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Free convection experiments in water and deuterated mixtures at temperatures including the density maxima

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Abstract—An apparatus designed to perform free convection experiments in cylindrical liquid samples under strictly controlled boundary conditions is described Convection experiments are carried out by measuring at the centre of the sample temperature vs time, as monitored by a thermocouple and a computer on-line device The system water–deuterated water has been investigated in temperature ranges including the density maxima of the samples and compared, only in the case of pure water, with theory Previously observed anomalies of the convective behaviour in this range are confirmed in the form of typical 'plateaux' and thoroughly examined to provide new information about the density maximum of isotopic mixtures A new effect of a faster cooling appears, near the maximum density, when the boundary temperature is brusquely increased

1. INTRODUCTION

THE STUDY of convective phenomena in water contained in cylindrical cells with the axis vertical has demonstrated to be particularly interesting either in steady state conditions [1] or, more recently, in systems far from steady state [2–7].

Our interest is concentrated on free convection in cylinders with a large height/diameter ratio and on phenomena occurring in the vicinity of the density maximum of water and its mixtures with deuterium oxide.

For systems of this kind a theory has been recently developed and published [7], based on a model of convection which subdivides the fluid in two parts the central nucleus and the 'couche' or boundary layer, moving with opposite velocities [2]. In ref. [7] a third intermediate region has been considered to join smoothly the nucleus and the boundary layer: the effects of the density maximum were calculated for a non-Boussinesq fluid by means of a set of functions which account for the velocity variations of the nucleus at various heights.

In the literature the peculiar behaviour of convection in water near its density maximum is reported for a spherical bulb by Codegone [8]. Preliminary measurements in cylinders are due to Sonnino [9], showing the existence of slowing down of the temperature vs time curves near 5°C The main difficulties met in these experiments are generated by the intrinsic vorticity of the system which gives rise to scarcely reproducible results

In this paper we start describing an apparatus designed to minimize undue perturbations and obtain data on free convection in ranges including the density maximum The convective cell is maintained at rest and the temperature at its walls changed by moving thermostatic fluids. In this way we avoid a possible cause of nonreproducibility due to the movements of the cell passing from one bath to the other when the free convection experiment is started.

Moreover, the initial temperature step which produces convection is automatically and reproducibly repeated to provide comparable results on different days

New data on convection in water and its mixtures with heavy water are presented and compared with theory only for cooling at the centre of the cell

A memory effect, which to our knowledge has never been reported in the literature, is observed near the maximum density

Moreover, using an original criterion of positioning

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NOMENCLATURE

k second expansion coefficient for the density function
t time
T temperature
T_s boundary condition for temperature T
z generic level of the liquid in the cell measured from the top

Greek symbols
β_k first expansion coefficient for the density function
ρ density of the liquid

the density maxima of mixtures based on the analysis of convective data, we show a possible deviation from ideality of these isotopic mixtures

2 DESCRIPTION OF THE APPARATUS

The method adapted to obtain reproducible boundary and initial conditions in the fluid is shortly resumed in the following points

(i) the cell is maintained at rest during the whole experiment,
(ii) its temperature at the walls is controlled by thermostatic fluids circulated as fast as possible around it;
(iii) convection is set up by the fastest possible temperature change obtained at a programmed instant,
(iv) temperature at the cell centre is continuously measured and recorded during the whole experiment

Since our fluidic method is not quite flexible as far as the cell diameter choice, we have built the apparatus around a cell of 40 mm diameter, suitable to observe the peculiar convective behaviour of water near its density maximum, as indicated by previous preliminary measurements [7].

The cell C is made of copper tubing machined to a thickness of 2 mm for a length of 123 mm, the lower end of it fits precisely in a nylon cylinder N_1 carrying an O-ring gasket G to provide tightness Similarly, the upper end is closed with a nylon stopper and O-ring gasket (Fig 1), the sample height is 93 mm. The lower nylon cylinder is part of a piece N_2 which supports a 2 in PVC tube B around the cell and the connections A to a 1 in. tubing This reduction from 2 to 1 in. allows the fluid coming from below to circulate around the cell at approximately the same speed as in the 1 in tubing The shape of the connection is machined to favour the fastest possible temperature change in the cell walls when the thermostatic fluid temperature is switched from TA to TB. Above and below the 1 in tubes are connected to L-three way valves VI and VO which can be pneumatically actuated to switch the circulating fluid from bath A to B or vice versa (Fig 2)

This operation requires about 0 3 s, fast enough compared to the duration of an experiment, typically 200 s for half temperature step decay

