

## Beyond oceanography

After Melvin Stern let the double-diffusive genie out of the bottle in 1960, it did not take long for his ideas to spread from oceanography to fields as diverse as astrophysics, geology, chemistry and numerous other physical and engineering sciences. As we think of it, conditions for double-diffusion are not particularly restrictive. All that is needed is a fluid with two or more density components that diffuse at different rates – a very common configuration that is perhaps even more widespread in nature than pure one-component media. At least one of these components should be stratified in the unstable sense (why not?) and there is the potential application for double-diffusion. The following review of double-diffusive applications is intentionally focused on several illustrative examples. Our objective is to reflect the breadth of the subject but at the same time we strive to avoid redundancy. In various applications, under the outer shell of different nomenclature, parameters and scales, lies the universal dynamical core. The key questions and challenges are similar and the knowledge acquired in one discipline is often transferable to others.

The variability of double-diffusive patterns in different media is largely caused by a wide range of two key non-dimensional parameters – the Prandtl number ( $Pr$ ) and the diffusivity ratio ( $\tau$ ). The typical values of  $(Pr, \tau)$  relevant for the most common applications are indicated in Figure 12.1. The Prandtl number varies by at least ten orders of magnitude and the diffusivity ratio varies by at least eight. Nevertheless, several basic double-diffusive characteristics are fairly stable. Figure 12.1 presents the non-dimensional linear salt-finger growth rate (a) and the flux ratio (b) as functions of  $\tau$  and  $Pr$  for  $R_\rho = 2$ . As previously, we use the standard system of non-dimensionalization (1.11). Neither the growth rate ( $\lambda$ ) nor the flux ratio ( $\gamma$ ) are particularly sensitive to the diffusivity ratio, provided that  $\tau \ll 1$ . The dependence on  $Pr$  is bimodal. For high and moderate Prandtl numbers ( $Pr \geq 1$ ), growth rates and flux ratios are constrained to the relatively narrow intervals of  $0.1 < \lambda < 0.3$  and  $0.5 < \gamma < 0.85$ . However, both  $\lambda$  and  $\gamma$  become small in the limit  $Pr \rightarrow 0$ .

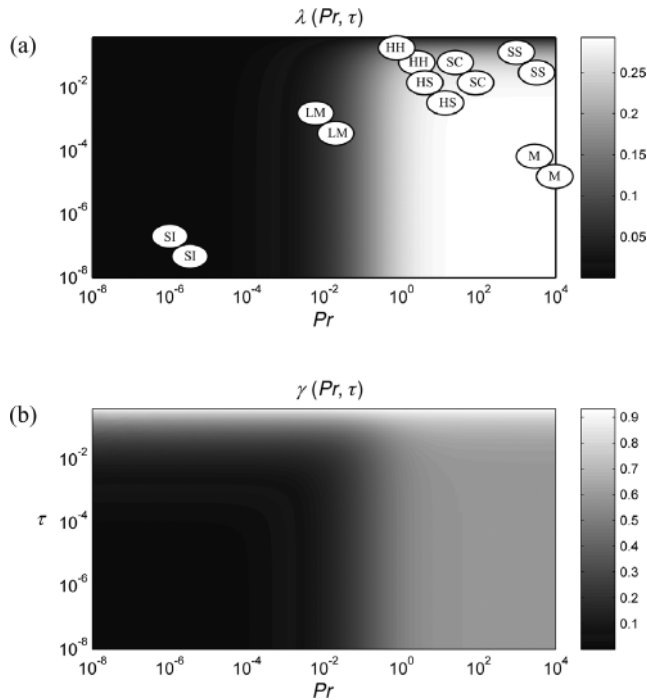


Figure 12.1 Linear characteristics of vertical fastest growing fingers at a density ratio of  $R_\rho = 2$  as functions of the Prandtl number and the diffusivity ratio. (a) The non-dimensional growth rate. Regions in the parameter space occupied by various double-diffusive systems are indicated as follows: SI – stellar interiors, LM – liquid metals, HS – heat–salt, SC – semiconductor oxides, HH – humidity–heat, SS – salt–sugar and M – magmas. (b) The flux ratio. After Schmitt (1983).

The fundamentally nonlinear quantities are more difficult to evaluate. For instance, we are unaware of any fully validated unified theory of double-diffusive transport for arbitrary  $(\tau, Pr)$ . The great majority of studies are regime-specific and some regions of the parameter space have been explored better than others. The oceanographic heat–salt case has been subjected to the most intense scrutiny (although the author could be biased), but other fields are rapidly catching up. Several non-oceanographic examples are discussed below, in no particular order, and the first item on our list is the astrophysical case of extremely low Prandtl number and diffusivity ratio.

## 12.1 Astrophysics

### *Semiconvection*

As astrophysicists have suspected for quite some time (Kato, 1966), double-diffusion is likely to play a fundamental role in the dynamics and evolution of

massive stars and giant planets. Stellar and planetary systems are phenomenologically different and will be discussed separately. Both forms of double-diffusion, diffusive and fingering, are active and can lead to observable consequences. However, so far, more attention has been paid to diffusive convection, which in astrophysical literature is usually referred to as semiconvection (Spiegel, 1969, 1972). Semiconvective regions are most commonly found outside the convective core of stars. These regions contain a mixture of hydrogen and helium; heavier elements are also present but in most applications play a lesser dynamical role. There are several scenarios for the development of semiconvective zones (e.g., Merryfield, 1995). For instance, in the main-sequence stars with masses between roughly  $10 M_{\odot}$  and  $30 M_{\odot}$  ( $M_{\odot}$  denotes the solar mass) the hydrogen-burning convective region shrinks. This process leaves behind a radially increasing hydrogen mass fraction, leading to an unstable chemical composition. Temperature, on the other hand, decreases and therefore has a destabilizing effect, which mirrors the diffusive configuration in high-latitude oceans. In astrophysical terms, the semiconvective region is Ledoux stable but Schwarzschild unstable – the Ledoux criterion quantifies the stability of radial adiabatic displacements; the Schwarzschild criterion is the analogous condition based only on the thermal density component.

It is interesting and perhaps surprising that stellar dynamics can be adequately modeled using the Boussinesq equations (1.1). The Boussinesq approximation is justified for phenomena operating on scales that are less than the pressure scale height, which for stars is typically one-tenth of their radius. Semiconvection – a relatively small-scale phenomenon – is expected to fall into this category. Another common approximation neglects the local nuclear energy generation, since the nuclear core spans only a small fraction of the interior. While it is comforting to know that geophysical and astrophysical systems are described by the same set of equations, the difference in governing parameters does affect the physical properties of double-diffusion. The compositional diffusivity in stars is extremely low in comparison with the thermal diffusivity ( $\tau \sim 10^{-6} - 10^{-8}$ ); viscosity is predominantly radiative and also small ( $Pr \sim 10^{-7} - 10^{-4}$ ). Thus, the hierarchical orders of governing parameters in stellar ( $\tau < Pr \ll 1$ ) and oceanic ( $\tau \ll 1 < Pr$ ) contexts are different. The immediate consequence of low  $Pr$  is that the range of density ratios for the linearly unstable stratification (2.5) is very wide:

$$1 < R_{\rho}^* < R_{\rho_{\text{cr}}}^*, R_{\rho_{\text{cr}}}^* = \frac{Pr + 1}{Pr + \tau} \sim \frac{1}{Pr} \gg 1. \quad (12.1)$$

In this regard, the astrophysical case is simpler than the geophysical. In the ocean, where  $R_{\rho_{\text{cr}}}^* \sim 1.1$ , the initiation of diffusive convection is attributed to fundamentally nonlinear mechanisms (Veronis, 1965, 1968). In contrast, the origin of semiconvection in stars and planets is clear; it is the linear instability of large-scale

gradients. Hence, the relevant spatial and temporal scales can be determined by considering the linearly fastest growing modes. The corresponding wavelength of primary instabilities is on the order of  $l_{\text{fg}} \sim 500$  km and the  $e$ -folding time is  $t_{\text{fg}} \sim 10^5$  s (Merryfield, 1995). Note that  $l_{\text{fg}}$  is still much less than the thickness of the stellar semiconvective zone ( $\sim 10^5$ – $10^6$  km) and therefore diffusive mixing is usually treated as a local process operating in the effectively unbounded gradient.

Numerous pieces of indirect evidence suggest that semiconvection is critical for the internal structure and evolution of core-convective stars of various sizes and its inclusion in large-scale stellar models helps to meet the observational constraints (e.g., Crowe and Mitalas, 1982; Langer, 1991). More quantitative estimates in astrophysics are difficult to come by. The major impasse is the lack of reliable flux laws. Not only the numerical values of transport but even the functional forms of such laws are highly uncertain. The situation is exacerbated by the absence of terrestrial fluids satisfying the condition  $(Pr, \tau) \ll 1$ , which precludes the laboratory modeling of semiconvection. One of the big unknowns is the stratification pattern: it is not clear whether the semiconvective region remains smoothly stratified or breaks into a series of mixed layers, as one could anticipate from the oceanographic studies (Chapter 8). Both possibilities have been considered. Theory developed by Langer *et al.* (1983) assumes that mixing is driven by destabilization of growing oscillatory modes, which collapse without forming permanent staircases. An alternative view was articulated by Spruit (1992), who proposed the staircase model of semiconvection. In order to determine the heat and compositional transport, several ad hoc assumptions were made about the thickness of layers and interfaces. Progress in this direction was stalled by the lack of effective means for testing the proposed transport models.

Given the lack of viable alternatives, the approach based on direct numerical simulations (DNS) has become increasingly popular. The standard Fourier-based spectral model appears to be best suited for studies of semiconvection (e.g., Mirouh *et al.*, 2012). The obvious limitation of the numerical approach is that the dissipation scales of heat, composition and momentum in stars are dramatically different – by as much as four orders of magnitude. Even modern state-of-the-art models cannot simultaneously resolve such a range of scales and the choice of the Prandtl number and diffusivity ratio is dictated by the feasibility of simulations. Transport estimates in such circumstances can only be obtained through extrapolation towards the realistic parameters.

