

# High precision balance from salt and water and the slow swelling of ping-pong balls

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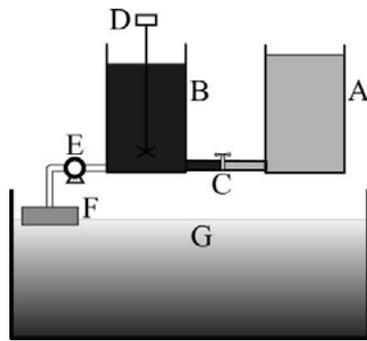
## Abstract

Density gradient columns are the most accurate type of equipment for determining unknown densities. Commercial equipment is designed for chemical engineering practice, where the typical sample size hardly exceeds a few grams. The accuracy of measurements crucially depends on the precision of height determination. Here we demonstrate that stratified salt water in much larger containers (used for experiments in geophysical fluid dynamics) is perfectly suitable for accurate density measurement of large samples. Even height determination has an increased reliability because the large free fluid surface serves as an excellent calibration level. The efficiency is illustrated by revealing a subtle effect where celluloid ping-pong balls slowly absorb water and swell, changing the total density by a few thousandths only.

## 1. Introduction

‘... In the bottom of a vessel I placed some salt water and upon this some fresh water; then I showed them [some friends] that the ball [made of wax] stopped in the middle of the water, and that, when pushed to the bottom or lifted to the top, would not remain in either of these places but would return to the middle. ...’ recollected Galileo when under house arrest by the Inquisition during the last years of his life [1]. This short note is probably the first written description of a density gradient in a fluid and its ‘application’. Some 300 years later, Linderstrøm-Lang demonstrated that density stratification can be exploited for extremely accurate density measurement [2]. Three decades later, Oster and Yamamoto concluded a

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**Figure 1.** Schematic diagram of the double-bucket technique: A, fresh water tank; B, salt water tank; C, connecting tube with tap; D, mixer; E, rotary pump; F, floating sponge; G, experimental tank of linear density-stratified filling.

review on density gradient techniques with the following [3]: ‘In this age of complicated instrumentation it is refreshing to know that a simple and inexpensive device, namely, the ordinary density gradient column, exists which is capable of measuring a fundamental property of matter to differences of one part in ten million’. Besides traditional chemical engineering [3], applications are abundant in fields ranging from the textile industry [4] through soil science [5] and marine biology [6–8] to pathology [9, 10].

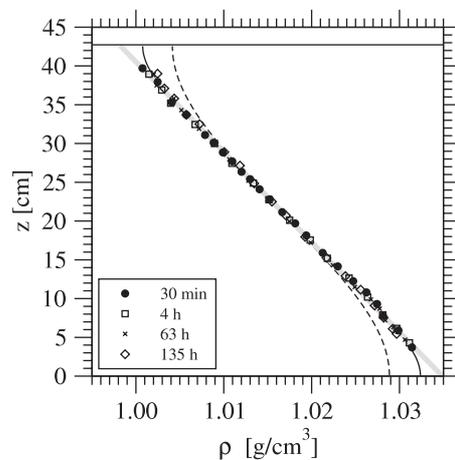
A usual density gradient column in its simplest form contains two miscible fluids, which covers in excess the density range to be investigated. They are slowly mixed in a long (50–70 cm) cylindrical glass tube (with a diameter of a few millimetres) such that the density of the resulting mixture decreases linearly with the height in the tube. The unknown density of a specimen is determined from its equilibrium position with a high accuracy.

The second largest ‘producers’ of stratified fluids are almost certainly laboratories for geophysical fluid dynamics. Density stratification in the atmosphere and oceans results in a plethora of exciting phenomena far from our everyday experiences, such as damping of vertical motions, internal oscillations and waves, trapping of buoyant plumes, zigzag instability, etc [11]. Fortunately, most of these unusual forms of motion can be demonstrated on a laboratory scale by means of relatively simple methods [11]. The probable reason why such experiments are regularly demonstrated only at university level is that a full explanation requires sometimes complex background knowledge; even details of easily accessible, spectacular phenomena are not fully understood yet.