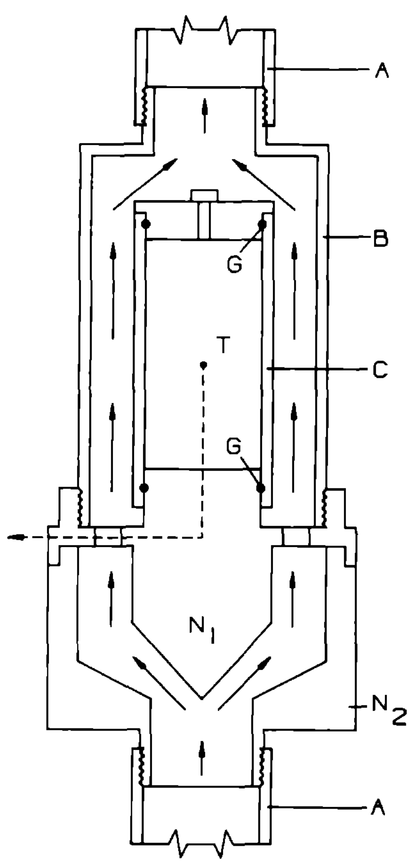

Fig 1 Apparatus detail of the sample cell

The remaining fluidic circuit is straightforward (Fig 2) two 1 in pumps PA and PB ensure a continuum circulation of thermostatic fluids from baths A, B and two additional L-valves VA and VB, pneumatically actuated at the same instant of VI and VO complete the temperature switching setup.

The tubes, the pumps and the valves and the sample holder S are covered with insulating materials to reduce heat input from ambient

Baths A and B are maintained within ± 0.1 C at two different constant temperatures by means of standard automatic electronic units TUA and TUB (Ascon Co), driven by Pt100 thermometers Temperatures as low as -5°C can be attained by a 1 5 hp refrigerator R and the buffer tank C, which provides A and B with

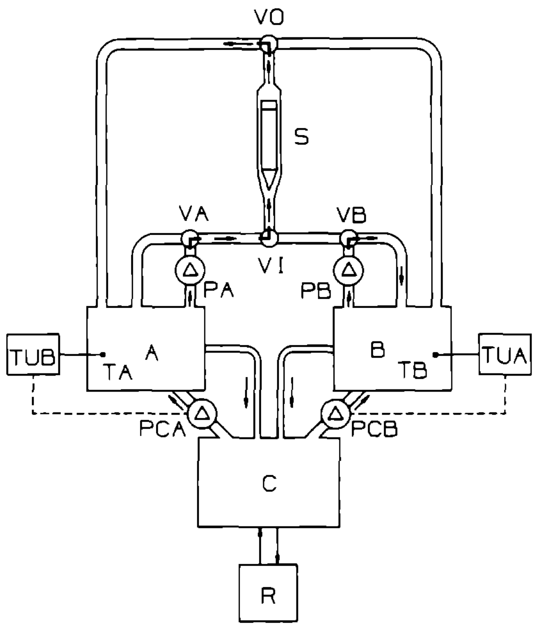

FIG 2 Schematic of the thermostatic system with automatic switching of flow

the appropriate amount of cold liquid by means of pumps PCA and PCB

The temperature at the cell centre is measured by a copper–constantan thermocouple T (Fig 1) the wires of which pass through a hole in the bottom nylon piece N_1 and sealed with waterproof silicone glue

The thermocouple signals are amplified 1000 times by means of a low noise integrated circuit (AD521JD by National) and carried to an Olivetti M24 computer through a Labmaster 16 bit board

Data are automatically averaged over a 1/8 s period and recorded a 1000 s run consists of about 8000 data obtained from 400000; a precision of 0 01°C is attained in most experiments In particular, at the thermocouple, a temperature stability of 0.01 C is observed for periods of 20 s, with occasional faster drifts amounting to 0 02°C in 20 s

The response time of the thermocouple in water is about 0 1 s (90% of the signal), determining our choice of the rate of sampling The fluidic temperature switching is actuated from the computer's board The total duration of the experiment and the instant of temperature switchings are recorded with a precision of 1 and 0.1 s, respectively Intermediate times are deduced using as a time basis the total duration divided by the number of data recorded, introducing a possible error of less than 0.1 s on the relative position of two subsequent data

3. EXPERIMENTS WITH WATER AND ITS DEUTERATED MIXTURES

We have studied five different systems

(S1) pure water with natural deuterium abundance (1/6666),

(S2) 25% volume D_2O–75% volume H_2O,

(S3) 50% volume D_2O–50% volume H_2O,

(S4) 75% volume D_2O–25% volume H_2O,

(S5) 99 75% D_2O (Merck Co., D.F R.).

