Density profile in convection of water near 4 °C

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Data on cylindrical free convection in water near $4^{\circ}C$ are compared with a theory previously developed for a fluid having a density maximum. The main features of experimental curves are well reproduced by theory and it is shown that the typical temperature arrests observed in free cooling of water are due to the particular profile of the density which propagates from the boundary layer inside the bulk of the fluid (the central nucleus). Here, we report a density behavior shown by water in convective state.

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I. INTRODUCTION

In previous works we have described a general theory of free convection in a cylinder for fluids submitted to a horizontal thermal gradient [1-3]. In Refs. [1] and [2] we have studied non-Boussinesq fluids having a monotonic behavior of the density versus temperature. Experimental data of temperature versus time obtained in our laboratory were compared with theory only in Ref. [1] in the case in which water is placed in a temperature range not including 4 °C where, as is known, it behaves as any other fluid.

In Ref. [3] we have taken into account fluids having a density maximum, such as water. Typical temperature arrests were observed either on cooling or on warming of the samples submitted to free convection. These arrests were observed at temperatures quite symmetric with respect to the density maximum and used to determine this datum for heavy-water mixtures [4].

Other experiments on pure water were also performed in narrower temperature ranges around the maximum to study the large (20%) asymmetries introduced in convection by the rather small (8 parts per million in the 0° to 8 °C range) asymmetries in the density curve [5].

Here we shall show a comparison between a further development of the theoretical solution of Ref. [3] and experimental data in the maximum-density region of water.

Such a comparison is carried out to provide complete information about the density profile in space-time for free convection in water confined in a cylindrical reservoir. In Sec. II we briefly describe an improved version of the theory published in Ref. [3]. The comparison of the theoretical solutions to experimental data and conclusive remarks are presented in Secs. III and IV, respectively.

II. MATHEMATICAL TREATMENT

Before we describe and discuss the experiments, it is useful to introduce the theoretical model of convection and give the main information about the results already obtained with this model. Free convection at a wall having a different temperature from the surrounding fluid is usually described in terms of density gradients in the gravity field. The fluid close to the wall starts its motion shortly after a temperature difference is created between the wall and the fluid itself. In fact, due to thermal conduction, a thin layer of the fluid is heated or cooled and its density, if no anomalies are presented by this property, becomes correspondingly lower or higher than the surroundings.

Near a warmer wall, a fluid starts to move upwards, while near a colder one, the motion is downward. The thin layer moving at the wall is the well-known boundary layer. If the fluid is contained in a hollow cylindrical cell with its axis vertical and well-conducting lateral walls, in order to maintain continuity in the fluid, the motion at the walls must be counterbalanced by an opposite motion on the axis. This gives rise to the so called "nucleus" in the scheme of Fig. 1, observed and described by Mouton and De Roeck [9].

In the Appendix of Ref. [3] we studied the case in which water contained in a cylindrical vessel is initially at rest and at a temperature T_0 . The lateral wall of the cylinder is conductive and the top and bottom plates of



FIG. 1. Model of convection in a fluid contained in a hollow cylinder with conducting lateral walls. The arrows indicate the fluid motion in the boundary layer and in the nucleus in the case of initial higher density at the walls.

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the cell are insulating. The thermostat is at temperature T_s . This implies an approximately constant temperature gradient across the boundary layer which is formed after a few seconds of convection. We can then assume a linear temperature distribution between the fluid and the walls at initial time. To consider a temperature range including the density maximum of water, we fit by a parabola the initial density profile versus temperature [6]. More complex functions might be used in larger temperature ranges [7]. The choice of the state equation determines the initial (i.e., $t = t_0$) profile of density versus space [3]. It will be the dynamics of the system to perturb the linear temperature distribution.

The values of T_0 and T_s are set, on the basis of experimental evidence, at about 8 °C and 0 °C, respectively. In fact, as already shown in previous papers [4,5,7], the typical temperature arrests in free-convection curves appear only when a quite large temperature range including the density maximum is considered.

