

Measurement of the solid fraction in the crystallization of a binary melt

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Measurements are described of the profile of solid fraction in the mushy layer that is formed when aqueous solutions of sodium nitrate are cooled and crystallized from below. The method relies on the measurement of electrical resistance in a conductivity cell, one electrode of which is a thin horizontal wire situated in the mushy layer. As the solid fraction increases with time, it insulates an increasing fraction of the length of the wire and increases the resistance. The results show an encouraging degree of consistency with the theoretical predictions of Worster. Inclusion in the theory of the effects due to the difference in density between the solid and liquid phases may enhance the agreement between the theoretical and experimental results even further.

1. Introduction

The phase change from liquid to solid plays a central role in a wide variety of natural, industrial and laboratory processes. The study of phase changes has thus attracted not only scientists working in specific disciplines such as metallurgy, geophysics and crystal growth, but also applied mathematicians who have attempted to build general quantitative models of the various processes. All such models, and the assumptions built into them, need to be tested against experimental data before one can be confident of their predictions. This is particularly so if one wishes to apply the theoretical concepts to situations inaccessible to direct experimental measurement, for example at the growing boundary between the solid inner core and the liquid outer core of the earth. Part of

the aim of the work reported in this paper is to carry out a measurement of the local ratio of solid to liquid in the mushy zone of a laboratory experiment with aqueous solutions and to compare the results of these measurements with the predictions of previously reported theoretical calculations. Chen and Chen [1] have recently used X-ray tomography to measure the solid fraction in a mushy layer at the end of an experiment. In the current paper we report on a series of measurements of both the spatial and temporal evolution of the solid fraction. In order to make measurements periodically throughout the experiments, we have constructed an instrument that we hope will be of more general use than to just this particular application.

When a binary fluid is cooled and solidified from a horizontal plane boundary, a morphological instability of the interface between solid and liquid usually occurs. The resulting solid phase that grows from the liquid usually forms in a so-called mushy layer. In this region there exist both a liquid phase and a solid, crystalline phase.

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Early theoretical work on mushy layers centers on the Scheil equation [2] which relates the local solid fraction to the local temperature. A later model developed by Huppert and Worster [3] allows predictions to be made of the total solid fraction in terms of the external parameters of the system by treating the mushy layer as a continuum, with the physical properties of the solid and liquid being averaged over the depth of the layer. Experiments in which an aqueous solution of sodium nitrate was cooled from below, in which case both the thermal and compositional profile within the mushy layer are stable, showed that this approach gives an accurate prediction of the rate of advance of the interface between the mushy layer and the liquid, although both the temporal and spatial variations of the ratio of solid to liquid throughout the mushy layer were neglected in the model.

Worster [4] presented a more detailed theory from which the solid fraction ϕ can be predicted as a function of both time and distance normal to the cooled boundary. Solving the equations of the model numerically, he showed that, over the parameter range covered by the experiments of Huppert and Worster [3], both models predicted the growth rate of the mushy layer well, and they disagreed with each other by less than the uncertainty of the experiments.

Huppert and Worster also calculated the temperature profile in the mushy layer and obtained good agreement between these calculations and their experimental measurements. Their determination of the profiles of solute concentration in the upper part of the mushy layer also confirmed the predicted values near the interface between the mushy layer and the liquid. Unfortunately, they were unable to make satisfactory measurements deep within the mushy layer.

The purpose of the work which we describe here was twofold. First, we wished to apply an additional test to the theory by measuring the solid fraction ϕ throughout a mushy layer. Further, we wished to build an apparatus that could measure the solid fraction in mushy layers generally and which could be used in other studies. The experiments were conducted under conditions almost identical to those used by Huppert and Worster [3]. Aqueous solutions of sodium nitrate with

mass concentrations between 5 and 18 wt% were cooled from below with a boundary temperature of -14°C , and the solid fraction ϕ was measured at three fixed distances z_i ($i = 1, 2, 3$) above the cooled boundary. Both forms of the theory described above give solutions in terms of a similarity variable $\eta = z/(4\kappa t)^{1/2}$, where z is the height above the cooled boundary, t is time, and κ is the thermal diffusivity of the solution. In particular, they predict that the depth h of the mushy layer is given by $h = 2\lambda(\kappa t)^{1/2}$, where λ is a constant that depends upon the imposed conditions of the experiment. Hence, if the similarity solution is valid, measurements at different times of ϕ at the three separate heights should map out the single profile $\phi(\xi)$, where $\xi = z/h$.