Nevertheless, simulations have brought much needed insight into the dynamics of semiconvection and particularly into the conditions of layering (Rosenblum *et al.*, 2011; Mirouh *et al.*, 2012). Overall, the astrophysical situation has proven to be quite similar to the oceanographic case. Extensive exploration of the numerically accessible parameter range – small but not too small  $(Pr, \tau)$  – revealed that layering

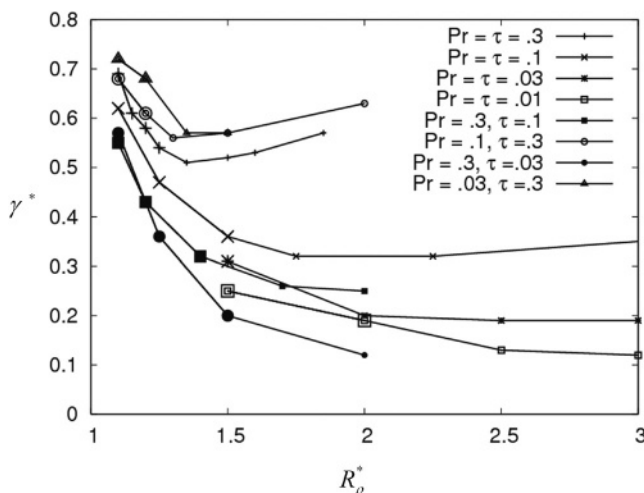


Figure 12.2 The equilibrium diffusive flux ratio as a function of the diffusive density ratio in a series of DNS. The experiments resulting in layering are marked by larger symbols. From Mirouh *et al.* (2012).

can occur in low- $Pr$  systems and that it is caused by the  $\gamma$ -instability (Chapter 8). Typical patterns of the flux ratio, estimated from small-domain simulations, are shown in Figure 12.2; the runs resulting in spontaneous layering are indicated by larger symbols. These experiments indicate that the decrease of the flux ratio with the density ratio is a necessary and sufficient condition for the formation of semiconvective staircases. In all cases considered, the layering condition  $\left(\frac{\partial \gamma^*}{\partial R_\rho^*} < 0\right)$  is met for sufficiently low diffusive density ratios ( $1 < R_\rho^* < R_{\rho^*}^*$ ). Note that in the astrophysical ( $Pr \ll 1$ ) case, it is critical to incorporate into the flux ratio  $\gamma^*$  the contribution from the molecular heat flux (a secondary effect for high  $Pr$  applications). The  $\gamma$ -instability modes developing in this parameter range grow at a rate consistent with the theoretical prediction (8.11), eventually transforming the background stratification into a well-defined staircase.

However, the analogies between the astrophysical and oceanographic cases (Chapter 8) do not end here. Layers that form first are thin and unsteady (Fig. 12.3). They undergo a series of merging events, in which strong interfaces grow further at the expense of weaker ones. Weak interfaces gradually erode and eventually disappear, following the B-merger scenario described in Section 8.4. The characteristic size of steps correspondingly increases in time until there is only one interface left within the limits of the computational domain (Fig. 12.3). Such evolutionary similarities of layering across different forms of double-diffusion (fingering/diffusive) and parameter ranges (low/high  $Pr$ ) are truly striking. They are indicative of the robust and universal nature of thermohaline layering.

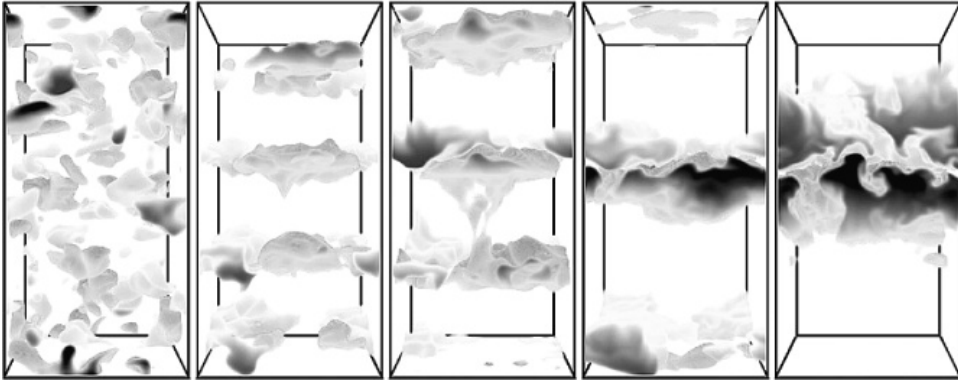


Figure 12.3 Direct numerical simulation of diffusive convection in the astrophysically relevant (low  $Pr$ ) regime. Shown is the perturbation of the composition at various times. Note the formation of the well-defined layers and their sequential mergers. From Rosenblum *et al.* (2011). See color plates section.

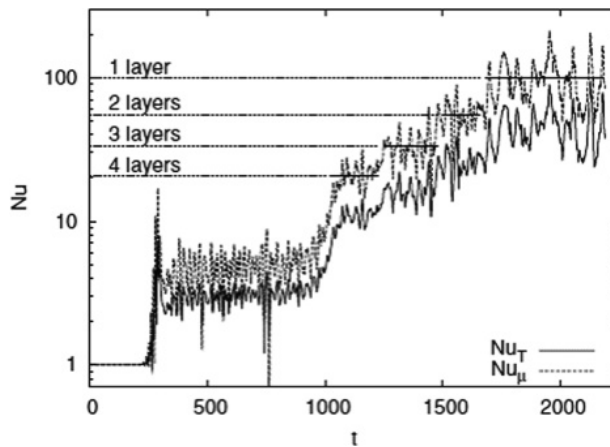


Figure 12.4 Time record of the thermal (solid line) and compositional (dashed line) fluxes. Note the systematic increase in the fluxes associated with layer-merging events. From Rosenblum *et al.* (2011).

As in the ocean (Schmitt *et al.*, 2005; Radko, 2005), formation of a staircase and the sequential layer-merging events dramatically increase the vertical transport (Fig. 12.4), which poses a major challenge for parameterizing semiconvection. In the non-layer-forming regime ( $R_\rho^* > R_{\min}^*$ ), transport could be deduced from small-domain DNS. For instance, Mirouh *et al.* (2012) notes that the available simulations (Fig. 12.5) can be adequately described by a universal analytical expression:

$$Nu - 1 = (0.75 \pm 0.05) \left( \frac{Pr}{\tau} \right)^{0.25 \pm 0.15} \frac{1 - \tau}{R_\rho^* - 1} (1 - r), \quad (12.2)$$

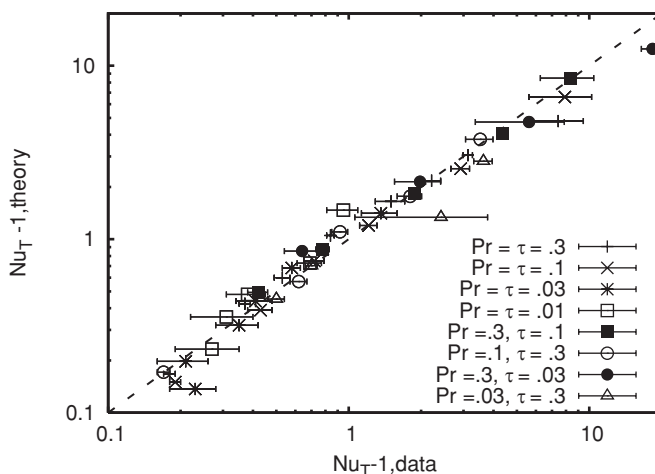


Figure 12.5 Comparison between the theoretical prediction of heat transport (12.2) and the corresponding numerical data. From Mirouh *et al.* (2012).

where

$$r = \frac{R_{\rho}^* - 1}{R_{\rho \text{cr}}^* - 1}. \quad (12.3)$$

The analysis in Mirouh *et al.* offers a promising starting point for the non-layering part of the problem. Future simulations, better resolved and capturing a wider range of  $(Pr, \tau)$  will undoubtedly refine these flux laws and improve the accuracy of extrapolations, but the direction such research should take is well defined.

The way forward in the layering regime ( $R_{\rho}^* < R_{\rho \text{min}}^*$ ) is less clear. It is safe to assume that heat and compositional fluxes in the staircase exceed the smooth-gradient values, but by how much? These fluxes sensitively depend on the equilibrium height of steps – the point where mergers are arrested (Fig. 12.4). However, the theory of layer equilibration is currently at a highly qualitative stage (Radko, 2005). Its applicability to the astrophysical regime is particularly uncertain, given the lack of observational guidance. Layer-merging significantly slows down as a staircase coarsens. The mergers of thick steps occur on time scales that are much longer than the growth period of primary instabilities. Therefore, the prospects of DNS-modeling the entire merging sequence and the ultimate stable state are problematic. On the positive side, limited numerical accessibility is likely to stimulate new theoretical developments. As we have seen so often in the past, the failure of brute-force methods inevitably creates fertile grounds for the birth of highly original ideas and unorthodox approaches.

Compared to the stellar case, modeling semiconvection in giant planets poses a lesser challenge. Planetary Prandtl numbers and diffusivity ratios are moderate ( $Pr, \tau \sim 0.01$ ) and the dissipation scales of heat, composition and momentum are not

too dissimilar. Therefore, reliable semiconvective transport models for planetary dynamics could appear in the not-too-distant future (Mirouh *et al.*, 2012). Semiconvection in giant planets is a subject of growing interest in astrophysics and models of this nature are urgently needed. The possibility that semiconvection can regulate both thermal and compositional mixing has been recognized since the seventies (Salpeter and Stevenson, 1976; Stevenson and Salpeter 1977; Stevenson, 1985). However, only recently has the community started to shift from the crude purely adiabatic view of giant planets (as reviewed by Guillot, 2005) to the new generation of evolutionary models incorporating semiconvection (Chabrier and Baraffe, 2008; Leconte and Chabrier, 2012). The transition was triggered by a combination of two factors. First, our physical understanding of double-diffusion reached the level where we can start developing and tentatively applying semiconvective transport models with a better than shot-in-the-dark chance of success. Another impetus comes from observations. The Galileo and Cassini missions enabled detailed measurements of the compositions of the atmospheres of Jupiter and Saturn. Extrasolar planet surveys provided statistically significant data on their composition and global characteristics, and future missions will undoubtedly expand the already impressive body of information. The possibilities are now opening to firmly connect semiconvection theory with observations. It is a win–win proposition that will concurrently improve physical interpretation of data and afford the observational validation of mixing models.

The impact of semiconvective mixing on the structure and evolution of giant planets could be profound and multifold. Semiconvection has been considered as the plausible origin of the low observed heat flux of Uranus (Gierasch and Conrath, 1987), of the high metallicity of the envelopes of Uranus and Neptune, and of the erosion of the core of Jupiter and Saturn (Guillot *et al.*, 2004). Non-adiabatic models have been proposed to explain the uncharacteristically large observed radii of some transiting exo-planets (Chabrier and Baraffe, 2008). The inclusion of semiconvective dynamics in evolutionary models (Leconte and Chabrier, 2012) improves the agreement with observations and leads to more reliable estimates of the size of the convective layers. While the full description of Jovian (gas giant) dynamics has to await development of accurate mixing parameterizations, it is possible to draw several general conclusions (Leconte and Chabrier, 2012) that are robust and not sensitive to the details of a semiconvective model. In particular: (i) Jovian planets might be significantly more enriched in heavy elements (by 30–60%) than previously thought; (ii) their interior heat content might be much larger; and (iii) the inner temperature profile significantly departs from the adiabatic profile.

Leconte and Chabrier (2012) emphasize that the significance of semiconvection is not limited to its effects on the current compositional and thermal structures of



giant planets. Taking semiconvection into account can impact our understanding of planet formation and their cooling properties. For instance, if new semiconvective models substantially modify the estimates of heavy material content, the planet formation theories should be revised accordingly. New results suggest an early and more efficient capture of planetesimals in the protoplanetary nebulae of giant planets. Another revision of the conventional chronology of giant planets is required to reflect the less efficient heat transport, a consequence of the semiconvective inhibition of convective mixing. The associated larger heat content and the possibility of significant core erosion also directly impact the planet cooling histories.

