Pattern formation in solutal convection: vermiculated rolls and isolated cells

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Abstract

Observations of the peculiar behaviour of a drink of liqueur topped with cream led us to perform experiments showing that the instability is a convection phenomenon that arises through destabilizing surface-tension forces. The convection is solutal: driven by gradients of concentration of a solute, rather than by heat gradients as in the more commonly studied thermal convection. The convective patterns, vermiculated rolls and isolated cells, are quite unlike the usual planforms. They are associated with an elastic surface film, and the Marangoni number is high, characteristic of solutal convection. We have conducted further experiments that reproduce these patterns in simpler working fluids.
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1. Introduction

A remarkable phenomenon, illustrated in Fig. 1, was brought to our notice by a reader's question in *New Scientist* magazine: "One of the recommended ways of drinking the liqueur *Tia Maria* is to sip it through a thin layer of cream. If the cream is poured onto the surface of the drink, to a depth of about 2 millimetres, and left to stand for about two minutes, the surface begins to break up into a number of toroidal cells. These cells develop a rapid circulation pattern which continues even if some of
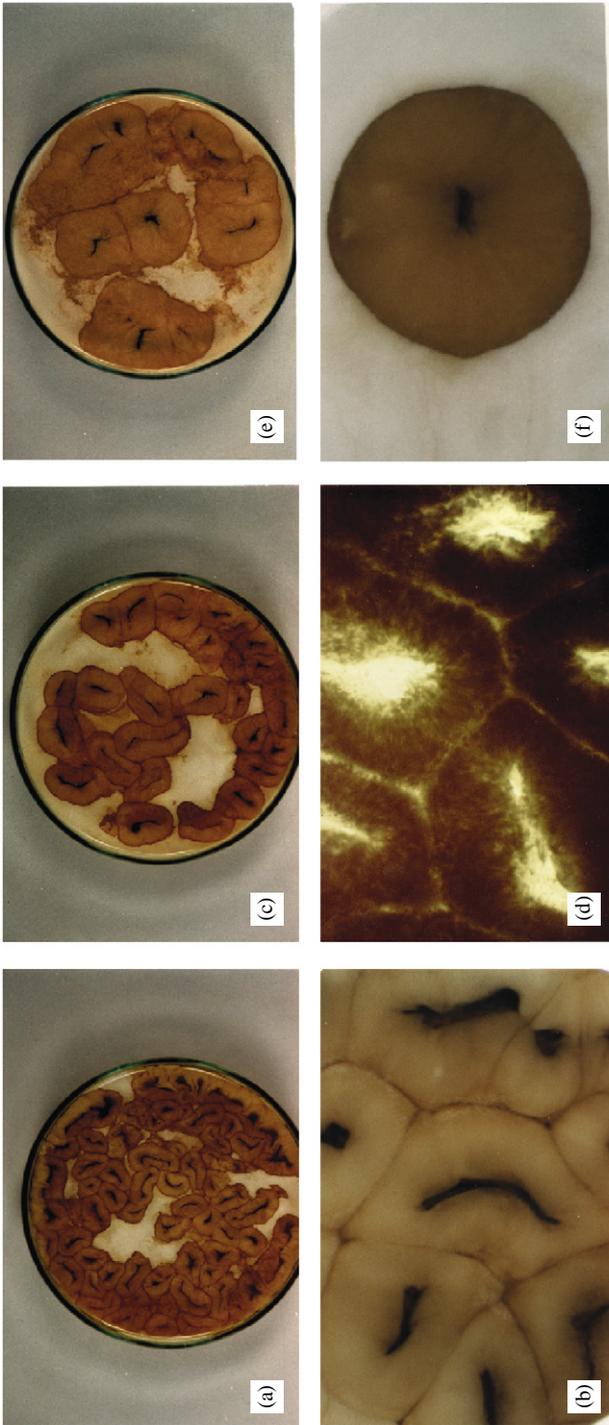
Fig. 1. Pattern formation in *Tia Maria*; the Petri dish is 9 cm in diameter. At the centre of each cell low-surface-tension liquid laden with ethanol is rising from the interface of the *Tia Maria* with the cream; the cell centres are dark in the photographs with the high concentration of *Tia Maria* there. Liquid then travels outwards at the surface, mixes with cream and so becomes lighter in colour, and higher in surface tension as its concentration of ethanol decreases, until it falls again at the edge of each cell. Above the centre of each cell, there is a depression in the liquid surface. (a) Vermiculated rolls in cream over a lower layer of the liqueur *Tia Maria*. (b) Detail of vermiculated rolls. (c) Cells of intermediate form and size in a deeper cream layer. (d) Detail of these (lighting by transmission rather than reflection as in the other images). (e) Large, isolated rounded cells in a deep layer of cream on *Tia Maria*. (f) Detail of large isolated cell. (Other liqueurs such as *Kahlua* work just as well as *Tia Maria*.)

