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An optical study of thin interfacial liquid films using total reflection of light

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Abstract. The light totally reflected at the interface between a glass prism and a liquid (water) of lower index can be partly transmitted as a droplet of liquid of larger index (oil) approaches this interface. By using the variation of the reflected intensity, one can study the static structure and the thickness variation of the intermediate water film in a range of thickness of a few 10 Å to 10^2 Å. A preliminary experiment is presented together with the optical technique.

1 Introduction

Total internal reflection in a glass prism of high refractive index in contact with a thick liquid film of lower refractive index has been applied with success to the study of the properties of the liquid near the interface on a thickness of the order of $\lambda/10$ to λ (λ being the wavelength of the reflected light). We have used this method previously in an extensive study of nematic liquid crystals to measure such properties as the refractive indices, the molecular alignment induced by the solid surface or by an external field, and the effect of hydrodynamic flow (Rivière 1984; Rivière & Levy 1979, 1981). The technique has also been used for the study of polymer solutions in the vicinity of a solid where modifications of concentration and configurations are obtained (Allain et al. 1982). The analysis makes use of the properties of the evanescent wave in the liquid medium which has a smaller refractive index, n_W, than the solid one, n_P. However, if the liquid film is thin and bounded by another material of larger refractive index, n_O, the tail of the evanescent wave will give rise to transmitted light in the second material; consequently, the intensity reflected at the glass-liquid interface will decrease. This wave effect, fairly similar to quantum tunneling, and already described in Newton's "Optika" (1717), is called frustrated total reflection (FTR). We use it here to study the approach of a liquid oil drop ($n_O = 1.402$) to a solid prism ($n_P = 1.9078$) when the drop is separated from the prism surface by a water film of lower index ($n_W = 1.333$).

The experiment is described schematically in Fig. 1a. A parallel He-Ne laser beam is totally reflected by the lower horizontal surface of a glass prism in contact with water. A buoyant oil droplet approaches the glass surface from below. We record the variation of the reflected beam intensity as the residual water film becomes thinner. On the other hand, after the droplet has reached static equilibrium we can measure the water film profile by moving the beam contact point along the interface at constant incidence angle.

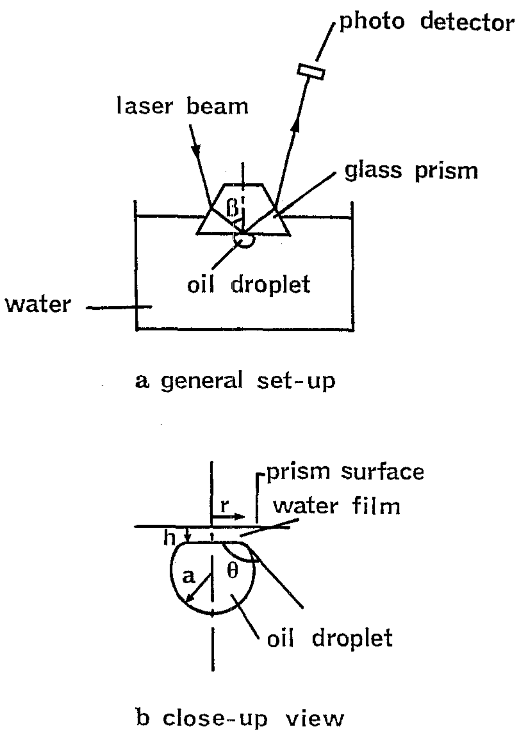

Fig. 1 a and b. Schematic of the experiment: the monochromatic HeNe laser beam *L* is totally reflected at the prism-water interface. The variation of the reflectivity measured on a photodiode *PD* is recorded as an oil droplet approaches the interface. Inset: schematic geometry of the droplet in the region of closest approach

This preliminary study shows the potential of the method for studying static and dynamic properties of films and droplets in contact with solid walls which is a subject of large present theoretical interest.

In such wetting problems, the role of the first few hundred angstroms of fluid near the solid, where molecular effects are dominant, is essential. It is also of importance in many fields of applied sciences (Dussan & Davis 1974). In particular, the present experiment addresses the problem of immiscible displacement in porous rocks with is an important issue in the oil industry. It provides a coarse simulation of the formation of primary oil reservoirs where tiny oil droplets had to gather on rock surfaces while expelling water. Previous experiments (Jacquin 1983; Dussan & Davis 1974) have shown a large variety of hydrodynamic behaviors of oil droplets near a solid surface. When the surface is tilted, a drop can stick to it. In other instances, it can slide easily suggesting the presence of a residual water film. The present work addresses the problem of the existence of this interfacial film.

