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Holographic visualization of convection during thermotransport: application to microgravity experiments

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Abstract. The performance of two microgravity measurements of the Soret effect in molten salt mixtures has led us to analyse their insufficiencies, essentially in terms of hydrodynamic diagnostics. As a consequence, and after preliminary measurements on Earth of the Soret effect on a particular class of vitrifying liquids by means of a holographic technique, we propose, in collaboration with two other groups, a new microgravity experiment on molten salt mixtures. The scientific interest and feasibility of this new experiment are analysed in detail. New solutions are given to overcome the experimental problems of such an experiment which should provide decisive proof of non-convective experimental conditions in space for molten salts.

Keywords: Soret, thermal diffusion, molten salt, microgravity, holography

1. The spatial relevance of mass thermotransport property measurements in liquids

Among the classes of mass-transport phenomena in liquids, thermal diffusion (the Soret effect) is related to a particularly large number of scientifically and technologically pressing questions. This effect is characterized by the existence of a spontaneous matter flux in an inhomogeneously heated fluid mixture, this flux tending to separate the constituents [1]. The scientific interest of thermal diffusion lies in microscopic as well as macroscopic considerations. Firstly, it is a nonequilibrium cross property, which still needs a lot of work on phenomenological modelling, especially for multicomponent systems [2]. Secondly, the molecular bases of the Soret effect are still vague and no statistical theory is able to show even a qualitative agreement with experiment [3]. But the interesting results of recent molecular-dynamics numerical simulations permit one to expect fruitful theory/experiment comparisons [4].

From a more industrial point of view, whenever multicomponent liquids are submitted to long-lasting temperature gradients, they are liable to experience thermal diffusive flows, modifying the distribution of the species concentration. Among the cases where this effect has been emphasized, we can mention the elaboration of high-technology materials (solidification of semiconductors [5]), the production or purification of light metals (electrolysis of aluminium, lithium, etc [6]) and the optimization of petroleum extraction (by modelling of the hydrocarbon distribution in the reservoirs [7]).

So, knowledge of quantitative values of the Soret coefficient (which is the parameter characteristic of the phenomenon) for a wide domain of materials, in various thermodynamic conditions and physical configurations is needed for the above-mentioned basic and applied purposes. Unfortunately, reliable values of these coefficients have proved to be very difficult to obtain. For example, agreement was only found recently regarding the values of the Soret coefficient of the well-studied toluene/n-hexane mixture measured by different techniques [8].

The experimental determination of Soret coefficients in binary mixtures, denoted $S_T$, is obtained by measuring the steady concentration gradient produced by the imposition of a constant and uniform temperature gradient. This concentration gradient achieves a stationary state when thermal diffusion and interdiffusion (which tends to rehomogenize the mixture) exactly compensate each other. However, the mechanical stability of such non-isothermal liquids is hard to guarantee. Indeed, the free-convection critical temperature gradient may be easily exceeded and a convection pattern may attenuate or even completely change the concentration gradient [9]. In addition, even in a globally diffusive regime, small experimental defects in the cell unavoidably exist and are the source of transverse temperature gradients, which initiate localized convection loops that disturb the measurements [10]. Several attempts to compensate for this gravity-induced convection have been
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made, but they can only be used for a highly restricted number of materials \[11\]. Under these conditions, the only opportunity of obtaining disturbance-free reference values of \( S_T \) are microgravity measurements. Facing this necessity of reduced gravity, experiments have been performed in sounding rockets and in the space shuttle.

Here we present our knowledge of the problems and solutions for the measurement in space of the Soret coefficient for a particular class of material, the molten salts.