Here we demonstrate that a laboratory tank filled with stratified salt water can be perfectly used for precise density measurement. The longevity of the density gradient is a consequence of the much larger fluid volume (~100 l) compared with the usual gradient columns (~100 ml), thus changing samples and similar manipulations mean much smaller relative perturbation. An accurate height measurement is supported by the presence of the large free fluid surface, providing a good quality horizontal reference level. An additional benefit of large volume is that specimens can be much bigger. It is worth emphasizing that the total cost of the necessary equipment is less than one-tenth of a medium class laboratory purpose density column. The resolution of the method is demonstrated by studying a subtle effect: the wall material of ping-pong balls (celluloid) slowly absorbs water resulting in swelling, and the increasing volume slightly decreases the overall density of the balls. This slow process is revealed by tracking the floating height of the balls, which turned out to be increased in our stratified fluids by 10–20 cm during the observations of several days.

## 2. Linear density stratification

Continuously stratified fillings are routinely produced by the ‘double-bucket’ or ‘two-tank’ method (figure 1) proposed originally by Fortuin [12] in 1960. The simplest version is made



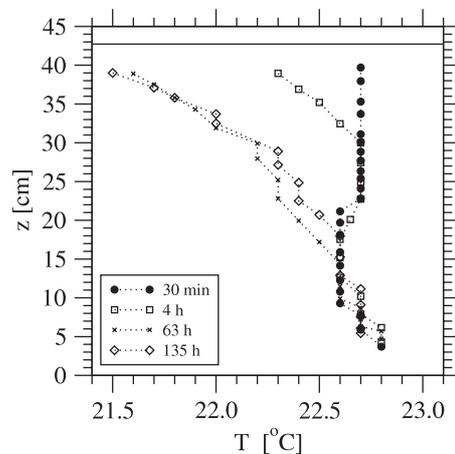
**Figure 2.** Density profile in a stratified tank measured at different times (see legend) after filling. The fitted grey line is the inverse of the function  $\rho(z) = az + b$ , where  $a = -0.00086 \pm 0.000072 \text{ g cm}^{-4}$  and  $b = 1.0349 \pm 0.00006 \text{ g cm}^{-3}$ . The thin black curve indicates the effect of diffusion after 135 h; the dashed curve is the prediction for 1 month waiting time.

from two containers joined by a tube, one for fresh water and the other for a homogeneous salt solution. The connecting tube has a tap which is closed during fill and has a U shape in order to block immediate cross flow at opening the tap. One of the containers has an outflow with a pump; in our case this is bucket 'B' (see figure 1). When fluid is pumped out from this side, the level difference drives fresh water from bucket 'A' through the connecting pipe. The solution in 'B' is continuously homogenized by a mixer. The filling of an experimental tank is performed through a floating sponge minimizing turbulent mixing at the nozzle. The advantage of such a simple set-up is that the linearity of density profiles is very robust in tanks of vertical walls and constant cross sections. A more elaborate technique with computer-controlled peristaltic pumps makes it possible to build up any statically stable density profile in tanks whose planform areas vary with the vertical coordinate [13].

An example of linearly stratified salt water filling in a tank of  $80 \times 40 \times 50 \text{ cm}^3$  is shown in figure 2. Density profiles are usually determined by measuring conductivity as a function of height. Most of the commercial electrode heads are supplied with a temperature sensor as well for an automatic temperature compensation. Although there are conversion formulae between salt concentration and measured conductivity in the literature [14], it is better to perform direct calibrations. When concentration and temperature are known, density can be calculated by means of empirical equations of states [15] which are usually given in polynomial forms. Alternatively, a set of calibrated glass floats can be used to determine density at a few levels.

A remarkable aspect of such a linear stratification is its temporal stability. The diffusion coefficient of NaCl at low concentrations [16] is  $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , but we do not really have a good impression of the speed of spontaneous homogenization in a quiescent fluid. Figure 2 illustrates that repeated measurements did not indicate significant changes during one week (note that a few centimetres at the top and bottom is not measurable because of boundary effects), in spite of the fact that the volume was manipulated during the experiments reported below. The solution of the diffusion equation predicts homogenization starting from the boundaries, but the linear profile survives weeks in the bulk (see figure 2).

