

## NL3469 Thermo-diffusion effects

In fluid mixtures a temperature gradient can drive a concentration current or generate a concentration gradient depending on boundary conditions. This thermo-diffusion effect—nowadays referred to as the Soret effect or Ludwig–Soret effect—was first reported by Carl Ludwig in 1856 and by Charles Soret in 1879. They observed an increase (decrease) of salt concentration at the cold (hot) end of a tube filled with salty water (Ludwig, 1856; Soret, 1879). The reciprocal effect that a concentration gradient drives a heat flow or generates a temperature gradient was first reported by Louis Dufour in 1872 for gas mixtures in a porous medium. Theoretically these and similar effects are most conveniently captured within the Onsager theory of irreversible macroscopic processes, in which generalized thermodynamic forces and resulting fluxes are linearly related to each other (de Groot & Mazur, 1962; Landau & Lifshitz, 1959).

In the last 20 years or so it has become clear that the linear Soret effect plays a dominant role in the nonlinear behavior of convective pattern formation in binary fluid mixtures (Platten & Legros, 1984; Cross & Hohenberg, 1993; Lücke et al., 1998). Consider the typical Bénard configuration of a horizontal fluid layer of height  $d$  that is heated from below in a homogeneous gravitational field,  $\mathbf{g} = -g \mathbf{e}_z$ . Strongly heat-conducting impermeable horizontal plates impose a vertical temperature difference ( $\Delta T > 0$ ) such that  $T = T_0 \pm \Delta T/2$  at  $z = \mp d/2$ .  $T_0$  is the mean temperature of the fluid layer. At small  $\Delta T$  the laterally homogeneous quiescent conductive state is stable with the linear temperature profile  $T_{cond}(z) = T_0 - \Delta T z/d$ . In a mixture like, for example, ethanol dissolved in water this conductive temperature gradient generates as a consequence of the Soret effect a concentration gradient, so that

$$C_{cond}(z) = C_0 + S_T C_0 (1 - C_0) \Delta T z/d. \quad (1)$$

Here  $C = \rho_1/(\rho_1 + \rho_2)$  is the mass concentration of the solute which is in our example the lighter component.  $C_0$  is its mean,  $S_T$  the Soret coefficient, and  $k_T = T_0 C_0 (1 - C_0) S_T$  the thermo-diffusion ratio. The Soret coupling between temperature and concentration fields (cf. below) is most conveniently measured in terms of the separation ratio  $\psi = -S_T C_0 (1 - C_0) \beta / \alpha = -(k_T / T_0) \beta / \alpha$ . Here  $\alpha$  and  $\beta$  are the thermal and solutal expansion coefficients of the total mass density  $\rho_1 + \rho_2 = \rho = \rho_0 [1 - \alpha(T - T_0) - \beta(C - C_0)]$  of the mixture for small deviations of  $T$  and  $C$  from their mean. Positive  $S_T$  corresponding to negative  $\psi$  (for mixtures like ethanol-water where  $\alpha$  and  $\beta$  are positive) implies a concentration increase (of the lighter component) near the cold upper plate and a decrease near the warmer lower plate and vice versa for  $S_T < 0$  ( $\psi > 0$ ). Note that in experiments  $\psi$  can easily be varied, say between -0.6 and 0.25 by varying  $T_0$  and  $C_0$ .

Convection is described by the balance equations

$$\nabla \cdot \mathbf{u} = 0 \quad (2a)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) \mathbf{u} = \sigma \nabla^2 \mathbf{u} + R\sigma (\delta T + \delta C) \mathbf{e}_z - \nabla p \quad (2b)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) T = \nabla^2 T \quad (2c)$$

$$(\partial_t + \mathbf{u} \cdot \nabla) C = L \nabla^2 C - L\psi \nabla^2 T \quad (2d)$$

for mass (2a), momentum (2b), heat (2c), and concentration (2d) in the Oberbeck–Boussinesq approximation.  $\delta T$  and  $\delta C$  in (2b) denote deviations from the mean  $T_0$  and  $C_0$ , respectively. Lengths are scaled with  $d$ , time with the vertical thermal diffusion time  $d^2/\kappa$ , and the velocity field  $\mathbf{u} = (u, v, w)$  with  $\kappa/d$ , where  $\kappa$  is the thermal diffusivity of the mixture. Temperatures are reduced by  $\Delta T$ , concentration by  $\Delta T\alpha/\beta$ , and pressure  $p$  by  $\rho_0(\kappa/d)^2$ .