### *Fingering convection*

While astrophysicists are more concerned with semiconvection, it is generally accepted that stellar stratification often becomes susceptible to fingering as well. It is less clear whether its mixing intensity is sufficient to substantially change the composition of stars on the evolutionary time scale. The answer requires knowledge of the relevant flux laws. Early theoretical attempts to predict fingering transport in the astrophysical context (Ulrich, 1972; Kippenhahn *et al.*, 1980) were based on uncertain assumptions and, furthermore, produced mutually inconsistent estimates of the transport. The oceanographic flux laws are in much better shape but, due to the differences in molecular characteristics, their application to astrophysical phenomena is unwarranted. Numerical simulations of fingering are also problematic due to the disparity of the dissipation scales of heat, momentum and composition. Thus, the obstacles for the development of a consistent theory (or at least a simple recipe) for finger-driven transport largely mirror the complications in dealing with semiconvection in stars.

On the positive side, similar problems can be tackled by similar methods. For instance, fingering convection has been successfully modeled in the numerically accessible range, which was followed by imaginative extrapolations of results to realistic values of  $(Pr, \tau)$ . As in semiconvection, the Fourier-based spectral model is a weapon of choice for astrophysicists, which makes it possible to avoid artificial contamination of the results by inappropriate boundary conditions (Denissenkov, 2010; Denissenkov and Merryfield, 2011b). One of the success stories was reported by Traxler *et al.* (2011b), who noted that simulations in the numerically accessible parameter range can be described using the universal expression for the eddy diffusivity of the composition  $K_\mu$ :

$$K_\mu = 101 \sqrt{\nu k_\mu} \exp(-3.6r)(1-r)^{1.1}, \quad (12.4)$$

where  $k_\mu$  is the molecular compositional diffusivity,  $\nu$  is viscosity and

$$r = \frac{R_\rho - 1}{\tau^{-1} - 1}. \quad (12.5)$$

An important caveat is that the flux law (12.4) was obtained for the smooth-gradient model. The assumed absence of staircases is consistent with the existing numerical simulations and theoretical arguments. For instance, the flux ratio monotonically increases with the density ratio implying the absence of  $\gamma$ -instability, the most common cause of step formation (Chapter 8). This argument, however, has to be considered with caution since the linear stability of a uniform gradient does not completely preclude spontaneous layering, which could be driven by fundamentally nonlinear processes (diffusive layering in high-latitude oceans being a prime example). Until the absence of fingering staircases in stellar atmospheres is proven, it is perhaps prudent to interpret (12.4) as a lower bound for the finger-driven transport. Overall though, despite all their current limitations and uncertainties, numerical studies have significantly advanced our understanding of the importance of fingering in astrophysics. In particular, all simulations consistently support two major qualitative conclusions: (i) the heat transport by fingers in stellar atmospheres is negligible but (ii) the compositional transport is substantial and can affect the evolution of stars and their observable characteristics.

One of the examples of finger-induced effects in stellar dynamics involves the planetary pollution conundrum. Central stars of planetary systems tend to exhibit surprisingly high metallicity – an intriguing observation, begging for a mechanistic explanation. Two distinct proposals have been considered. It is possible that metallicity is primordial: the planetary systems could be formed more easily in a higher metallicity disk. The accretion hypothesis, on the other hand, assumes that the planet formation mechanism is independent of the disk metallicity and the enhancement is caused by subsequent planetary infall. The most common criticism of the accretion idea is based on the lack of correlation between the size of the stellar convection zones and their metallicity. If the accretion mechanism is dominant, stars with thinner convection zones should be polluted more. The size of the outer convection zone rapidly decreases with stellar mass and therefore the relative metallicity enhancement should be larger for heavy stars (Laughlin and Adams, 1997). However, such correlation has not been detected. It is an interesting counter-argument for the accretion theory but is it sufficiently rigorous? Recent studies suggest that the mechanics of planetary pollution could be more complicated (Vauclair, 2004; Garaud, 2011; Theado and Vauclair, 2012). The added metallicity does not necessarily stay trapped in the outer convection zone, but could be drained into the interior of a star. The likely mixing mechanism is double-diffusive, by metallic fingers.

Using the flux law (12.4), Garaud (2011) successfully modeled the radial large-scale distribution of composition and demonstrated that fingering serves as an effective regulator of surface metallicity. The first post-infall stage is convective mixing, triggered by the accretion of planetary material in a thin surface layer of a star. This brief period is followed by a much longer fingering phase, during which the metallicity is drained deep into the interior. Garaud notes the sensitive dependence of the finger-induced dilution rates on the star size: the larger the star, the faster metallicity is removed from the surface. The enhanced post-impact metallicity in large stars could be compensated by faster dilution into the interior. This fundamentally double-diffusive effect could explain the lack of systematic variation of metallicity with star size – the original argument against the accretion hypothesis. In view of this result, the debate over accretion and the primordial dynamics of planetary pollution is bound to shift in a different direction. While the size–metallicity correlation argument no longer appears convincing, taking into account double-diffusive mixing poses a problem of a different kind. The double-diffusive draining of the metal-rich material into the stellar interior leaves only a fraction of the initial metallicity excess in the surface convective layer – much smaller than the average observed overmetallicity (Theado and Vauclair, 2012). Thus, the question is still open of how to explain the enhanced metallicity in central stars of planetary systems. Another suggestive finding of Theado and Vauclair (2012) and Garaud (2011) is that the fingering region can extend downward to the lithium-burning region, which could help to rationalize recent observations (Gonzalez 2008; Israelian *et al.*, 2009) of lower lithium abundances in planet-bearing stars.

There are several other scenarios of stellar evolution in which fingering could play a major role. For instance, red giants are known to experience extra mixing in their convectively stable radiative zones, separating the hydrogen-burning shell from the bottom of the convective envelope. A promising physical mechanism for this extra mixing is fingering convection. The evolutionary model that takes into account parameterized finger-induced mixing (Charbonnel and Zahn, 2007) appears to be consistent with numerous spectroscopic measurements of surface composition in low-mass red giants after they reach bump luminosity. On the other hand, the estimates of transport suggested by recent finger-resolving DNS (Denissenkov, 2010; Traxler *et al.*, 2011b) fall by at least an order of magnitude below the levels required to explain observationally inferred extra mixing. The inconsistency can be caused by two factors (or their combination). The DNS could underestimate mixing due to their present inability to operate in the realistic parameter range. Likewise, one cannot rule out the possibility that the extra mixing in red giants is associated with a yet undetermined non-double-diffusive transport mechanism and that the agreement of

the finger-based model of Charbonnel and Zahn (2007) with observations is coincidental.

Fingering convection has also been implicated in the mixing of carbon-rich material deposited at the surface of a star in a mass-transferring binary (Stancliffe *et al.*, 2007). It is generally assumed that the material accreted from a no longer visible companion of such stars remains on the surface and does not mix with the interior. However, the new material has higher mean molecular weight than the original stellar composition and therefore is likely to drive fingering convection. Stancliffe *et al.* (2007) suggests that the ensuing mixing rapidly transfers the accreted material deep into the star interior, affecting up to 90% of its volume. As a result, the surface abundance of carbon decreases by nearly an order of magnitude relative to the non-fingering estimates. Some of the accreted carbon-rich material mixes into the high-temperature interior region where CN-cycling occurs. Therefore, the finger-based model also displays a substantial increase in the abundance of nitrogen in the period after the surface convection zone extends to the layers that have gone through nuclear fusion (the first dredge-up). Taking into account finger-driven transport makes it possible to bring the predicted values and evolutionary patterns of carbon/iron and nitrogen/iron ratios into close agreement with observations, something that the non-double-diffusive version of the model fails to accomplish.

## 12.2 Geology and geophysics

I hope we all enjoyed this brief voyage to space – time to go back to the Earth and take a look at signs of double-diffusion in its interior. There are several geophysical systems that have been considered as likely sources of double-diffusive phenomena. The most frequently discussed examples include magma chambers (Huppert and Sparks, 1984; Clark *et al.*, 1987; Toramaru and Matsumoto, 2012) and the core–mantle boundary (Kellogg, 1991; Hansen and Yuen, 1994; Buffett and Seagle, 2010). In addition, diffusive convection driven by hydrothermal forcing can occur in individual groundwater wells (Love *et al.*, 2007) and, on much larger scales, throughout the Earth's crust (Schoofs *et al.*, 1999, 2000). Magma chambers have been studied more extensively for reasons of observational accessibility and will be discussed here first.

The term magma chamber refers to an underground pool that contains molten rock under high pressure. The liquid material in a magma chamber can fracture the solid material around it and create outlets, occasionally reaching the surface of the Earth and resulting in a volcanic eruption. Magma chambers are located 1–10 km below the Earth's surface and their obvious locations are directly under active volcanoes. The most natural thermal structure of a magma chamber is the one in which it is cooled at the upper surface. Thus, the thermal component of density

is unstable. At the same time, numerous studies of volcanic rocks suggest that magma chambers are often characterized by stable compositional gradients. The major components of silicate melts are only weakly diffusive ( $\tau \sim 10^{-3} - 10^{-8}$ ), which creates favorable conditions for diffusive convection (e.g., Huppert and Sparks, 1984; Hansen and Yuen, 1995).

The early studies of double-diffusion in a geological context were motivated by observations of well-defined layers commonly seen in igneous rocks (Fig. 12.6). Their similarity to thermohaline staircases in the ocean has led to a suggestion that layers were formed in the liquid state of rocks by double-diffusive processes (Huppert and Turner, 1981; Kerr and Turner, 1982). However, closer inspection of igneous layering reveals signatures of several distinct mechanisms (reviewed by Naslund and McBirney, 1996), and hopes for a universal explanation for all or even most incidences of layering are likely to be disappointed. It also remains unclear how the layered liquid can transform into a layered solid without major disruptions of regularity. Nevertheless, the double-diffusive hypothesis remains among the most popular explanations of layering. The major challenge for igneous petrologists is to develop techniques for identification, by the composition and textural patterns of layered rocks, the likely origin of layering. Meeting such a challenge requires familiarity with the basic (and possibly not-too-basic) physics of double-diffusive convection.