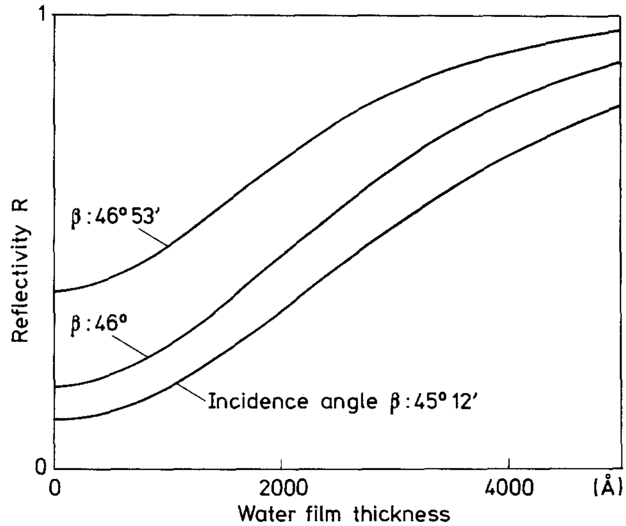

Fig. 2. Variation of the reflectivity as a function of the water layer thickness h (in Å) with the incidence angle. The indices of the three layer system used are n_P (prism) = 1.9078, n_W (water) = 1.331, n_O (oil) = 1.402

2 The frustrated total reflection

When an electromagnetic plane wave propagates from a high refractive index medium (glass prism, n_P) to a less refractive one (water, n_W) it is totally reflected when the incidence angle is larger than a critical value β_W given by Snell-Descartes law with $\beta_W = \arcsin(n_W/n_P)$. In the lower index medium, there exists an evanescent wave decaying exponentially with the distance from the interface. The decay length ranges from infinity at β_W to values of the order of λ as the incidence angle increases; this suggests a method to probe the index profile in the liquid, e.g. with a polymer solution (Allain et al. 1982) by using deconvolution techniques.

In an interface with a third medium (oil, n_O) is close enough to the glass-water surface, part of the wave will be transmitted if $n_W < n_O$ and if an initial angle intermediate between β_W and $\beta_O = \arcsin(n_O/n_P)$ is used. The reflectivity R at the prism interface decreases with the interface thickness h, for sufficiently small h (typically $< \lambda$). According to Heavens (1965), and for the case of TM polarization used in the present experiments, R is given by:

$R = R \times R^*$ with

$$R = (r_W + r_O\, e^{-2i\delta})/(1 + r_W r_O\, e^{-2i\delta}),$$

where

$$r_W = \mathrm{tg}(\beta_2 - \beta)/\mathrm{tg}(\beta_2 + \beta), \quad n_P \sin\beta = n_W \sin\beta_2 \qquad (1)$$

$$r_O = \mathrm{tg}(\beta_3 - \beta_2)/\mathrm{tg}(\beta_3 + \beta_2), \quad n_P \sin\beta = n_O \sin\beta_3$$

and

$$\delta = \frac{2\pi}{\lambda} n_W h \cos\beta_2 .$$

We present in Fig. 2 a set of reflectivity curves as a function of film thickness h for the materials used in the present experiment.

3 Experimental set-up and measurement accuracy

3.1 *Experimental procedure*

An oil drop is generated at the tip of an upward oriented syringe needle. Once it has reached a diameter of about 10 mm, the droplet detaches itself from the needle and slowly rises through the water bath towards the lower surface of the glass prism wich is used for the reflectance measurements. Three types of measurements are performed during the experiment:

(1) While the droplet is moving and approaching the prism surface, we monitor the variations of the light reflectivity at a constant incidence angle for a fixed location at the expected impact point of the oil droplet on the surface. This dynamical measurement of the variation of the local thickness of the water film with time gives us informations on the balance of forces determining the fluid flow dynamics in the film. Increasing the volume of the drop very slowly and carefully adjusting the orientation of the needle is a key factor for avoiding deviations of the droplet trajectory during its rise time and obtaining the expected impact point.