2. Thermoelectric Soret measurements in molten salts in space

Numerous techniques are available for the measurement of the Soret coefficient in molten salt mixtures, and are \textit{a priori} usable in space:

- throughout direct measurements of the steady concentration gradient, in various configurations (shear cell \[12\], flow cell \[13\], etc), are widely used thanks to their simplicity. But their major drawback is their invasive character: taking samples from the liquid for concentration evaluation is impossible during the diffusion, so kinetic measurements are lacking. Therefore, we are compelled to turn towards nondestructive techniques;
- classical optical methods are very attractive (beam deflection method \[14\], classical interferometry \[15\], etc). One of their limitations is their relatively low accuracy compared with electrical measurements and their absolute requirement of high optical quality surfaces (flatness and polishing);
- new subtle optical methods such as classical Rayleigh scattering \[16\], thermal diffusion forced Rayleigh scattering \[17\], fibre optic spectroscopy \[18\], etc are presently in their infancy and have not provided enough results to be reliably validated. Furthermore, they often need several runs for one measurement, advanced data processing (filter, fits, etc) and the use of delicate thermophysical properties in computations, which makes remote real-time measurements difficult;
- finally, from our point of view, electrical methods (thermoelectric \[19\], conductimetric \[20\], etc) are the best candidates for spatial measurements, combining a high level of accuracy, a relatively handy procedure convenient for a spatial utilization, and the access to real-time measurements. Indeed, these characteristics were the main requirements influencing the choice of technique.

Therefore, we performed two thermoelectric Soret experiments in the eutectic mixture AgI0.72/KI0.28 in the Spacelab during the D1 and D2 flights of the space shuttle (1985 and 1993) \[21\]. This system of molten salts was chosen for at least three reasons:

- firstly, the presence of the silver ion enables the convenient use of reversible silver electrodes (no interface electrical capacitance);
- secondly, it exhibits a particularly low melting point (238 °C) which was required for reduced energy consumption in the shuttle;
- thirdly, it exhibits the properties of an ionic superconductor in the solid state, which is of interest in the field of solid-state batteries.

The main experimental problems that had to be solved were the following:

- the mixture being unavoidably solid during the storage at ambient temperature prior to the flight, the expansion due to the temperature increase and extra volume due to the solid–liquid transition had to be absorbed in order to avoid any free volume. The solution adopted to fulfil this requirement was the use of a porous ceramic crucible surrounding the liquid;
- the liquid and electrodes had to be totally electrically isolated in order to avoid any short circuit between the electrodes, through the frame;
- during the flights, all the experiments were required to have a triple screen between the liquid and the Spacelab in order to insure the astronauts’ safety. A sketch of the device is given in figure 1. This device was integrated in the gradient heating facility (GHF) furnace developed by CNES for several flights.

Figure 2 displays the typical evolution of the Soret-induced thermopower during the D2 experiment. This experimental behaviour can be fitted by well known laws in
order to give access to the steady-state value (at infinite time). The stationary concentration difference in the mixture, $\Delta c_\infty$, is then calculated from the difference between the initial $c_0$ and the final $c_\infty$ thermopowers. The Soret coefficient is then given by $S_T = 1/c(1 - c) \times \Delta c_\infty / \Delta T$; $c$ being the initial concentration and $\Delta T$ the applied temperature difference.

Although a few improvements might be made for future flights, these first experiments can be considered a success from the technical standpoint. However, several important questions remain from the scientific point of view, as we explain below. The two main results were as follows:

- the direction of the effect in the mixture was measured reliably for the first time: $S_T$ is positive, i.e., conventionally, the silver ions migrate towards the cold end of the cell;
- the quantitative value of the Soret coefficient was determined: $S_T = 1.0 \times 10^{-3} \ K^{-1}$.

But alongside these successes, we encountered the following limitations:

- the characteristic time of the Soret experiment, $\tau$, is linked directly to the interdiffusion coefficient $D$ through the formula $\tau = h^2/(\pi^2 D)$, $h$ being the diffusion length. A computation of $\tau$ from diffusion measurements carried out on Earth gave a value of 1 h. The actual measured value of 4 to 5 h, corresponds to a diffusion coefficient, $D$, which is then four times smaller than expected. This was the initial reason for performing a new experiment on flight D2, with a much longer duration than the ‘too short’ D1 experiment;
- as can be assessed from the D2 curve given in figure 2, the thermoelectric power deviated from the expected exponential behaviour for several hours during the course of the experiment. The actual origin of this discrepancy is still unknown but it could be linked to the thermal regulation of cooling fluid in the Spacelab, as well as variations in the vacuum. The experimental consequences are unknown;
- the Soret coefficient was also estimated from a chemical determination of the concentration distribution in the quenched mixture after return to Earth. The discrepancy between the chemical and electrical values was about 40%, which has not yet been clearly explained.