There are several features that distinguish the dynamics of geological double-diffusive systems from their oceanographic and astrophysical counterparts. One peculiarity is that molten rocks are highly viscous. Viscosity depends on the magma temperature and its silica content. In different types of magma, viscosity can vary by up to ten orders of magnitude – a remarkably wide range for any physical parameter. However, even for the least viscous magmas, viscosity exceeds thermal diffusivity by more than four orders of magnitude ( $Pr \geq 10^4$ ). Generally, the disparity in the dissipation coefficients leads to significant complications for analytical and numerical modeling, as we have seen in the astrophysical examples. However, the effectively infinite Prandtl number of geological systems appears to simplify the dynamics. Non-dimensionalizing Boussinesq equations (1.1) using the standard system (1.11) and taking the limit of high Prandtl number ( $Pr \rightarrow \infty$ ) reduces the governing equations to

$$\begin{cases} -\nabla p + (T - S)\vec{k} + \nabla^2 \vec{v} = 0, \\ \frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T = \nabla^2 T, \\ \frac{\partial S}{\partial t} + \vec{v} \cdot \nabla S = \tau \nabla^2 S, \\ \nabla \cdot \vec{v} = 0. \end{cases} \quad (12.6)$$

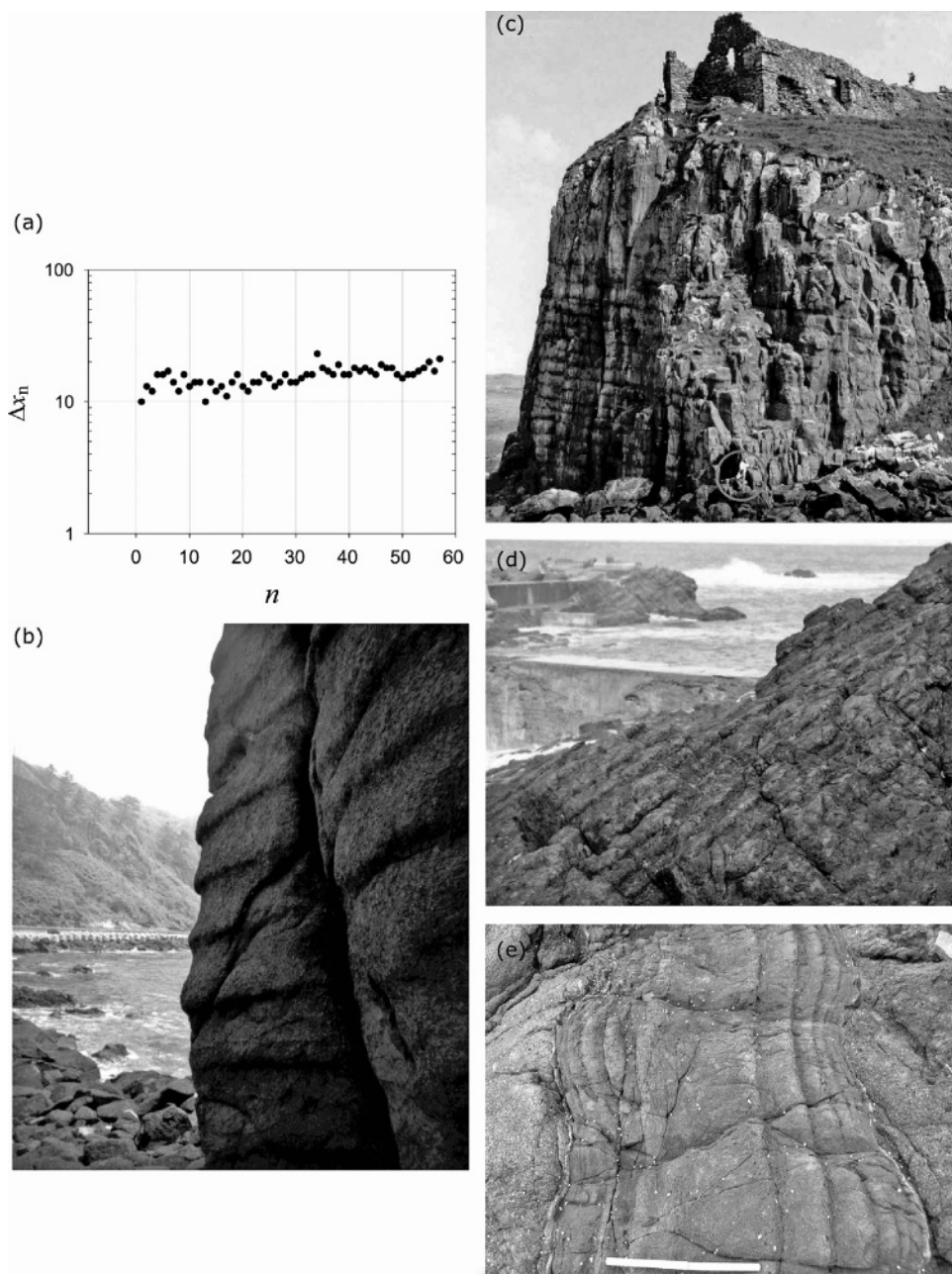


Figure 12.6 (a) Typical variability in layer thickness (m) in observations. (b)–(e) Selected examples of cyclic layering. From Toramaru and Matsumoto (2012).



Thus, the nonlinearities in this limit are retained in the equations for temperature ( $T$ ) and composition ( $S$ ) but not in the momentum equations, which can facilitate analytical and numerical developments. The high Prandtl number version of the standard Boussinesq model (12.6) adequately reflects the qualitative properties of geological flows. However, if precise quantitative information is sought, geologists often employ the so-called extended Boussinesq version, in which the temperature equation is modified to include viscous and adiabatic heating.

The asymptotic high Prandtl number system has been successfully modeled numerically. For instance, Hansen and Yuen (1989, 1995) used it to examine the propensity of double-diffusive magmas to form layers. Analogous to the oceanographic case, the ability of such systems to maintain preexisting layers and to create new ones from un-layered states is controlled by the density ratio, as are the cooling rates of magma. The numerical solutions obtained by Hansen and Yuen exhibited rich phenomenology. Interesting effects include the coexistence of stratified and homogeneous layers, as well as transient layering followed by convective overturns. While layering was readily developing in the diffusive case, it did not occur in the analogous fingering systems. Viscous heating was shown to have a significant impact on double-diffusive convection. The variation in viscosity across the magma chamber could also be of major importance (Turner and Campbell, 1986) but is rarely incorporated in modeling studies.

Aside from high viscosity (a simplifying factor), another distinguishing characteristic of geological fluid dynamics is the possibility of crystallization (a complicating factor), which occurs when the melt cools. Crystallization is one of the major mechanisms for the initiation and maintenance of double-diffusive convection. On the most fundamental level, crystallization affects the fluid dynamics of magma by the so-called differentiation effect – the production of compositional gradients in the initially homogeneous media. There are at least two common mechanisms for crystallization-driven differentiation. The first one is the crystal settling, in which stratification is caused by the displacement of crystals relative to a melt. The second, and perhaps more likely (Turner and Campbell, 1986) mechanism involves the growth of crystals at the boundaries of a magma chamber, which selectively depletes the fluid adjacent to newly formed crystals of certain chemical components. For instance, the crystallization of dense olivine after cooling generates residual liquids of lesser density. Crystallization in magmas causes much larger changes in melt density than the associated temperature changes. Thus, if cooling is applied at the upper surface, the residual melts in the upper layers become colder and lighter, due to a different composition, than the magma in the lower part of the chamber. This creates favorable conditions for diffusive convection. Since crystallization and boundary cooling are generic attributes of magma dynamics, double-diffusive processes of one form or another should be ubiquitous in magma

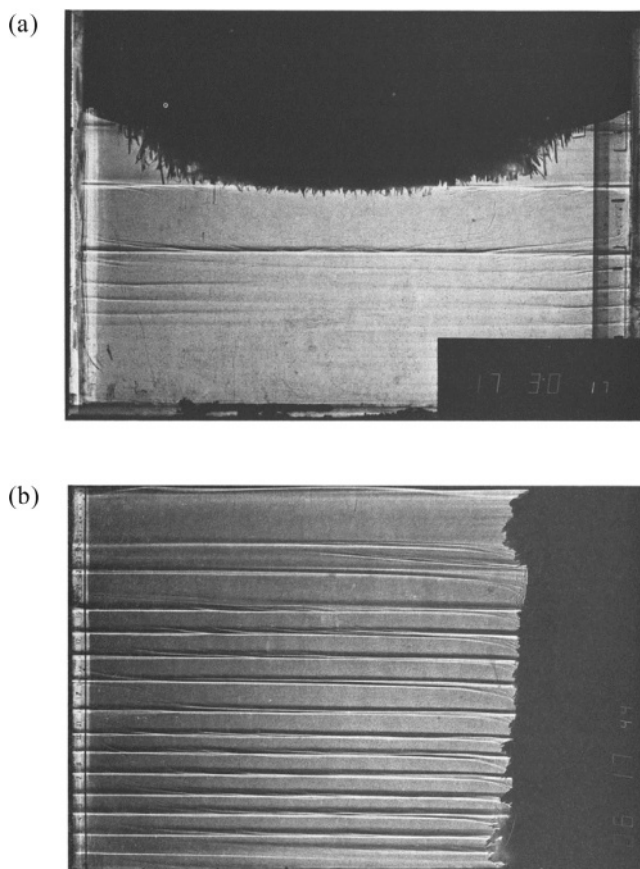


Figure 12.7 Shadowgraphs of crystallization. (a) Crystallization of  $\text{Na}_2\text{CO}_3$  in a constant vertical concentration gradient cooled from above. (b) A vertical concentration gradient cooled from the side. From Chen and Turner (1980).

chambers. Melting and assimilation of the solid boundaries of magma chambers can lead to analogous dynamic sequences – differentiation, double-diffusion and, ultimately, formation of layers.

Much of our understanding of the combined systems involving crystallization and double-diffusive processes comes from the analogous laboratory experiments with crystallizing aqueous solutions. Figure 12.7a presents an experiment in which a tank containing sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution was cooled at the top (Chen and Turner, 1980). Regardless of its initial stratification pattern (e.g., gradient or homogeneous) the system eventually developed a well-defined set of diffusive layers. Laboratory experiments have been highly effective in terms of emphasizing the coupled nature of the convective/crystallization dynamics. The term “convective fractionation” is commonly used in geological literature to describe



processes involving convection of residual fluids away from fixed growing crystals. Figure 12.7a presents one of many examples of such coupled phenomena – crystallization induces double-diffusive layers and these layers, in turn, influence the subsequent growth of the crystals. As a result, layers in the crystallized matter are well defined and characterized by a significant variation in properties. Several interesting attempts have been made to represent the coupled dynamics of magma chambers in the numerical models (Oldenburg *et al.*, 1989; Oldenburg and Spera, 1991) using simple parameterizations of crystallization. Most recently, Toramaru and Matsumoto (2012) developed a one-dimensional numerical model based on double-diffusive dynamics as well as the kinetics of diffusion-limited crystallization. They were able to reproduce major features of layering observed in a number of locations, including such subtle characteristics as the spatial trends in layer thickness.

Two-dimensional effects play an important role in double-diffusive systems with crystallization. The crystallization can happen on one or several surfaces simultaneously and so can erosion of solid boundaries. In some cases, heat escapes through the top of a chamber, in others through the sidewalls and the floor. Figure 12.7b presents an experiment in which cooling and crystallization occur at the vertical boundary. The fluid released by crystallization in this case is less dense than the original mixture and, since the density is dominated by the compositional content, the light and cold fluid rises along the wall. Both laboratory experiments and field observations suggest that boundary currents of this type are laminar over their whole depth for a wide range of chamber sizes and magma types. The boundary current continuously supplies cold and light fluid upward, slowly building up diffusive stratification in the chamber. The combination of vertical and horizontal destabilizing temperature gradients leads to the formation of a series of double-diffusive layers clearly visible in Figure 12.7b. In a certain parameter range, crystallization leads to a denser residual fluid, which can flow downward forming double-diffusively stable stratification (cold and compositionally dense fluid below the warm and compositionally light). Nevertheless, layering in this case is still possible due to thermohaline interleaving (Chapter 7) driven by the lateral gradients introduced at the cooled boundary (Leitch, 1990). The interleaving can be particularly spectacular in the case of preexisting stratification. The presence of sloping boundaries adds a new element of complexity to the problem and affects the patterns of secondary double-diffusive structures (Martin and Campbell, 1988). Another set of double-diffusive processes is triggered by the formation of convective chimneys, which focus upwelling currents into narrow vertical channels (Tait and Jaupart, 1992).