(2) After the droplet has reached its equilibrium position (the typical stabilisation time is 15 minutes), we analyse the variations of the reflectivity with incidence angle at a fixed location close to the minimum thickness point. This static measurement allows us to determine precisely the minimum thickness of the residual water

film. At the same time, we get a precise value of the oil refractive index, thus allowing us to correct the previous dynamic film variation measurements.

(3) Finally, by scanning the incidence point of the measurement beam across the contact surface between the glass and the oil droplet, we determine the horizontal profile of the water film thickness between the oil droplet and the prism surface. For practical reasons, this measurement is performed using a constant incidence angle.

3.2 Measurement sensitivity and accuracy

The sensitivity of this film thickness detection method is first limited by that on the measurements of the reflectivity coefficient R. Absolute variations of R by less than 0.005 can be detected in the whole range $0 < R < 1$ (Laser beam insensity fluctuations are smaller than this). Using the characteristic curves shown in Fig. 2, this corresponds to a thickness detection threshold of 250 Å. There are two main causes of uncertainty:

(1) The experimental accuracy is mainly limited by uncertainties on the incidence angle determination (typically 1′). In addition, the laser beam has a slight intrinsic divergence. The measured reflectivity variation with the incidence angle corresponds to a convolution between the angular distribution of the laser beam (gaussian for the TEM_{00} mode) and the theoretical reflectivity curves shown in Fig. 2. The corresponding variation of the incidence angle at a given reflectivity is about 3′.

(2) The beam diameter is finite. The thickness measurement is therefore averaged over an elliptical area with a width of about 2 mm at the interface between the prism and the droplet.

4 Experimental results and interpretation

4.1 Measurements of the residual film thickness after the droplet stabilization

Fig. 3 shows two strongly different reflectivity time variation curves obtained for two different prism surface cleaning procedures.

Curve a corresponds to a surface simply cleaned with ethanol before drying: no significant deviation from the zero thickness curve is observed and the film thickness is, therefore, lower than the experimental uncertainty of 250 Å.

Curve b corresponds a surface carefully cleaned using a sulfochromic acid mixture. A residual film thickness of 700 ± 200 Å is measured.

It is possible that the sulfochromic acid treatment has introduced some roughness in the prism surface which should be taken into account as an average deviation in the determination of h. Systematic experiments will require an independent study of the state of the solid surface.

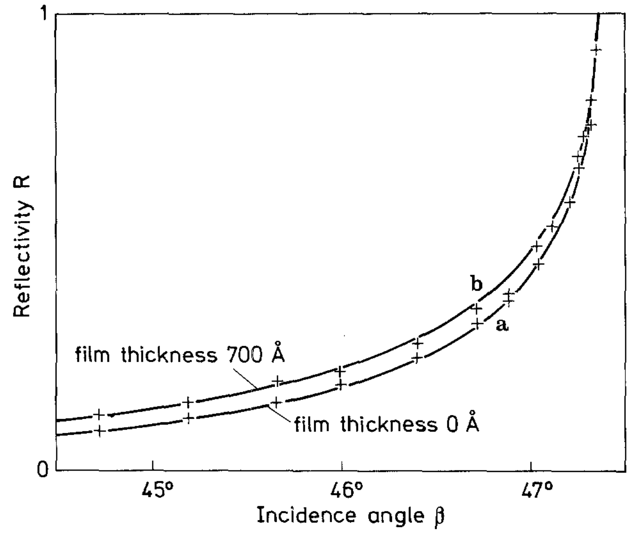

Fig. 3. Variation of reflectivity of the beam as a function of the incidence angle β in quasi static conditions. The experimental data are represented by +; the calculations are given on continuous curves. Curve **a**: the experimental points are not distinguishable from the theoretical curve when the prism has been washed with ethanol. Curve **b**: the prism was thoroughly cleaned with a sulfochromic mixture. The theoretical curves correspond to values $h = 0$ Å (curve **a**); $h = 700$ Å (curve **b**)

