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Colloquium

European Space Agency experiments on thermodiffusion of fluid mixtures in space★

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Abstract. This paper describes the European Space Agency (ESA) experiments devoted to study thermodiffusion of fluid mixtures in microgravity environment, where sedimentation and convection do not affect the mass flow induced by the Soret effect. First, the experiments performed on binary mixtures in the IVIDIL and GRADFLEX experiments are described. Then, further experiments on ternary mixtures and complex fluids performed in DCMIX and planned to be performed in the context of the NEUF-DIX project are presented. Finally, multi-component mixtures studied in the SCCO project are detailed.

1 Introduction

Diffusive processes are ubiquitous in daily life and in natural processes, and play a key role in the transformation and mixing of fluid mixtures. In this context, the term diffusion is used to describe the relative motion of a species with respect to the other and can be caused by a concentration difference (isothermal diffusion), by a temperature difference (thermal diffusion) [1,2] or by a pressure gradient (barodiffusion) across the mixture. Such mixing processes in fluid mixtures have a high scientific and industrial interest in oil reservoirs, where all the above-mentioned effects contribute to the initial distribution of the (millions of) components of the mixture that forms crude oils. For instance, the temperature gradient that develops inside reservoirs can reach an average value of around $3\,^{\circ}\mathrm{C}/100\,\mathrm{m}$ which induces thermal diffusion and should be taken into account for the prediction of hydrocarbon composition, as it is an important factor that contributes to the reservoirs exploitation strategies [3].

Another consequence of diffusion is the development of non-equilibrium fluctuations in liquid mixtures. Fluids show random fluctuations in density and/or concentration even in thermal equilibrium. The intensity of these fluctuations is strongly enhanced when fluids are exposed to a thermal gradient. This is easier to observe in weightlessness, as gravity dampens this phenomenon on Earth especially for large fluctuations, and the confirmation of the latter phenomenon was the main objective of the GRADFLEX experiment [4]. The fundamental understanding of transport processes occurring in non-equilibrium fluid systems applies to a wide range of physical phenomena, ranging from crystal growth to pharmaceutical production. The understanding of diffusion processes at the mesoscopic scale and the development of applications based on non-equilibrium fluctuations are the objective of the Giant Fluctuations experiment (also known as NEUF-DIX [5]). The related flight instrumentation is at the moment under development. The first round of experiments will be performed on-board the International Space Station in 2021 or later.

The paper is structured as follows: first, the experiments on binary mixtures (IVIDIL and GRADFLEX) will be presented; second, we will show experiments on compounds that are more likely to be found in nature. These are for example ternary mixtures, already studied in DCMIX, and that are planned for NEUF-DIX. Finally, the thermophoresis of typical multi-component mixtures of interest for oil reservoirs are shown in the last section dedicated to the SCCO experiment.

2 IVIDIL

Space presents the benefit of the lack of gravity. But while buoyancy is negligible, external vibrations, or g-jitter, are always present on microgravity platforms and may give rise to convective currents therefore affecting the measurements. Their effect may be especially dangerous for long-lasting experiments such as the ones that involve the diffusion and thermodiffusion phenomena.

This was one of the main motivations behind IVIDIL (Influence of Vibration in Diffusion in Liquids), a project proposed to the European Space Agency (ESA) in 2000 by an international team including the Microgravity Research Centre of ULB (Brussels, Belgium), the Institute of Continuous Media Mechanics UB RAS (Perm, Russia) and Ryerson University (Toronto, Canada) and coordinated by the Brussels team. The experiment IVIDIL has been performed in 2009-2010 on-board the ISS, inside the SODI instrument mounted in the Glovebox at the ESA Columbus module. Along with the impact of on-board g-jitter, another target of the study concerns the response of binary mixtures to vibrational forcing when the density gradient results from thermal and compositional variations. Depending on the sign, the Soret effect can strengthen or weaken the overall density gradient and, consequently, the response to vibrational forcing.

The experiments were carried out in a cubic cell with differentially heated walls, which was filled with a water-isopropanol mixture and subjected to translational vibration in the direction perpendicular to the temperature gradient. Several experiments were conducted without imposed vibrations. The cell arrangement is shown in fig. 1 and the highlighting point of the design is that the external transparent walls are shaped in the form of two prisms (fig. 1(c)), allowing optical observations along two perpendicular directions (fig. 1(b)).

The IVIDIL experiment provides one of the first quantitative observations confirming that the daily on-board environment of the ISS does not perturb diffusion-controlled experiments. Experiments with two binary mixtures were reproducible on different days, even in different months, and thus in a different environment, and provided a separation of the components equivalent to that obtained from numerical simulations without perturbations.

We demonstrated that, unlike g-jitter, imposed vibrations with constant frequency and amplitude do affect the diffusion process. High-frequency periodic forcing with a zero mean value causes time-averaged flows, which substantially affect the regime of mass transfer in a fluid. The evolution of the mean flows is the result of a nonlinear interaction between thermal, solutal and vibrational effects. The concentration pattern in fig. 2 obtained in the course of the experiment on the ISS indicates the features of a four-vortex flow structure created by vibrational convection.

While IVIDIL examined a binary solution, it paved the way for more complex mixture research on orbit by showing that g-jitter would not affect the results and the measurements of the transport coefficients are reliable [6–8].