However, most of our data refer to S1, i e. pure water The deuterated mixtures, as we explain further on, have been investigated only to achieve information about the temperature of the density maximum for such isotopic systems

In Fig. 3 is represented a typical free convection experiment of cooling (A), showing an evident anomaly at about 5°C when compared with the curve (B) obtained by submitting the same sample to the identical initial and boundary conditions and hindering convection by adding a 3% weight cotton fibre in

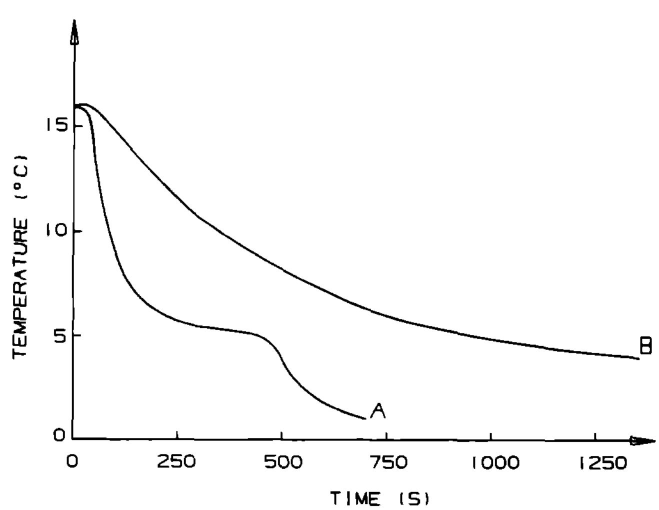

FIG. 3. (A) Temperature vs time convective curve measured at the centre of the water sample (B) Experiment with the same conditions of (A) but with 3% weight of cotton to hinder convection Note the absence of a plateau in this case

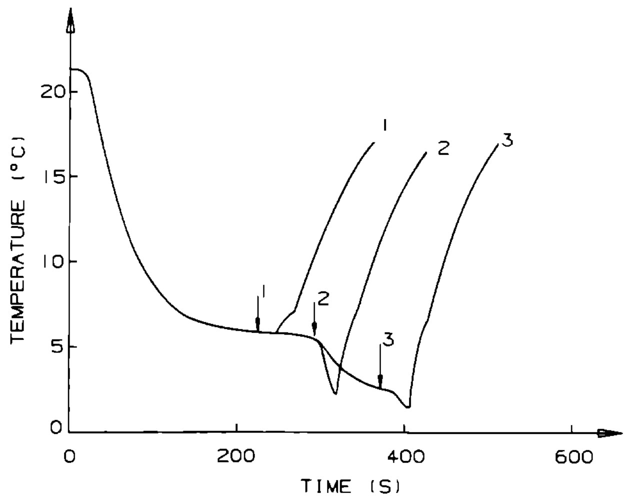

Fig 4 Memory effect of convection The arrows indicate the instants of temperature switching at cell walls (1) absence of a faster cooling rate, (2) the largest evidence of a faster cooling rate, (3) a smaller evidence of a faster cooling rate approaching the lower limit for the effect ($T < 2$°C)

the cell volume Moreover, the shape of this convective curve (A) is very different from the ones previously observed in temperature ranges not including the density maximum of water, which show only one inflection point and are very similar (apart from the rate of cooling) to the conduction curve (B).

In Fig 4, which is a sample of several experiments not reported for brevity, we show a quite curious effect observed by applying the temperature switching towards warming to the cell at different positions of the cooling curve

- in position 1, on the typical 'plateau', a $\simeq$20 s delay is followed by a rapid warming with a kink;
- in position 2, at the end of the plateau, and in position 3, far below the plateau, we note a fast rate of cooling (*even faster* than the normal rate[1]) followed by the warming curve · the delay is of about 20 s at 5 C and 40 s at 2 5 C

These observations which, to our knowledge, have never been reported in the literature of fluid dynamics, reflect the intrinsic complexity of convection in the central region of the cell and may be interpreted only through a detailed analysis based upon the complete Navier–Stokes equation for a non-Boussinesq fluid in non-linear conditions

If the switching on cooling is operated at temperatures lower than about 2°C, no faster cooling is observed, but a plateau on the warming curve is equally present at a temperature substantially symmetric with respect to 4°C (Fig. 5(a))

