

Dissipative Structures in Demixing Binary Liquid Systems

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The demixing of a horizontal fluid layer of far-critical composition in the presence of a vertical temperature gradient can cause the formation of dissipative structures and thereby lead to a regular distribution of the precipitate. The occurrence of these convective structures is explained with the model of a Rayleigh-Bénard instability (RBI) which is driven by parallel gradients of temperature and concentration. The distribution of the precipitate is a synergetic effect of the macroscopic convective pattern and the local action of the Marangoni flow at the surfaces of the drops. If boundary conditions prohibit an RBI, the distribution of the precipitate also becomes inhomogeneous in course of time; however, in this case no regular pattern is observable and the inhomogeneities develop mainly due to the Marangoni convection near the surfaces of the larger drops that have settled at the boundary of the sample volume.

Key words: Fluid phase decomposition, Dissipative structures, Precipitate organization, Rayleigh-Bénard instability, Marangoni instability.

Introduction

The investigations of phase decomposition or hydrodynamic instabilities may be an access to processes leading to self-organization and to the development of chaos in systems far from equilibrium. The opening of the near space to experimental work on reduced gravity conditions has given a fresh impetus to these investigations due to the fact that now phenomena become observable which on earth are hidden by dominant gravitational effects [1, 2].

Our investigations are concerned with phase decomposition in fluid mixtures, to which various phenomena can contribute. In a previous paper [3] we reported the appearance of dissipative structures in a demixing thin layer of the binary system cyclohexane + methanol, which is accompanied by the corresponding organization of the precipitate. These patterns are supposed to be caused by a gravitational hydrodynamic instability and not by spinodal effects [4, 5]. Meanwhile the investigations have been continued to identify the driving forces of the structure formation.

Experimental

The experimental setup is described in detail elsewhere [6].

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The sample cell (Fig. 1) had to be improved, however, in order to make possible the application of a defined vertical temperature gradient to the thin fluid layer, which is of cylindrical shape (diameter = 25 mm, depth = 2 mm). For this purpose the temperatures of the two sapphire windows, which have good thermal conductivity and form the upper and the lower boundaries of the sample volume, respectively, must be controlled independently. Therefore the hollow screws that support the sapphires were closed with glass windows and the resulting two little chambers were connected to two thermostats which pump turbulently flowing water through the cavities. A thermocouple is used to measure the temperature difference. To perform a pressure jump induced decomposition the sample cell is filled with the homogeneous fluid mixture. The inlet of the cell is closed by a membrane of Kalrez (Du Pont) to prohibit any contact between the sample liquid and the pressure medium. Then the cell is connected to the pressure supply (Fig. 2) and the desired values of the initial pressure and the temperature difference are adjusted. A period of 30 minutes is given to the sample in order to allow the formation of a stationary temperature gradient and the appearance of a (thermal) convective instability. After valve 2 has been closed, a defined pressure is generated inside the left part of the supply. Its magnitude is chosen to lead to the desired final pressure value in the sample cell, when after the sudden opening of valve 2 the pressure equilibration that needs some milliseconds has fin-