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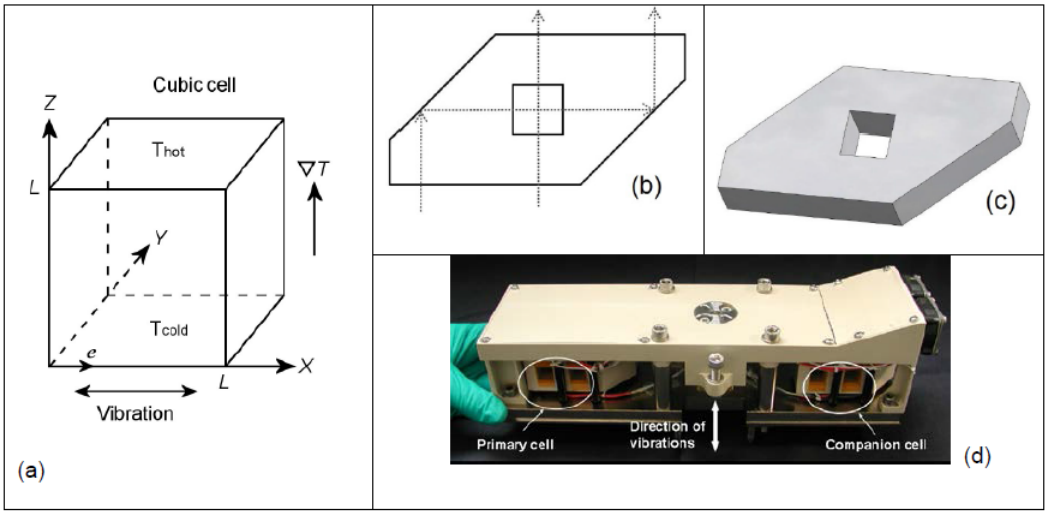

Fig. 1. The IVIDIL cell arrangement: (a) the sketch of the cubic cell filled with mixture; (b) top view of the experimental cell (note that the front view corresponds to a beam that travels directly through the cell); (c) actual view of the experimental cell; (d) the cell array (by courtesy of QinetiQ Space nv).

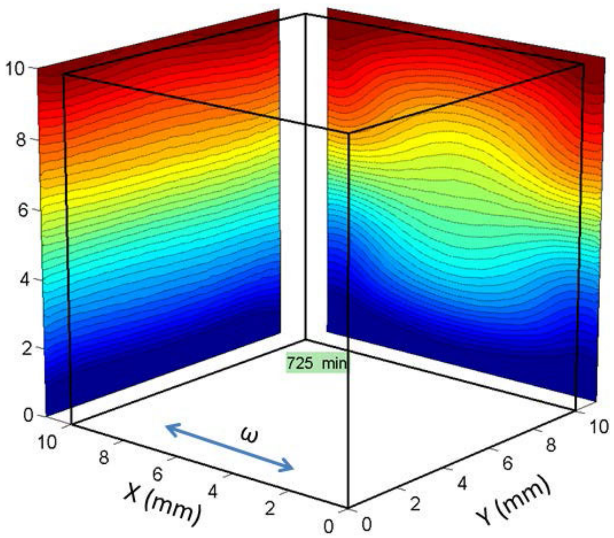

Fig. 2. The concentration field in two perpendicular views at the end of the experiment; the amplitude of vibration is $A = 68\,\mathrm{mm}$, the frequency is $f = 1\,\mathrm{Hz}$ and the temperature difference between top and bottom is $T = 10\,\mathrm{K}$.

3 GRADFLEX

Most of the space experiments on non-equilibrium fluids under the action of a temperature gradient have investigated macroscopic states. A notable exception is represented by the experiments of the GRADFLEX project, which studied non-equilibrium fluctuations induced in a fluid under the action of a steady temperature gradient. GRADFLEX was a joint effort of ESA, which developed the flight hardware and took care of the flight, and NASA, which contributed to the development of the experiments. The existence of non-equilibrium fluctuations in single-component fluids under the action of a temperature gradient was predicted theoretically at the beginning of the 80s (see [9] and references therein). In particular, a seminal article by Ronis and Procaccia [10] showed that Landau's Fluctuating Hydrodynamics can be extended successfully to describe the statistical properties of non-equilibrium fluctuations. Theoretical models assume that the thermal agitation of the fluid generates velocity fluctuations having exactly the same features in equilibrium and out of equilibrium. These fluctuations couple to the temperature gradient and, as a result, the microscopic displacement of a parcel of fluid gives rise to a non-equilibrium temperature fluctuation. The same mechanism was predicted to be effective in the case of a binary liquid mixture under the action of a temperature gradient. In this kind of system, the thermal stress imposed to the fluid generates a steady concentration gradient due to thermodiffusion. Therefore, in the case of a binary mixture velocity fluctuations couple both to the temperature and concentration gradient to give rise to non-equilibrium temperature and concentration fluctuations. Theoretical models predict that the power spectrum of non-equilibrium fluctuations is proportional to the square of the gradient and diverge as q^{-4} at small wave vectors q [9]. The experimental verification of the theoretical predictions required a series of challenging experiments with small angle dynamic light scattering [11–14]. Experiments provided a thorough confirmation of the theoretical predictions, but were not able to access wave vectors smaller than $1000\,\mathrm{cm}^{-1}$ or less. Further theoretical work showed that at very small wave vectors of the order of $100\,\mathrm{cm}^{-1}$ non-equilibrium fluctuations are strongly affected by the gravitational force [15,16]. The basic mechanism is that the density fluctuation associated with a temperature or concentration fluctuation gives rise to a buoyancy force that provides an additional mechanism for the relaxation of the fluctuation. This additional mechanism is reflected in the fact that the q^{-4} divergence of the static structure factor of fluctuations is suppressed by the gravity force, and the power spectra saturate at a constant level at wave vectors smaller than a characteristic roll-off wave vector determined by gravity and by the fluid properties. The experimental verification of this result was initially considered not feasible. However, the usage of a state-of-the-art ultra-low angle light scattering diagnostics allowed a full characterization of the static power spectrum of non-equilibrium concentration fluctuations at small vectors, thus confirming that the gravity force significantly affects the features of non-equilibrium fluctuations [17,18]. At the same time, experiments performed with shadowgraphy on a simple fluid under the action of a temperature gradient below the critical Rayleigh number investigated how the non-equilibrium fluctuations are related to the features of the macroscopic convective state [19,20]. Indeed, gravity can either amplify or quench non-equilibrium fluctuations, depending on whether the macroscopic density gradient present inside the fluid is parallel (stable case) or anti-parallel to gravity (unstable case). The amplification of non-equilibrium fluctuations generated in the unstable configuration was further studied in binary mixtures, confirming the presence of a characteristic lengthscale dictated by the gravitational force [21]. In the stable configuration, the strong action of gravity at small wave vectors can determine the presence of propagating modes. These have been first reported in non-equilibrium temperature fluctuations in a simple mixture [22] and, very recently, for the non-equilibrium fluctuations in a binary mixture undergoing a thermodiffusion process [23].