The experiments were performed in an air-conditioned laboratory; nevertheless, fluid temperature was continuously tested. The appropriate profiles are shown in figure 3. The initial uniform distribution evolved to a weak gradient because of evaporative cooling, even though the tank was covered between the experiments. Note that such an inverted temperature



**Figure 3.** Temperature profiles for the same filling as in figure 2 measured at the same time as density with an accuracy of  $\pm 0.1$  °C. Note that the horizontal scale covers 1.5 °C only.

profile cannot be stable in a homogeneous fluid; gravitational equilibrium is not possible without a salt concentration gradient.

### 3. Swelling of ping-pong balls

As is clear from figure 2, ideal floats for revealing motion in a stratified fluid have a slightly higher density than fresh water. Besides calibrated glass beads (they are rather expensive), ping-pong balls filled with some ballast turned out to be very practicable for our experiments.

The table tennis ball is one of the last products made from celluloid, a plastic formed by treating cellulose nitrate with camphor and alcohol [17]. Celluloid was the first important synthetic plastic (production began in 1869) and was widely used as a substitute for more expensive substances. It is highly flammable and has been largely superseded by newer plastics with more desirable properties. The rigorous specifications of the International Table Tennis Federation (ITTF) do not exclude other plastics [19], but apparently ball producers have not been able to replace celluloid yet.

In order to get an idea of the level of standardization of ping-pong balls, let us quote a few rules from the ITTF technical leaflet of June 2003 [19]:

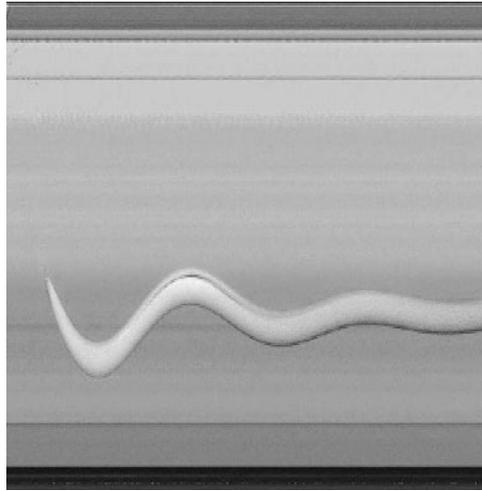
*Weight.* Law 2.3.2 specifies 2.7 g, but any weight between 2.67 and 2.77 g is acceptable for any one ball. No more than 1 ball out of the 24 sampled may be outside this range. The standard deviation may not exceed 0.03 g.

*Size.* The minimum diameter of every ball must be at least 39.50 mm, and its maximum diameter must not exceed 40.50 mm. The standard deviation of the average diameter may not exceed 0.06 mm.

*Sphericity.* The sphericity of any ball must be less than 0.35 mm, and the sample mean sphericity must be less than 0.25 mm. [The sphericity of a ball—more correctly the lack of sphericity—is the absolute difference between its minimum and maximum diameters.] The standard deviation of sphericity must be less than 0.06 mm.

*Bounce conformity.* All 24 balls must rebound to a height of not less than 240 mm or more than 260 mm when dropped from a height of 305 mm on to a standard steel block.

We used the officially recognized Japanese brand Nittaku in our experiments. Control measurements confirmed that all the parameters are well within the permitted intervals. The density of wall material is 1.54–1.71 g cm<sup>-3</sup> depending on the nitrogen content [18], thus a nominal wall thickness of  $d = 0.33$  mm can be estimated. Since the average volume is around



**Figure 4.** Time-slice image of an oscillating ping-pong ball filled with water in a linearly stratified fluid. The white trace has a thickness of 40 mm; the horizontal axis covers a time interval of 22 s.

32 cm<sup>3</sup>, a filling with fresh water by means of a hypodermic needle results in a float in the required density range (the small hole is sealed after injection).

When a ping-pong ball filled with water is carefully dropped into the stratified fluid at the top, it accelerates until drag forces become strong enough to brake falling. Then a slow oscillation sets in around the equilibrium level, where the densities of the ball and the surrounding fluid perfectly match. This damped oscillation is visualized in figure 4 by time-slice imaging, where a vertical column of pixels is cut out from consecutive digitalized video frames and merged sideways to form a time series representation. The appearance of the trace of the ball ‘out of the blue’ is a consequence of horizontal drift caused by vortex shedding in the wake. The dynamics of falling spheres in a stratified fluid has many interesting details, but this is beyond the scope of the present paper.