2. Experimental method

The solid fraction ϕ is the local ratio of the volume which is solid to the total volume. The volume concerned must be small compared with that of the mushy layer as a whole, but sufficiently large to include representative contributions of both solid and liquid phases. In this experiment ϕ is expected to vary only with the dimensionless vertical coordinate ξ , so it can be appropriately thought of as the volume fraction of solid within a thin horizontal layer which spans the mushy layer. Division of this thin layer into many narrow parallel strips shows that ϕ can also be thought of in this case as the fraction of a horizontal line that is embedded in the solid phase, and this view forms the basis of the measurement technique.

The experimental arrangement employed is shown in fig. 1. Three thin platinum wires of 0.32 mm diameter were stretched at heights z_i above the cooled boundary. In the experiment with 17.8% concentration, the z_i were chosen to be (10, 20, 30) mm, but otherwise they were set at (5, 15, 25) mm. Each of these wires in turn formed one electrode of a conductivity cell, the other electrode in each case being a carbon block of relatively large surface area suspended in the solution about 150 mm above the cooled boundary. As cooling proceeded, the mushy layer grew up past the wires, and the ice growing around them reduced the length of

wire in contact with the fluid. The major assumption in interpreting the experiment was that the cell constant of each conductivity cell, that is, the product of its resistance and the conductivity of the fluid, was inversely proportional to the fraction $(1 - \phi)$ of the length of the wire immersed in the fluid. The technique also relies on the fact that the conductance in the solid is negligible compared with that in the liquid.

This assumption needs to be discussed, as there are two potential sources of error: (i) the presence of a fine wire in the supercooled liquid just ahead of a growing crystal might have affected the freezing process, for example by providing a preferred site for crystal growth, and (ii) the geometry of the spaces which were occupied by fluid between the growing crystals is unknown, and might have affected the electric field and its associated current in such a way as to change the current which

flowed from any given short length of the wire, even though its potential was unchanged and it remained immersed in fluid of constant conductivity. These problems will now be discussed in turn, before going on to examine the results of the measurements in the next section.

Firstly, the effects of a wire on the formation of crystals would be most easily seen near the time when the crystal interface first reached the wire. Visual inspection of the ice crystals at that stage of the experiments showed no abnormality near the wire, provided steps were taken to prevent heat being conducted along it between the measurement region and warmer or colder levels of the experimental tank. For this reason, the insulated copper wire, which was connected to one end of the platinum wire and which provided the electrical connection to it, was arranged to run horizontally for a length of about 60 mm before

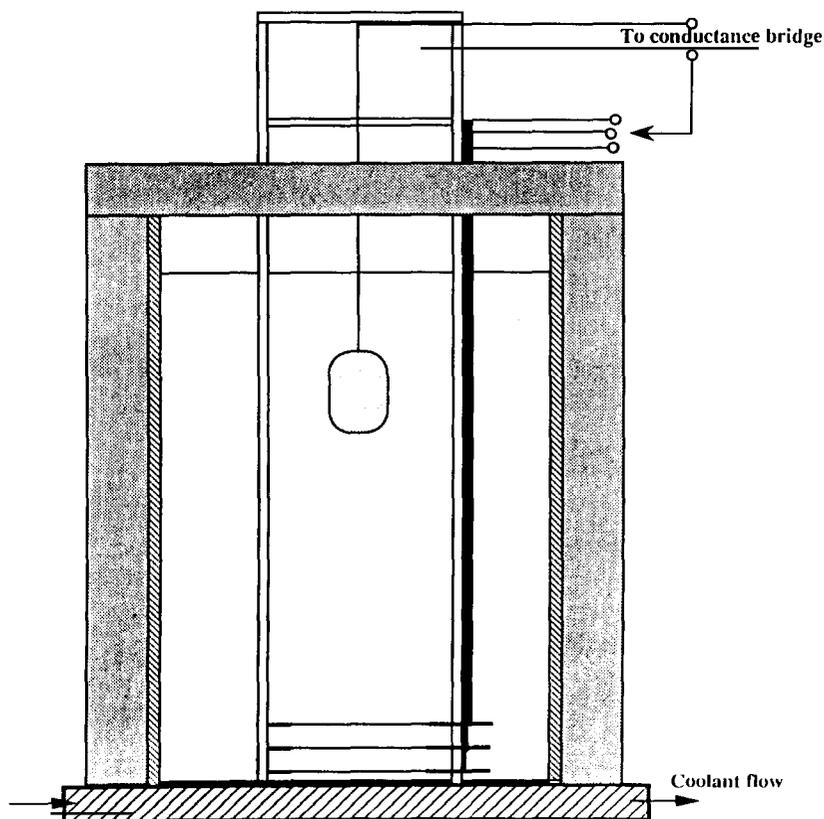


Fig. 1. The experimental arrangement.

