded by rigid and free surfaces is performed in the case of nonlinear Soret effect.

## 2. Formulation of the problem

The system under consideration is a thin layer of a binary mixture liquid placed on a horizontal rigid plate and subjected to a constant vertical temperature gradient. The liquid is in contact with the ambient gas phase of constant temperature $T_a$. On the flat free surface, the surface tension is given by (3) and Newton's cooling law with a liquid–gas heat transfer coefficients $h$ is assumed, i.e.

$$-k\frac{\partial T}{\partial z} = h(T-T_a). \tag{4}$$

The bottom wall is kept at constant temperature $T_w$. The mixture density is assumed constant and the buoyancy effect is neglected in comparison with the surface tension-driven one. All the mixture's transport properties, except the Soret diffusion parameter $\tilde{S}_T$, are considered constant. Both boundaries of the layer are impermeable for each mixture's component.

In the unperturbed steady state, the temperature and concentration distributions are ($\beta_1 \neq 0$)

$$T_{st}(z) = T_w - \beta z,$$
$$c_{st}(z) = c_w + \left(\frac{\beta_0}{\beta_1} + c_w\right)[\exp(S_T\beta\beta_1 z) - 1]. \tag{5}$$

Here $z$ is the coordinate measured from the plate upward, $\beta$ is the constant adverse temperature gradient, being positive (negative) for heating from below (above), and $c_w$ is the solute concentration at the layer's bottom. The latter value cannot be considered as prescribed because it results from the simultaneous heat and mass transport processes. It is defined through the mean solute concentration across the layer,

$$\frac{1}{d}\int_0^d c_{st}(z)\,\mathrm{d}z,$$

where $d$ is the layer depth.

Let us define the parameter $S_1 \equiv S_T\beta\beta_1 d$, which is the non linear contribution of the Soret effect. For positive $S_1$, the concentration $c_{st}(z)$ increases with $z$ and the concentration gradient is positive, while for negative values of $S_1$, the concentration decreases with increasing $z$ and the gradient is negative. It is important to note that the concentration gradient on the interface depends also on this parameter.

If $\beta_1 > 0$, the product $S_T\beta$ has the same sign as the parameter $S_1$. Hence, the concentration gradient increases from the lower boundary to the upper one in mixtures with positive Soret coefficient when the layer is heated from below ($\beta > 0$) or in mixtures with negative Soret coefficient if the heating is from above ($\beta < 0$). Different signs of $S_T$ and $\beta$ results in negative values of $S_1$, and then, the concentration gradient across the layer is negative either for heating from below if $S_T < 0$ or for heating from above when $S_T > 0$.

For concentrated solutions with reversal in the sign of Soret effect, $\beta_1$ may easily be as large as $\pm 10$. For values of $S_T$ ranging usually between $\pm 10^{-2}$ and $\pm 10^{-3}$ K$^{-1}$, and temperature gradients ranging from 1 K/cm (for metallic melts) to 100 K/cm (in thin layers of organic solutions), one must consider values of $S_1$ between $\pm 0.1$ to $\pm 10$ to face all practical and experimental situations.

Because the concentration gradient across the layer is not constant, as in the case of linear Soret effect, we introduce the following quantity

$$\psi_\sigma = \frac{\left(\frac{\partial\sigma}{\partial c}\right)_0 (\nabla c_{st})_{z=0}}{\left(\frac{\partial\sigma}{\partial T}\right)_0 (\nabla T_{st})_{z=0}} = \frac{\alpha_c(\nabla c_{st})_{z=0}}{\alpha_T\beta} = S_T\frac{\alpha_c(\beta_0+\beta_1 c_w)}{\alpha_T}, \tag{6}$$

named as 'Marangoni separation factor'. It is a physical parameter characterizing the properties of the binary mixture. The Marangoni separation factor is expressed below by the ratio of the thermal and solutal Marangoni numbers. For some dilute organic solutions, for example, $\alpha_c/\alpha_T$ is about $10^2$ K and for the typical range of the Soret coefficient mentioned above, the separation factor varies from about $\pm 0.1$ to $\pm 1$.

