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The effect of natural convection in liquid phase mass transport coefficient measurements: the case of thermosolutal convection

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Abstract—This paper focuses on the effect of natural convection on the accuracy of diffusion coefficient measurements in concentrated liquid alloys. This convective effect is modelled using the concept of effective diffusivity, introduced in a former work for the case of dilute systems. Our computer simulations support the validity of this approach and show that it is very difficult in practice to reach conditions of negligible convective solute transport. The possibility of realizing the measurements of diffusion coefficients in microgravity is also discussed. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

The modelling and the understanding of a variety of processes rely on the knowledge of transfer coefficients. However, an accurate measurement of these parameters is very difficult, especially when the diffusivities are very low, e.g. for the case of liquid phase solute transport. Indeed, the unavoidable convective flows induced by the interaction of density gradients with gravity often lead to significant errors. An open question is thus to assess the possibility of realizing these measurements on earth, the alternative being to carry out the experiments in space where the intensity of gravity is reduced by a factor ranging from 10^3 to 10^6.

The most commonly used methods for liquid metals or semiconductors are the long capillary or shear cell techniques [1]. In both cases, for isothermal diffusion coefficient measurements, a one-dimensional concentration step is followed over time in its development, and the sample is solidified at the end of the experiment. A compositional average is taken over slices normal to the capillary axis and the resulting concentration profile fitted by a Gaussian error function under the assumption that the diffusion coefficient is independent of concentration.

In practice, thin vertical capillaries are generally used to limit convective solute transport. However, our former work on the topic [2] indicates that an optimized set-up is necessary to guarantee purely diffusive conditions in dilute alloys, since unavoidable lateral temperature gradients always induce fluid motion. To reach such a conclusion, we relied on a coupled numerical-scaling analysis approach and

showed that the error induced by the convective motion scaled with the square of the non-dimensional product $Gr \times Sc$, where the Grashof number Gr measures the intensity of the flow and the Schmidt number Sc the ratio between viscosity and diffusivity.

We also found that an 'effective' diffusion coefficient could be used to understand the physics of transport phenomena; indeed, even with significant convective flow, the simulated composition profiles keep a Gaussian error function appearance. In practice, this means that there is no way to determine *a posteriori* whether a given experiment has been carried out under favourable conditions. In all cases, the output of the procedure yields the effective diffusion coefficient, which may be significantly higher than the actual diffusion coefficient.

In this paper, we focus on concentrated systems where, according to a mechanism proposed by Hart [3], the coupling between the thermal and solutal fields may lead to a significant reduction of the convection velocity. Using numerical and scaling arguments, we shall show that the effective diffusivity formalism can also be applied in concentrated systems and discuss the practical implications in terms of attainable accuracy in ground based and space experiments.

EFFECTIVE DIFFUSIVITY AND SOLUTAL DAMPING

As carried out previously [2], we modelled the actual, cylindrical geometry with an idealized, two-dimensional planar cell schematized in Fig. 1. In the present problem, the lateral temperature difference acts as convective driving force. The fluid velocity **V**, solution to the Navier–Stokes equations, contributes to mass transport and the solute conservation equation can be written as

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NOMENCLATURE

C	alloy composition	$\mathbf{V}$	velocity vector
C_0, C_1	end concentrations of the diffusing couple	W	longitudinal velocity component
D	actual diffusion coefficient	X, Z	transverse and longitudinal coordinates.
D^*	apparent diffusion coefficient		
D_0^*	apparent diffusion coefficient without solutal stabilization	Greek symbols	
G	longitudinal composition gradient	β_S	solutal expansion coefficient
g	gravity	β_T	thermal expansion coefficient
Gr	Grashof number, $Gr = \beta_T g \Delta T_H H^3 / v^2$	ΔC	maximum concentration range of diffusing couple, $\Delta C = C_1 - C_0$
H, L	width and length of the cavity	ΔT_H	lateral temperature difference
M	Hart's parameter, $M = (-Ra_S/4)^{1.4}$	$\delta(t)$	length scale of established longitudinal concentration gradient
p	pressure		
Ra_S	solutal Rayleigh number $Ra_S = \beta_S g G H^4 / vD$	v	kinematic viscosity of the fluid
		ρ	mass density of the alloy
Sc	Schmidt number, $Sc = v/D$	ς	velocity reduction with solutal stabilization.
t	time		