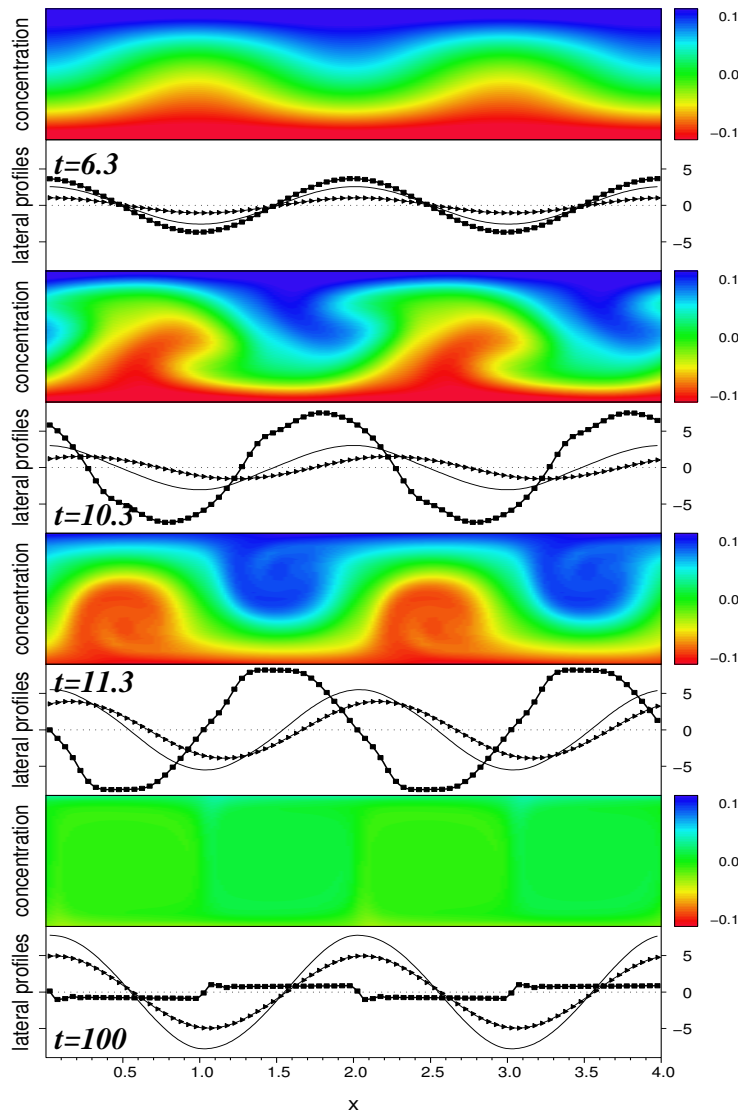
The Dufour effect that provides a coupling of concentration gradients into the heat balance is discarded since it is relevant only in a few gas mixtures and possibly in liquid mixtures near the liquid–vapor critical point.

Besides the Rayleigh number  $R = \frac{\alpha g d^3}{\nu \kappa} \Delta T$  measuring the thermal driving force, three additional numbers enter into the field equations: the Prandtl number  $\sigma = \nu/\kappa$ , which is of order 10 for ethanol-water mixtures at room temperature, the Lewis number  $L = D/\kappa \simeq 0.01$ , and the separation ratio  $\psi$ . Here  $\nu$  denotes the kinematic viscosity and  $D$  the concentration diffusivity.

The concentration field is responsible for the significantly larger complexity of binary mixture convection compared to pure fluids. It causes the richness of spatiotemporal properties of the convective structures, of the bifurcation behavior, and of the transient growth of convection. The Soret-generated concentration variations  $\delta C$  influence the buoyancy, i.e., the driving force for convective flow in (2b). The flow in turn mixes by advectively redistributing concentration. This nonlinear advective mixing in developed convective flow is typically much larger than the smoothing by linear diffusion—the Péclet number measuring the strength of advective concentration transport relative to diffusion is easily of the order of a few thousand. Thus, the concentration balance is strongly nonlinear giving rise to boundary layer behavior and strongly anharmonic concentration field profiles in the horizontal direction, as in Figure 1. In contrast, the momentum and heat balances remain weakly nonlinear close to onset as in pure fluids, implying only smooth and basically harmonic variations,  $\sim e^{i\mathbf{k}\cdot\mathbf{x}}$ , as the critical modes, c.f. Figure 1.