## 3. Solution of the problem

The linear stability problem is solved in usual manner. The solution of the perturbed equations of continuity, momentum, energy and solute diffusion is searched in normal modes,namely

$$[w', T', c') = [W(z), \theta(z), C(z)] \exp[\omega t + i(a_x + a_y)], \quad (7)$$

where $t$ is the time, $w'$ is the normal velocity, $T'$ and $c'$ are the temperature and concentration perturbations. $W(z)$, $\theta(z)$ and $C(z)$ are unknown amplitudes, $\omega$ is the frequency, $a_x > 0$ and $a_y > 0$ are the wave numbers in $x$- and $y$-directions, parallel to the plate. This leads to the following set of equations written in dimensionless form

$$\left[\frac{\omega}{Pr} - (D^2 - a^2)\right](D^2 - a^2)W = 0,$$

$$[\omega - (D^2 - a^2)]\theta = W,$$

$$\left[\frac{\omega}{Le} - (D^2 - a^2) + S_1 D\right]C$$

$$= S\exp(S_1 z)\left[-\frac{1}{Le}W + (D^2 - a^2 + S_1 D)\theta\right]. \quad (8)$$

Here $D \equiv d/\mathrm{d}z$ stands for differentiation with respect to $z$, $Pr \equiv \mu/\rho\chi$ is the Prandtl number, $Le \equiv D_c/\chi$ is the Lewis number, $\mu$ being the dynamic viscosity, $\chi$ the thermal diffusivity and $a \equiv \sqrt{a_x^2 + a_y^2}$. Length, time, velocity, temperature and concentration have been scaled by the quantities $d$, $d^2/\chi$, $\chi/d$, $\beta d$ and $c_w$ respectively. The quantity $S = S_1 + S_0$ is related to $\beta_1$ through $S_1$ and to $\beta_0$ through $S_0 \equiv S_T\beta\beta_0 d/c_w$. Later it is shown that $S$ is not important parameter in this study.

The boundary conditions to equations (8) are

$$z = 0\begin{cases} W = 0, DW = 0, \theta = 0, \\ (D - S_1)C = SD\theta; \end{cases} \quad (9)$$

$$z = 1\begin{cases} W = 0, \\ D^2 W = Ma_T a^2\theta + LeMa_c a^2 C, \\ (D + Bi)\theta = 0, \\ (D - S_1)C = -S\exp(S_1)D\theta, \end{cases} \quad (10)$$

where the thermal Marangoni number $Ma_T \equiv (\alpha_T\beta d^2)/\mu\chi)$, the solutal Marangoni number $Ma_c \equiv (\alpha_c c_w d/(\mu D_c)$ and the Biot number $Bi \equiv hd/k$ are introduced. The first condition (10) expresses the non-deformability of the upper free boundary of the layer and the second one follows from the balance of the tangential forces on it.

Although the coupling of temperature and concentration fluctuations by the Soret effect is recognized to yield oscillatory convection in some cases, in the present paper we restrict ourselves to the case of stationary convection, when $\omega = 0$, and left the overstability for future study. For stationary instability, the Prandtl number is not important but the Lewis number, due to the nonlinear Soret effect, influences it.

Equations (8) with homogeneous boundary conditions (9) and (10) are solved analytically in terms of exponential function. The solution of this eigenvalue problem yields a relationship between the parameters and the wave number, written in the form

$$Ma_T = \Phi_0(a; Bi) + Ma_c S\Phi(a; S_1, Bi, Le), \quad (11)$$

where

$$\Phi_0(a; Bi) = \frac{8a(\sinh a\cosh a - a)(a\cosh a + Bi\sinh a)}{\sinh^3 a - a^3\cosh a}, \quad (12)$$

$$\Phi(a; S_1, Bi, Le) = \frac{\exp(S_1)}{S_1^2}$$
$$\times\left\{-S_1^2 Le + \Phi_0(a; Bi) + \frac{4(a\cosh a + Bi\sinh a)}{\sinh^3 a - a^3\cosh a}\right.$$
$$\left.\times\left[\frac{2(\lambda_1 - \lambda_2)\sinh a}{(\exp\lambda_2 - \exp\lambda_1)}[-a + \cosh a(\exp\lambda_1 + \exp\lambda_2)] + a^2\right]\right\} \quad (13)$$

$$\lambda_1 = \frac{S_1}{2} + \sqrt{\left(\frac{S_1}{2}\right)^2 + S^2},$$

$$\lambda_2 = \frac{S_1}{2} - \sqrt{\left(\frac{S_1}{2}\right)^2 + a^2}. \quad (14)$$

Expression (11) contains, in particular, Pearson's solution [8] for thermocapillary instability of a layer of a pure liquid when the mass flux is absent ($Ma_c = 0$). Takashima's result [9], corresponding to the case of linear Soret effect, is recovered for very small, but non-zero, value of $S_1$.

## 4. Discussion of the results

For given binary fluid, both thermal and solutal Marangoni numbers cannot be treated as independent parameters because the temperature gradient imposed induces a corresponding concentration distribution across the layer. But, the ratio of those numbers, namely the Marangoni separation factor, is usually considered as independent of the thermal condition. The third important parameter $S_1$ introduced in this study, cannot be assumed independent of the thermal Marangoni number because $\beta$ participates in their definitions. Nevertheless, considering the parametric analysis as an exploration of possible situations, we study below the behavior of $Ma_T$ varying the separation factor and $S_1$ independently of each other.