The GRADFLEX project was carried out to investigate non-equilibrium fluctuations in simple fluids and binary mixtures under micro-gravity conditions. Theoretical models based on linearized hydrodynamics predicted that in the absence of gravity, the q^{-4} divergence of fluctuations would continue until a wave vector set by the sample size was reached [24]. GRADFLEX involved two separate samples [25], each of which was contained in a thermal-gradient cell, where transparent thermally conducting plates allowed the non-equilibrium fluctuations to be visualized and measured using quantitative shadowgraphy [26,27]. One of the setups was optimized to provide accurate quantitative results on non-equilibrium temperature fluctuations in CS_2. The other setup was optimized for the investigation of non-equilibrium concentration fluctuations in a binary mixture of 9100 MW polystyrene polymer diluted at a 2% weight fraction concentration in toluene. GRADFLEX was hosted on the FOTON M3 spacecraft, which orbited the Earth for two weeks in 2007. After a stabilization time, non-equilibrium fluctuations in space were triggered by suddenly imposing a temperature gradient. In the case of the binary mixture thermodiffusion determined the gradual development of a concentration gradient.

GRADFLEX showed that the amplitude of non-equilibrium concentration fluctuations in the absence of gravity is several orders of magnitude larger than that measured on Earth (fig. 3). A quantitative analysis of the structure factor of non-equilibrium concentration fluctuations showed that the theoretical results obtained with

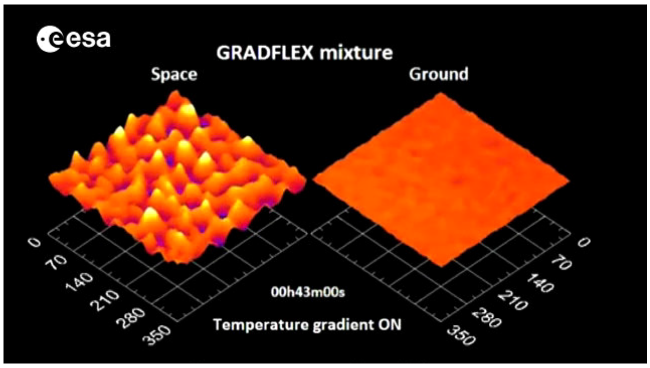

Fig. 3. Comparison between the fluctuations occurring on Earth (right) and in space (left) during a thermodiffusion process in a polymer solution. Data were recorded by the GRADFLEX experiment during the flight of Foton-M3. Credits: ESA-Gradflex Team [4].

linearized hydrodynamics [9,24] are fully compatible with the experimental spectra under ideal conditions, that is small concentration gradients and steady state [4]. A similar result was found for the temperature fluctuations in a simple fluid [28]. Simulations of transient thermodiffusion performed under conditions similar to those employed in GRADFLEX showed that the imposition of a temperature gradient is followed by the development of a most unstable mode, which grows with a scaling law similar to that encountered in spinodal decomposition [29]. The poor statistical sample of the experimental results collected during transient thermodiffusion in space did not allow to confirm this result yet. One of the most important results of GRADFLEX is that the power spectrum of non-equilibrium fluctuations diverges as q^{-4} down to very small wave numbers, of the order of a few cm^{-1}. The power law behaviour suggested the presence of a scale-invariant structure [30], but further theoretical analysis showed that the anisotropy of the system gives rise instead to a self-affine structure of the fluctuations [31]. A further analysis of the results obtained during the experiments on thermodiffusion in a binary mixture in the absence of gravity showed that the opportunity of measuring simultaneously the power spectra of temperature and concentration non-equilibrium fluctuations paves the way for the development of diagnostic methods using the non-equilibrium as a tool to determine the transport coefficients of mixtures [32].