These three limitations might have three different causes, but what handicaps the interpretation is that these measurements were performed ‘blind’. The spatial environment should have provided convection-free diffusion but we had no chance to check whether this was the case, and the troubles encountered might originate from convective flows due to residual gravity. Thus, it is necessary to perform a new experiment which will allow us to visualize the mass fluxes during the diffusion. In this way, the spatial relevance of this kind of experiment can be properly demonstrated.

3. Preliminary holographic Soret measurements on Earth

First we made an exhaustive examination of the possible techniques which could provide, in the same experiment, a physical measurement (determination of the concentration gradient) and a mechanical observation (check of the absence or presence of convective flows). The most powerful method fulfilling these requirements and permitting measurements in space is holographic interferometry. Of course, it has the advantage of an interferometric technique: i.e., the recording of the refractive index evolution (due to temperature or concentration in our case) is visualized through interference fringes. But above all, it permits one to work without any physical reference system: the latter is simply replaced by a three-dimensional recording of the studied system at a given time on a so-called reference hologram. So the reference time can be changed during the course of the experiment. Furthermore, high optical quality is not an absolute requirement for the majority of the device components.

A preliminary phase of experimentation on Earth was essential because the holointerferometric procedure has not been established for Soret experiments. As specified above, thermal diffusion on Earth is mostly disturbed by gravity-induced non-diffusive fluxes. So we had to use a ‘trick’ to compensate for buoyancy effects. The one chosen was inspired from chemical experiments but had never been used before in this case: an instability spontaneously develops in free convection if buoyancy forces due to the thermal gradient exceed the dissipative effects (viscosity and heat diffusion). Therefore, taking advantage of our in-depth experience of vitrifying liquids [22], we can enhance the viscosity instead of reducing the gravity. Indeed, liquids of this type exhibit a high increase in their viscosity when the temperature is decreased. We eventually chose the (LiCl, H₂O) mixture, thus remaining in the ionic liquid class. The main experimental questions to be clarified were the following [23]:

Figure 3. Evolution of the concentration fringes with time in the mixture (LiCl, 9.7 H₂O) during a thermodiffusion experiment. $T_{cold} = -26.5^\circ C$, $\Delta T = 6.1^\circ C$ (from 0 to 202 h).
temperature and concentration variations in time are both diagnosed in holointerferometry by the same fringes, implying comparable refraction index changes, so the problem of decoupling arises. The first possible solution was the use of two-wavelengths holointerferometry, where a comparison of the two sets of fringe patterns, corresponding to each wavelength, permits one to deconvolve the solutal and thermal contributions [24]. Unfortunately, this technology is not programmed for any future flight facility scheduled over the coming years. So we had to discard this type of technical solution and find a physical one. It then transpires that heat and mass transport exhibit characteristic times that have considerably different orders of magnitude. This is quantified by the Lewis number, \( Le = D/DT \), \( D \) being the interdiffusion coefficient and \( DT \) the thermal diffusivity. \( Le \) is of the order of \( 10^{-5} \) in liquids. According to this timescale difference, in our system the temperature fringes appear in about half an hour, amounting to the establishment of the temperature gradient. We consider that the mixture remains homogeneous during this time, which is short compared with the diffusion time. After recording a new reference hologram, the newly appearing fringes can be attributed to the concentration evolution. The time duration of this process is about one week;

- another point to deal with was the unusual simultaneity of the diffusion measurement and the hydrodynamic diagnostic. A purely diffusive Soret experiment is shown in figure 3 in (LiCl, 9.7 H\( _2 \)O) with \( T_{ad} = -10^\circ C \) (the last temperature difference value corresponds to steady convection).

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Figure 4. Evolution of the concentration difference (between top and bottom of the cell) with time for the experiment shown in figure 3.

Figure 5. Isotherms obtained for the respective temperature differences of 0 °C, 4.9 °C and 10.8 °C along a cell heated from the bottom and containing the mixture (LiCl, 9.7 H\( _2 \)O) with \( T_{ad} = -10^\circ C \) along a cell heated from the bottom and containing the mixture (LiCl, 9.7 H\( _2 \)O) with \( T_{ad} = -10^\circ C \) (the last temperature difference value corresponds to steady convection).