turning upwards and passing out of the top of the tank. Without this precaution, ice was noticeably slower to form near the wire.

Secondly, the geometry of the liquid-filled spaces between the crystals could not be observed directly. The fact that current continued to flow to the wire in these experiments even when the wire was above the base by only 10% of the depth of the mushy layer shows however that the spaces remained connected to the solution above the mushy layer. Furthermore, the ice crystals tended to grow as nearly vertical plates, which is a favourable geometry for this method. However, when a wire is surrounded by a homogeneous solution, current flow is radial and most of the resistance occurs where the current paths converge, within a few radii of the wire. It is probable that the ice crystals introduced some additional constrictions into the current paths, further from the wire, thereby increasing the resistance.

We cannot distinguish between errors produced by these two effects. However we show below that a correction can be made for their combination, which we shall refer to as the geometrical error.

3. Measurements

After a number of trial runs, four experiments were conducted. In each case a uniform aqueous solution of sodium nitrate at room temperature

was cooled at its base as rapidly as our equipment would allow to -14°C (in about 90 min). This boundary temperature was then held constant. The eutectic temperature and concentration for such solutions are -17.8°C and 38.5 wt%, so no solid composite layer was formed at the boundary. The mushy layer, consisting of ice crystals growing upwards through a concentrated solution, always extended to the cooled boundary.

The essential difference in external parameters between the four experiments was in the concentration of the initial homogeneous solution, values of which were 5.6, 10.75, 15.0 and 17.8 wt%. Data from the first of these cases will be presented in detail to show the treatment applied in all of them.

Fig. 2a shows a plot of h^2 versus time for this experiment. The time scale is clock time, and the arrow indicates the time at which the supply of coolant to the base of the tank began. The first ice appeared 16 min later, and the graph shows that for the next 80 min its growth differed somewhat from the theoretical result that $h \propto t^{1/2}$. In fig. 2b the temperature of the base of the tank is plotted against time, and it can be seen that the initial failure to conform to the similarity solution was due to the relatively slow cooling of the base. Once the base temperature became steady, the expected growth rate was established.

Fig. 3 shows graphs of the resistance associated with each of the three wires as a function of time

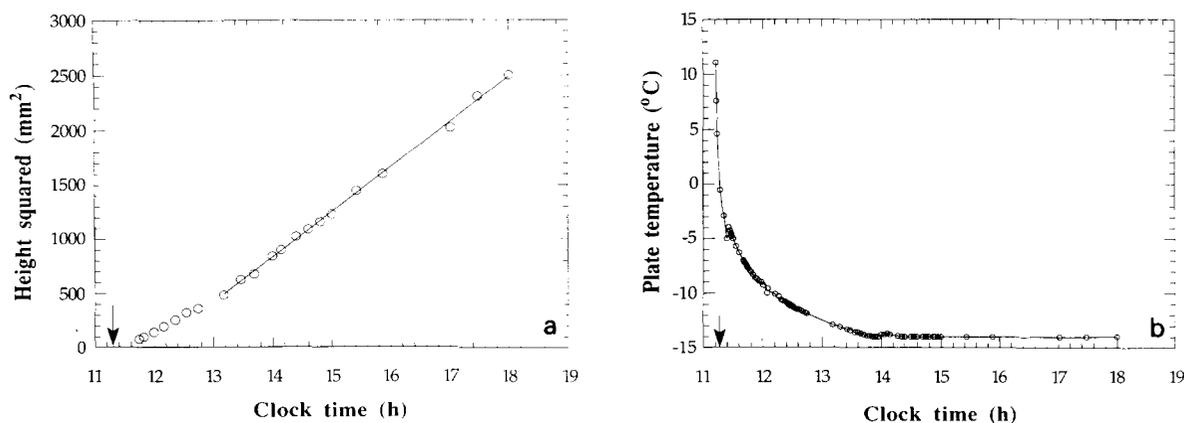


Fig. 2. (a) The square of the height of the mushy layer versus (clock) time. (b) The temperature of the base plate versus (clock) time. The arrow in both figures indicated the time of commencement of the experiment.