4 DCMIX

Most fluids in nature are truly multi-component and contain significantly more than just two components. Because of the experimental and theoretical complexity, thermodiffusion data until very recently existed almost exclusively for binaries. Since thermosolutal convection in triple-diffusive ternary mixtures can be detrimental for experiments and is difficult to predict and to identify, the need for microgravity experiments was recognized in order to establish a set of convection-free reference data for

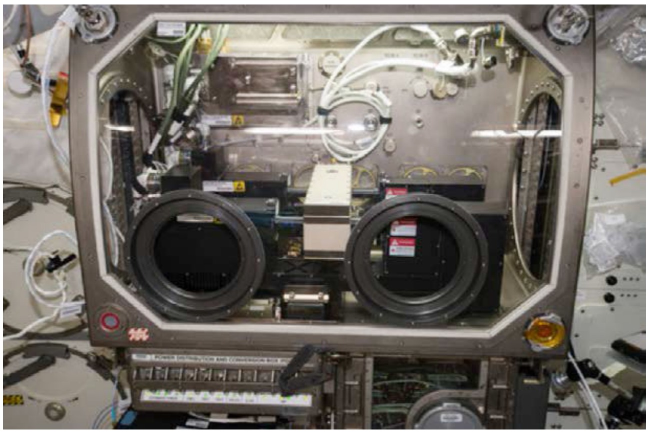

Fig. 4. Microgravity science glovebox with SODI and the DCMIX3 cell array inserted. Courtesy Qinetiq Space.

ground-based experiments. This led to the multinational DCMIX project of ESA and Roscosmos with the aim to perform thermodiffusion experiments on carefully selected ternary mixtures in the SODI instrument, a digital Mach-Zehnder interferometer aboard the ISS (fig. 4).

DCMIX is organized into so far four measurement campaigns. The first one, DCMIX1, was carried out in 2012 with the aim to establish a firm basis by investigating the so-called Fontainebleau benchmark system n-dodecane/isobutylbenzene/tetralin, whose binary pairs had already extensively been characterized before [33]. The second campaign, DCMIX2, took place in 2014 with toluene/methanol/cyclohexane. This mixture shows a miscibility gap in a certain region of the composition space (fig. 5) and a critical point. DCMIX3, flown in 2016, is the first aqueous system containing water/ethanol/triethylene glycol. Already water/ethanol-binaries of this system show sign changes of the Soret coefficient. The last campaign so far, DCMIX4, was launched to the ISS in late 2018 and the experiment is still ongoing. This campaign includes three additional mixtures similar to DCMIX2 in conditions that are closer to critical one, one mixture containing fullerene and a polymer in a mixed solvent as a model fluid with two well separated mass diffusion timescales.

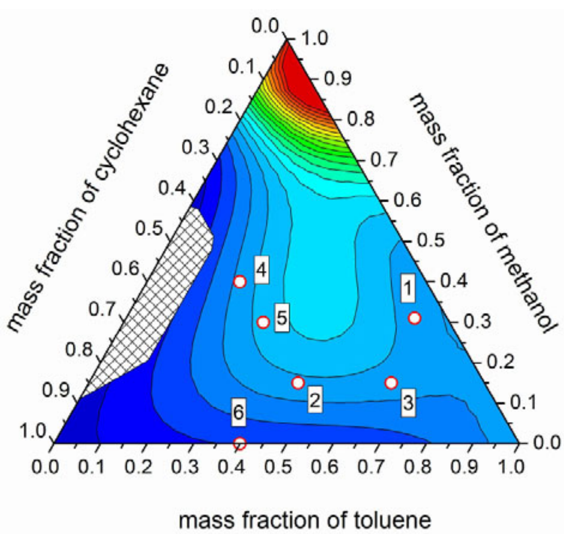

Fig. 5. Ternary DCMIX2 composition diagram indicating the 5 ternary and 1 binary samples. The hatched area on the left side is the miscibility gap. The color encodes the condition of the contrast factor matrix (increasing from blue to red) [34].

The DCMIX project has not only led to a series of successful microgravity experiments but also developed into a nucleus for diffusion and thermodiffusion research on multi-component systems on ground. The major part of the knowledge about thermodiffusion in ternary mixtures available today in the literature has been acquired within the framework of the DCMIX project, from which more than 120 scientific publications and approximately ten PhD Theses have emerged. An illustrative example and an excellent result from the DCMIX1 campaign is the benchmark for a 0.8-0.1-0.1 mass fraction tetralin/isobutylbenzene/n-dodecane mixture, where a good agreement between different processing schemes for the microgravity data and also between microgravity and ground based experiments could be established [35]. Encouraged by the successful microgravity experiments and the validation of the ground-based 2-OBD technique, the Soret coefficients were measured for the DCMIX1 system on a dense grid in the composition triangle [36]. Interestingly, isobutylbenzene changes its migration direction depending on the composition of the other two components. This sign change in a ternary mixture could be related to the thermophobicity concept originally developed for binaries [37].