$$\partial C/\partial t + (\mathbf{V} \cdot \nabla)C = D\nabla^2 C \qquad (1)$$

with D standing for the diffusion coefficient. For the concentrated systems considered in this text, the fluid velocity $\mathbf{V}$ depends on solute repartition. Quite generally, assuming that the mass density of the alloy is given by $\rho = \rho_0 [1 - \beta_T(T - T_0) + \beta_S(C - C_0)]$ and that the Boussinesq approximation holds, the Navier–Stokes equations can be written as

$$\partial \mathbf{V}/\partial t + (\mathbf{V} \cdot \nabla)\mathbf{V} = -\nabla p/\rho_0 + v\nabla^2 \mathbf{V}$$
$$+ [1 - \beta_T(T - T_0) + \beta_S(C - C_0)]\mathbf{g} \qquad (2)$$

with p, β_T, β_S, v and $\mathbf{g}$, respectively, standing for the pressure, thermal and solutal expansion coefficients, kinematic viscosity and gravity. To fully specify the problem, one also needs the continuity equation, that for an isochore fluid reduces to

$$\nabla \cdot \mathbf{V} = 0. \qquad (3)$$

We used the same boundary and initial conditions as previously [2], namely

$$t = 0 \quad C = C_0 \quad Z \leqslant L/2 \quad C = C_1 \quad Z > L/2$$
$$(4)$$

$$\text{top/bottom walls} \quad \partial T/\partial Z = 0 \quad \partial C/\partial Z = 0 \quad \mathbf{V} = 0$$
$$(5a)$$

$$\text{left wall } (X = 0) \quad T = T_0 \quad \partial C/\partial X = 0 \quad \mathbf{V} = 0$$
$$(5b)$$

$$\text{right wall } (X = H) \quad T = T_0 + \Delta T_H \quad \partial C/\partial X = 0$$
$$\mathbf{V} = 0. \qquad (5c)$$

The heat transport equation was also solved numerically, but with low Prandtl number fluids, such as metals or semiconductors, the ratio of thermal to solutal diffusivity is very high and a limited convection—by solute transport standards—should not affect the heat flow. Indeed, we have seen [2] that a constant lateral temperature gradient was established between the side walls.

In our previous work [2], we showed scaling analysis arguments that the additional contribution to the diffusion coefficient coming from convective transport scaled with the non-dimensional group $\bar{W}^2 H^2/D^2$, $\bar{W}$ standing for the lateral average of the vertical velocity component. This result was confirmed by means of numerical simulations so that the 'effective' diffusion coefficient D^*, i.e. the one that would be deduced from the composition profile at the end of the experiment assuming purely diffusive conditions, could be written as
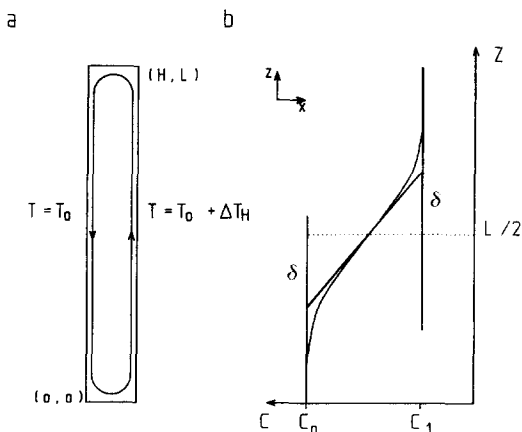

Fig. 1. Sketch of the model cavity and typical vertical composition profile.

$$D^* = D[1 + \alpha \bar{W}^2 H^2 / D^2], \qquad (6)$$

α being a numerical constant introduced to match the numerical results. In the dilute alloy problem considered previously, $\bar{W}$ scaled with the thermal Grashof number, so that the group $\bar{W}^2 H^2 / D^2$ was seen to be proportional to the square of the product of the Grashof and Schmidt numbers, defined as

$$Gr = \beta_T g \Delta T_H H^3 / v^2 \quad Sc = v/D. \qquad (7)$$

In order to test the validity of equation (6) in the presence of solutal damping, we need to estimate the reduction of velocity induced by the coupling of the mass and momentum transport equations. To do so, we rely on the work of Hart [3] who, dealing with the quite different problem of sideways diffusive instability, had previously considered a configuration similar to that of Fig. 1. Assuming the vertical composition gradient G to be constant, he obtained an analytical, parallel flow solution to the set of equations (1)–(3) and (5), the non-dimensional velocity being given by

$$W = [\cosh{(Mx)} \sin{(Mx)}$$
$$- A \sinh{(Mx)} \cos{(Mx)}] / 2M^3 B, \qquad (8)$$