the *Tia Maria* is sipped through the cream. How and why do these cells develop and what is the energy source?" [1]. To which the editor adds the comment: "This is a truly astonishing effect … 'Rapid circulation pattern' does not do justice to the series of eruptions that convulse the surface of the cream as the liqueur bursts through from beneath".

Here we show that the source of these patterns is convection, but not of the common, thermally activated, variety; a temperature gradient is not necessary. It is instead solutal, driven by the tensoactivity of the ethanol that makes up 26.5% of the liqueur. We estimate the Marangoni and Rayleigh numbers, and the adsorption and elasticity numbers due to a surface film, which indicate that this convection is operating at extreme regimes far from normal thermal convection experiments, and we discuss their influence on the unusual pattern morphology. Lastly, we present laboratory experiments that we have performed with different solvents and solutes to explore for different levels of the driving force this pattern-formation mechanism.

Beyond displaying curious and beautiful patterns in an unusual context, this example of convection is noteworthy for how the patterns formed differ from those, such as hexagons or rolls, commonly observed. A shallow layer of cream gives wormlike *vermiculated rolls* (Fig. 1a) that writhe about, bifurcate, and coalesce. In deeper layers they become more rounded *isolated cells* (Fig. 1e). These, with inactive regions between them, are not so mobile, but they drift slowly, and may periodically die away and reform. The appearance of these unusual patterns is linked to the presence of a blocking layer at the liquid surface that hinders surface renewal; fatty components of the cream fulfil this rôle in the *Tia Maria* system. In some of the earliest work on thermal convection from the 1910s–1930s, similar phenomena were noted by Dauzère [2], Bénard [3], and Avsec [4]. Evidently, in their investigations a surface layer was also present; Dauzère, for example, performed his experiments with beeswax boiled with water or an alkali, which produced a film of material that blocked access to the surface from the bulk. In solutal convection, Herrera [5], in the 1940s, observed vermiculated rolls so similar to swarming protozoa that he saw in them a possible origin of life! In the 1960s Linde and Schwarz [6] saw similar patterns with a tensoactive solute passing between two liquids, as did Berg [7] studying evaporative solutal convection. More recently, though, a surface layer has been seen solely as an undesired stabilizing effect to be avoided in thermal convection experiments.

2. Solutal convection

Whether concentration or heat driven, Bénard–Marangoni convection is the name given to surface-tension-driven convection [8]. The theory has been built up from two contrasting viewpoints: that in which convection affects both boundaries of a thin fluid layer, the shallow layer limit [9], and, on the other hand, a fluid layer of infinite extent, having an interface with another fluid layer also of infinite extent [10]. In this, the deep layer limit, convection affects only a boundary layer of finite depth adjacent to the interface. These two strands were joined in later theoretical work that models the full problem of two interacting fluid layers, and includes the effects of buoyancy

along with surface tension [11]. Bénard–Marangoni convection can then be described by a few dimensionless parameters, the most important of which is the Marangoni number Ma giving the ratio between surface tension and viscous forces. For solutal convection, $Ma = \sigma_C \, \Delta C \, d/(\eta\kappa)$, where $\sigma_C = \partial\sigma/\partial C$ is the derivative of surface tension σ with concentration, ΔC the change in concentration across the convecting layer, d the depth of the layer, η the viscosity of the liquid, and κ the molecular diffusivity. Apart from a surface-tension-driven instability, in all convection on Earth, there is also the possibility of instability occurring through density differences giving rise to Rayleigh–Bénard convection [8]. We can describe this with another dimensionless parameter, the Rayleigh number Ra giving the ratio between buoyancy and viscous forces. For solutal convection, $Ra = \rho g \beta_C \, \Delta C \, d^3/(\eta\kappa)$, where in addition to terms previously defined, g is the acceleration due to gravity, ρ is the fluid density, and $\beta_C = 1/\rho \, \partial\rho/\partial C$ the volume expansion coefficient. For Ma or Ra greater than a critical value, the steady diffusive state becomes unstable as the concentration difference overcomes dissipative effects, and the fluid begins to convect.