The DCMIX2 experiments in the binary companion cell with a toluene-cyclohexane mixture continued the comparison of microgravity and earthbound results. The experiments in the orbital laboratory showed that the Soret coefficient of the toluene/cyclohexane system ($C = 0.40$) is negative within the investigated temperature range and its absolute value $|S_T|$ decreases with increasing temperature [38]. This made it possible to validate rare ground-based data for binary systems with a negative Soret coefficient, measured by the Thermal Diffusion Forced Rayleigh Scattering (TDFRS) method [39]. The further examination of the orbital data led to the intriguing result of a temperature independent thermodiffusion coefficient D_T for this mixture.

The analysis of the DCMIX2 ternary mixture in cell 1 has established a linear dependence of the Soret coefficients on the mean temperature [34]. Such a finding was reported for the first time for ternary mixtures. Examination of the cells with other compositions (*i.e.*, cells 2, 4, 5) exhibited an increase of the Soret coefficient towards the demixing zone by at least one order of magnitude. This suggested to push the analysis closer to the demixing zone as is currently done in the DCMIX4 campaign.

Besides the actual measurements of transport coefficients, the possible methodologies to process raw data from the Soret experiments in ternary mixtures were thoroughly analyzed using DCMIX2 data (fig. 6). The two best approaches found were used to investigate the dynamics

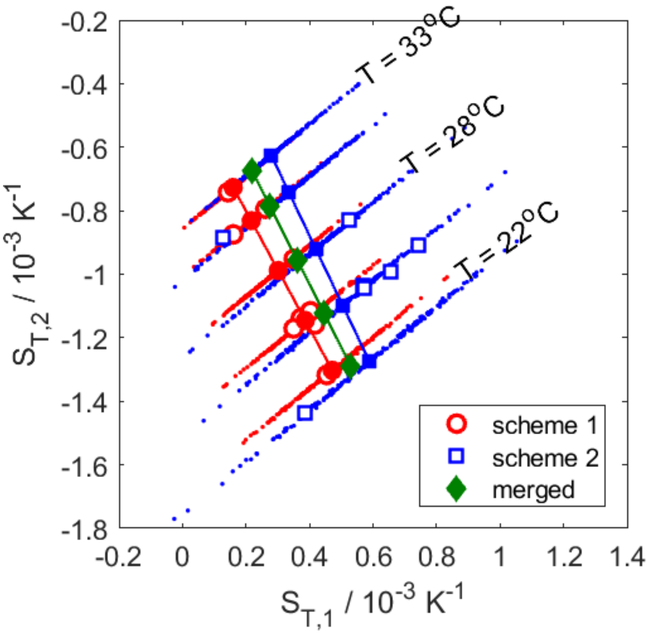

Fig. 6. Comparison of ternary Soret coefficients obtained by two best approaches (open symbols) and their possible scattering due to an error of separation obtained by Monte Carlo simulation (dots). Closed green rhombi present final merged values [34].

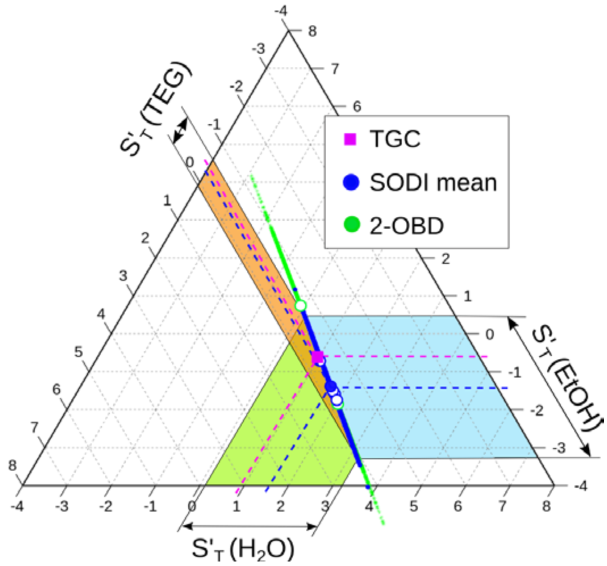

Fig. 7. Soret coefficients for DCMIX3 (cell 2, 25 °C) as measured on ground (TGC, 2-OBD) and in space. Monte Carlo simulation of error propagation [40].

of the error propagation. Remarkably, the error bar of the SODI experiment forms a very elongated ellipsoid instead of an isotropic cloud around the solution, which is an indication of highly correlated errors. This specific characteristic of the measurements makes the determination of the Soret coefficient particularly sensitive to the experimental conditions and is partly related to the choice of the two wavelength available in the actual SODI apparatus.

The evaluation of the DCMIX3 data is still work in progress. Nevertheless, a very good agreement could already be achieved between DCMIX3 results and thermogravitational column (TGC) and optical beam deflection (2-OBD) measurements [40,41]. Particularly for the latter, the optical contrast factors have turned out to be critical and their accurate measurement and theoretical modelling needs to be advanced further [42]. Figure 7 shows results for cell 2 of DCMIX3 in comparison with TGC and 2-OBD measurements. The unfavorable condition of the contrast factors leads to the well-known elongated ellipsoidal confidence regions, in particular for the 2-OBD ground experiments. The agreement of the centers and orientations of these confidence regions strongly supports the compatibility and correctness of all experiments. From the projections onto the axes it is seen that not all Soret coefficients are affected by the experimental uncertainties in the same way. This is a very encouraging result, showing that even under less favorable conditions the extraction of certain Soret and thermodiffusion coefficients is still possible with a decent accuracy [40].