where $A = \tan{(M/2)} / \tanh{(M/2)}$ and $B = \sin(M/2)/\sinh{(M/2)} + \cosh{(M/2)}/\cos{(M/2)}$ are constants depending on the sole parameter

$$M = (-Ra_S/4)^{1/4}$$

Ra_S being the solutal Rayleigh number, $Ra_S = \beta_S g G H^4 / v D$. The lateral composition difference induced by the thermal flow tends to reduce the density gradient and thus the mean velocity, and we can define a damping factor

$$\zeta = \bar{W} / \bar{W}(Ra_S = 0). \qquad (9)$$

In the above expression, $\bar{W} (Ra_S = 0)$ is the average velocity of the thermally driven parallel flow, equal to (v/H) $(Gr/192)$ [2]. From equations (8) and (9), we get

$$\zeta = \frac{96}{M^4} f(M) \qquad (10)$$

with $f(M)$ equal to

$$\frac{|\sinh{(M/2)} \cosh{(M/2)} + \sin{(M/2)} \cos{(M/2)}}{|\sinh{(M/2)} \cosh{(M/2)} + \sin{(M/2)} \cos{(M/2)}|} \cdot$$
$$\frac{- \sinh{(M/2)} \cos{(M/2)} - \sin{(M/2)} \cosh{(M/2)}|}{}$$

However, Hart's analysis cannot be applied directly to our present diffusion coefficient measurement problem, the main difference being that the vertical composition gradient G is neither uniform (see Fig. 1b), nor constant in time. To build a link between our transport configuration and Hart's results, let us assume that at the end of the experiment

$$G = (\Delta C/2)/\delta(t), \qquad (11)$$

ΔC standing for the difference between the top and

bottom concentrations, $\Delta C = C_1 - C_0$, and $\delta(t)$ for the length scale of the central region where the composition gradient is established (see Fig. 1). In our previous work [2], the numerical simulations yielded

$$\delta(t) \simeq 1.8(D^* t)^{1/2}. \qquad (12)$$

It should be noted that the factor 1.8 in the above expression can be identified with $\sqrt{\pi}$, as proposed by Carslaw and Jaeger for the related problem of heat diffusion in a semi-infinite solid [4]. We could then derive the solutal Rayleigh number and the damping factor ζ to fit the effective diffusivity formula [equation (6)]. However, since $\delta(t)$ depends on D^*, we would face an implicit equation; for the sake of simplicity, we shall take $D^* = D$ in equation (12), a hypothesis certainly valid when convection is not too strong.

The assumptions required to derive a damping factor in our present transport configuration may seem questionable, but we shall later see that the rather arbitrary choices of equations (11) and (12) have only a limited impact on the final result. Back to the effect of thermosolutal convection on effective diffusivity, inserting equation (9) in equation (6) yields

$$D^* = D[1 + \alpha \zeta^2 \bar{W}^2 (Ra_S = 0) H^2 / D^2]. \qquad (13)$$

For a clear presentation of the results, it is interesting to introduce the effective diffusion coefficient without solutal stabilization D_0^*. Rearranging equations (6) and (13), we get

$$(D^* - D)/(D_0^* - D) = \zeta^2. \qquad (14)$$

For low values of M, D^* should remain close to D_0^*, whereas at large M, one should eventually fall back on the true diffusion coefficient D. The ratio on the right hand side of equation (14) should thus vary between 0 and 1, depending solely on M. In other words, the perturbation induced by thermally driven convection is accounted for by the D_0^* parameter and the effect of solutal stabilization should simply be the square of the damping factor.

NUMERICAL SIMULATIONS AND DISCUSSION

To test these predictions, we performed numerical simulations of the coupled momentum and mass transfer problem formulated by equations (1)–(5). As carried out previously, we used the FIDAP finite element code, implemented on an HP 730 workstation. Typical mesh dimensions were 26×3 (nine-nodes quadrilateral elements). We chose a quasi-Newton method, with implicit time scheme to obtain the solution. The model cavity was sufficiently long to ensure that the results did not depend on the aspect ratio H/L. As carried out in ref. [2], the apparent diffusion coefficient D^* was estimated from a error function best fit procedure at the end of the simulated experiment.