Much of the theory that has been developed for Bénard–Marangoni and Rayleigh–Bénard convection may be transferred between the thermal and solutal cases, by interchanging temperature with concentration dependencies. But solutal convection has additional effects, for unlike heat, a material species may accumulate at the surface. A surfactant, or surface-active solute, is a particularly marked instance of this. The resulting surface film is elastic, this property being termed Gibbs elasticity [12,13]. Of course, a surface film can also be present in a thermal convection experiment, where instead of being the transferring solute itself, it is a foreign substance. The first work to include a surface film in the theory of surface-tension-driven convection considered such an insoluble foreign film [14]. Further theoretical work including a soluble surface film has followed the same two paths as the theory of surface-tension-driven convection; with studies of both the shallow [15,16] and deep-layer limits [17], as well as later work integrating the two viewpoints [18]. The adsorption number $N_A = \Gamma_0/(\Delta C \, d)$, where Γ_0 is the surface concentration of surfactant, is the ratio of the effectiveness of bulk diffusion to adsorption in transferring mass to the surface. This and the elasticity number, $E_S = Ma \, N_A = \sigma_C \Gamma_0/(\eta\kappa)$, the ratio of Gibbs elasticity to viscosity, describe the presence of a surface film of a substance soluble in the bulk fluid.

If we insert approximate values of the parameters for *Tia Maria* diffusing into a cream layer of depth 2 mm ($d = 2 \times 10^{-3}$ m, $\sigma_C \, \Delta C = \Delta\sigma = 5 \times 10^{-2}$ N m^{-1}, $\eta = 10^{-3}$ N s m^{-2}, $\kappa = 10^{-9}$ m^2 s^{-1}, $g = 10$ m s^{-2}, $\rho = 10^3$ kg m^{-3}, $\beta_C \, \Delta C = \Delta\rho/\rho = -0.2$), we obtain estimates for the Marangoni and Rayleigh numbers in the system of $Ma \approx 10^8$, $Ra \approx -10^7$. Such a high Marangoni number would be difficult, if not impossible, to attain in thermal convection, while the large negative Rayleigh number implies that buoyancy is opposing surface tension. Factors not considered in this estimate are that the concentration gradient will be nonlinear, and that the thickness of the layer affected by convection may vary. Where there are multiple levels of cells within cells, with different affected thicknesses, each level will see a different Marangoni number. Despite the high Marangoni number, here there is not classical high-Reynolds-number Kolmogorov turbulence arising from the convective transport of momentum when $Re = vd/v \gg 1$ (v being a characteristic

velocity). As the nonlinearity occurs through the convective transport of solute, the Péclet number is high, $Pe = vd/\kappa \gg 1$, but because the Schmidt number $Sc = v/\kappa$ is also high (e.g., of order 10^3 in the *Tia Maria* system), the Reynolds number may be rather small: in the limit Ma large and $Sc \to \infty$, $Pe \to \infty$ but $Re \to 0$. We can also estimate the adsorption number (we suppose $\Gamma_0 = \Delta C\,h$, where h is the surface layer depth $h \approx 5 \times 10^{-9}$ m) as $N_A = h/d \approx 5 \times 10^{-6}$, and the elasticity number $E_S = \Delta\sigma\,h/(\eta\kappa) \approx 250$. These values of E_S and N_A should raise the critical Marangoni number for the onset of convection by one to two orders of magnitude, from 10^2 to between 10^3 and 10^4 [16]. While the surface film is not effective in hindering convection, it manifests itself, nevertheless, in the pattern morphology.

3. Laboratory experiments

Tia Maria and cream form a complex multicomponent system. We aimed to discover whether the same structures are seen with simpler working fluids. It is instructive here to examine a plot of density against surface tension for some common liquid compounds. Using Fig. 2a as a guide, we designed experimental setups to investigate solutal convection phenomena in the *Ma–Ra* plane. The first is based on the use of a membrane (Fig. 2b). In the example we show here, we filled the lower chamber with ethanol, and to the upper we added a shallow layer of propane-1,2,3-triol. The membrane allows solute from the lower layer to diffuse into the solvent in the upper layer from below without permitting bulk mass flux, with the resulting convective patterns shown in Fig. 3a. A complementary technique we elaborated is with an acrylamide gel containing the solute (Fig. 2c). The working solvent is added on top of the gel, from which the solute is free to diffuse. We illustrate the results of an experiment with this set-up in Fig. 3b, where the solute is ethanol and the solvent, water. Convection cells form as the ethanol diffuses out of the gel into the water. A third technique is hygroscopicity-induced Bénard–Marangoni convection, in which water from the atmosphere above a liquid layer adsorbs onto the surface of a hygroscopic liquid, increasing the surface tension and causing instability. We show convection cells that result with $2,2',2$-nitrilotriethanol as the working fluid in Fig. 3c.