4.2 Theoretical estimates of the equilibrium water film thickness between the prism and the oil drop

The value of the equilibrium film thickness can, in principle, be used to estimate the molecular forces arising due to the presence of the water film. Using a schematic representation of a spherical cap drop (Fig. 1 b) bounded by a flat surface parallel to the glass plate, we can write an approximate balance of forces as:

$$\Delta\varrho\, g\, V - 2\pi\, a\, \gamma \sin\theta = (\Pi_{VdW} + \Pi_e)\, \pi\, a^2 .$$

The first term in Eq. (1) is the buoyancy force applied to the drop ($\Delta\varrho$ is the difference between water and oil densities, $\Delta\varrho = 0.033$ g/cm^3). The second term is the capillary over-pressure in a spherical drop of radius a. The two terms on the right of Eq. (1), Π_{VdW} and Π_e are due to the molecular interactions between the solid and the film.

The Van der Waals forces lead to a disjoining pressure Π_{VdW}, which, in the case of a flat non-polar film of thickness h, is given by (Chen 1984):

$$\Pi_{VdW} = -B/h^4 \quad (\text{for } h \sim 500\ \text{Å}).$$

For a flat film of thickness h, the electric double layer disjoining pressure, Π_e, is:

$$\Pi_e = D\, e^{-kh} \quad (\text{for } k\, h > 1)$$

($1/k$ being the Debye length).

Without getting into the detailed nature of Van der Waals and electrostatic interactions, we can show that the order of magnitude of the equilibrium thickness obtained in the case of a "clean" surface (prism washed with a sulfochromic acid mixture) gives a reasonable order of magnitude for the Van der Waals pressure values involved with $h = 700$ Å, $a = 0.5$ mm, and a typical value: $B = -10^{-19}$ erg · cm. We get:

$\Pi_{VdW} \sim 42$ dyne/cm², to be compared with
$\Delta\varrho\, g\, a \sim 17$ dyne/cm², (hydrostatic pressure) and
$2\,\gamma/a \sim 80$ dyne/cm², (capillary pressure).

Therefore all these three pressure terms are of the same order of magnitude as required to obtain a mechanical equilibrium. The relative influence of the electrical double layer forces compared to the others should be evaluated in systematic experiments by varying the water salinity. When its value increases, the Debye length decreases at the same time as the influence of the electric double layer forces does.

Moreover, due to the strong dependence of the force terms on h a precise determination of this parameter would be needed to evaluate the Van der Waals force constant.

4.3 Static water film thickness profile measurements

The curves of Fig. 4 have been obtained using the correspondence between R and h given in Fig. 2 by keeping the incidence angle of the laser beam constant and monitoring the variations of the reflectance with the location of the incidence point.

A typical profile for a single oil droplet obtained after the film thickness has reached equilibrium is shown in Fig. 4a. The thickness is averaged over the laser beam width (2 mm). The uncertainty is particularly large near the edges of the water film.

Figure 4b has been obtained after the coalescence of two oil droplets deposited successively very near each other. Although the two droplets have joined into a single one, the film thickness profile shows clearly a slowly decaying dimple in the middle of the contact film which can be observed even after 10 minutes. (In principle one should consider the effect of the curvature of the film on the reflectivity but the angle between the film upper surface and the prism is always very small.)

This result can be related to the macroscopic observations of Platikanov (1964), Burril and Woods (1969) and Sheludko (1967) on the shape of droplets approaching plane surfaces. At distances of the order of several 10 Å, sizable dimples are observed on the lower surface; the corresponding water volume cannot get quickly evacuated outside due to the very large flow resistance of the film at small thicknesses.

4.4 Dynamic film thickness measurements during the approach of the droplet towards a plane surface

In these measurements, we keep both the beam incidence point and the angle constant and we monitor the variations of the reflectivity with time. Two distinct regimes appear on Fig. 5: first a very fast decrease of thickness h, then a slower variation regime.