Simulations were carried out for two different thermal configurations, corresponding to values of the
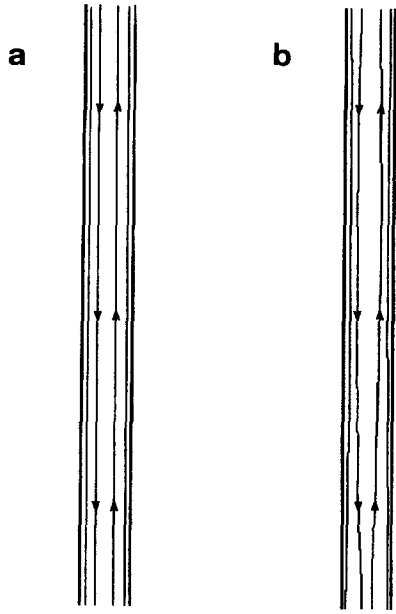
Fig. 2. Vertical velocity contours in the middle part of the cavity as obtained from the FIDAP simulations in the case $Gr = 3$ for two values of the solutal stabilization [(a) $\beta_S \Delta C = 10^{-5}$, $HV_{max}/v = 2.3\ 10^{-2}$ and (b) $\beta_S \Delta C = 10^{-1}$, $HV_{max}/v = 3\ 10^{-3}$].

Fig. 3. Variation of $(D^* - D)/(D_0^* - D)$ with $\beta_S \Delta C$ (symbols: numerical data for two values of the Grashof–Schmidt product (*: $GrSc = 90$, · $GrSc = 360$), full line: scaling analysis). Duration of the experiment: 1000 s.

$Gr \times Sc$ product of 90 and 360, the associated relative errors, i.e. $(D_0^*/D) - 1$, being, respectively, 2 and 32% [2]. The physico chemical parameters used were $\beta_T = 10^{-4}\ K^{-1}$, $v = 3.6\ 10^{-7}\ m^2\ s^{-1}$, $D = 1.2\ 10^{-8}\ m^2$ s^{-1}, the cavity width and length being, respectively, $H = 7.5\ 10^{-4}$ m and $L = 0.1$ m. The main parameter in the present study is the product $\beta_S \Delta C$, that characterizes the efficiency of solutal damping.

The major change with respect to the dilute alloy configuration solved in ref. [2] concerns the hydrodynamic field. At high values of $\beta_S \Delta C$, a significant damping is observed around mid-cavity where the axial composition gradient is high. On the other hand, in the end parts, no stabilization occurs and the fluid velocity is governed by the thermal Grashof number of equation (7).

As a consequence, the body force in the Navier–Stokes equations being dependent on the Z-coordinate, the conditions for purely unidirectional flow are not fulfilled. Indeed, for $\beta_S \Delta C \geqslant 10^{-2}$, the velocity field is significantly distorted (see Fig. 2), but it should be noted that the convective loop never breaks down into smaller cells.

Shown in Fig. 3 is the variation of $(D^* - D)/(D_0^* - D)$ with $\beta_S \Delta C$ for the two thermal configurations studied, the duration of the simulated experiment being held constant, $t = 1000$ s. Up to $\beta_S \Delta C = 10^{-2}$, both series of numerical points lie very close to the curve representing ζ^2, ζ being computed from equation (10). At higher $\beta_S \Delta C$, the damping is much less efficient than predicted, but this may be understood from the structure of the convective pattern.
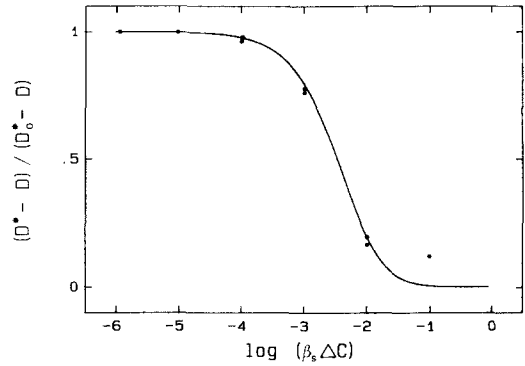
Indeed, as noted by Hart [3], at high values of M (or in our case $\beta_S \Delta C$), the flow is localized in thin boundary layers of extent M^{-1} along the cavity walls. With regards to the scaling analysis of ref. [2] that led to equations (6) and (14), such a structure violates the assumption of regular variation of both velocity and composition across the cavity. Another possible explanation is that, as shown in Fig. 2, the flow is not purely parallel at high $\beta_S \Delta C$ and so the conclusions drawn may thus not be valid.