We have been able to view in these experiments the bifurcation and coalescence of cells, as we had seen previously in *Tia Maria*. Cells in shallow layers are elongated vermiculated rolls, while the large rounded cells in deeper layers have a dead zone around them, suggesting that they exhaust the concentration gradient in their vicinity. On occasion, these isolated cells form, die away, and reform periodically. The breakdown of convection can be accounted for by the supply of solute being insufficient to satisfy the demands of the cell, so convection periodically breaks down until the supply is replenished. In some experiments, smaller secondary cells may be observed within primary cells, drifting outwards with the flow until they disappear in the subduction zone at the outer edge of the parent cell. We believe this hierarchical structure of cells within cells to arise when one level of cells is not sufficient to exhaust the concentration gradient.
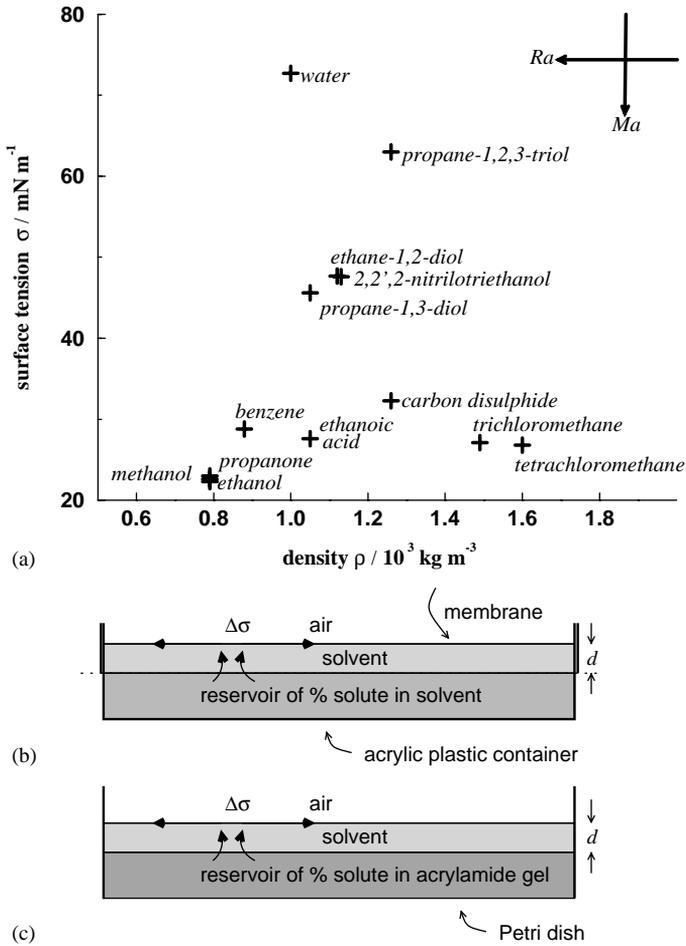
Fig. 2. (a) The surface-tension-density parameter plane for common liquid compounds. Data [19,20] are for 20°C, and surface tensions are against air. For those pairs of liquids that are soluble, we can use this plot to design experiments in solutal Bénard–Marangoni and Rayleigh–Bénard convection. Mentally locating the crosshairs over any given datum, we can consider this liquid as the solvent and estimate the Marangoni and Rayleigh numbers for any given solute diffusing into a layer of this solvent from below. For example, ethanol is far below and to the left of water, so the Marangoni and Rayleigh numbers for ethanol in water are large and positive, whereas propane-1,2,3-triol is below and to the right of water, so the Marangoni number is positive but the Rayleigh number negative for propane-1,2,3-triol in water. (b and c) Experimental set-ups (these, together with the working fluids, are brought to thermal equilibrium in the laboratory to remove any temperature gradients): (b) The membrane technique. We use a nylon membrane with a 0.45 μm pore size, and hold it taut horizontally between two chambers, the upper of which we fill with the working solvent, and the lower with the working solute at a given concentration in the solvent. (c) The gel technique. To prepare the gel with ethanol, for example, as the working solute, we use three aqueous solutions prepared with distilled water and analytical-grade reagents. We mix 20 ml of solution A (16% propenamide and 0.8% N,N'-methylenebis(2-propenamide)), 9.6 ml of solution B (10% 2,2′,2-nitrilotriethanol and 36% ethanol), and 6.4 ml of solution C (10% ammonium peroxydisulphate) in a petri dish (all percentages by weight). The mixture polymerizes into a gel with a level surface, from which the ethanol, not being chemically bound, is free to escape. We then add a layer of the working solvent on top of the gel.
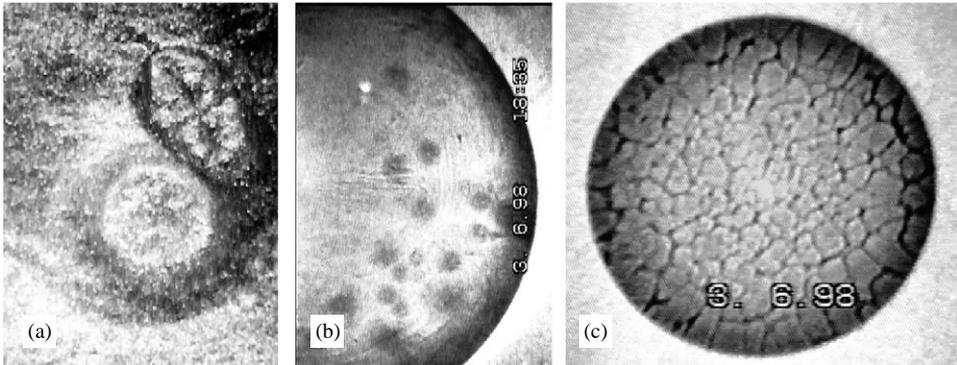
Fig. 3. (a) Large, isolated convection cells formed in a solutal Bénard–Marangoni convection system using a membrane allowing an ethanol solute to diffuse into a propane-1,2,3-triol solvent ($Ma \approx 10^7$, $Ra \approx 10^6$, $N_A \approx 10^{-6}$, $E_S \approx 10$). Visualization is with aluminium flakes. (b) Round, isolated cells in water on an ethanol acrylamide gel ($Ma \approx 10^7$, $Ra \approx 10^6$, $N_A \approx 10^{-6}$, $E_S \approx 10$). Visualization is by shadowgraphy. (c) Network of convection cells in hygroscopic Bénard–Marangoni convection with 2,2′,2-nitrilotriethanol ($Ma \approx 10^5$, $Ra \approx -10^4$, $N_A \approx 10^{-6}$, $E_S \approx 0.1$), visualized using shadowgraphy.