(1) The first regime has been analyzed in several theoretical works. A crucial input in these analyses is the change of shape of the flattened surface of the drop, as it approaches the solid surface, which controls the creeping flow of water in the space between the oil and glass

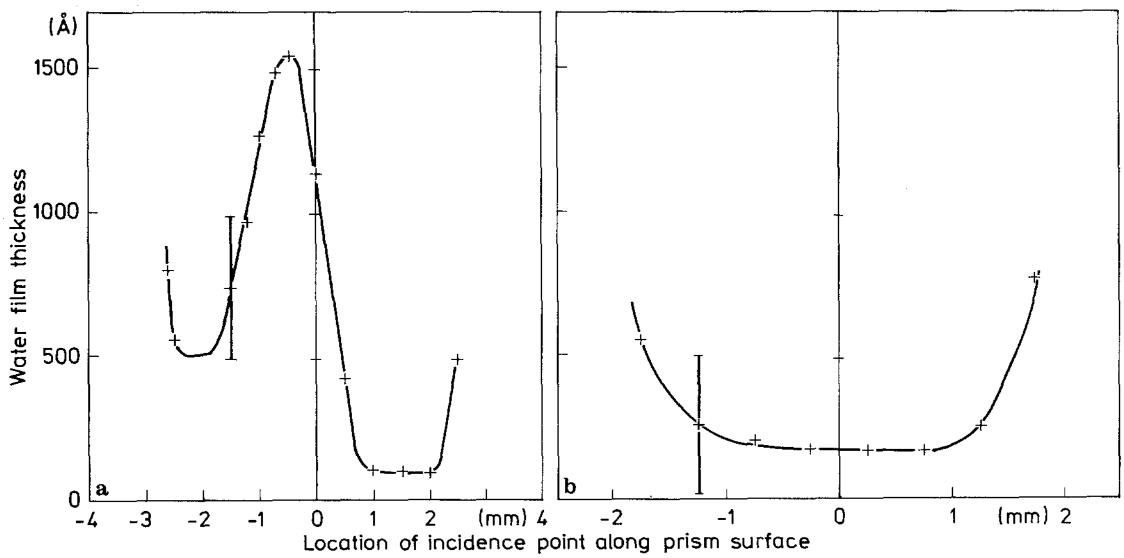

Fig. 4a and b. Quasi-equilibrium film profile obtained by displacing the beam parallel to itself. The observed bump (**b**) is due to the coalescence of two droplets on the surface whereas **a** shows a flat profile. The sensitivity of this measurement can be greatly improved by using a narrower beam

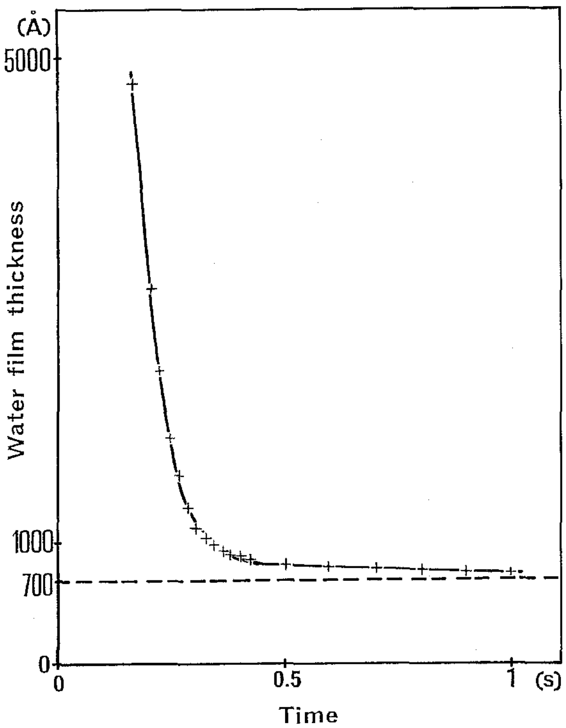

Fig. 5. Variation of the thickness of the water film as a function of time (the origin of time is arbitrary) as it approaches the prism surface. The asymptotic value (~ 700 Å) does not vary appreciably at longer times (a few 10^2 s)

surfaces. The simplified analysis of Siggia (1979) replaces the sphere by a flat disk of radius $A(t) = \sqrt{a\,h(t)}$ varying with time and gives a law.

$$\mathrm{Log}\,[h(t)/h(t_0)] \sim (t_0 - t)\,.$$

Another classical limit approximation (Charles and Mason 1960) uses flat disk of constant radius and leads to a different regime $h(t) \sim t^{-1/2}$. In addition, it is expected that dimples are present in the center of the contact area zone, the bumpy region at the edge being induced by the radial outward flow of water. This makes difficult to identify precisely a thickness variation law from our local observations.