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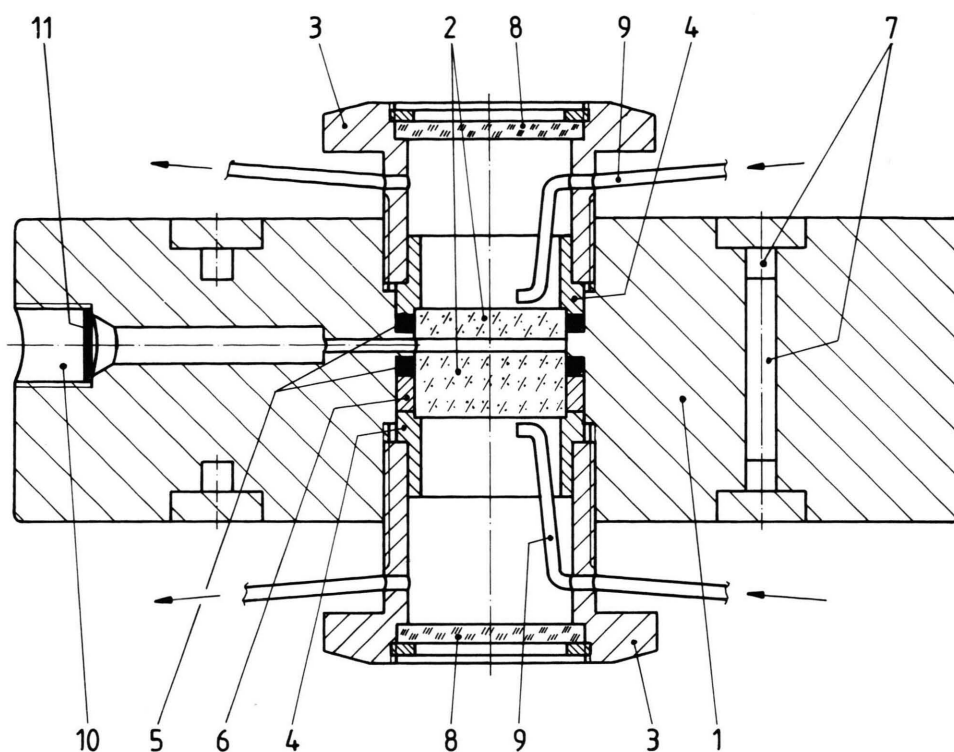


Fig. 1. Sectional view of the sample cell, 1 annular steel body, 2 sapphire windows, 3 hollow screws, 4 rings supporting the windows, 5 O-ring seals, 6 spacer, 7 channels for the temperature control of the body, 8 glass windows, 9 channels for the temperature control of the sapphire windows, 10 inlet boring, 11 membrane.

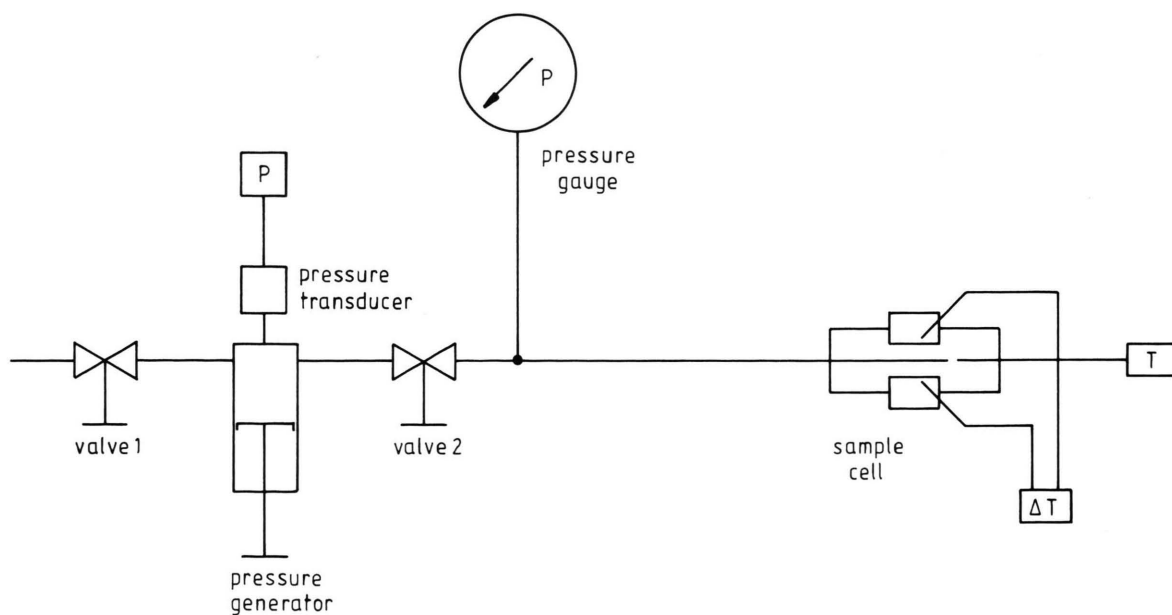


Fig. 2. Schematic drawing of the experimental setup.