As is well known, to have a well-formulated problem from a mathematical point of view, it remains only to specify the initial condition for the density [8]. Physically, this reflects the fact that the state of the wall can only constrain the temperature and velocity of the fluid at the wall, whereas the behavior of the density close to the wall is entirely determined by the internal dynamics of the system.

Once the boundary conditions are specified, the dynamics of the system is determined by solving the five hydrodynamic equations (continuity, Navier-Stokes, and Fourier). However, to simplify the mathematical complexity of the problem, we had to assume the convective model of Fig. 1, which subdivides the fluid into two regions: the boundary layer and the central nucleus. This allowed us to apply two different mathematical methods to solve these two problems [9,3].

Of course, these two regions are physically connected and it is easy to show that they are mathematically related by the continuity equation for velocity fluxes [2,3]. Let us now report the final results.

The temperature T(z,t) on the vertical axis of the cylinder is expressed as a function of the depth z and t, starting from the initial temperature T_s :

$$T(z,t) = T_s + \Delta T , \qquad (1)$$

with

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

and

$$\rho(z,t) = \rho(T_s) + S , \qquad (3)$$

$$S(z,t) = \sum_{n=-\infty}^{n=+\infty} \alpha_n \exp(in\pi z/h) \exp[inx(t)], \qquad (4)$$

$$\alpha_n = (1/2h) \int_{-h}^{+h} [\rho(z, t_0) - \rho(T_s)] \exp(-in\pi z/h) dz ,$$
(5)

$$t = \frac{1}{a} \int_0^x \frac{d\xi}{G^{1/3} \left[\frac{h}{\pi} \xi + \delta \right]} .$$
 (6)

 β_k and k are, respectively, the first and second coefficients of the density ρ expansion with temperature, and G is a function of x expressing the initial condition for the temperature step. Moreover, h and δ are, respectively, the height of the cylinder and the thickness of the boundary layer, and a is a dimensional constant which depends on the transport coefficients. Note that Eq. (6) provides variable x as a function of time in an implicit form.

Of course, Eq. (4) can be rewritten as

$$S(z,t) = \sum_{n=-\infty}^{n=+\infty} \alpha_n \exp\left[(in\pi/h) \left[z + \frac{h}{\pi} x(t) \right] \right], \quad (7)$$

or, by taking into account Eq. (5), as

$$S(z,t) = \rho \left[z + \frac{h}{\pi} x(t), t_0 \right] - \rho(T_S) .$$
(8)

In other words, function S coincides with the initial density profile but not calculated at point z but at point $z'=z+x(t)h/\pi$. Physically, the density solution has the same profile as the one it had at the initial time $t=t_0$ but deformed in space-time according to the law $z'=z+x(t)h/\pi$. Thus, we see that the role played by variable x is unusual since the phenomena examined here is completely determined by the time evolution of x given by Eq. (6). Briefly, both temperature T and density ρ are, at any instant, only functions of variable x. Since x shows properties connected with the time evolution of the phenomenon and measures in some way the degree of advancement towards equilibrium [2], we called it a "clock function" [10]. Its general role in nonequilibrium thermodynamics has been discussed elsewhere [10,11].

The velocity, pressure, and density profiles can be also found by using the central-nucleus model [3]. However, temperature measurements are simple and accurate. Then, we prefer to test the validity of our theory published in Ref. [3], comparing the experimental temperature data versus time to the theoretical profile.

III. COMPARISON WITH EXPERIMENTS

The apparatus consists of a copper cell (3.6 cm diameter, 9.2 cm length) filled with water and surrounded by a circulating thermostated fluid. At a given instant, by a convenient valve switching, this fluid is suddenly replaced by another fluid thermostated at a different temperature. After this instant, free convection takes place within the cell.