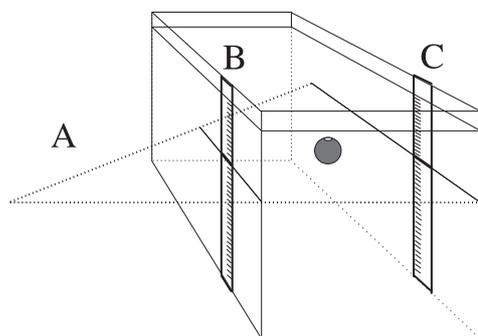
Viscous drag damps oscillations in a few minutes, then the vertical position of the floating ball should be determined. Figure 5 illustrates a simple, accurate but inexpensive method for measuring height deep in the tank. The basic tool is a light sheet produced by a cylindrical lens fixed to a small diode laser; high power is not necessary at all. Two plastic rulers are positioned to the front and the rear walls of the glass tank such that the meniscus of the free surface is used for precise levelling. The horizontal light sheet (calibrated by the free surface as well) is moved downward until a bright spot remains only on the top of the floating balls. Height is recorded when the two readings on both rulers are the same. With this method the accuracy of height measurement is better than  $\pm 0.5$  mm, which means a nominal precision of  $\pm 4.2 \times 10^{-5}$  g cm<sup>-3</sup> for density measurement in the given stratified medium.

In the course of experiments we observed that fresh balls did not float at an equilibrium level; their vertical position increased monotonically after cessation of oscillatory motion. In order to understand this slow process, we performed systematic investigations with different balls; the result is summarized in figure 6.

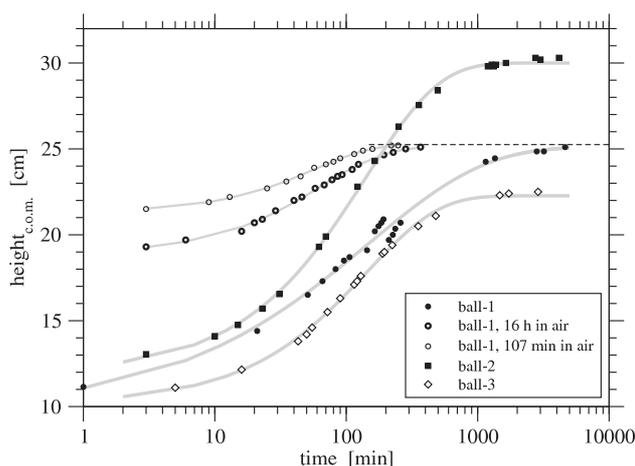
We found that the monotonic rise of fresh balls is a continuously decelerating process, which can be fitted with a stretched exponential function:

$$z(t) = \Delta \left[ 1 - \exp\left(-\left(\frac{t}{\tau}\right)^\alpha\right) \right] + z_0, \quad (1)$$

where the numerical values of the parameters for three balls are given in table 1. Stretched exponentials are commonly used to describe kinetic processes in strongly disordered systems.



**Figure 5.** Schematic diagram for measuring height of a floating object. A, horizontal laser sheet; B, front ruler; C, back ruler. (For details, see text.)



**Figure 6.** Centre of mass height of test balls (see legend) as a function of waiting time in a density stratified fluid. Grey lines are stretched exponential fits by equation (1). The dashed line indicates the approximate wet asymptotic height for ball 1.

The function in equation (1) was introduced in the 19th century by Rudolf Kohlrausch to describe the relaxation of electrical polarization in glassy materials [20]<sup>5</sup>. More than a century later, Williams and Watts [21] rediscovered this function to fit the relaxation of electrical variables in glassy dynamics. Since then, the Kohlrausch–William–Watts function has dominated in the description of stretched relaxation. A large number of physical systems have been shown to present such behaviour [22], and, consequently, a number of theories have been proposed to explain it [23].