Another interesting parameter of the solutal damping efficiency problem is the duration of the experiment. Its effect on $(D^* - D)/(D_0^* - D)$ is presented in Fig. 4, the numerical data (symbols) being obtained from simulations carried out at $\beta_S \Delta C = 10^{-2}$. The agreement with the curve representing ζ^2 is again satisfactory, and it appears clearly that the $t^{-1/2}$ dependence of the Rayleigh number leads to a significant decrease of the damping efficiency with time.

It should be kept in mind that numerous underlying assumptions were made to account for the solutal damping effect via equation (14). For instance, we only consider a snapshot at the end of the experiment, and one might have thought that an integration over the duration of the process might have been necessary. However, in all the cases where the damping factor
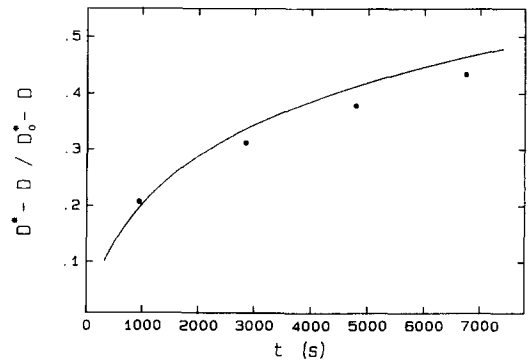

Fig. 4. Variation of $(D^* - D)/(D_0^* - D)$ with the duration of the experiment for the case $GrSc = 90$ and $\beta_S \Delta C = 10^{-2}$ (symbols: numerical data, full line: scaling analysis).

depends moderately on M (e.g. up to $\beta_S \Delta C = 10^{-3}$ in Fig. 3), such an averaging would not dramatically alter the results.

Similarly, due to the 1/4 power law dependence of M on Ra_S, a modification of either $\delta(t)$ or G in equations (11) and (12)—for instance through a relaxation of the condition $D^* = D$—would have a minor effect on M. Thus, even if the stabilization of the flow depends on the position along the cavity, our arbitrary choices for equations (11) and (12) can be considered reasonable.

Besides, it should be stressed that the aim of our theoretical approach is not to get accurate estimates of the apparent diffusion coefficient (that is the purpose of the numerical simulations), but rather to understand the physics of the transport phenomena. In this sense, the point at $t = 1000$ s in Fig. 4 should not be considered significantly 'better' than the others, the key result being the similar trend between the ζ^2 curve and the numerical data.

The overall good agreement between theoretical predictions and numerical results can be taken as an indication that, in concentrated systems, the additional convective transport scales with the square of the average fluid velocity, as observed previously [2] for the case of dilute alloys. Having gained confidence in the validity of our approach, we can now proceed to a discussion of the practical implications in terms of attainable accuracy of diffusion coefficient measurements.

A look at Figs. 3 and 4 will convince the reader that even if some progress may be achieved, it is very difficult in practice to reach the purely diffusive transport conditions. Moreover, in a simulation performed with $\beta_S \Delta C = 0.5$ and $t = 1000$ s, the error function fit of the obtained composition profile was not very good, and the deduced D^* was seen to be *higher* than for the case $\beta_S \Delta C = 0.1$. Thus, a more efficient damping is no guarantee of a better diffusion coefficient estimate.

To build a link between our modelling and the experimental conditions, let us turn to an estimation of typical $\beta_S \Delta C$ values in experimental conditions for metallic or semiconducting liquid alloys. It is important to keep in mind that the error function fit can only be done if the diffusion coefficient is independent of concentration. The difference between the end compositions $\Delta C = C_0 - C_1$ should thus be limited, an absolute value $\Delta C = 5$ wt% being a maximum.

Concerning β_S, under the assumption of volume additivity, reasonable for liquid systems, the solutal expansion coefficient can be estimated from the formula giving an alloy mass density

$$\rho = \rho_A \rho_B / (x_B \rho_A + x_A \rho_B), \qquad (15)$$

where x_A, ρ_A, x_B, ρ_B are the mass fractions and mass densities of component A and B, respectively. Simple algebra indicates that β_S will vary between $\rho_A/\rho_B - 1$ and $\rho_B/\rho_A - 1$. In practice, the heavier component in the diffusing couple should of course be placed at the

bottom, otherwise the solutal effect would be destabilizing.

In liquid metal alloys, the difference between the mass densities of the constituents may be quite high, leading to β_S values, expressed in inverse weight fraction ranging from 0.1 to 2. On the other hand, β_S is much smaller in semiconductors of the same class (III–V, II–VI), of the order of 0.05, with the exception of germanium in silicon ($\beta_S = 1.2$). For typical experimental conditions, the product $\beta_S \Delta C$ thus ranges between 10^{-4} and 10^{-1}.