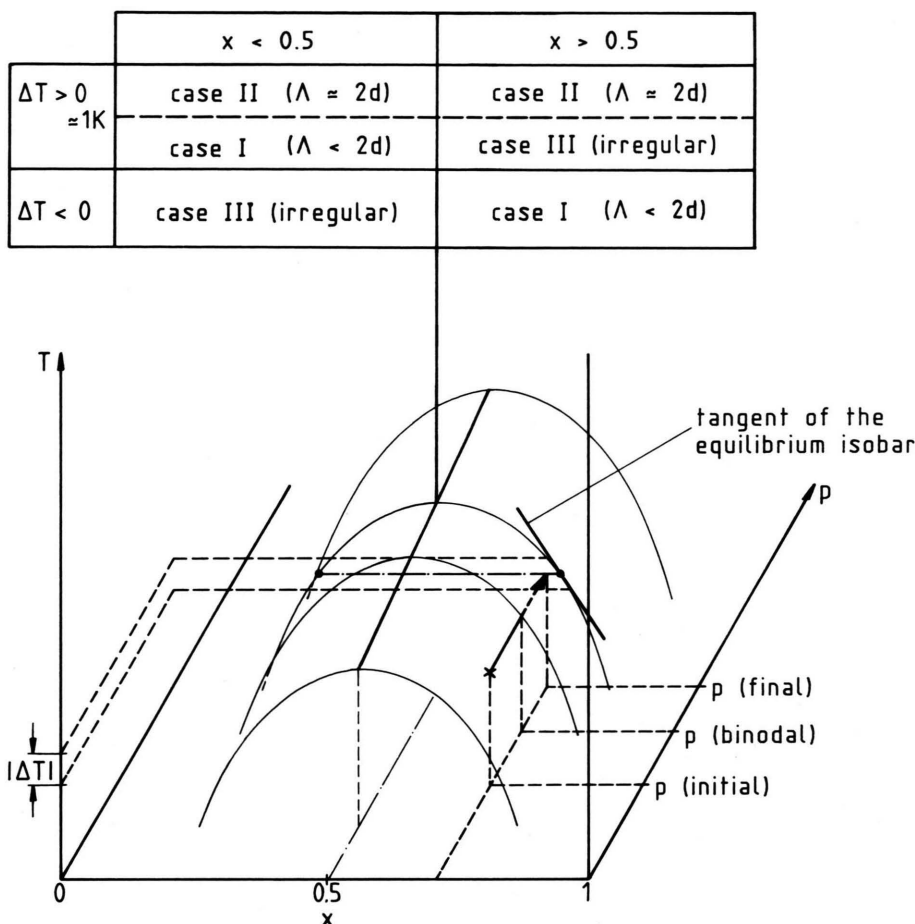


Fig. 3. Summary of the phenomenological results. The table shows the appearance of the different kinds of dissipative structures (see text) in the demixing system cyclohexane + methanol due to the experimental conditions. Below the table the miscibility gap is presented schematically. The arrow symbolizes an exemplary pressure jump into the gap on the cyclohexane-rich side ($x > 0.5$). The dots represent the equilibrium phases after the jump at the mean temperature of the fluid. According to the slope of the equilibrium isobar the temperature gradient results in a concentration gradient inside the bulk phase. x = mole fraction of cyclohexane, ΔT = temperature difference = $T(\text{lower}) - T(\text{upper})$, Λ = wavelength of the regular structures, d = depth of the fluid layer, T = temperature, p = pressure.

ished. The value taken for the final pressure ensures that the demixing of the fluid occurs in the whole sample volume.

The fluid layer is illuminated from below and the behaviour of the fluid is documented from above by a video camera either directly or through a microscope. For the experiments the system cyclohexane + methanol was chosen, which exhibits a liquid-liquid miscibility gap that increases with pressure (upper critical solution temperature at normal pressure = 318 K; critical mole fraction = 0.5). It is distinguished by the fact that the equilibrium phases are quasi-isopycnic (density difference $\approx 5 \text{ kg/m}^3$). Consequently a fast de-

position of the precipitate after phase splitting is inhibited and the system may serve as a model for substances of greater density difference under reduced gravity conditions, which are of interest, e.g., in material science [1].