- first, the reliable determination of the evolution of the Soret coefficient with temperature (from \(-60^\circ C\) to 0°C) and concentration (from 0.5 to 9 mol kg\(^{-1}\)) of lithium chloride in aqueous solutions enables us to test several theories. When dealing with the interpretation of characteristic features of the thermal diffusion (inversion of the effect with temperature, existence of a minimum with concentration) these theories were missing experimental confrontation, since reliable experiments were lacking. Some relevant physical processes playing significant roles in this effect have now been demonstrated;

- second, in order to test the ability of our procedure to highlight convective disturbances, we studied the hydrodynamic behaviour of (LiCl, H\( _2 \)O) in our cell geometry (30 \( \times \) 10 \( \times \) 10 mm\(^3\)) [23]. We especially investigated the \( \Delta T > 0 \) and \( \Delta C > 0 \) domain of the stability diagram (heated from below and with salt migrating downwards), where amazing convection patterns occur (see figure 6). Although many studies of such thermosolutal convection exist, very few have been undertaken in such a confined configuration, most of them having been made in the well known Rayleigh–Benard geometry [26].

Finally, this preliminary phase yielded the confirmation that Soret experiments on Earth are extremely difficult to perform in liquids with standard viscosity, since convection arises too easily.
4. Preparation of holographic measurements of the Soret effect in molten salts in space

As a consequence of its long experience of microgravity measurements on molten salts and in the holographic technique, our group has proposed, to ESA, a combined holographic interferometry and thermoelctric study of the thermodiffusion process appearing in molten salt solutions, in the International Space Station (ISS). This proposal has been made in collaboration with the group from RWTH Aachen (J Richter) and with a group specialized in hydrodynamics (D Henry and H BenHadid from the École Centrale de Lyon).

4.1. Choice of the mixture

Obviously, the choice of mixture is crucial to the study. In the class of the binary mixtures of molten salts with a common anion, we have pointed out the suitability of AgNO₃/KNO₃ for six main reasons:

- simplicity. From a physical and chemical point of view, it is a simple mixture with well known transport properties, phase diagram, thermal expansion, electrical and thermal conductivity, thermodiclectric power, viscosity, etc;
- melting point. This liquid exhibits a particularly low melting point (eutectic point 130 °C) compared with other liquids of this class, which guarantees both low-energy consumption of the heating facility in the ISS, and the possibility of making optical measurements without the problems associated with high temperature, especially in the space environment;
- optical transparency. This fluid is completely transparent in the visible range, which is not the case for the mixture used during preceding flights, AgI/KI, which shows a large absorption band, variable with temperature, in the visible range. This permits an optimization of the holointerferometric diagnostic;
- comparison with preceding experiments. The choice of AgNO₃/KNO₃ will permit a comparison with the AgI/KI measurements during the D1 and D2 flights. The discrepancy (or coincidence) of their Soret coefficients will highlight the part of the anion during the diffusion mechanism in these two very similar systems;
- the silver anion enables the use of reversible silver electrodes for the thermoelctric measurements (no interface electrical capacitance);
- no particular hazard is posed by ingestion, or vapour inhalation. This condition is important in the confined space-laboratory environment. Corrosion reactions must be avoided by the use of silica, glass or corrosion-resistant alloys (Hastelloy C-276).

4.2. Facility

ESA has ordered the design and fabrication of a facility with the aim of supporting scientific microgravity research in the field of fluid physics: the Fluid Science Laboratory (FSL) [27]. It is a flexible, highly modular facility to be housed in the Columbus Orbital Facility (COF), which is the European module of the ISS. Compared with older systems such as HOLOP [28, 29], it presents new and up-to-date possibilities. The FSL facility fulfils most of our experiment requirements except for the digital image holography (DIH) technique [30], for which the reference state can be chosen among all the recorded states of the system. In addition, DIH produces high-contrast interferograms even if the experimental conditions are not ideal, compensating for the influence of additional light sources and the effects of thermal deformation of the interferometer in the course of the experiment; this is particularly true in the case of long-duration experiments such as we propose here (30 h). The interference fringes produced by DIH can be interpreted in the same way as those from real-time holography. Therefore, this particular technique is required by our group and collaborators in order to refine the possibilities of classical holography, which is permitted by the FSL. In addition to DIH, adaptive filter algorithms for interference patterns of diffusion measurements [31] will permit the confident detection of signal peaks represented by interference fringes, avoiding misinterpretations of the experimenter, and could possibly lead to automatic diffusion measurement, if desired.