To summarize, the feedback interplay between (i) the Soret-generated concentration variations that are sustained against mixing and diffusion by externally imposed and internal temperature gradients, (ii) the resulting changes in the buoyancy, and (iii) the strongly nonlinear advective transport and mixing causes binary mixture convection to be rather complex not only with respect to its spatiotemporal properties but also concerning its bifurcation behavior.

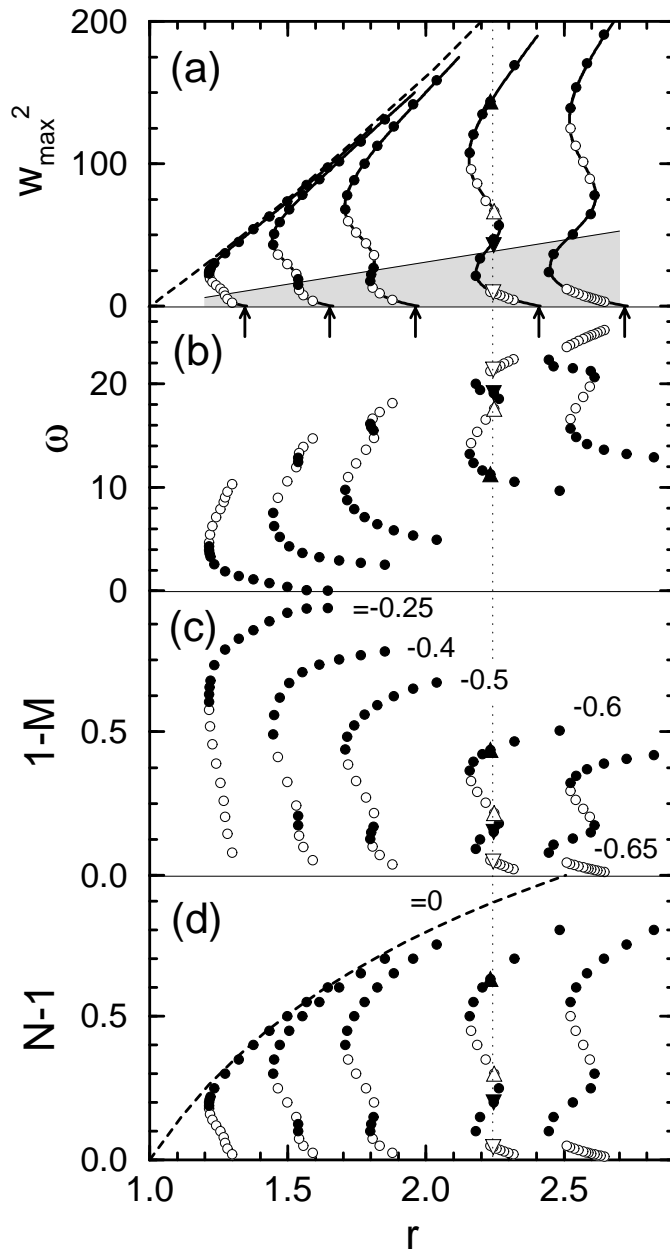
Take for example  $\psi < 0$  where the Soret-induced separation requires higher heating to destabilize the conductive state than for a pure fluid characterized by  $\psi = 0$  (for a review of the multitude of convection states appearing for destabilizing positive  $\psi$  see, for example, Huke et al. (2000)). Then the off-diagonal coupling between solutal buoyancy and advection of Soret-induced concentration variations described above generates oscillations—traveling waves (TW) of horizontally propagating rolls occur via a subcritical Hopf bifurcation whenever  $\psi$  is sufficiently negative. The bifurcation properties of such oscillatory TW states are shown in Figure 2 for different  $\psi$  as a



**Figure 1.** Evolution of convection after perturbing the quiescent conductive state. The concentration distribution in a vertical cross section of the fluid layer is displayed by color-coded plots where highest concentration was initially at the top, and lowest at the bottom. Wave profiles at midheight,  $z = 0$ , are shown for the fields of vertical velocity  $w$  (thin lines),  $40\delta T$  (lines with triangles), and  $400\delta C$  (lines with squares). The final TW propagates to the left. Parameters are  $L = 0.01$ ,  $\sigma = 10$ ,  $\psi = -0.25$ ,  $r = 1.42$ , and wavelength  $\lambda = 2$ . For better visibility two wavelengths are shown.

function of the reduced Rayleigh number  $r = R/R_c^0$ , where  $R_c^0 = 1707.76$  marks the convective onset in pure fluids. With increasing flow intensity (Figure 2a) the fluid gets more mixed while simultaneously the TW frequency decreases (Figure 2b) as the flow intensity and the Nusselt number (Figure 2d) approach the pure fluid reference values. Here the mixing is measured by the reduced spatial variance  $M = \sqrt{\langle \delta C^2 \rangle / \langle \delta C_{\text{cond}}^2 \rangle}$  of the concentration.