The first preliminary results of DCMIX4 obtained via real-time telemetry have shown a significant slowing-down of a diffusion process with a slight temperature decrease (from 25 °C to 20 °C) for the mixture toluene/methanol/cyclohexane for the composition closest to the demixing zone.

5 NEUF-DIX

The GRADFLEX project allowed to establish that non-equilibrium fluctuations in fluids under the action of a temperature gradient are strongly affected by gravity. Experiments performed in space showed that the absence of gravity led to the development of large amplitude non-equilibrium fluctuations during a thermophoretic process, in agreement with the predictions of Fluctuating Hydrodynamics. The investigation of these non-equilibrium fluctuations under non-ideal conditions that cannot easily tackled with linear theories is of great fundamental and applicative relevance. In particular, the investigation of non-equilibrium fluctuations in complex fluids is of great interest in the biomedical and industrial fields, where several processes occur at the mesoscale in multi-component mixtures. For this reason, non-equilibrium fluctuations in complex fluids under microgravity conditions will be investigated on the ISS in the framework of the NEUF-DIX (non-equilibrium fluctuations during diffusion in complex liquids) “Giant Fluctuations” project of ESA [5], currently in the *B* phase, under development for flight. The project is part of the SciSpacE Physical Sciences roadmap of ESA on Soft or Complex Matter. It involves academic partners (Chinese Academy of Sciences, University of New York, University of Pau, University of Milan, University of Bayreuth and University Complutense of Madrid), together with industrial partners (NanoTemper Technologies GmbH) and the Chinese and European Space Agencies.

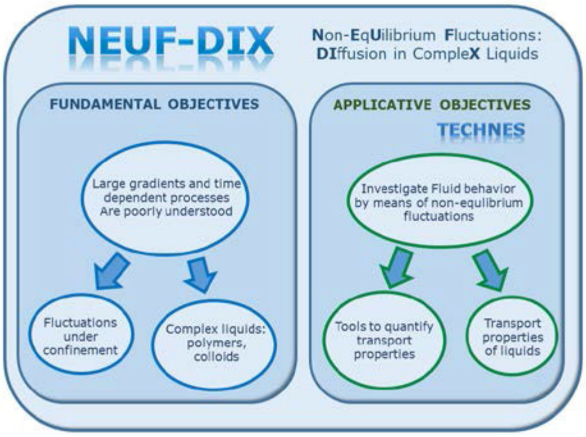

Fig. 8. Fundamental and applicative objectives of the NEUF-DIX project. Applicative objectives will be pursued within the TechNES project funded by ESA in the framework of the Microgravity Application Promotion Programme.

The project envisions both fundamental and applicative objectives, summarized in fig. 8. The most important fundamental goal is the investigation of non-equilibrium fluctuations and transport processes in complex multi-component mixtures under conditions for which theory is currently not capable of providing reliable predictions, such as large gradients and transient phenomena. The focus is on the investigation of non-equilibrium fluctuations in complex liquids, because of the rich phenomenology that can be attained by tuning the interactions in such systems. The availability of experimental results collected in the absence of gravity will allow the development of diagnostic tools based on non-equilibrium fluctuations and aimed at the determination of the thermophysical properties of multi-component complex mixtures. This result will be achieved by working in close collaboration with NanoTemper Technologies Gmbh within the framework of the technology transfer project TechNES (Technologies for Non-Equilibrium Systems) recently funded by the Microgravity Application Promotion Programme of ESA.

The NEUF-DIX project will comprise a set of challenging experiments that will be performed on the International Space Station in 2021–2024. The experiments scheduled for the first flight of the project reflect the advancements in the field of non-equilibrium fluctuations achieved during the last ten years. A first important experiment, strictly connected to DCMIX4, will involve the investigation of non-equilibrium fluctuations in a complex mixture including a diluted polymer. Thermodiffusion in ternary mixtures cannot be investigated on Earth, due to the presence of double diffusion processes that can lead to the destabilization of the sample, even in the presence of an initially stable density profile. By investigating non-equilibrium (NE) fluctuations in space one can have direct access to the different physical phenomena involved in transport processes (mass diffusion, Soret and thermal diffusivity coefficients as well as viscosity [43,44]). Therefore, we expect to get more insight in the diffusion and thermo-diffusion processes, a goal particularly elusive in multi-component systems starting with ternaries. The same sample prepared at a much higher polymer concentration will allow to investigate the glass transition in a ternary mixture including a polymer. The goal is to investigate how glass transition and chain entanglement affect non-equilibrium temperature and concentration fluctuations. The slowing-down occurring when the glass transition is approached affects both the isothermal Fickian and the thermodiffusion coefficients. However, local friction cancels out in the Soret coefficient, which nicely follows the concentration scaling predicted by the blob model [45]. This cancellation of friction resembles the situation observed in metals for the constant ratio between the electronic contribution to the thermal and the electrical conductivity. The slowing-down of diffusive transport by the glass transition is in sharp contrast to the critical slowing-down near a consolute critical point, where the Soret coefficient diverges whereas the thermodiffusion coefficient remains unaffected [46].