A series of dynamically interesting effects in magma chambers are associated with the time dependence of the filling pattern. It is believed that large magma

chambers are not filled by a single large pulse but by several smaller pulses over an extended period of time, which by itself could lead to layering. Most significantly, the non-uniform filling can produce a rich array of thermal/compositional configurations, many of which are likely to develop active double-diffusive convection. For instance, even the timing of a new pulse can determine the convective pattern. Fractionation of tholeiitic magma has a non-monotonic effect on density. First, the density decreases due to crystallization of olivine and bronzite. However, as lighter elements start to crystallize, density increases again beyond the original density of the primitive magma. Finally, crystallization of iron–titanium oxides leads to another reversal of the density trend. Thus, depending on the cooling history of the magma, the new material could be lighter or denser than the old fractionated magma. As a result, magma can convect, double-diffuse or cool off without mixing.

The periodic replenishment of magma chambers leads to several plausible scenarios in which finger-favorable stratification is produced (e.g., Campbell, 1996). For instance, the new pulse of magma that enters the chamber may be significantly colder and therefore denser than the magma already present in the chamber. But if the new magma is compositionally lighter, fingering convection ensues. In view of this possibility, double-diffusion has been considered as a cause of columnar finger-like structures occasionally observed in basaltic rock formations (Kantha, 1980, 1981). Double-diffusion may also occur when the chemical content of the adjacent magmas is dissimilar and individual components diffuse at different rates. In this case, the circulation is controlled by the diffusion of two or more chemical components, rather than by temperature and composition, giving rise to a wide range of processes that can be grouped under the heading of multicomponent convection (Huppert and Sparks, 1984).

Geometry is also important for circulation in the replenished chambers. If the new material is light and enters the chamber through a relatively narrow inlet at the bottom boundary, then “filling box” mechanics (Baines and Turner, 1969) will be engaged. The replenishing magma will first float towards the surface of the chamber and then gradually spread downward, creating finger-favorable stratification. Turner and Campbell (1986) point out that different dynamics are expected for funnel-shaped and inverted-funnel chambers. The gravitationally stable but possibly double-diffusive stratification is likely to be better developed in the case of the normal funnel due to the channeling effect of the inward-sloping walls. The aspect ratio of a chamber fundamentally affects the fluid dynamics of magma, as do numerous other factors not mentioned in this review. Overall, the variety of possible configurations in magma chambers is astounding, and each scenario is associated with a distinct set of physical process and circulation patterns. Being primarily an oceanographer, I may be running the risk of sounding a bit disloyal to my chosen field, but it seems that geological systems offer an extraordinarily

wide spectrum of intriguing and largely unresolved double-diffusive problems. The sheer number of possibilities may be unmatched by any other application.

We should also add that the interest in double-diffusion of magma goes far beyond intellectual curiosity. Understanding the fluid dynamics of magma chambers aids in the recognition of precursors to volcanic eruptions, assists with mineral exploration, and addresses the associated environmental problems. The mixing processes that occur between different types of magma coming into direct contact are particularly significant in this regard. Knowledge of the mixing rates is important for designing petrogenetic models, which are used to infer the origin and structure of igneous rocks. The especially intense mixing of mafic and felsic magmas could cause an increase in pressure and trigger eruptions. However, the mixing rates in magma chambers are highly variable, which makes their prediction difficult. There are numerous examples of effective mixing of different types of magma. A parallel stream of evidence suggests that distinct magmas frequently coexist in close proximity to each other, maintaining their individual characteristics for long periods of time (e.g., Turner and Campbell, 1986). The systematic analysis of the conditions that control mixing of magmas, particularly double-diffusive mixing, is a prerequisite for development of quantitative evolutionary models and is the subject of ongoing research.

In addition to magma dynamics, there are several other geological systems in which double-diffusion is expected to arise and affect circulation patterns. In particular, the dynamics of the core–mantle boundary (CMB) has been a focus of much interest and research activity (Hansen and Yuen, 1994; Montague and Kellogg, 2000; Lay *et al.*, 2004). The CMB is involved in the thermo-chemical coupling of the mantle and the core and thus plays a major role in the planetary thermo-chemical evolution. One of the key variables controlling planetary heating is the CMB heat flux. Current estimates of this flux are poorly constrained, partially because of the complex and not fully understood fluid mechanics of this region. Seismic studies find evidence of a seismic discontinuity 150–450 km above the CMB, which suggests the presence of a thermo-chemically distinct boundary layer, known as the D'' layer. This region is highly heterogeneous in chemical composition and temperature, which provides a favorable environment for double-diffusive instabilities.

The influence of diffusive convection on the structure, heat flux and chemical transport characteristics of the D'' layer has been emphasized by numerous studies. Without the stabilizing compositional gradients, this region would be strongly unstable and therefore susceptible to rapid destruction and entrainment into the lower mantle. Several modeling studies (e.g., Montague *et al.*, 1998, Montague and Kellogg, 2000) have examined the stability of the D'' layer and concluded that order one (or higher) values of the diffusive density ratio are required to maintain

its structural integrity. Hansen and Yuen (1988) argued that the observed pattern of topographic variations of the CMB could be attributed the fundamentally double-diffusive instabilities of the D'' layer. Samuel and Farnetani (2003) showed how the presence of a dense diffusive layer at the base of the mantle can profoundly affect the convective pattern in its interior. For instance, it provides a plausible explanation for the observationally inferred persistence of geochemical heterogeneities in a vigorously convecting mantle for billions of years. Inclusion of the thin diffusively convecting layer, acting as a thermo-chemical barrier, in the numerical models of the mantle (Farnetani, 1997) reduces the typical excess temperature of the plumes reaching the surface, bringing it into agreement with the inferences based on petrological models.

Buffett and Seagle (2010) suggest that diffusive processes should be active in a stratified layer at the top of the core, which is maintained by diffusion of light elements through the CMB. These authors develop a physical model for the evolution of this diffusive layer. Stratification is assumed to be close to density neutral but staircase-like in temperature and composition. The overall thickness of the stratified region is set by a balance between its diffusive spreading and the adverse tendency associated with the inner core growth and nucleation. The model predicts thickness of 60 to 70 km, although the accuracy of this estimate is difficult to ascertain. The significance of the diffusive layer is related to its control of the transfer rates of the light elements (oxygen and silicon) into the core interior.

Double-diffusion in porous media has already developed into an actively developing discipline in its own right (Nield, 1968; Taunton *et al.*, 1972; Griffiths, 1981; Green, 1984; Chen and Chen, 1993; Diersch and Kolditz, 2002; Zhao *et al.*, 2008; Trevelyan *et al.*, 2011; among many others) but the primary applications of such studies are geophysical. Porous double-diffusive convection is likely to occur in the dendritic mushy zones, formed during the cooling and crystallization of magmas. Another application, on much larger scales, is related to the motion of hydrothermal flows in the Earth's crust. The hydrothermal circulation extends to depths of about 10 km and is affected by both thermal and haline chemical buoyancy. The temperature stratification is maintained by geothermal heating and regional variations in salinity are inevitable due to active geochemical processes, seawater intrusion or contaminant disposal. There are a number of key physical differences between the homogeneous and porous media. Unlike heat, solute cannot diffuse through a solid matrix. As a result, temperature perturbations disperse more rapidly in porous media, which greatly reduces the effective diffusivity ratio. Even more unusual are the advective effects: chemical components are advected by the velocity of the liquid component but heat is effectively transported by the much slower average velocity of the media. Thus, the fluid dynamics of porous systems can be both double-diffusive and double-advective. Mechanical

dispersion is a new and significant form of mixing that appears in porous material due to the obstructions a fluid element experiences on a particular flow path. Momentum balance is better represented by Darcy's law (Darcy, 1856) and its extensions, rather than by the Boussinesq model commonly used for homogeneous media. The porosity values (the fraction of volume occupied by fluid) in the crust are generally low ( $\phi \sim 10^{-4} - 10^{-1}$ ) and therefore the circulation patterns and the consequences of porous double-diffusive processes differ from their homogeneous counterparts.

The most natural double-diffusive configuration for fluids circulating in the Earth's crust is diffusive convection – geothermal heating from below destabilizes the system whereas the chemical gradient is stabilizing – and this case has been studied more extensively. As expected, numerical simulations (Schoofs *et al.*, 1999, 2000) reveal that diffusive effects often lead to the formation of well-defined horizontal layers with nearly uniform temperature and composition. However, for typical geological parameters, diffusive convection in low-porosity media appears to be more disorganized than in pure-fluid systems. Chaotic features include irregular transitions from layered to non-layered stratification patterns. Phase (liquid/vapor) separation is another common and important process in hydrothermal settings and the inclusion of multi-phase effects can considerably affect double-diffusive flow patterns and transport characteristics (Geiger *et al.*, 2005). In this complicated and highly nonlinear system, the conventional governing parameters (such as the density ratio and the Rayleigh numbers) tend to lose some of their controlling influence on the dynamics of diffusive convection, giving way to parameters characterizing phase transitions and permeability of the media. Diffusive convection in the Earth's crust has significant implications for ore deposit formation and mineralization in hydrothermal systems, for sedimental history of subsiding basins, for groundwater pollution, and for heat transport at mid-ocean ridges. Fingering convection in porous media has also been considered (e.g., Imhoff and Green, 1988) as one of the possible scenarios of groundwater contamination in which warm, chemically laden solute overlies cooler, fresher and denser groundwater.

### 12.3 Chemistry

Numerous fluid dynamical processes in nature, including several geophysical and astrophysical phenomena, are accompanied by chemical reactions. These reactions add a new level of complexity to double-diffusive convection. The double-diffusive system ceases to be conservative; not only do density components diffuse and advect but they can be produced internally. The possibility of strong interactions between chemical kinetics and fluid dynamics has been recognized for quite some time (e.g., Dewel *et al.*, 1983; Pojman and Epstein, 1990). However, research activities

in this field have greatly intensified in the last decade or so. A new lease on life for chemical double-diffusion was brought by a fuller appreciation of the depth and richness of coupled hydro-chemical systems.

Some effects are straightforward and could be easily anticipated. If an exothermic autocatalytic reaction results in a product that is compositionally denser than the reactant solution then compositional and thermal changes have opposing influences on density – the antagonism that lies at the heart of double-diffusive dynamics. Such configurations arise in the nitric acid–iron(II), chlorite–thiosulfate, chlorite–tetrathionate, chlorate–sulfite, chlorite–thiourea, and bromate–sulfite autocatalytic fronts: the products contract while the reaction is exothermic. Free radical polymerizations also fall into the same category: they are very exothermic and form polymer products that are denser than the original monomers (Pojman *et al.*, 1992). Thus, if a chemical front is spreading downward (product above the reactant) then the system becomes susceptible to fingering. In the case of an ascending front (product below the reactant), the conditions could favor diffusive convection. Of course, the occurrence of double-diffusive convection in such systems is not guaranteed. Depending on the values of governing parameters, the system could also become buoyantly convective (top-heavy) or completely stable, but our main interest lies in the classical double-diffusive configurations (bottom-heavy and unstable). If the front spreads very slowly, allowing enough time for double-diffusive convection to fully establish, and if advective-diffusive effects are more significant than the chemical forcing, then the dynamics reduces to that of classical non-reactive systems. The role of chemical reactions in such cases is limited to creating the background stratification that supports double-diffusive convection.