The adiabatic pressure jump that induces a sudden demixing of the fluid also causes a small temperature jump that can, however, be neglected here because of the rapid relaxation of temperature disturbances in comparison to the time scale of mutual diffusion or the formation of new dissipative structures.

Convection of the bulk fluid was observed by the motion of microscopic droplets which are too small to

be influenced remarkably by buoyancy or Marangoni effects.

Experiments were performed for different choices of the composition of the mixture (x = mole fraction of cyclohexane = 0.15, 0.20, 0.35, 0.65, 0.80), the value and the direction of the temperature difference ($-2 \text{ K} \leq \Delta T \leq 3 \text{ K}$, where $\Delta T = T(\text{lower}) - T(\text{upper})$) and the depth of the pressure jump into the miscibility gap ($2 \text{ MPa} \leq p(\text{final}) - p(\text{binodal}) \leq 6 \text{ MPa}$).

Results

Our investigations resulted in a manifold of patterns, which we have divided into three phenomenological cases.

No strong influence of the pressure jump magnitude was observed on the morphology of an appearing pattern. On the contrary, the composition of the liquid and the temperature difference applied are decisive for its regularity, size and form. The table in Fig. 3 gives a summary of the different cases as a function of the experimental conditions.

The behaviour of the precipitate is reported in detail elsewhere [7], so we will concentrate here upon the macroscopic pattern formation only.

Case I

The fluid layer is at rest prior to the pressure jump. After the jump that induces demixing in the whole sample a homogeneous turbidity is observed, which a few minutes later begins to show some regular inhomogeneities. In the nascent state of pattern formation a roll-shaped structure may occur (the three-dimensional motion of the small droplets is perceptible under the microscope); however, in the long run a cellular pattern appears.

The wavelength λ , i.e. the size of the spatial periodicity of the structure, is smaller than $2d$, where d means the depth of the fluid layer. In most experiments λ is found to be in the range between d and $1.5d$. Detailed quantitative investigations concerning the wavelengths of the appearing patterns are in progress. The reciprocal time τ^{-1} (where τ is the time that passes between the demixing and the first noticeable macroscopic pattern formation) is taken as a rough measure of the growth rate. It increases monotonically with the absolute value of the temperature gradient (Fig. 4).

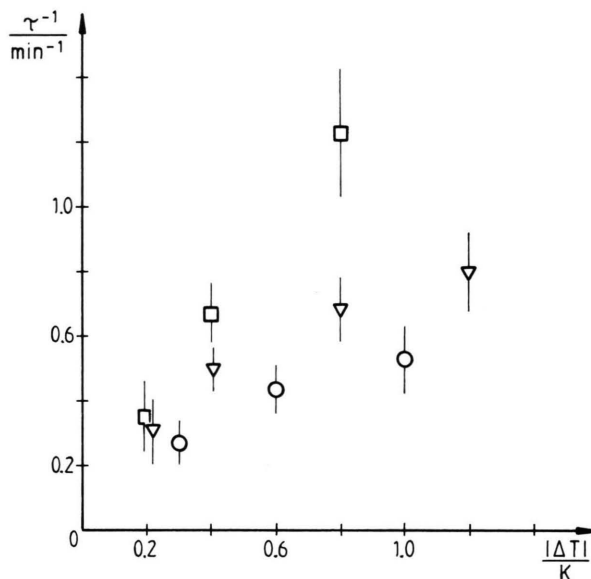


Fig. 4. τ^{-1} vs. absolute value of the temperature difference $|\Delta T|$ (where τ = time that passes between demixing and occurrence of the macroscopic pattern) for various compositions; mole fraction of cyclohexane = 0.15 (○; $\Delta T > 0$), 0.35 (□; $\Delta T > 0$), 0.65 (▽; $\Delta T < 0$).

This case includes the structures reported earlier [3]. The later state is similar to that presented in Fig. 5b.