A remarkable scientific problem that emerged during the last decade is connected to the forces generated by the confinement of non-equilibrium fluctuations. When fluctuations are spatially long ranged their intensity is affected by the presence of boundaries. Likewise, the presence of such long-ranged fluctuations affects the boundaries, inducing forces on them. These effects are generically known as pseudo-Casimir forces [47,48]. When a fluid or a fluid mixture are in global thermodynamic equilibrium, fluctuations are only long ranged in the close vicinity of the respective critical points, where equilibrium Casimir forces have been measured. As a consequence of the generic long-ranged nature of non-equilibrium fluctuations, recent theoretical research predicted the existence of a novel, yet unobserved, non-equilibrium (NE) Casimir effect that would be much more intense than the equilibrium critical one [49–51] and is present even far from critical points. The most likely method for detecting the presence of fluctuation-induced forces would be by using colloidal particles as probes. In the framework of the Neuf-Dix project we will investigate how the non-equilibrium concentration fluctuations in a binary liquid mixture affects the spatial distribution of colloidal particles dispersed into it. Although this method does not allow to measure directly the force determined by the confinement of the fluctuations, it would allow to achieve a first experimental confirmation of the presence of these forces. Indeed, the investigation of non-equilibrium fluctuations in dense colloidal suspensions represents a stimulating scientific topic by itself. This is due to the fact that until now the investigation of non-equilibrium fluctuations has been limited and focused mostly onto polymer suspensions [4,29,32], dilute colloidal suspension [52,53], and only very recently dense colloidal suspensions [54]. On the theoretical side, the only available theory for concentration NE fluctuations in a dense colloid was published in 1994 by Schmitz [55] and much can be done in this respect with new approaches such as for instance Dynamic Density Functional Theory [56]. Therefore, the investigation of non-equilibrium fluctuations in colloidal suspensions represents a promising, almost unexplored, experimental field.

The investigation of how non-equilibrium fluctuations under confinement affect the interactions between macromolecules has relevant implications on the understanding of the stability of protein solutions, with potential applications in the biomedical industry. Protein drugs are beneficial since they generally own higher specificity and fewer side-effects than conventional chemical drugs. However, protein drugs are much more complex than small molecules and introduce new challenges in the development of drugs. Protein-protein interactions can give rise to opalescence, phase separation, and sometimes undesirable rheological properties. Aggregated proteins are considered to be one of the major risk factor for protein drug immunogenicity. Aggregation processes are complex, and the interplay between molecular structure, association, aggregation, denaturation and formulation conditions are not well understood on the molecular level. Hence, there is a lack of knowledge to bridge protein structure and formulation conditions with physical stability of these proteins. Thermal diffusion methods like the microscale thermophoresis (MST) [57] are already established to study biomolecular solutions, but measurements on Earth can be strongly affected by convective motions. Therefore, one aim of NEUF-DIX project will be the investigation of how non-equilibrium fluctuations affect the stability of a protein solution under microgravity conditions.

So far, non-equilibrium fluctuations have been investigated mostly at steady state or during quasi-stationary processes [58], such as free diffusion [54,59–61]. A key open question is represented by the behaviour of the fluctuations during the transient leading to the development of a steady macroscopic concentration gradient in a binary liquid mixture. Recent simulations [29] investigated the development of NE fluctuations induced by thermodiffusion in a solution of a polystyrene polymer in toluene under microgravity. The conditions mirrored those found in the GRADFLEX experiment [4]. The simulations agree only partially with the results of the space experiment, due to the poor statistical sample available during transient diffusion. Thus, future experiments will require a better statistical characterization of the transient state. This will be achieved both by iterating the experiment and by using a suspension of large colloidal particles or polymer to slow down the kinetics sufficiently to allow the investigation of the slow development of a concentration gradient induced by thermodiffusion.

6 SCCO

Context, objectives and issues

SCCO (Soret Coefficients in Crude Oil) is an ambitious project that begun in 1994 and was associated with three different microgravity experiments since then [62–64]. The last one, named Shi Jian 10 (SJ10)-SCCO which is the subject of this section, has flown in April 2016. This long-lasting project is the result of a unique partnership between the European Space Agency and China's National Space Science Center, Chinese Academy of Sciences with the help of academics from France (Université de Pau et des Pays de l'Adour, Université de Paris-Sud and CNRS), Spain (Mondragon Unibertsitatea and Universidad Complutense), United Kingdom (Imperial College London), China (Institute of Mechanics, Chinese Academy of Sciences) and industrialists from France (TOTAL) and China (PETROCHINA, RIPED).

Fig. 9. The six SCCO cells contained in the C-Box.

SCCO project aimed at investigating thermodiffusion of multi-component mixtures of petroleum interest under reservoir thermodynamic conditions, *i.e.* high pressures. It is still an open problem from the modeling/simulation points of view and the reliable ground-based measurements on more than binary mixtures are still scarce, despite very recent progresses on both aspects [65]. From the application viewpoint, this project was motivated by the fact that, in oil and gas reservoirs, thermodiffusion is one of the main processes that governs the vertical distribution of species along the geothermal gradient [66,67].

Experimental details

The SCCO-SJ10 experimental set-up consists of six small and sturdy titanium cylinders put in a C-Box, see fig. 9, and containing about 1.2 ml of fluids each. Each cell is divided into two halves, which are linked by an initially open valve. During the orbital flight, about 270 hours long of operational time, the boundaries of every cell were maintained at two different temperatures (35.85 °C and 65.88 °C), so as to induce thermodiffusion inside the fluid contained therein. At the end of the flight the central valves in all cells were closed separating each fluid sample in two fractions (a "hot" and a "cold" part). More details can be found in ref. [64].