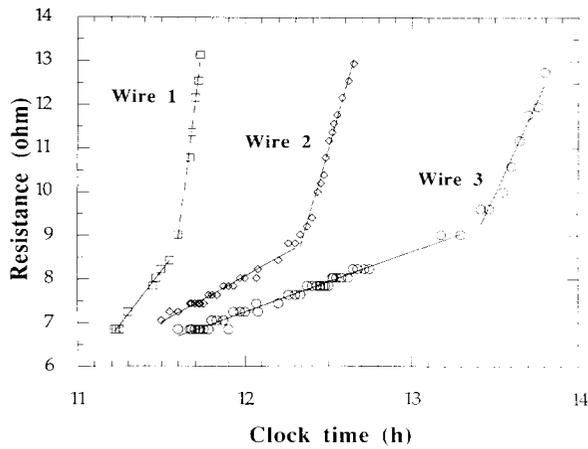


Fig. 3. The resistance versus time for the three wires.

in this experiment. In each case there are two regions of interest in the graph: an initially slow, approximately linear growth, and a final rapid growth. Initially, the resistance increased slowly due to the reduction of temperature ahead of the mushy layer, and after the transition it was affected strongly by the growth of ice crystals which insulated an increasing proportion of the wire. The resistance R_0 when the ice first arrived at the wire is indicated by the intersection of the trend lines before and after the transition. According to our assumed relationship between the solid fraction and the cell constant, we may therefore write

$$1 - \phi = \gamma_0 R_0 / \gamma R \tag{1}$$

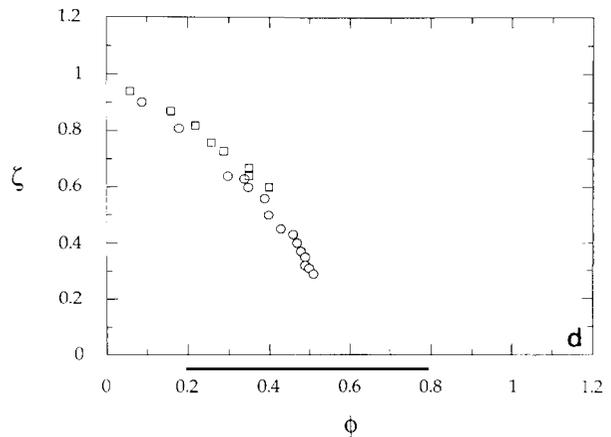
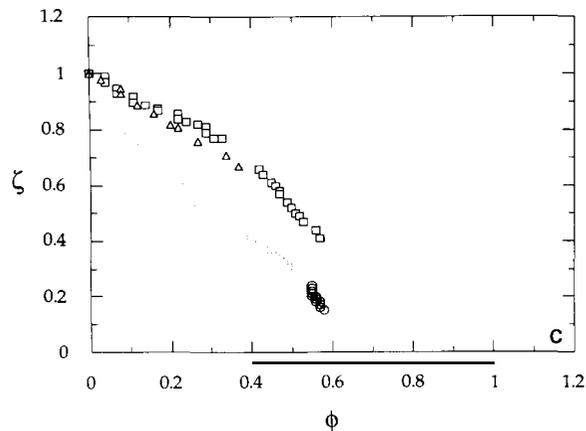
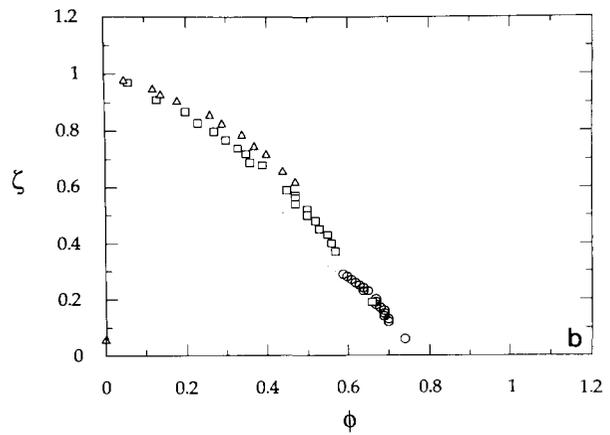
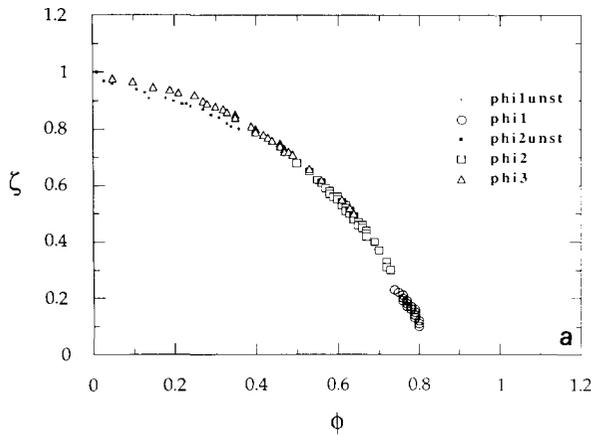