(2) At lower thicknesses, the resistance to flow increases fast and the slope of the $h(t)$ curve decreases. This regime remains to be studied and should depend crucially on the surface state of the surfaces as we have already seen that the final thickness depended on the glass surface preparation.

In particular if the surface treatment introduce local changes in the roughness of the prism surface the hydrodynamics in the lubrication regime could be modified.

5 Conclusion

This paper shows that the frustrated total reflection technique can probe the static and dynamic properties of liquid films over the range of 250–4,000 Å. The role of this thickness range in wetting phenomena where both hydrodynamic and molecular effects have to be taken into account has been recently emphasized (De Gennes 1985). The experiments presented here should be carried out systematically particularly in connection with their possible use for measuring the disjoining pressure due to Van der Waals interactions. In addition it would be of importance to characterize the dynamics of the drop as it rises and its detailed shape as it approaches the prism since this controls the dynamics of the lubrication film. This technique has been used in particular in the related problem of ascent of a small sphere using standard stroboscopic techniques (Bourrier et al. 1984).

Some technical improvements can be made to increase the range of the experiments:

- The use of a thinner laser beam can give a more precise profile of the film at equilibrium but a compromise must be made to limit the beam divergence.
- By using a converging beam on the prism surface and a linear array of photodiodes as detector, one can get more precise information on the thickness heterogeneities of the film.
- An expanded parallel beam covering a large area of the prism can yield a dynamic profile of a drop while it approaches the prism down to a few 10^2 Å.

The present technique has a range comparable to the classical interferometric method (formation of localized fringes) discussed in particular by Sheludko (1967) for molecular films of comparable thickness.

We conclude by mentioning two possible extensions of the present work: by using molecules which can be excited by the evanescent wave, one can probe the molecular state of the thin interfacial film (Allain et al. 1982). Another extension of the present technique using the optical excitation of surface plasma waves can improve the accuracy and limit of resolution (Rivière 1984). The prism is covered initially with a thin (500 Å) metal film and the light wave in grazing incidence in this film can excite surface plasmons at the metal-liquid interface (Raether 1977). The reflectance is modified by this resonance effect and slight variations in the liquid film properties strongly influence the shape of the reflected intensity curve. Using this technique, 50 Å liquid films can be detected. However the presence of the metal surface must be included in the description of the wetting behavior.

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Technical notes

Detection of roll transitions in thermal convection

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1 Introduction

Natural convection at small buoyant potential in a fluid layer heated below and cooled above is characterized by two-dimensional flow structures. For laboratory experiments in rectangular containers, the two-dimensional motion is comprised of longitudinal rolls aligned parallel to the shorter side. Flow structure evolution in this regime involves a successive loss (gain) of rolls with increasing (decreasing) buoyant potential. This note describes a technique by which to determine transition of convection roll patterns for evolutionary experiments with gases in rectangular containers.

2 Problem background

Magnitude of the buoyant potential is defined by the Rayleigh number, $Ra = (g\,\beta/\nu\,\alpha)\,d^3\,\Delta T$, in which g, β, ν, and α are respectively the gravitational acceleration, fluid thermal expansion, kinematic viscosity, and thermal diffusivity. The Rayleigh number is defined for a fluid layer of depth d with imposed temperature difference ΔT. As the buoyant potential is a linear function of temperature difference between lower and upper surfaces, evolutionary experiments are usually produced by using slow heating and cooling rates.

The evolutionary behavior of thermal convection in horizontal fluid layers is well-established in theory (Busse 1978) and in experiment (Willis et al. 1972; Oertel 1980; Behringer 1985). Starting from an initially quiescent condition, the onset of convection in rectangular containers with quasi-steady heating appears in the form of square longitudinal rolls parallel to the shorter side. Transitions in flow structure with increasing Rayleigh number are dependent upon the test fluid, container size, experimentally realized boundary conditions, and prior dynamic behavior.

Roll diameter growth (decrease in number of rolls) with increasing Rayleigh number for gases in infinite horizontal layers is induced by the skewed varicose instability mechanism (Busse and Clever 1979). The skewed varicose instability causes periodic pinching and bulging of convection rolls, with the eventual loss of a roll or roll pair with increased heating as the fluid layer opts for minimum complexity (Normand et al. 1977). Two