Similar behaviours, with plateaux at different temperatures, are observed in mixtures of water with heavy water (Figs 5(b)–(e)) In fact, it is well known that heavy water presents a density maximum at about 11 2 C [10] however, the position of maxima for mixtures is not available in the literature

We may obtain this information from our con-

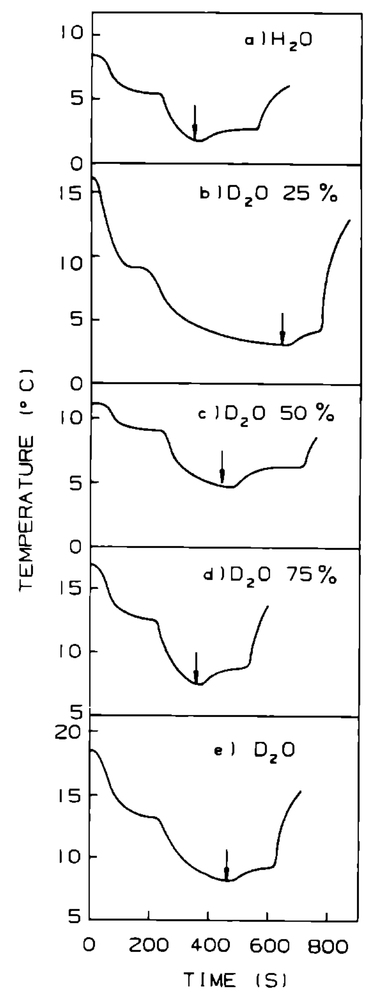

Fig 5 Double plateaux in water–heavy water mixtures The arrows indicate the instants of temperature switchings at cell walls Note that in limiting cases (H_2O and D_2O) the position of the density maximum is close to the middle point of the two plateaux (4 1 and 11 2 C, respectively)

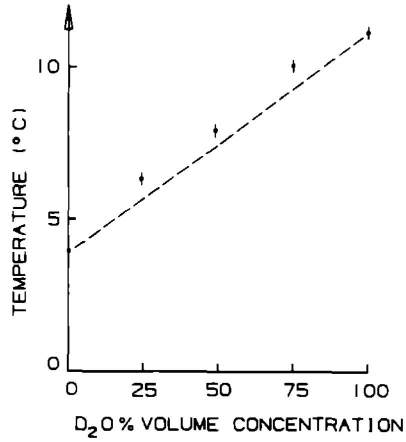

FIG. 6 Behaviour of the temperature of maximum density of water–heavy water mixtures, calculated from convective plateaux

vection data by assuming that the average of the plateaux temperatures is close to the position of the maximum density. This proves to be true for the limiting cases (H_2O and D_2O); if we apply this criterion to our data we obtain the graph shown in Fig. 6, where a straight line does not fit the intermediate maxima positions, indicating a possible non-ideal mixture behaviour

4. THEORETICAL REMARKS AND CONCLUSIONS

It is possible to explain theoretically the observed peculiar form of the free convection curves $T(z, t)$ (where z is the half sample height) in fluids with density maxima. To reach this goal we use our theory, previously published [7], suitably modified to fit our data.

This theory is valid for any boundary conditions, so that we have first introduced the appropriate functions describing our experimental conditions as far as the temperature steps initially applied to the samples These functions are identical to those indicated for the asymptotic solution analysed in ref. [7] On the contrary, to fit our data, appropriate boundary functions for the density must be considered, very different from those reported in ref. [7]. In fact it is evident that the turbulent convective flow modifies the form of the density curve at least by a few parts per million, which is very relevant in the density maximum region, due to the peculiar form of our solution, where the expansion coefficient k is at the denominator

$$T(z, t) = T_s + \frac{\beta_k \pm \{\beta_k^2 - 4k[\rho(z, t) - \rho(T_s)]/\rho(T_s)\}^{1/2}}{2k}.$$

Without giving details of the numerical solutions, we show a fit of only one typical cooling curve in Fig 7 The main features of the convection curve are quite well reproduced by theory and the agreement with experimental data is fair

More refined calculations and measurements to obtain data at various levels of the sample are in progress and will be published soon

We are also trying to explain by our model the interesting memory effect reported here, but the complexity of the boundary equations to be chosen is enormous