By introducing the separation factor (6), written as $\psi_\sigma \equiv SMa_c/Ma_T$, into (11), the thermal Marangoni number is represented by

$$Ma_T = \frac{\Phi_0(a; Bi)}{1 - \psi_\sigma\Phi(a; S_1, Bi, Le)}. \quad (15)$$

The stability results are applied to organic solutions in contact with air, for $Bi = 0.1$ and $Le = 10^{-2}$. Typical (absolute) values of the separation factor are of order of unity.

Figures 1 and 2 represent neutral stability curves, calculated from (15), for $\psi_\sigma = 1$ and $\psi_\sigma = -1$, respectively, and various values of $S_1$ between $-2$ and $+2$. This range is sufficient to show the influence of $S_1$ on the stability of thin layers of liquid mixture. It is well known that positive values of $\psi_\sigma$ correspond to a physical situation where both thermal and solutal configurations tend to destabilize the layer. The behavior of the curves shown in Fig. 1, is the same as in the case of the linear Soret effect ($S_1 \to 0$). Moreover, the minimum value of $Ma_T$ decreases when $S_1$ is increased. This tendency is also seen in Fig. 3 representing the critical thermal Marangoni number, $Ma_{T,\min}$ and the critical wavenumber, $a_{\min}$, as functions of $S_1$ for various positive values of the separation factor. The decrease of the critical wavenumber corresponds more and more to the case of pure solutal instability: because of impervious boundary conditions, it tends towards zero.

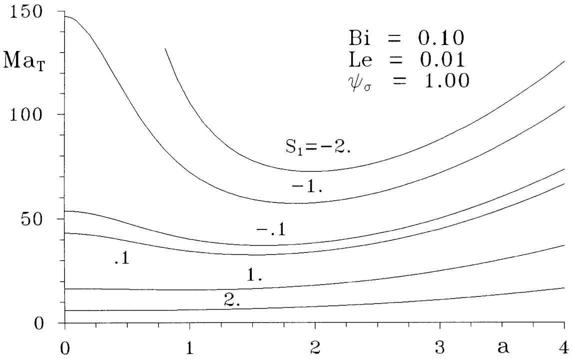

Fig. 1. Neutral stability curves for $\psi_\sigma = 1.0$, $Bi = 0.1$, $Le = 0.01$ and various values of $S_1$.

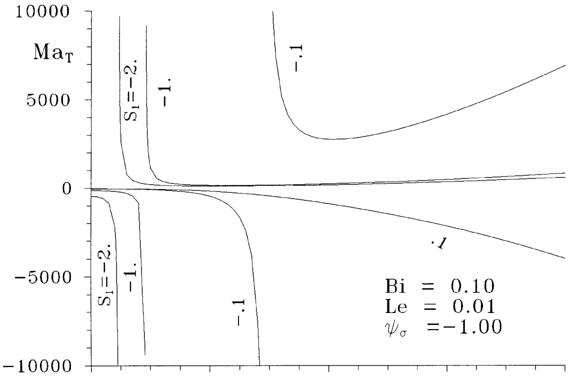

Fig. 2. Neutral stability curves for $\psi_\sigma = 1.0$, $Bi = 0.1$, $Le = 0.01$ and various values of $S_1$.

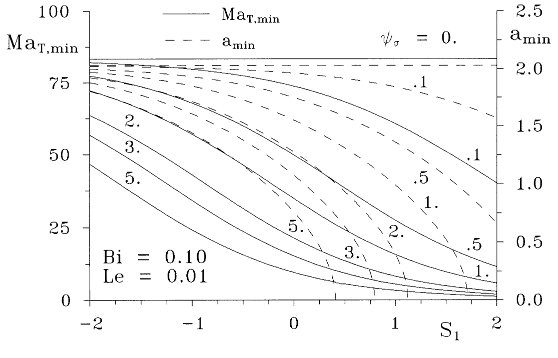

Fig. 3. Critical thermal Marangoni and wave numbers vs $S_1$ for $Bi = 0.1$, $Le = 0.01$ and positive values of $\psi_\sigma$.

The situation for negative values of $\psi_\sigma$, shown in Fig. 2, is more complex, because both positive and negative thermal Marangoni numbers may lead to steady convective instability as it is already found in the case of linear Soret effect. When $Ma_T$ is negative, instability sets in with a wavenumber of zero, and no qualitative modification of the neutral stability curves is observed when the nonlinear Soret effect is taken into account, although significantly different amplitudes are obtained by varying the parameter $S_1$.