Figure 1 shows the complex spatiotemporal concentration redistribution during the



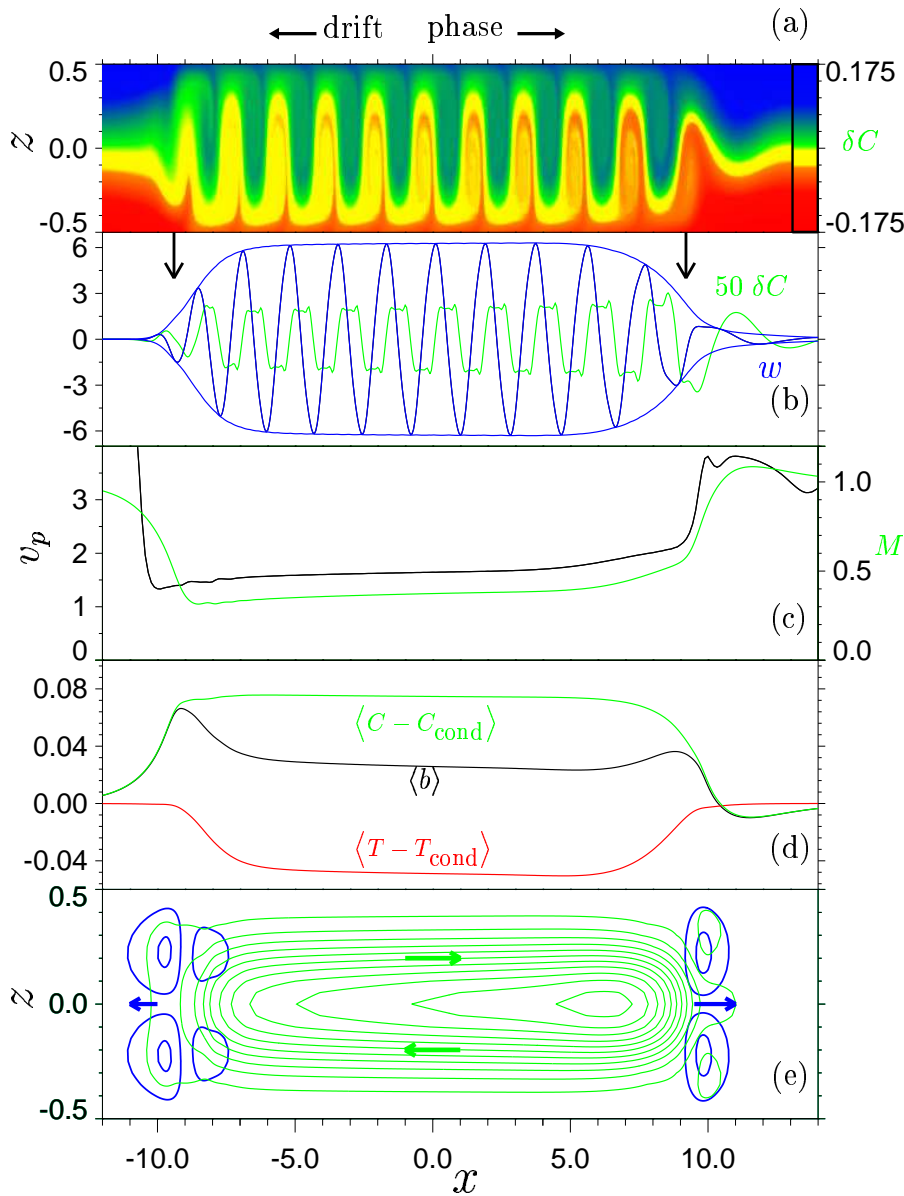
**Figure 2.** TW-bifurcation diagrams for different Soret coupling strength  $\psi$ : (a) squared maximal vertical flow  $w_{max}^2$ , (b) frequency  $\omega$ , (c) degree of mixing  $1 - M$ , and (d) convective contribution to the Nusselt number  $N - 1$  vs reduced Rayleigh number  $r$ . Stable (unstable) TW states are marked by filled (open) symbols. Arrows mark Hopf thresholds  $r_{osc}$  for onset of TW convection. The  $\psi = 0$  pure fluid limit is included in (a) and (d) by the dashed line. TW states on the vertical line are discussed in more detail in Hollinger, Büchel & Lücke (1997). Only states in the shaded region of (a) are weakly nonlinear. Parameters are  $L = 0.01$ ,  $\sigma = 10$ , and  $\lambda = 2$ .