However, most frequently, chemistry introduces a series of new and fundamentally coupled phenomena. Pojman *et al.* (1991) emphasize the impact of double-diffusive processes on the structure and propagation velocity of the chemical front, supporting their arguments by experiments with the iron (II)–nitric acid system. The rate of propagation of a chemical front is set by a balance between the diffusion of the reacting material and the intensity of the chemical reaction. The double-diffusive processes, salt-finger or diffusive, dramatically accelerate the transfer of properties across the front relative to molecular diffusion, which increases the speed of the front by up to two orders of magnitude. The descending (fingering) fronts are more distributed and generally propagate at higher speeds than the ascending ones. The motion of the front, in turn, can affect the double-diffusive circulation patterns. A number of studies have modeled, experimentally and numerically, the fluid dynamics of chlorite–tetrathionate reactive fronts (Bansagi *et al.*, 2003, 2004; Toth *et al.*, 2007), and examples of fingering are shown in Figure 12.8. Kalliadasis *et al.* (2004) noted that fingers formed in the descending fronts are frequently characterized by a “frozen” cellular structure, and – unlike non-reactive fingers – remain

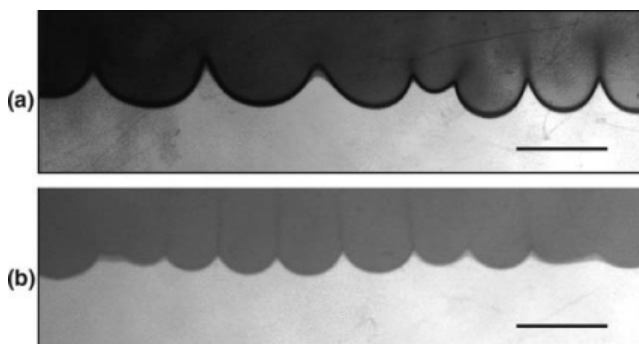


Figure 12.8 Images of fronts propagating downward. Darker regions represent the product solution and lighter the reactant. The black bar corresponds to 5 mm. From Bansagi *et al.* (2004).

spatially constrained to a narrow high-gradient interface and do not penetrate into the homogeneous interior.

Even more subtle and intriguing phenomena have been reported by D'Hernoncourt *et al.* (2006, 2007a,b), who argued that double-diffusive destabilization of the ascending exothermic chemical fronts is possible even when both temperature and compositional gradients are overall stabilizing. This counterintuitive effect is driven by the interplay between chemistry and fluid dynamics. When a fluid particle is displaced from the upper (warm and light) region occupied by the product-rich material into the reacting zone, it rapidly adjusts its temperature but not its compositional content. Thus, it is less engaged in chemical reactions than the surrounding reactant-rich fluid. The particle receives less heat chemically, becomes denser, and continues to sink. The positive feedback implies the existence of a new type of fingering instability, which does not arise in non-reactive media. More detailed analysis reveals that the chemical instability takes the form of small-scale cellular structures located in the reacting front and that it is highly sensitive to the diffusivity ratio. This instability is most obvious in doubly stable configurations. However, the chemical modes are also present in double-diffusive regimes, where they can substantially broaden the parameter space of instability. Of particular theoretical interest are the mixed instabilities that critically depend on both chemical and classical double-diffusive mechanisms.

Of course, temperature need not be the main diffusive component, and innumerable possibilities exist for double-diffusive effects driven by the differences in diffusivities of individual chemical components. For instance, Rica *et al.* (2010) performed a series of experiments with acid-catalyzed chlorite–tetrathionate reactions in a horizontally propagating front. Thermal effects on buoyancy were largely negligible, yet the purely compositional double-diffusion was sufficiently vigorous



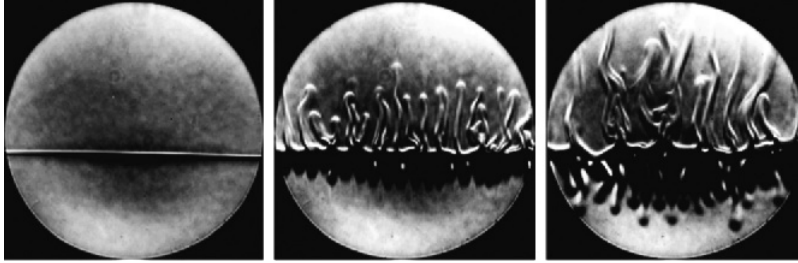


Figure 12.9 Evolution of the interface between a solution of HCl on top of a solution of CsOH. A snapshot was taken every minute. The field of view is 3 cm. From Almarcha *et al.* (2011).

and profoundly affected the patterns and evolution of the system. A number of studies have focused on the instabilities of the interfaces between solutions containing different reactants (Zalts *et al.*, 2008; Almarcha *et al.*, 2010a,b). Such configurations are more complicated and phenomenologically rich than the systems with an initially homogeneous reactant and typically are more unstable. The dynamics of such systems are controlled by the relative densities and diffusivities of both reactants and their product.

Interesting examples were presented by Almarcha *et al.* (2011), who performed a series of experiments on the neutralization of a strong acid by a strong base in an aqueous solution. By systematically varying the initial concentrations and the type of base reactant, various forms of buoyancy-driven circulation were produced and systematically examined in the Hele-Shaw cell. Figure 12.9 presents an experiment in which a solution of hydrogen chloride (HCl) was placed in the upper layer and caesium hydroxide (CsOH) in the lower layer. Since  $\text{H}^+$  is the fastest diffusing cation and  $\text{OH}^-$  the fastest diffusing anion, the product of the reaction diffuses slower than both of these reactants. Thus, for suitably chosen experimental parameters (density decreases upward but gently enough not to quench double-diffusion) it is possible to induce the circulation pattern that is concurrently controlled by diffusive convection in the upper layer and by fingering in the lower layer. These dynamics are easily identifiable in Figure 12.9 by irregular plumes rising above the interface and narrow fingers spreading downward. Thermal effects in this experiment are of marginal significance. The evolutionary pattern shown here is one of several possible outcomes; depending on the reactants and their concentration, circulation can be limited to diffusive plumes in the upper solution only or to fingers in the lower solution. However, the hybrid system (Fig. 12.9) is of particular interest since it conjoins in a single experiment the adversary diffusive and fingering phenomena. The simplicity and elegance of the experimental setup in this case is



afforded by the clever use of chemical reactions to control fluid dynamics – a nice example of an effective and truly multidisciplinary approach.

## 12.4 Materials science and engineering

Over the years, double-diffusion has become recognized as an important process in quite a few industrial applications and is currently the subject of intense research activity in these areas. The general philosophy of engineering studies is conspicuously dissimilar to that of more basic physical sciences. In most industrial problems, double-diffusion is regarded as an undesirable phenomenon: it compromises the quality of metal alloys, increases the chances of rollover in liquid gas tanks, and adversely affects the performance of solar ponds. Engineering research is motivated by the “know your enemy” principle, which actually can be an even more effective driver than the intellectual curiosity of a physicist or a mathematician. However, the pragmatic engineering attitude has introduced a strong bias towards the solution of immediate practical problems, leading the field a bit astray from analyzing the fundamentals of double-diffusive dynamics. In this section, we discuss two representative examples of industrial applications: solidification of metal alloys and double-diffusive effects in solar ponds.

### *Solidification of metal alloys*

There are several ways in which double-diffusion comes into play in solidifying systems. On the most primary level, it affects the morphology of the liquid/solid interface (Coriell and Sekerka, 1981; Schaefer and Coriell, 1984; Lan and Tu, 2000). The geometric complexities of dendritic solidifying zones can be ultimately traced to small-scale instabilities of initially planar interfaces. The significance of such instabilities in the dynamics of solidification has long been known (Langer, 1980), and their ability to create intricate patterns is truly impressive. The exquisite shape of a snowflake, incredibly complex and precise, is perhaps the most common and striking example of the spontaneous evolution of a two-phase interface. In some cases, the instability is purely morphological; it is driven by capillary effects, diffusion kinetics and thermodynamic constraints. However, the interfacial instabilities become very different in the presence of buoyancy-driven circulation in the liquid layer. The fluid dynamical and morphological instabilities are intrinsically linked by the boundary conditions at the interface and their interaction becomes particularly intricate in doubly diffusive media (Coriell *et al.*, 1980; Nguyen Thi *et al.*, 1989; Anderson *et al.*, 2010). New morphological/double-diffusive unstable modes emerge and profoundly affect the evolution of an interface. Somewhat

counterintuitively, these coupled instabilities can occur even when both diffusing substances in the liquid region are stably stratified. The double-diffusive version of the classical phase-change problem is phenomenologically rich and offers new physical routes to the breakdown of the interface and the formation of dendrites.

An example of a more industrially motivated type of double-diffusive research in metallurgy is given by studies of freckle formation in metal alloys. Freckle defects are the segregation channels that are formed during directional solidification of alloys, and their occurrence remains a major problem in the casting industry. For instance, freckles can severely weaken superalloy turbine blades for high-temperature applications. The rejection rate of turbine blades due to macrosegregation defects can be as high as 40%. It is generally accepted (Giamei and Kear, 1970; Sarazin and Hellawell, 1988; Hansen *et al.*, 1996) that freckles are caused by buoyancy-driven circulation – convection or double-diffusion. The latter is commonly referred to in metallurgical literature as thermosolutal convection. The dynamics of freckling is analogous to the convective fractionation effect that occurs in magma chambers (Section 12.2); it involves the interaction between the morphology of solidification and fluid dynamics.

When the alloy is cooled from below and liquid released during solidification is compositionally light, the zone immediately above the mushy solidifying layer becomes susceptible to fingering. The buoyancy-induced circulation plays a dual role in the dynamics of solidification: it directly causes the segregation of the material and also provides a mechanism for the transport of dendritic fragments from the mushy region into the bulk liquid. Surviving fragments become nuclei for solidification and block the parental dendritic front. The resulting inhomogeneities of the solid material can be substantial, profoundly affecting its mechanical characteristics. A series of such finger-driven freckles is clearly visible on the surface of a superalloy ingot shown in Figure 12.10. Similar adverse double-diffusive effects often compromise the production of chemically homogeneous crystals used in the electronics industry.

The closed character of casting systems poses obvious constraints on the direct measurement of solidification in metal alloys. To address the observational limitations, two lines of inquiry have been actively pursued. The older traditional approach (e.g., Copley *et al.*, 1970; Sample and Hellawell, 1984; Hansen *et al.*, 1996) involves the analysis of transparent aqueous analogs followed by the extrapolation of the results to opaque metallic systems based on the post-mortem examination of fully solidified samples. The major problem with this method is that the analogies between the metallic and aqueous systems are very qualitative. Prandtl numbers and diffusivity ratios differ by orders of magnitude and, consequently, so do the double-diffusive fluxes. Typical incubation periods in solidifying metals are very brief compared to crystallizing aqueous systems, which makes the



Figure 12.10 An example of freckling in a metal alloy. From Hansen *et al.* (1996).

extrapolation attempts even more questionable. Experimental uncertainties, combined with computational advancements over the past few decades, have led the casting community to become increasingly more interested in the numerical modeling of solidification (reviewed by Voller *et al.*, 1990; Beckermann, 2002; among others).