Fig. 4. Uncorrected values of solid fraction versus fractional height. Legend for all plots as in (a); small points show unsteady data, large points are steady data for each of the three wires. (a) $C = 5.6\%$; (b) $C = 10.75\%$; (c) $C = 15.0\%$; (d) $C = 17.8\%$. Data depicted by circles are taken from the lowest platinum wire, data depicted by squares are from the middle wire of the array, and data depicted by triangles are from the uppermost wire.

at any later time, where ϕ and R are the solid fraction and resistance at that time, and γ_0 and γ are the corresponding fluid conductivities.

As a first approximation, we may assume that the conductivity of the fluid is constant. Fig. 4a shows the resulting estimates of ϕ plotted against the dimensionless height ζ_i of the wire concerned, where $\zeta_i = z_i/h$. In this experiment $z_i = (5, 15, 25)$ mm. It is clear from fig. 2a that the mushy layer had already grown to a depth of at least 20 mm by the time the conditions had been established for the similarity solution to apply. Thus for the lowest wire, points with $\zeta_1 > 0.25$ have been indicated by small dots only. Similarly for the second wire, points with $\zeta_2 > 0.75$ have been indicated separately. Figs. 4b to 4d show corresponding graphs for the other three experiments.

The data points plotted in fig. 4 display an important property: all of the points acquired during the period when $h \propto t^{1/2}$ collapse to a single curve, the results from all three wires being consistent. This is strong evidence for the validity of the similarity solution. The appearance of this property in all four experiments, as shown in fig. 4, confirms that for given external conditions of base temperature, initial concentration and initial temperature, $\phi(\zeta)$ is a function that is independent of time.

A second property which appears to be confirmed by the experiment is that $\phi(\zeta)$ tends smoothly to zero at $\zeta = 1$. This too is consistent with the theory of Worster [4] for this case, but it is not obvious a priori that there will be no discontinuity in ϕ at this point.

These are the major results of the experiment. However, subject to certain assumptions, we can derive additional information by considering the first-order corrections

4. First-order corrections

The graphs plotted in fig. 4 display a satisfactory collapse of each set of raw data. Two corrections are necessary, however, to allow a comparison with the theory. The data need to be corrected firstly for the variations in the actual conductivity

of the fluid, which is dependent on the temperature and concentration, and secondly for the geometrical error.

First, we shall make the correction for the change of conductivity of the fluid with depth in the mushy layer. Since this is a higher-order correction, we can calculate it to sufficient accuracy by assuming that the concentration and temperature there are both linear functions of ζ ; fig. 4 of Huppert and Worster [3] provides justification for this assumption. The conductivity at 20°C as a function of the concentration C was evaluated by least squares as a cubic polynomial $\gamma_1(C)$ from data in Weast [5]; the expression, valid up to a concentration $C = 40\%$, is

$$\gamma_1(C) = 0.9809C - 1.79 \times 10^{-2}C^2 + 1.13 \times 10^{-4}C^3 \pm 0.1 \Omega^{-1} \text{ m}^{-1}.$$

Our own measurements showed that in the range of interest the dependence of γ on temperature is nearly linear and that $\gamma = \gamma_1(1 - 0.015T')$ to an adequate approximation, where T' is the temperature deficit below 20°C. The resulting correction increases the estimates of ϕ by about 0.2; it is less at the top and bottom of the layer than near the centre.