4.3. Experimental problems arising from space experiments and new solutions

Let us analyse, briefly, the main experimental problems occurring when a liquid diffusion experiment is performed in space. The first problem arises from the absolute necessity of total cell filling, the second problem derives from the parasitic presence of bubbles on the cell walls during optical measurements, and the third problem concerns convective instabilities.
4.3.1. Total cell filling. 100% cell filling is necessary in order to avoid any free-surface effect leading to Marangoni convection. Care must be taken to deal with the volume increase of the salt when melting (about 5%), combined with the normal thermal expansion (from 1 to 5%, depending on the working temperature). Several possibilities exist for solving this kind of problem. As stated above, we have already tested a method of absorbing the extra volume by the use of a controlled porosity alumina cylinder surrounding the salt [21]. This solution cannot be considered as fully satisfactory, due to insufficient knowledge of the evolution of the thermal diffusion experiment. This new apparatus, which was designed by CNES and COMAT Industry, will be tested on Earth in the near future and then adapted to its continuous help, especially to F Gonzalez and D Buso and COMAT Industry for helpful discussions leading to the new Earth apparatus, which could be the precursor of the future ISS diffusion experiment facility.

4.3.2. Absence of bubbles on the optical walls. The small bubbles which get stuck on the cell optical walls come from initially dissolved gas or simply from the saturated vapour pressure, the bubbles’ total volume possibly being increased by a cell filling defect. Previous Earth and space experiments performed by our collaborators have brought this problem to our attention [28]. In the case of aqueous solutions used at room temperature, careful filling and closure of the cell at the same temperature allows one to avoid these two problems (the presence of bubbles and incomplete filling). As molten salts cannot be kept in the liquid state ($T \geq 130^\circ C$) during the storage time prior to the flight, one has to seek an alternative type of solutions. We are currently working on an Earth facility in which the bubbles stuck on the optical wall can be removed by an energetic stirring induced by a fan situated at one end of the cell. This stirring also has the advantage of enhancing homogenization before the initiation of the thermal diffusion experiment. This new apparatus, which was designed by CNES and COMAT Industry, will be tested on Earth in the near future and then adapted to microgravity with the help of experiments performed during short microgravity sequences in the Airbus A300-Zero g from CNES-NOVESPACE during parabolic flight.

4.3.3. Hydrodynamic stability. This issue can be dealt with on Earth by means of numerical simulations applying confined thermostal convection to the microgravity environment. These computations will additionally constitute a major part of the calculations of the ideal size (aspect ratio) of the experimental cell by finding the best compromise between mechanically stabilizing dimensions and optical constraints.

5. Conclusion

We have shown that an in-depth knowledge of the transport parameters of liquids is of fundamental importance both for basic research and from an industrial point of view. Among those parameters, the Soret coefficient, characteristic of the thermodiffusion process, is one of the most difficult to obtain due to the quasi-impossibility of obtaining the mechanical stability of non-isothermal liquids on Earth except for a limited number of materials. A special type of liquid combined with the holographic technique has allowed us to obtain non-gravity-disturbed Earth thermal diffusion measurements as well as a hydrodynamic diagnostic. So, except for this highly restricted number of materials, there is a need for microgravity measurements, particularly in the case of molten salts, the physical characteristics of which lead them to be mechanically unstable. In addition, even with the use of special Earth techniques, the reliability of such an approach also has to be tested.

Two initial blind microgravity experiments performed during the D1 and D2 flights have shown the need for a hydrodynamic diagnostic and have led us to propose, in collaboration with two other groups, a new thermal diffusion experiment in the ISS with a holographic visualization. This experiment will be based on a new approach combining in situ measurement techniques, with continuous optical control as a guarantee of reliability. This will provide decisive proof of non-convective experimental conditions in space for this kind of experiment.

Acknowledgments

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