Numerical models of solidification have been developed since the 1960s (Flemings and Nereo, 1967, 1968a,b). However, the early models were principally deficient in their focus on the solute redistribution during solidification contraction; double-diffusive effects were not taken into account. As a result, these models failed to capture the essential mechanisms for the formation of freckles. The next generation of numerical models appeared much later (Benetton and Incropera, 1987; Beckermann and Viskanta, 1988). The entire casting system, including its liquid, mushy and solid components, was treated using the unified formalism of volume-averaged equations. The differences in types of media were taken into account by assuming spatially variable permeability, which removed the need to model the evolution of the liquid/mushy interface. The ability of these models to explicitly represent double-diffusive effects substantially improved their predictive capabilities.

However, several significant challenges remain. Mesoscale solidification models are only as good as the macroscopic parameterizations they assume for all essential microscopic processes, including nucleation, microsegregation, thermal/solutal undercooling and solid movement. The development of accurate parameterizations – currently an active area of research – is necessarily conditioned by progress in the physical understanding of solidification microdynamics (e.g., Heinrich and Poirier, 2004). In this regard, it is interesting to note that double-diffusion is also engaged on the microscale level. Double-diffusively induced currents inside interdendritic regions affect the dendrite growth and pattern formation. Taking the thermosolutal circulations into account reduces the spacing between the adjacent dendrites (Spinelli *et al.*, 2004, 2005), which impacts the macroscopic properties of the mushy zone.

Another major difficulty is associated with the wide range of dynamically important scales present in double-diffusive convection, from the solute dissipation scale to the characteristic size of the casting domain. The modeling of freckle segregation with mesh adaptation schemes (Sajja and Felicelli, 2011) appears to be particularly promising in this regard. A different set of complications arise in modeling multicomponent alloys. The analysis of generalized solidification models developed for multicomponent systems (e.g., Schneider and Beckermann, 1995) has revealed that additional elements induce substantial changes in the convective patterns and macrosegregation dynamics. This finding has brought into question earlier attempts to model multicomponent systems with binary models. Overall though, I am happy to report that, despite all the obstacles, the field of solidification modeling is rapidly advancing. In the not too distant future we can expect development of reliable computational models that can guide innovation in the casting industry. The ultimate goal of such models is to reduce or even eliminate the need for the expensive and time-consuming experimental trial-and-error stage in the design of ingots and castings.

### ***Solar ponds***

The first impression of a person trying to figure out the operating principle of a solar pond is that this device is nothing more than the diffusive convection experiment, reproduced on a large scale and industrially utilized. The essential dynamical component of solar ponds is the initially introduced stable salinity stratification. The relatively shallow layer of water (1–4 m) in solar ponds is nearly translucent to solar radiation and therefore much of the radiant solar heat is absorbed at the bottom. As a result, water in deep regions of a solar pond is much warmer than that near the surface. In the absence of salinity stratification, this would lead to convective overturns and rapid homogenization. However, salt maintains a stable

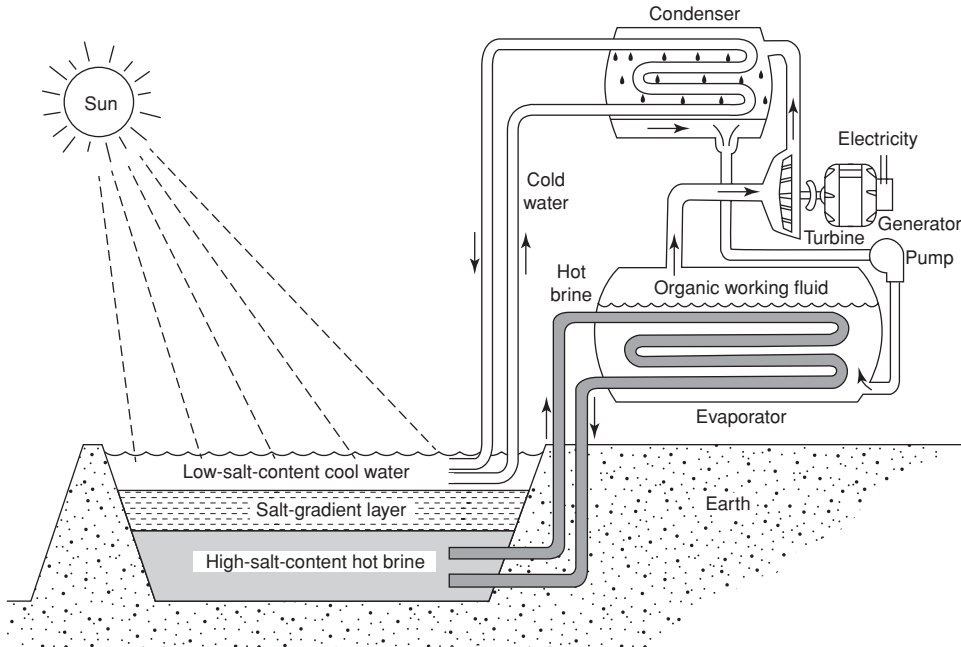


Figure 12.11 Schematic diagram of a power-generating solar pond.

density distribution, the circulation is minimal, and heat remains trapped in the lower layer. Thermal energy collected in this manner can be used for various applications, such as heating, desalination, refrigeration, drying and electric power generation (Fig. 12.11). While in this section we focus on artificial solar ponds, it should be mentioned that there are natural examples of solar pond dynamics, such as the saline Solar Lake in the Sinai Peninsula of Egypt.

Salty, warm and dense water that is located below cold, fresh and buoyant sounds very familiar – it is the configuration prone to diffusive convection. But does this mean that double-diffusion has found a new practical use in the form of solar ponds? Not exactly. The mixing induced by diffusive convection can transport heat to the surface, where it would be rapidly lost to the atmosphere. This could seriously compromise the dual purpose of a solar pond as a thermal energy collector and as a heat storage mechanism. Once again, double-diffusion shows its dark side and should be avoided in solar ponds by all means. This is not a trivial task since the medium (heat–salt) is fundamentally double-diffusive and therefore the solar pond problem has stimulated a fair amount of research. Designing solar ponds and making proper maintenance decisions requires clear understanding of the conditions that can trigger double-diffusive convection and of its consequences (Tabor, 1980, 1981).

Typically, a solar pond consists of three distinct regions (Fig. 12.11): (i) the top mixed layer, which is relatively cool and fresh, (ii) the warm and salty bottom mixed layer and (iii) the non-convective zone (NCZ) separating the two mixed layers. The primary purpose of the NCZ is insulation. The temperatures in the lower layer can reach as high as 90 °C, whereas the upper layer is in equilibrium with the ambient atmosphere, typically at about 30 °C. Maintenance of large top-to-bottom temperature differences ( $\Delta T$ ) is essential for the efficient extraction of energy in solar ponds. According to Carnot's theorem,  $\Delta T$  controls the maximum theoretical efficiency of energy extraction from a high-temperature reservoir (Carnot, 1824). In this regard, the insulation between upper and lower mixed layers is critical and the foremost consideration for the design of solar ponds is to minimize heat transport through the NCZ. This implies that two conditions are met: (i) the inevitable molecular diffusion should be the only source of heat transport through the NCZ and any form of turbulence should be avoided; and (ii) temperature gradients should be low, which means that the NCZ region should occupy a large fraction of a solar pond, typically about half of its depth.

Both requirements lead to interesting engineering challenges. As discussed in Chapter 4, diffusive systems with relatively low density ratios ( $R_\rho^* < \tau^{-1/2}$ ) tend to spontaneously evolve to a statistically steady configuration in which convecting layers are separated by a thin interface. In order to avoid this scenario, salinity concentration in the lower layer should be very high ( $R_\rho^* > 10$ ). This complicates the maintenance of solar ponds, requiring continuous brine injection in the lower layer, the removal of salt crystals and surface washing (Ouni *et al.*, 2003). But even if the density ratio is kept high, convective motions in the lower mixed layer can still lead to the gradual erosion and/or vertical drift of the NCZ (Zangrando and Fernando, 1991; Karim *et al.*, 2011). The life expectancy of solar ponds due to breakdown of the NCZ is about 10–15 years, after which the solar pond has to be drained and refilled in order to continue its operation. The destruction of the gradient region occurs by means of local instabilities at the lower boundary of the NCZ, induced by bottom-layer convection. To some extent, the problem could be mitigated by introducing the initial salt stratification that minimizes the strength of such instabilities – an interesting fluid dynamical problem in its own right. Karim *et al.* (2011) also suggest that the durability of solar ponds can be substantially increased by introducing a grid that would suppress the convective vortices in the lower layer. Implementation of thin horizontal membranes in solar ponds to prevent the vertical transport of salt is another interesting idea, which is currently at the research and development stage.

Another pressing problem for the operation of solar ponds, which is also double-diffusively induced, involves the generation of lateral interleaving at the sidewalls (Akbarzadeh and Manins, 1988; Jubran *et al.*, 1999). The relatively small-scale



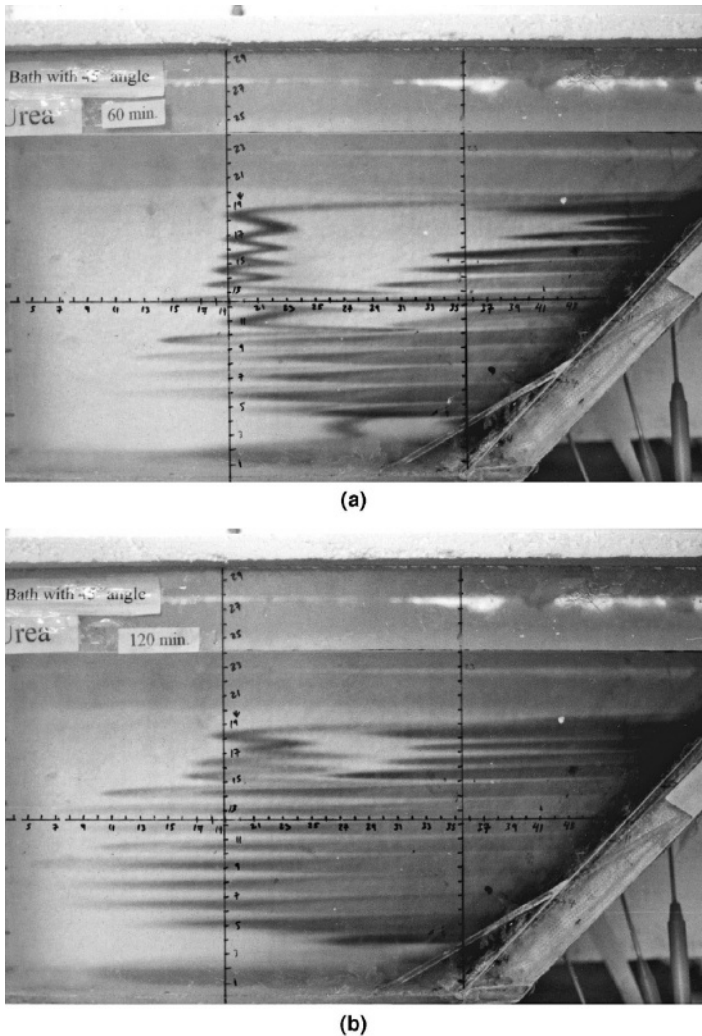


Figure 12.12 Interleaving in a solar pond with inclined sidewalls. From Jubran *et al.* (1999).

intrusive structures, driven by heat absorbed at the sidewalls, can lead to substantial changes in the overall stratification of the NCZ. If this effect is not accounted for, the gradient zone can become unstable, which would ultimately lead to the destruction of the NCZ. Sidewall interleaving is a generic property of diffusively stratified systems (Chapter 7). Intrusive currents could be particularly intense in solar ponds with inclined walls, which are often used to minimize the ground heat loss and to eliminate shadows. Figure 12.12 shows a series of nearly horizontal layers spreading from the sidewalls into the interior of a solar pond. Their progression is

quite rapid and effects on the stability of the NCZ could be profound. As a way of reducing the adverse consequences of sidewall interleaving, Jubran *et al.* (1999) suggest several measures: (i) usage of high angles of sidewalls; (ii) experimentation with different types of salts – intrusions are sensitive to the molecular properties of the media; and (iii) increasing the roughness of sidewalls, which has a detrimental effect on intrusions.