growth of oscillatory convection at slightly supercritical heating. The growth starts generically from perturbations of the conductive state that contain the two critical Hopf modes for counterpropagating TWs with roughly equal amplitudes. First they linearly superimpose to form SW-like oscillations of growing amplitude with the large Hopf frequency. But then they compete via nonlinear advection with each other: at a critical SW amplitude advective breaking of the concentration wave triggers a very fast flow-induced transition from SW to TW convection with anharmonic profile, large phase velocity, and large amplitude of the concentration wave. Finally, advective mixing and diffusive homogenization slow down the TW as the concentration differences between left and right turning rolls slowly decrease.

In mixtures with sufficiently negative  $\psi$  there are also uniquely selected stable LTW states of localized, i.e., spatially confined TWs. They occur at small subcritical heating where extended TWs cannot exist and where the conductive state is strongly stabilized by the Soret effect. Such a strongly nonlinear LTW (Figure 3) is robustly sustained by a complex concentration redistribution process. Therein flow-induced mixing locally reduces the Soret separation and thereby increases the buoyancy to levels that suffice to drive well mixed fluid flow there: In Figure 3 positive (negative)  $\delta C$  is sucked from the top (bottom) boundary layer into right (left) turning rolls as soon as they become nonlinear under the trailing LTW front. This happens when the vertical velocity  $w$  roughly exceeds the local phase velocity  $v_p$  (left arrow in Figure 3b) so that regions with closed streamlines appear Hollinger, Büchel & Lücke (1997); Lücke et al. (1998). Within them “dark” (“gray”) concentration is transported predominantly in the upper (lower) part of the layer to the right. Mean concentration, on the other hand, migrates mostly to the left along open streamlines that meander between the closed roll regions and that follow the global mean in Figure 3a. The *time averaged* current of  $\delta C$  (gray lines in Figure 3e) reflects the mean properties of this transport. Since positive and negative  $\delta C$  (mean) is transported away from (towards) the left trailing front mean concentration accumulates there and causes a strong drop of  $M(x)$ . In the same way the leading front’s concentration variations and with it  $M(x)$  are strongly increased even beyond the conductive state’s values. Thus, unlike TWs LTWs do not reach a balance between  $\delta C$  injection, advective mixing, and diffusive homogenization on a constant level of small  $M$ . Rather LTW rolls collapse under the leading front when  $v_p$  has grown up to  $w$  (right arrow in Figure 3b). Thereafter concentration is discharged and sustains ahead of the leading front a barrier of  $\langle \delta C \rangle$  that prevents the expansion of the conductive state into the LTW.

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*See also* Thermal convection



**Figure 3.** Broad LTW of length  $l=17.4$ : (a) Concentration deviation  $\delta C$  from global mean (pale gray) in a vertical cross section of the layer. (b) Lateral wave profiles at midheight,  $z=0$ , of  $\delta C$  (gray), vertical velocity  $w$  (black), and its envelope. At the arrows  $w_{max} = v_p$ . (c) Mixing number  $M$  (gray) and phase velocity  $v_p$  (black). The variation of the wavelength  $\lambda(x) = 2\pi v_p(x)/\omega$  is the same since the LTW frequency  $\omega$  is a *global* constant. (d) Time averaged deviations from the conductive state at  $z=-0.25$  for concentration (upper), temperature (lower), and their sum ( $\langle b \rangle$ ) measuring the convective contribution to the buoyancy. (e) Streamlines of time averaged concentration current  $\langle \mathbf{J} \rangle = \langle \mathbf{u} \delta C - L \nabla(\delta C - \psi \delta T) \rangle$  (gray) and velocity field  $\langle \mathbf{u} \rangle$  (black). The latter results from  $\langle b \rangle$  and documents roll shaped contributions of  $\langle \mathbf{u} \rangle \delta C$  to  $\langle \mathbf{J} \rangle$  under the fronts and the associated  $\langle \delta C \rangle$  redistribution. Thick black and gray arrows indicate  $\langle \mathbf{u} \rangle$  and transport of positive  $\delta C$  (alcohol surplus), respectively. Thus, in the lower half of the layer negative  $\delta C$  (water surplus) is transported to the right. Parameters are  $L = 0.01$ ,  $\sigma = 10$ ,  $\psi = -0.35$ ,  $r = 1.346$ .

**Further Reading**

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