4. Discussion

Thermal Bénard–Marangoni convection experiments cannot explore far above the onset of convection, since this would require either an unphysically large temperature difference, or a deep fluid layer. However, in thermal convection in deep layers— on Earth at least—buoyancy forces dominate surface tension ($Ra/Ma \propto$ depth^2), so such experiments concern Rayleigh–Bénard, not Bénard–Marangoni convection. Solutal convection does not suffer from this restriction; it is possible to use a wide variety of solvents and solutes as convecting mixtures, and to choose their physico-chemical properties to change the Marangoni and Rayleigh numbers in the system independently to obtain purely surface-tension-driven convection, purely buoyancy-driven convection, or a mixture of the two. The experimentalist in thermal convection is denied this freedom of movement in the parameter plane, as the surface tension and density of the working fluid have a fixed relation. Moreover, solutal convection allows easier control over the boundary conditions, from impermeability to permeability (from insulation to conduction) at both the lower and upper surfaces and at the side walls. Surface films in thermal convection have been considered merely as contaminants. In solutal convection, on the other hand, Gibbs elasticity is an integral part of the physics. Marangoni numbers can be much larger in solutal convection than in the thermal case, because molecular diffusivities are generally much smaller than thermal diffusivities—Schmidt numbers are larger than Prandtl numbers. As such, surface films have a much lesser effect on inhibiting convection than in thermal experiments; what we have seen is that they modify the morphology of the patterns.

Acknowledgements

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