Before further discussing quantitative details, let us turn back briefly to the experiments in figure 6. The first data series for ‘ball 1’ (filled circles) has an apparent break at around 200 min. This is because we removed it when the rise was observed and performed some control measurements. Evaporative weight loss was immediately observed on a precision balance. It became clear, however, that the volume must be shrunken more strongly, since the equilibrium level decreased after the short stay in air. On the fourth day the ball seemingly

<sup>5</sup> This reference has so many deficient versions in contemporary literature that it might be worthwhile to note the following. (i) The author is Rudolf Kohlrausch and not his son Friedrich. (ii) The periodical has the full title *Annalen der Physik und Chemie*. The publisher of series I–VI (volumes 1–160) was J G Poggendorff, that is why older citations refer to it as *Poggendorff’s Annalen* or as we have done. (iii) The article appeared in two separate parts; this is indicated by the precise page numbers.

**Table 1.** Fitted parameters of equation (1) for the three test balls shown in figure 6.

	$\Delta$ (cm)	$\tau$ (min)	$\alpha$	$z_0$ (cm)
Ball 1	15.3	147.7	0.49	9.8
Ball 1 (16 h in air)	6.2	64.6	0.88	18.9
Ball 1 (107 min in air)	3.9	57.6	0.98	21.3
Ball 2	18.1	141.8	0.78	11.9
Ball 3	12.1	143.5	0.80	10.2

reached an asymptotic height; further rise could not be detected. The second and third series in figure 6 (empty circles) prove that the density change is proportional to the resting time in air; furthermore, it is reversible: the dashed line indicates that a given ball returns to the same height after a long enough wait. The two control series with ‘ball 2’ and ‘ball 3’ provide an impression of how quantitative details depend on the specific properties of specimens.

It was fairly easy to recognize the key process behind the increase of equilibrium height: the wall material of ping-pong balls absorbs water and swells such that the overall density decreases. Swelling is an important technological process, especially considering soils, wood, food products, etc, therefore the related literature is immense. Surprisingly, apart from notes that celluloid absorbs 1–2 wt% water in 1–2 days [24], we could not find a systematic scientific analysis. This might be due to the fact that celluloid is the oldest industrial plastic and basic properties were determined and published as early as the end of the 19th century. The situation is similar for volumetric changes: the basic problem that celluloid films shrink in air too dry has been reported many times, but we could not trace back even a single relevant paper on quantitative analysis.

We can estimate, however, the magnitude of expected density drop by using average parameters of standard ping-pong balls: outer diameter = 40 mm, mass = 2.7 g, density = 1.625 g cm<sup>-3</sup>, volume of wall material = 1.66 cm<sup>3</sup>, computed internal diameter = 39.33 mm, internal volume = 31.85 cm<sup>3</sup>, total initial weight = 34.475 g (with  $\rho_{\text{H}_2\text{O}}^{22.5^\circ\text{C}} = 0.99766 \text{ g cm}^{-3}$ ), initial density = 1.0288 g cm<sup>-3</sup>, expected initial height with respect to the bottom of the tank  $\approx 7.0$  cm. By assuming that the water absorption limit in the wall is 1–2 wt% (0.03–0.05 g) and that swelling is directly proportional to it (0.017–0.034 cm<sup>3</sup> in the wall) and uniform, we can compute the ‘inflated’ size: internal volume = 32.17–32.49 cm<sup>3</sup>, total volume = 33.845–34.180 cm<sup>3</sup>, total mass = 34.505–34.525 g. The expected final density should be in the range 1.010–1.020 g cm<sup>-3</sup>, accompanied by a height increase of  $\Delta = 10$ –20 cm. Empirical values in table 1 agree well with this elementary estimate.

In summary, the results seem to support the view that the celluloid wall material of table tennis balls absorbs 1–2 wt% water, and the ‘swelling coefficient’ is directly proportional to it. Furthermore, the observations revealed that the kinetics is stretched exponential with a characteristic time  $\tau \approx 140$  min and stretching exponent  $\alpha \approx 0.8$  for fresh balls. Repeated tests with the same ball indicated that the swelling is reversible and exhibits ageing:  $\tau$  decreases while  $\alpha$  increases during cyclic wetting–airing treatment.

Finally, we note that the salt–water system is very convenient for gradient columns in the density range 1.00–1.11 g cm<sup>-3</sup>, which might seem to be quite narrow and restrictive. This range, however, is very important itself, e.g. millions of organic materials have densities in this interval simply because their essential building blocks are proteins. Furthermore, the density range can be widened by using calibrated hollow containers; this is possible because there is practically no size limitation.

## Acknowledgments

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