Regarding the studied fluids, the SCCO-SJ10 experiment has been conducted on six different synthetic samples composed of linear alkanes, methane (C1), *n*-pentane (*n*C5), *n*-heptane (*n*C7) and *n*-decane (*n*C10), in a monophasic state under high pressures (between 300 and

Table 1. Measured thermal diffusion ratio in the two exploitable SCCO-SJ10 cells.

	k_{T_i}			
	C1	nC5	nC7	nC10
Liquid mixture	N/A	-1.36 ± 0.47	-0.02 ± 0.14	1.38 ± 0.62
Gas condensate mixture	-0.21 ± 0.17	0 ± 0.01	0.11 ± 0.09	0.1 ± 0.08

400 bars) and at an average temperature of 50.8 °C. Details regarding preparation, injection (pre-flight) and compositional analysis (post-flight) of the fluids mixture inside the cells can be found in [64].

Results and discussion

Over the six cells that were sent to space, only two were considered of not having suffered from leakage. One containing a liquid ternary equimolar mixtures composed of nC5, nC7 and nC10 at a pressure of 310 bars and one containing a quaternary mixture, a gas condensate, composed of C1 (96.5% in mol), nC5 (1.17% in mol), nC7 (1.17% in mol) and nC10 (1.17% in mol) at 350 bars.

From the mole fraction, Δx_i, the difference between the two compartments of the cells measured by gas chromatography, and assuming a linear response, it was possible to quantify thermodiffusion in the studied mixtures by computing the so-called thermal diffusion ratio of each species, i:

$$k_{T_i} = -T_{av} \frac{\Delta x_i}{\Delta T} \,. \tag{1}$$

Results, provided in table 1, indicate that thermodiffusion leads to a relative migration to the hot region of the lightest hydrocarbon for both mixtures as expected. What is more surprising is the magnitude of the thermal diffusion ratios.

The k_{T_i} values obtained for the quaternary mixtures exhibit an order of magnitude (about 0.1) which is consistent with experimental results on binary mixtures [65, 68] and with molecular dynamics simulations on such mixtures [64]. However, the thermal diffusion ratios for nC5 and nC10 in the ternary liquid mixture are one order of magnitude larger than those of the quaternary mixture, which remains to be elucidated.

Interestingly, when the thermodiffusion values obtained on the gas condensate are included into a simulation of an idealized one-dimension reservoir, it appears that thermodiffusion is able to counteract the influence of gravitational segregation on the vertical distribution of species [64]. Even more striking, combined with thermal expansion, thermodiffusion leads to a reversed density gradient which could result into an unstable fluid column, confirming previous findings on other oil and gas mixtures [69]. Thus, these results confirm that thermodiffusion data on multi-component mixtures are key quantities to determine the initial state of a petroleum reservoir.

7 Conclusions

The present paper provides a short review of the main experiments on thermodiffusion carried out in microgravity conditions in the framework of the ESA programmes enabling the utilisation of facilities on-board the ISS and other microgravity platforms. These experiments span over more than two decades and involve large international cooperative teams of scientists, from ESA member states and from partner space agencies which worldwide also contributed to their accomplishment.

The development of experimental activities on orbit has pushed for a strong experimental, theoretical and numerical activity on-ground as witnessed by the large number of related publications. As a result, the understanding and the quantification of thermodiffusion has strongly improved over time. While the measurement of the Soret coefficient was strongly controversial even for binary mixtures in the 90s, now a large amount of measurements on ternary mixtures have been performed and attempts have been done even on quaternary ones. The possibility of performing measurements in a gravity-free environment was crucial in most of the cited cases, in particular on more than binary mixtures, as convection and sedimentation would have made most of the measurements impossible. Among other, such measurements have helped to confirm the key impact of thermodiffusion to determine the compositional initial state of an oil and gas reservoir (SCCO). The impact of g-jitter and reboosting of the ISS has been shown to have limited impact on thermodiffusion experiments in most cases. Conversely, imposed vibrations with constant frequency and amplitude have been studied and their impact on diffusive processes has been demonstrated (IVIDIL). Last point, the impact of gravity on diffusive processes has been demonstrated through the GRADFLEX project and its implications to a large variety of thermo-physical processes will be investigated more in details through the upcoming NEUF-DIX series of experiments.

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Author contribution statement

MB, AVa, FC, VS, WK, AM, GG wrote the paper. MB, PAA, HB, JPB, MMBA, FC, JD, GG, HH, EK, JCL, FM, JMOZ, BR, SVV, AVe, RV, VV, SX, KZ, SM, OM have contributed to plan, develop or perform the SCCO experiment. YG, JCL, TL, SM, AM, OM, VS have contributed to plan, develop or perform the IVIDIL experiment. HB, MMBA, FC, CG, AE, JME, AFP, QG, YG, LGF, JG, EK, WK, EL, ALS, JCL, IL, TL, SM, AM, OM, JMOZ, JR, XR, IIR, MS, VS, TT, SVV, AVa, VY have contributed to plan, develop or perform the DCMIX experiment. DSC, RC, MG, SM, NM, OM, FJM, CJT, AVa, AVe, have contributed to plan, develop or perform the GRADFLEX experiment. MB, PB, HB,MC, RC, FC, AD, AFP, LGF, FG, EK, WK, OM, JMOZ, AVa, SX, DZ have contributed to plan and develop the NEUF-DIX experiment.

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