With a cell dimension of 10^{-3} m, a kinematic viscosity $v = 3 \ 10^{-7}$ m^2 s^{-1}, and a diffusion coefficient $D = 10^{-8}$ m^2 s^{-1} characteristic of semiconductors, the Ra_S obtained from equations (11) and (12) using a value of $\beta_S \Delta C = 10^{-3}$ and a process time of one hour is $Ra_S = -150$. The damping factor is then, from equation (10), $\zeta = 0.77$. Some solutal stabilization thus takes place, but not enough to reach the purely diffusive conditions.

For liquid metals, keeping $H = 10^{-3}$ m, $v = 3 \ 10^{-7}$ m^2 s^{-1}, $t = 3600$ s, but with $D = 2 \ 10^{-9}$ m^2 s^{-1} and $\beta_S \Delta C = 10^{-2}$, we get $Ra_S = -17000$ and $\zeta = 2.4 \ 10^{-2}$. The damping would thus be very efficient, but one should keep in mind that equation (10) significantly overestimates the solutal stabilization at large Rayleigh numbers, as was seen in Fig. 3.

In our previous paper [2], we showed that semiconductors were less sensitive to the effect of thermally driven convection, the key factor being their higher diffusivities. Solutal stabilization is here seen to be much more efficient for liquid metals, but whether purely diffusive mass transport conditions can be reached on earth remains more than questionable.

At this point, we may wonder whether the measurements of diffusion coefficients in concentrated systems may be carried out in space, since the interaction of the solutal gradients with the residual gravity will drive some convective flow. The velocity induced is governed by the solutal Grashof number $Gr_S = \beta_S g G H^4 / v^2$ and the additional contribution to mass transport should thus scale with $(Gr_S Sc)^2$.

One should be aware that $Gr_S Sc$ can be formally identified with the solutal Rayleigh number introduced earlier in this section, but the relevant physical mechanisms are totally different. Indeed, we have seen that in a vertical configuration, the effect of the axial composition gradient was to damp the fluid flow. On the contrary, in space experiments, this gradient is the convective driving force.

In a typical space experiment in the NASA space shuttle, gravity is about 10^{-4} weaker than on earth where, as indicated above, Ra_S is of the order of 150 for semiconductors and 17000 for metals. Relevant values of $Gr_S Sc$ are thus 1.5×10^{-2} and 1.7, respectively. In comparison with our previous work [2], the configuration may appear quite different, since it is the interaction of an axial density gradient with a transverse gravity that drives the fluid flow.

However, a closer look at the Navier–Stokes equa-

tions will convince the reader that the relevant convective source is the vectorial product $\nabla \rho \times g$, identical in both cases. We may thus assume that, as derived in ref. [2], the error induced by convection, $D^*/D - 1$, expressed in %, is equal to $(Gr_S Sc)^2/4050$.

It is then clear that for the derived values $Gr_S Sc = 1.5 \times 10^{-2}$ and 1.7, the space experiments do take place under purely diffusive transport conditions. However, one should be aware that in some special cases, where both the composition range ΔC and the solutal expansion coefficient β_S are large, the diameter of the capillary should be limited to guarantee the validity of the measurement, even in microgravity conditions.

CONCLUDING REMARKS

Our purpose in this work was to test the validity of the effective diffusivity concept, introduced in an earlier paper [2], for the case of transport coefficient measurement in concentrated systems, where the interaction between the hydrodynamic and solutal fields leads to a reduction of the convective velocity. The numerical results indicate that, as predicted by our scaling analysis [2], the error induced by the fluid motion scales with the square of the convective velocity. The effective diffusivity concept can thus be used to understand the physics of transport phenomena in both dilute and concentrated systems.

However, even if such a concept works well in diffusion coefficient measurement configurations, one should be aware that it cannot always be used to account for the additional convective transport. For instance, in the field of crystal growth, the solutal boundary layer ahead of the solidification interface that scales with D in purely diffusive conditions

becomes thinner [5], and not wider, as convection is increased.

Concerning the solutal stabilization of the flow, the key result is that even though some damping may be achieved, it is probably not sufficient to guarantee purely diffusive mass transport conditions. Measurements are thus very difficult to perform on earth, especially in the case of liquid metals that are more sensitive to convection. We also showed that clean reference data could always be obtained from measurements in microgravity.

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