Second, in order to correct for the geometrical error, we calculate quite separately the value ϕ_0 of ϕ which we should expect at $\zeta = 0$, that is, at the cooled boundary. Little vertical exchange of material can occur in the mushy layer, because the temperature decreases downwards in it and the solid and liquid phases are close to equilibrium at each level. It follows that the density of the liquid increases downwards, limiting any vertical advection. Our estimate of ϕ_0 is based on the assumptions that there is no vertical advection, and that the expansion associated with freezing is accommodated uniformly by both phases of the mushy layer. We consider a region near the cooled base containing some fixed mass M . Before cooling and solidification take place, this region has volume V_1 , say, density ρ_∞ and concentration C_∞ . In the final state, after cooling and solidification have occurred, the region is mushy with a solid fraction ϕ_0 and total volume V_2 . The liquid phase has concentration C_L and density ρ_L , while the

solid phase has concentration 0 and density ρ_S . Conservation of mass requires that

$$M = \rho_\infty V_1 = \rho_L(1 - \phi_0)V_2 + \rho_S\phi_0V_2, \quad (2a)$$

while conservation of solute is expressed by

$$C_\infty\rho_\infty V_1 = C_L\rho_L(1 - \phi_0)V_2. \quad (2b)$$

These two equations are readily solved for

$$\phi_0 = (C_L - C_\infty)/(C_L - \alpha C_\infty), \quad (2c)$$

where

$$\alpha = 1 - \rho_S/\rho_L. \quad (2d)$$

In the present case, $C_L = 33\%$, corresponding to a temperature of -14°C , $\rho_L = 1.25 \text{ g cm}^{-3}$ and $\rho_S = 0.92 \text{ g cm}^{-3}$. Hence $\alpha = 0.27$ and ϕ_0 may

Table 1

C (%)	ϕ_0	V_2/V_1
5.6	0.87	1.08
10.75	9.74	1.07
15.0	0.62	1.06
17.8	0.54	1.05

be calculated for each value of C_∞ , giving the values in table 1.

The amount by which the measured value of ϕ_0 , after correction for the variation of conductivity, exceeds this value is a measure of the geometrical error at $\zeta = 0$. We now need to estimate this error in the interior $0 < \zeta < 1$. Since the measurements are consistent with the existence of a simi-