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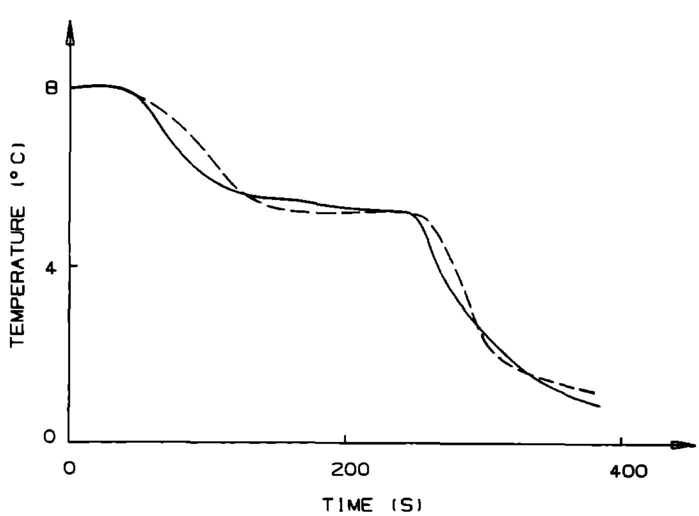

FIG 7 Comparison between a convection experiment and theory The dashed line indicates the theoretical curve calculated according to ref [7]

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EXPERIENCES DE CONVECTION NATURELLE DANS L'EAU ET DES MELANGES DEUTERATES A DES TEMPERATURES INCLUANT LE MAXIMUM DE DENSITE

Résumé—Un appareil est conçu pour étudier expérimentalement la convection naturelle dans des cellules cylindriques liquides avec des conditions aux limites strictement contrôlées Les expériences sont conduites en mesurant au centre de la cellule la température en fonction du temps par un thermocouple relié à un ordinateur en ligne Le système eau–eau deutératée est étudié dans des domaines de température qui incluent les densités maximales et on compare, seulement dans le cas de l'eau pure, avec la théorie Des anomalies déjà observées dans la convection sont confirmées par des "plateaux" typiques et elles sont soigneusement examinées pour obtenir des informations nouvelles sur le maximum de densité des mélanges isotopiques Il apparait un nouvel effet de refroidissement rapide, tout près du maximum de densité lorsque la température à la limite est brusquement augmentée

EXPERIMENTE ZUR NATÜRLICHEN KONVEKTION IN WASSER UND IN GEMISCHEN VON WASSER MIT SCHWEREM WASSER BEI TEMPERATUREN IN DER UMGEBUNG DES DICHTEMAXIMUMS

Zusammenfassung—Eine Vorrichtung fur Experimente zur freien Konvektion an zylindrischen Flussigkeitsproben bei streng festgelegten Randbedingungen wird beschrieben Bei den Versuchen wird die Temperatur im Zentrum der Probe durch ein Thermoelement und eine on-line-Computerverbindung aufgezeichnet Das System Wasser–schweres Wasser wurde in Temperaturbereichen in der Umgebung des Dichtemaximums untersucht und im Fall reinen Wassers mit der Theorie verglichen Schon fruher beobachtete Anomalien des konvektiven Verhaltens in diesem Bereich werden in Form typischer Plateaus bestatigt. Sie werden sorgfältig untersucht, um neue Informationen uber das Dichtemaximum von Isotopengemischen zu erhalten Ein neuer Effekt einer schnellen Abkuhlung wurde in der Nähe des Dichtemaximums beobachtet, wenn die Grenztemperatur abrupt angehoben wird

ЭКСПЕРИМЕНТЫ ПО СВОБОДНОЙ КОНВЕКЦИИ В ВОДЕ И ДЕЙТЕРИРОВАННЫХ СМЕСЯХ ПРИ ТЕМПЕРАТУРАХ, СООТВЕТСТВУЮЩИХ МАКСИМАЛЬНОЙ ПЛОТНОСТИ

Аннотация—Описывается установка, предназначенная для проведения экспериментов по свободной конвекции в цилиндрическом объеме при строго контролируемых граничных условиях. В экспериментах измерялось изменение температуры в центре образца в зависимости от времени с помощью термопары неавтономного вычислительного устройства Система вода-дейтерированная вода исследуется в диапазонах температур, включающих максимум плотности образцов, и сравнивается с теорией в случае с чистой водой. Подтверждено существование ранее наблюдавшихся аномалий картины конвекции в данном диапазоне, проявляющихся в виде типичного "плато", и проведено их тщательное исследование с целью получения новой информации о максимальной плотности изотопных смесей. При резком увеличении температуры на границе возникает новый эффект ускоренного охлаждения вблизи максимальной плотности.