Case II

No homogeneous turbidity is found after the jump. On the contrary, the distribution of the nascent precipitate is regular and indicates a roll-shaped convection in the bulk fluid that must have developed already before the jump (Fig. 5a). These structures always possess wavelengths of about $2d$ and often have the shape of concentric rings. We consider this kind of convection to be a thermal RBI mainly due to the following facts:

(i) The effect occurs if and only if the temperature difference exceeds a critical value of about 1 K. We have calculated the thermal Rayleigh number of our fluid

$$Ra_T = \frac{g d^3 \alpha \Delta T}{\nu a} \quad (1)$$

(with g = acceleration due to gravity, α = isobaric expansion coefficient, ν = kinematic viscosity, a = thermal diffusivity) and found it to exceed the critical value $Ra_c \approx 1700$ for onset of thermal convection in the range $0.8 \text{ K} \leq \Delta T \leq 1.1 \text{ K}$ [8].



Fig. 5a. Fluid layer just after the pressure jump. The wavelength of the roll-shaped convective pattern is about two times the layer depth. The black shadows that are superimposed on the structures in this and the following pictures originate from the thermocouple and the jets inside the cavities (see Experimental). The disturbance in the lower part of the picture is caused by the fluid inlet of the sample cell.

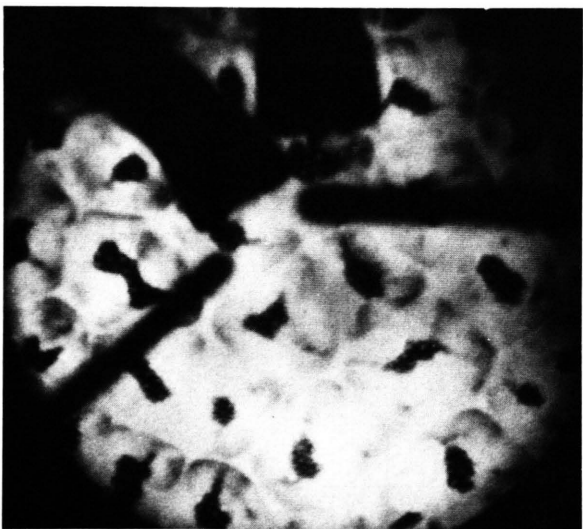


Fig. 5b. The same fluid layer after structure transformation. A cellular pattern has formed, which exhibits precipitated drops in the centres of the cells. As compared with Fig. 5a the wavelength is slightly reduced.

(ii) The dependence of λ on $\varepsilon = (Ra - Ra_c)/Ra_c$ agrees within some percent with the measurements of Croquette *et al.* [9], who used pure methanol and a sample volume of greater diameter.

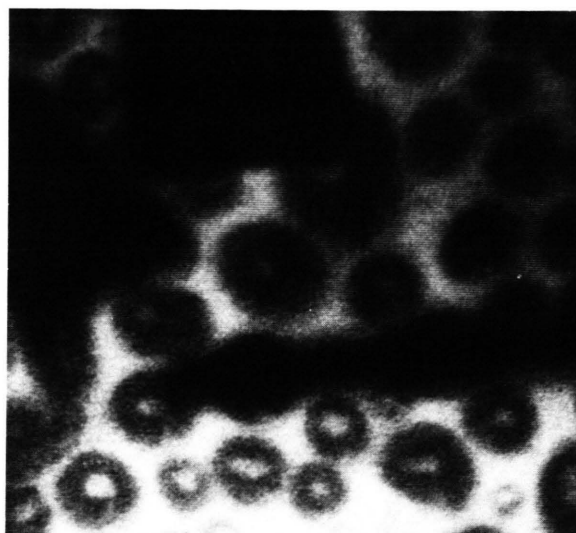


Fig. 6. Distribution of the precipitate in the absence of an RBI. Turbid rings of small droplets surround deposited larger drops.

In this case the demixing as a rule causes a structure transformation towards a cellular form, which in cyclohexane-poor liquid is accompanied by a reduction of λ (Fig. 5b).