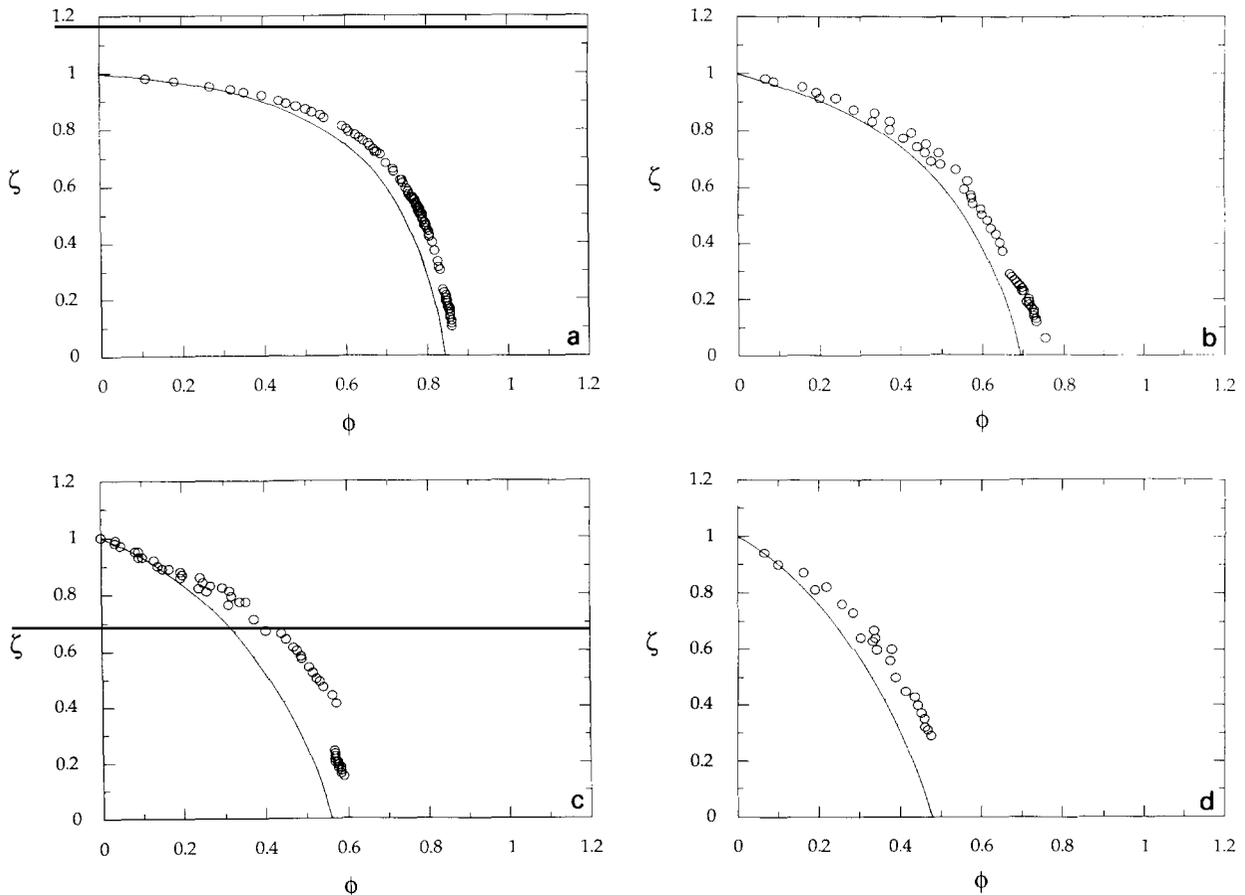


Fig. 5. Final estimates of profiles of solid fraction, ϕ . The curves represent the theoretical model of Worster [4] and the points are our adjusted measurements; (a)–(d) as for fig. 4.

larity solution in which $\phi(\zeta)$ is independent of time (after the initial transient cooling), it is likely that the first-order corrections are also dependent on ζ only. Indeed, if this were not so, the measurements from the three wires would not have collapsed onto single curves in fig. 4. We therefore take the simplest option and assume that the fractional correction to ϕ which is necessary at $\zeta = 0$ should be applied at all values of ζ . This procedure yields the profiles shown in fig. 5 as our best estimates. It may be noted that the downward correction of the measured values which this procedure introduces is similar in magnitude to the prior upward correction required by the variation of conductivity in the mush. Comparison of fig. 4 and fig. 5 shows that the nett effect of these two corrections is mainly seen near the centre of the mushy layer, where the estimate of ϕ is somewhat increased.

5. Discussion

Superimposed on the experimental profiles in fig. 5 are the profiles predicted by the numerical solution of the theoretical model of Worster [4]. It may be seen that in each case the theoretical curve predicts a value of ϕ_0 that differs from the value given by (2). This is because the theory assumes that the densities of the solid and liquid phases are equal, that is, $\alpha = 0$ in (2c). It is likely that this assumption is responsible for the entire difference between the curves, and that if the theory was recast to include the actual density differences, the experimental values would agree within their uncertainty.

We conclude that the continuum model of the mushy layer is a good one, but that allowance for the different densities of solid and liquid phases needs to be made in it. We note also that the technique described above for the measurement of solid fraction is a useful one, and should have applications in other circumstances, for example where no theoretical value of ϕ is available. Knowledge of the solid fraction may be particularly important in cases where the fluid in the

interstices of the mushy layer is in convective motion.

As an example of an important phase change which occurs on a large scale, we note that a large mushy layer is believed to exist at the outer extremities of the solid inner core of the earth. The idea, first put forward qualitatively by Braginskii [6], is that the slow solidification of the liquid outer core in this mushy layer results in the release of relatively less dense fluid which rises through the outer core. This flow through a conducting fluid in a rotating frame is thought to be responsible for the maintenance of the earth's magnetic field. Only the very beginnings of a quantitative analysis of the formation of the mushy layer and the resulting fluid motions have been undertaken, notably by Loper [7] and by Moffatt [8]. Any theoretical model of the mushy layer will be strengthened by the agreement of predictions of the model with results from laboratory experiments. We would hope that the instrument we have constructed and the approach we have outlined in this paper will be of use in this endeavour.

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