When $Ma_T$ is positive, the nonlinear Soret effect competes with thermal destabilization, and the critical thermal Marangoni number as well as the critical wavenumber increases with $S_1$. In Fig. 4 they are plotted against $S_1$ for different values of the separation factor. At fixed $\psi_\sigma$, denoted by $\psi_\sigma^*$, both curves tend to infinity when $S_1$ approaches some value $S_1^*$, given by the expression

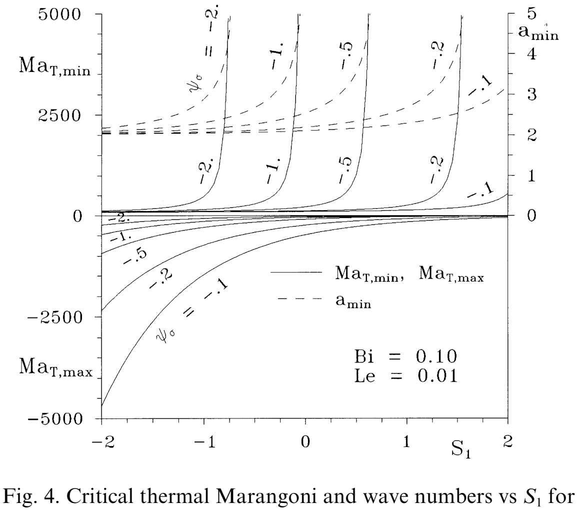

Fig. 4. Critical thermal Marangoni and wave numbers vs $S_1$ for $Bi = 0.1$, $Le = 0.01$ and negative values of $\psi_\sigma$.

$$S_1^* = \ln\left[\frac{-1}{(1+Le)\psi_\sigma^*}\right]. \tag{16}$$

One may conclude that for $S_1 \geqslant S_1^*$ the binary mixture is always stable to small stationary disturbances. For $Le = 0.01$, for instance, the value of $S_1^*$ increases from $-0.703$ to 2.293 when $\psi_\sigma^*$ varies between $-2.0$ and $-0.1$, becoming zero at $\psi_\sigma^* \simeq -0.98$. Hence, in the case of heating from below, layers of binary mixtures with the separation factor $\psi_\sigma \leqslant -0.98$ and positive, even small, values of the parameter $S_1$ will be unconditionally stable to stationary disturbances.

The critical thermal Marangoni number as a function of the separation factor is shown in Fig. 5 for different values of $S_1$. For positive $Ma_T$, the curves for negative $\sigma_\sigma$ are continuation of those for $\psi_\sigma > 0$. The increase of $Ma_T$ when $\psi_\sigma$ becomes more negative, is very fast, and the curves have a vertical asymptote $\psi_\sigma = \psi_\sigma^*$. Negative values of $S_1$ increase this domain and decrease the critical $Ma_T$, so that, stabilized steady convection is more likely to appear with negative nonlinear Soret effect. It is known however that when stabilization by the Soret effect is large, oscillatory instability should occur for values of $|\psi_\sigma|$ larger than $|\psi_\sigma^*|$, with a frequency of oscillation increasing with $|\psi_\sigma|$. That case of overstability will be considered in another paper.

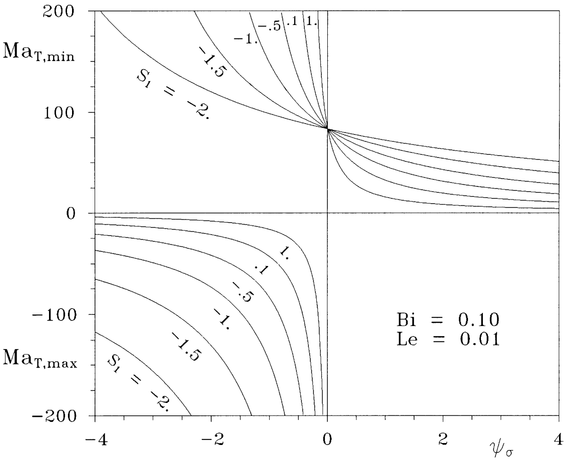

Fig. 5. Critical thermal Marangoni numbers vs $\psi_\sigma$ for $Bi = 0.1$, $Le = 0.01$ and various values of $S_1$.

The zero wavenumber instability appearing at negative thermal Marangoni number, on all the range of negative values of $\psi_\sigma$, is preserved when the nonlinear Soret effect is considered, because the instability is purely of solutal origin. However, as is seen from the behavior of the curves of $Ma_{\mathrm{T,max}}$ shown in Fig. 5, convective instability is now promoted by positive values of the nonlinear Soret effect parameter.

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