Case III

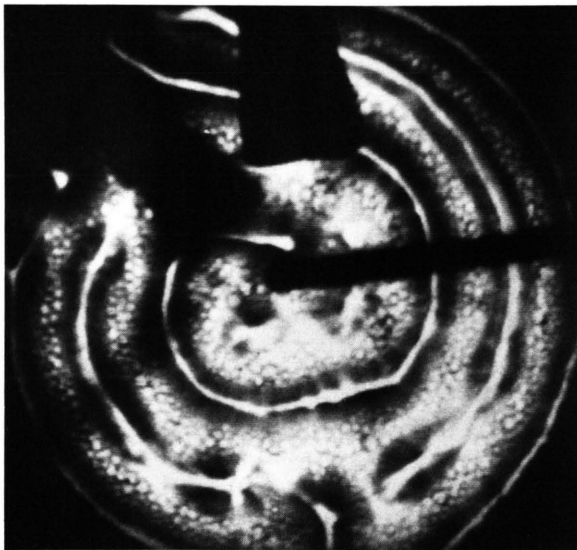
No regular patterns occur. Soon after the demixing comparatively large droplets settle on the warmer sapphire window and continue their growth. The remaining smaller ones concentrate near them forming a turbid ring around each of them (Fig. 6). At the surfaces of the large deposited drops convective flow towards the colder window is observed.

Common to all three cases is the fact that the precipitate at last accumulates in those regions where the bulk flow is directed towards the colder boundary.

Finally an amazing effect of pattern splitting should be mentioned, which sometimes has been found in case I or II if the fluid is cyclohexane-poor. It is illustrated in Fig. 7 and – schematically – in Fig. 8: In the region of an old convective roll where the bulk phase flows towards the colder window the direction of motion turns around. Meanwhile the axial region be-



(a)



(b)

Fig. 7. RBI pattern before (a) and after (b) splitting of the convective rolls.

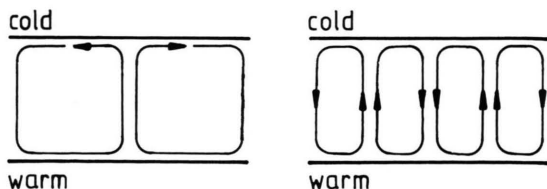


Fig. 8. Schematic illustration of pattern splitting.

comes the boundary of two new rolls, where now the flow is directed to the colder window; thereby λ is reduced to $\lambda/2$.

Discussion

In spite of the variety of observed patterns their occurrence can be explained qualitatively by a simple model.

Onset of the RBI

After the pressure jump into the miscibility gap the fluid separates into two phases, the compositions of which are given by the final pressure and the local temperature (Fig. 3). This means the temperature gradient causes a concentration gradient inside the bulk phase according to the slope of the respective equilibrium isobar

$$dx = \left(\frac{\partial x}{\partial T} \right)_{p, eq} dT. \quad (2)$$

In order to find the conditions that can give rise to an RBI after demixing we have set for the solute Rayleigh number according to Nield [10]

$$Ra_s = \frac{g d^3 \beta \Delta x}{\nu D} \quad \text{with} \quad \beta = \frac{1}{\varrho} \left(\frac{\partial \varrho}{\partial x} \right)_{T, p} \quad (3)$$

and ϱ = density of the bulk liquid, D = binary diffusion coefficient. In doing so we have neglected the influence of the precipitate on the hydrodynamics of the fluid layer. This simplification is considered to be acceptable within the scope of our semiquantitative description.

Inserting (2) into (3), the solute Rayleigh number can alternatively be written

$$Ra_s = \frac{g d^3 \beta}{\nu D} \left(\frac{\partial x}{\partial T} \right)_{p, eq} \Delta T \quad (4)$$

and so becomes – like the thermal one – a product of a factor containing fluid properties and the temperature difference applied. By this equation we have evaluated the critical temperature difference $(\Delta T)_c$ for which the Rayleigh number

$$Ra = Ra_T - Ra_s \quad (5)$$

exceeds 1700 and thus a two-component RBI should occur. Because of the much larger value of Ra_s in

comparison with Ra_T and the shape of the isobars in the phase diagram the critical temperature difference $(\Delta T)_c$

- (i) is positive for cyclohexane-poor liquids,
- (ii) is negative for cyclohexane-rich liquids and
- (iii) has an absolute value of the order of 10^{-1} K or less.