A thermocouple is placed along the z axis at 4.6 cm from the bottom, i.e., at the center of the cylinder. The electromotive force of the thermocouple is amplified, detected, and recorded by a standard computer on-line interface to provide temperature data accurate to 0.01 °C. Each recorded datum is averaged over 100 points with a period of about 0.2 s. A typical convection experiment lasts about 400 s, so that it consists of approximately



FIG. 2. Comparison between experimental data and theory for free convection in water: ——, temperatures measured at the center of a cylindrical cell (9.2 cm length, 3.8 cm diameter); **—**, calculated values according to the general theory of a convecting nucleus.

2000 data, or 200 000 points.

The experimental conditions, with reference to the region of interest, i.e., cooling curves between temperatures including the density maximum, are the following:

(i) The initial temperature of the fluid is uniformly constant, i.e., $T(t_0, z) = T_0$ for all levels z; (ii) the temperature of the thermal bath is $T_s = 0$ °C; and (iii) the continuum is initially at rest.

In Fig. 2 we report a comparison between the experimental temperature data (solid line) and the theoretical solution (dotted line). As can be seen, the main features of anomalous convection in water are well reproduced by our theory. We wish to point out the extreme sensitivity of the temperature trends to the actual form of the density field. This can also be explained theoretically by considering the equation which relates the temperature to the density [3]. This equation is strongly dependent on the initial density condition: Any small variations in the slope of the initial density choice, even slightly different from the parabolic one, induce large variations in temperature.

Considering the technological limitations of laboratory experiments [11], we have measured the density profile directly using the temperature data. To this end, we have assumed that: (i) the local-equilibrium hypothesis is valid [12], and (ii) the density dependence on pressure is negligible.

Assumption (i) is fully supported by moleculardynamics experiments on fluids confined in rectangular boxes and submitted to temperature gradients [13]. Assumption (ii) comes from experimental pressure-volumetemperature data for water [6]. Therefore, the density profile in space-time is simply obtained by inserting the experimental temperature versus time data into the following state equation:

$$\rho(z,t) = \rho(T_s) \{ 1 - \beta [T(z,t) - T_s] + k [T(z,t) - T_s]^2 \} .$$
(9)



FIG. 3. Density profile vs time: (a) Theoretical and (b) experimental behaviors in the middle of the cylinder.

In Fig. 3(b) the results of such a calculation, carried out on the data of Fig. 2, are shown. As can be seen, the experimental and the corresponding theoretical curves, reported in Fig. 3(a), are in excellent agreement.

The great sensitivity of convection to very small variations in the density distribution in the fluid is confirmed. In fact, the flat-top form of Fig. 3 modifies this distribution by about 15 ppm only. Without introducing this quite small density change, no temperature arrest is predicted by theory. As seen in Fig. 2, the temperature arrest perturbs the monotonic form of a cooling curve by more than 30%. Thus, even a slight variation of 1 ppm in the density profile would produce an appreciable modification in the temperature versus time dependence.

As a consequence, the peculiar form of the density profile shown in Fig. 3 suggests the following physical interpretation: The static density profile is perturbed by a few parts per million due to the motion of the fluid. Thus, just after the onset of convection, the cuspidated density distribution is created within the liquid near the walls in place of the parabolic one. According to our theory, this slightly perturbed boundary-layer density profile propagates into the nucleus modifying its shape in space-time and giving rise to the observed temperature arrest. Detailed calculations with other experimental curves will be presented elsewhere.

IV. CONCLUSIONS

We have shown, in a typical case of anomalous convection in water near its density maximum, the substantial validity of our previously published theory. By combining the experimental data with theoretical considerations, we have been able to measure and interpret the convective anomalies of water. The temperature arrests are described in terms of very slightly perturbed density profiles (about 15 ppm) generated in the boundary layer of water in a convective state. In our opinion, these small density variations revealed by experiments, and confirmed by theory, should be very difficult to detect using other techniques. We hope that the introduction of variable x(t), presented in Ref. [3], may be useful in approaching other complicated hydrodynamic problems.

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