Despite the numerous problems of this nature, solar pond technology is promising. The first solar pond experiments were made in the late 1950s, and by the 1970s significant progress had been made (Tabor, 1980). Solar ponds have been built and industrially operated in several countries (Israel, Australia, India and Tunisia, among others). For many years, solar ponds have been discussed as an attractive source of cheap energy in developing countries, most of which are located in warm low-latitude climates. However, the implementation of this idea has been disappointingly slow and small-scale. A new impetus for solar pond technology was brought about by the recent worldwide surge of interest in renewable energy. On the other hand, solar ponds now have to compete with other emerging technologies: solar panels, wind-driven turbines and bio-fuels. Whether solar ponds can survive and succeed in such a competitive environment depends on many factors, one of which is our ability to design reliable, low-cost but long-lasting systems. Progress in this direction requires complete understanding of the fluid dynamics of solar ponds and, particularly, of the ubiquitous double-diffusive effects.

## 12.5 Other applications

There are several applications of double-diffusive convection that are not easily classified into well-defined scientific disciplines and therefore are combined here under the hopelessly vague heading of “other.” For instance, archetypal double-diffusive dynamics are commonly realized during sedimentation in stratified fluids. Stratified sedimentation in itself is a broad multidisciplinary subject, largely motivated by environmental concerns. Specific applications include a variety of natural and industrial processes: dynamics of dust particles in the air, sedimentation in rivers and oceans, collective evolution of swimming microorganisms, dispersal of atmospheric pollutants, dilution of undersea sewage and dredged materials. If the background density stratification is gravitationally stable and the particle concentration decreases downward, the sedimenting particles could play the role of a destabilizing agent. The resulting instability takes a form dynamically analogous to fingering convection (Drake, 1971; Chen, 1997). These particle-driven dirt fingers have been studied experimentally in two-layer configurations (Green, 1987; Hoyal *et al.*, 1999), in a gradient stratification (Houk and Green, 1973) and at the base of spreading gravity currents (Maxworthy, 1999; Parsons *et al.*, 2001).



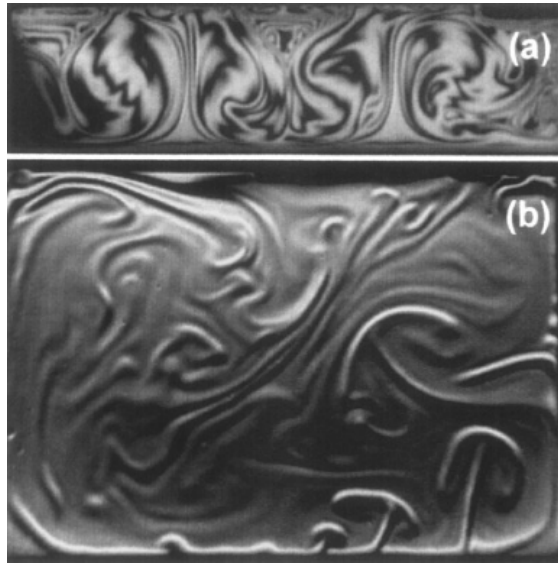


Figure 12.13 Flow patterns in soap films. (a) The steady circulation regime for the temperature variation of  $\Delta T = 15^\circ\text{C}$ . (b) Chaotic pattern realized for  $\Delta T = 45^\circ\text{C}$ . From Martin and Wu (1998).

All this talk about dirty fingers makes us yearn for some soap. Some peculiar examples of double-diffusion can be found among experiments with freely suspended soap films (Martin and Wu, 1998). At first, such experiments come across as a bit esoteric and frivolous, although undeniably entertaining. In reality, however, they carry the significant function of isolating essentially two-dimensional aspects of double-diffusive convection in the laboratory setting. In this regard, soap films offer an attractive alternative to the thin-gap (Hele-Shaw) experiments, where solid boundaries strongly impede flow, resulting in fundamentally frictional dynamics. The setup of soap film experiments is simple and circulation patterns are easily observable. Figure 12.13 shows the diffusive convection that occurs when a soap film is heated from below. The competing double-diffusive mechanisms in this case are the density reduction due to heating and the film's tendency to increase its thickness downward under the action of gravity. As the temperature difference between the bottom and the top of the film is gradually increased, the system first transitions from a stable steady state to a time-dependent state characterized by periodic oscillations of a standing-wave pattern. When the temperature difference is further increased, the system develops the steady circulation pattern presented in Figure 12.13a. This regular pattern changes once again for even larger temperature differences, resulting in the chaotic and disorganized state in Figure 12.13b. Overall, the dynamics and transitions observed in the soap film experiment follow

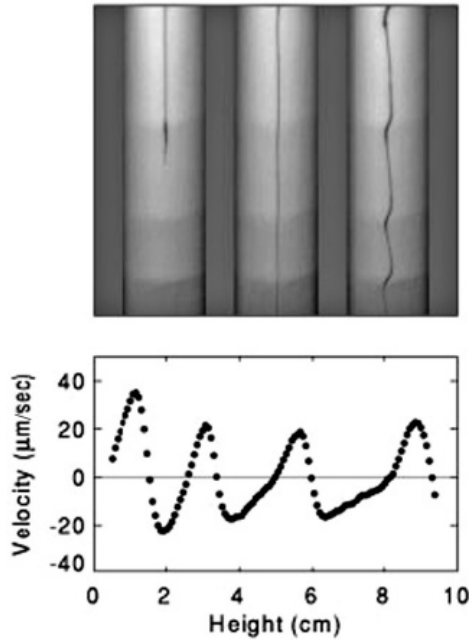


Figure 12.14 Direct visualization of convective flow in a stratified suspension. (Top) Evolution of stratified emulsion and formation of layers. The circulation pattern is revealed by the deformation of the initially vertical dye line. (Bottom) The horizontal flow velocity along the tube's center line as measured from the photographs above. From Mueth *et al.* (1996).

the scenario realized in the analytical and numerical studies of diffusive convection (Veronis, 1965, 1967).

An interesting example of double-diffusion at play is given by spontaneous layering of initially homogeneous colloidal suspensions in narrow containers. This effect has been known for more than a century (Brewer, 1884) but a clear physical explanation has eluded observers. Several mechanisms have been proposed to explain these observations, including spinodal decomposition, formation of streaming flows, and generation of Burgers shocks. However, a series of flow visualization experiments with creaming emulsions (Mueth *et al.*, 1996) finally provided strong evidence in favor of the double-diffusive mechanism of layering. These experiments demonstrated that each layer in a stratified suspension is associated with a convecting roll (Fig. 12.14). The circulation pattern was shown to be highly sensitive to the horizontal thermal gradient, which led Mueth *et al.* to suggest that the origin of the layers is the instability due to coupling between the vertical gradient in the concentration of suspended particles and the horizontal thermal

gradient. This mechanism is dynamically analogous to the thermohaline interleaving in laterally bounded fronts discussed in Chapter 7. The lateral gradients required to engage such dynamics are surprisingly low ( $\sim 10 \text{ mK m}^{-1}$ ) and could easily have been present in most, if not all, previous experiments with colloidal suspensions.

Double-diffusion in moist air is rarely invoked in the discussions of double-diffusive convection. The diffusivity ratio of humidity/heat is close to unity ( $\tau \approx 0.8$ ) and therefore double-diffusive effects are usually assumed to be secondary. This assumption has been questioned by Bois and Kubicki (2002, 2003), who pointed out that the dynamics of saturated air can differ from that of unsaturated systems. In the saturated case, the buoyancy-driven circulation is inherently coupled with the liquid/vapor phase change. Since the diffusivities of the liquid and gaseous phases are different, double-diffusive processes are readily engaged. Bois and Kubicki argue that the resulting instabilities come in the form of moisture fingers, dynamically analogous to salt fingers in the ocean. These moisture fingers, among other processes, could be responsible for the specific texture of “fleecy clouds” in the statically stable moist-saturated air. The oscillatory diffusive regime is also possible in the atmosphere but should not be as common as fingering under typical meteorological conditions.

The list of applications could go on and on. There is an immensely broad range of problems that have formal mathematical analogies with double-diffusive convection, although the physics may be dissimilar. One such problem is the analysis of Langmuir circulation – a system of shallow, counter-rotating vortices, commonly manifested by parallel streaks of foam and debris at the surface of a natural body of water. While this phenomenon is unrelated to double-diffusion of heat and salt, the governing equations that are used to describe Langmuir circulation are identical to the standard double-diffusive system. In this case, velocity and temperature play the roles of  $T$  and  $S$  respectively (Leibovich, 1983). Another example of isomorphism is presented by the so-called GSF (Goldreich–Schubert–Fricke) instabilities associated with differential rotation in stably stratified stars (Goldreich and Schubert, 1967). The difference in the rate of energy and lepton diffusion in post-collapse stellar cores can drive the neutron-finger instability, which could play a role in supernova explosions (Wilson *et al.*, 1986; Wilson and Mayle, 1993). Convection in a magnetic field is yet another field that has direct parallels with double-diffusive convection (Proctor and Weiss, 1982). A whole class of problems emphasizes the dynamically distinct roles of buoyancy components even when their molecular diffusivities are the same – the fundamentally two-component effects may occur due to the nonlinearities of a mixing model or the differences in boundary conditions (Welander, 1989; Ferrari

and Young, 1997). Another Pandora's Box opens when the difference in viscosities, rather than diffusivities, of mixing components is taken into account (Homsy, 1987). Such double-viscous systems are known to produce viscous fingering, a phenomenon that has apparent similarities to the buoyancy-driven fingering.

Undoubtedly, the exchange of knowledge between different fields, related by equivalent dynamics and/or by similar math, can be highly beneficial for all parties involved. But whether or not such analogue systems should be considered part of the core theory of double-diffusion is open to interpretation. In this monograph, we adopted a rather conservative approach – the “if it is not about heat and salt, then don't complain” principle. The whole grey area of related-to-double-diffusion studies has been mentioned in passing. The breadth of the subject is the author's only excuse. Considering that the number of articles published on the salt-finger subject alone already exceeds a quarter of a million (Google Scholar) it becomes apparent that any attempt to summarize the status of the field in a single book requires major sacrifices. The choices that have been made are unavoidably subjective and many of them might be unintentionally unfair. On this apologetic note, let us proceed towards the end. A couple of brief personal remarks in the next chapter will conclude our story.