Comparing this result to the table in Fig. 3 it is evident that the appearance of case I meets the conditions for which an RBI is expected. On the other hand, if no RBI is expected, the irregular patterns of case III are found.

The regular patterns that are observed in cyclohexane-rich mixtures under the influence of a great positive temperature difference do not contradict this model, because due to theory, instabilities, which may exhibit a complex behaviour, should develop in that domain [2].

Wavelength and Growth Rate of the RBI

Baines and Gill [11] calculated the wavelengths that occur preferentially at the onset of an RBI in the presence of linear gradients and their growth rates as functions of the state of the system in the (Ra_T, Ra_S) -plane. Although they presumed free boundaries (in contrast to the rigid boundaries in our sample cell) and of course a one-phase fluid, we have used their results to get a qualitative idea of the dependence of λ and τ^{-1} on the Rayleigh numbers.

In fact our observations meet roughly their predictions:

(i) Patterns of small wavelengths develop in the formerly quiescent fluid or are generated by splitting or during transformation of an old greater pattern, if Ra_S is negative and Ra_T is smaller than or about the critical value for onset of a pure thermal instability. If Ra_T is greater than this value λ is about $2d$.

(ii) τ^{-1} is found to increase with the absolute value of ΔT , i.e. with the penetration depth of the system into the instability region in the (Ra_T, Ra_S) -plane.

Planform of the RBI

The shape of an RBI is correlated to the deviation of the liquid properties from the vertical symmetry with respect to the horizontal midplane of the liquid layer [12]. Strong deviations, which should occur in our two-phase systems, cause a hexagonal planform. So the pattern transformations we have observed may

be the reaction of the system to the changes of the bulk phase properties after demixing and therefore may have an RBI-immanent origin. However, the droplets that accumulate at the centres or the corners of the cells, respectively, may also stabilize a cellular pattern compared to a roll-shaped one by the Marangoni flow surrounding them. For that reason the driving forces of the pattern transformations (and splittings) will be a topic of future work.

Organization of the Precipitate

Because a detailed description has already been given elsewhere [7] the distribution of the precipitate is only briefly discussed here.

Whereas small droplets follow the bulk flow, medium-sized ones are influenced strongly by the Marangoni flow at their surfaces until they become so large that buoyancy forces dominate. The medium-sized droplets accumulate in the regions where the bulk flow is directed to the colder boundary. There they float or – after growth – deposit on the windows of the sample cell. These regions can develop on the one hand due to an RBI and on the other hand due to Marangoni-driven flow that surrounds the larger drops, which have already settled on a window. The first case creates a regular organization of the precipitate and the second – due to the positions and the sizes of the settled drops given randomly – causes an irregular one. However, in both circumstances an inhomogeneous distribution of the precipitate results.

Conclusions

The far-critical phase decomposition of a thin liquid layer exposed to a vertical temperature gradient results in the appearance of new dissipative structures inside the formerly quiescent fluid. If a thermal instability is present before demixing, a change of the structure happens. The convective motion of the liquid gives rise to the corresponding organization of the precipitate that may be regular or irregular.

The irregular precipitate distributions in the quasi-isopycnic system used are mainly driven by interfacial effects: Each larger drop, which has deposited at the boundary, creates a flow that is directed towards decreasing temperature due to the Marangoni instability at its surface. Here smaller drops accumulate because of their own Marangoni-driven motion. The irregular-

ities of the drop deposition are reflected by the distribution of the precipitate.

The regular patterns can qualitatively be explained with regard to the conditions of formation, to their magnitude and to their form by the model of a two-component Rayleigh-Bénard instability which results from a concentration gradient that is parallel to the vertical temperature gradient and is formed after demixing due to the dependence of the equilibrium composition on the local temperature. Inside the RBI pattern the droplets – as above – concentrate in the regions where the bulk phase flows to the colder boundary. As a result the distribution of the precipitate becomes regular.

We are continuing our work to obtain more quantitative results, which will help us in the estimation to what extent a simplified RBI-based model can describe the regular structures and how far these patterns are influenced concerning their morphology and their dynamics by the Marangoni convection of the precipitate.

Acknowledgements

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