Book of Abstracts

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Contents

Programme	3
Oral Communications, Day 1 I. F. Torres, M. Mohsenzadeh, S. Xu., From concept to device: angingering the Soret effect for scalable	6
all-liquid thermal separation	6
Oral Communications, Day 2	9
B. A. Rudani, W. Briels, S. Wiegand - Whats is the nature of the Soret effect in sait solutions? Ali El Yazidi, Alain Bergeon, Mourad Echchadli, Charrier-Mojtabi M.C, Said Aniss, Abdelkader Mojtabi - Solar seawater desalination using thermogravitation	9
 C. O. Oko, B. Seta, M. M. Bou-Ali, V. Shevtsova, H. Bataller - Diffusion layer convection of two superimposed brines: experimental and theoretical approaches	14
national Space Station	16
 F. Bresme, J. D. Olarte-Plata - Nanoparticle thermophoresis: the impact of internal degrees of freedom and interfacial thermal resistance B. Hafskjold, S. Kjelstrup - Thermodiffusion and thermo-osmosis in membrane systems R. Gervassone, S. Buzzaccaro, R. Piazza - Optothermally-induced deformations in soft solids A. Bhattacharyay - Transport by diffusion gradient 	18 20 22 24
Oral Communications, Day 3	26
 A. Mialdun, M. Bou-Ali, V. Shevtsova - Transport properties of toluene-methanol-cyclohexanol ternary mixture obtained in DCMIX space experiment W. Köhler, D. Sommermann - Thermodiffusion of the ternary system polystyrene + toluene + cyclohexane 	$\frac{26}{28}$
A. Errarte, P. F. Arrolabe, A. Mialdun, I. Castellanos-Rubio, M. Munoz-Arias, M. Insausti, V. Shevtsova, M. Bou-Ali - Experimental analysis of absorption mechanisms in LiBr-H ₂ O solution	30
 T. Fiuza, M. Sarkar, J. Riedl, F. Cousin, G. Demouchy, J. Depeyrot, E. Dubois, R. Perzynski, V. Peyre - Inversion of the thermodiffusive properties of nanoparticles in mixtures of ionic liquid and water L. Garcia-Fernandez, O. B. Ferreiro, M. C. Garcia-Payo, E. Garcia-Merino, J. Contreras-Martinez, J. Garcia- Candido, R. Guerrero, M. Khavet - Effects of membrane porous structure on the performance of non- 	33
 isothermal separation process P. Fruton, H. Imuetinyan, E. Lisoir, C. Giraudet, F. Croccolo - Anomalous behaviour in out-of-equilibrium supercritical CO₂ 	$\frac{35}{37}$
Oral Communications, Day 4	41
A. T. Krüger, E. Sondermann, A. Meyer - Thermodiffusion in liquid $Ag_{60}Cu_{40}$	41
Marangoni convection in the absorption process	43
molecular dynamics simulation	45
convection in cylinders	47 49
hexanol/Toluene binary mixtures	51
gation of 2D colloidal quasicrystals	53 55 57
A. Sanjuan, V. Shevtsova, M. Bou-Ali - Thermodiffusion coefficients in quartenary liquid mixtures	58
Oral Communications, Day 5 M. Carpineti, S. Villa, C. Volpari, F. Croccolo, an A. Vailati - Molecular diffusion investigated with a cartesian	62
diver	62

M. Brizioli, S. Castellini, C. Giraudet, M. Carpineti, F. Croccolo, F. Giavazzi, A. Vailati - Experimental investigation of non-equilibrium fluctuations under non-stationary conditions	63
B. Seta, J. Spangenberg, M. Bou-Ali, V. Shevtsova - Role of cross-diffusion on double diffusion in ternary	
 system	67
and natural convection	69
lating an anticlinal geological fold under the action of a geothermal temperature gradient I. N. Cherepanov, B. L. Smorodin - Convection of a binary fluid mixture in the Hele-Shaw cell with modulated	71
heating	73
Poster	76
M. Mojtabi, M-C Charrier Mojtabi, A. Mojtabi - Enhancing species separation in a two sided lid-driven horizontal cavity	76
 A. Errarte, A. Mialdun, H. Badiar, D. Dubert, F. Gavaida, J. Massons, V. Snevtsova, M. Bou-All, X. Ruiz - Comprehensive analysis of PCM melting dynamics: thermogravitational convection and Marangoni flows L. De Port, O. Milark, P. Sabaa, E. Crossela, Dynamic differentia microscopy, investigating transport 	79
phenomena in the Fourier space	82
L. Sappl, C. N. Likos, A. Zöttl - Polymer thermophoresis by mesoscale simulations	85
S. Diaz-Luz, C. Garcia-Payo, L. Garcia-Fernandez, J. Contreras-Martinez, M. Khayet - Photothermal mem-	
brane distillation: harnessing solar energy for clean water production and desalination L. Garcia-Fernandez, P. Baaske, H. Bataller, M. Braibanti, M. Carpineti, S. Castellini, R. Cerbino, F. Croccolo, P. Fruton, F. Giavazzi, C. Giraudet, C. Heim, W. Kölher, C. Likos, A. Vailati, S. Xu - Giant	87
fluctuations in complex mixtures on the International Space Station	89
C. O. Oko, B. Sobac, F. Croccolo, H. Bataller - Measurement of salt diffusion coefficient as a function of	
concentration in a free-diffusion cell by interferometry	91
T. P. Lyubimova, S. A. Prokopev - Stability of quasi-equilibrium of a binary fluid-inclined layer under the action of high-frequency vibrations	03
H. Badfar, D. Dubert, A. Errarte, A. Sanjuan, B. Seta, J. Gavalda, J. Massons, M. M. Bou-Ali, V. Shevtsova,	50
X. Ruiz - On the thermocapillary and melting processes in PCM devices under terrestrial and micro-	
gravitatory environments	94
M. N. Ouarzazi, A. Sanjuan, K. An Ammar, V. Snevtsova, S. C. Hirata, M. M. Bou-An - Impact of the transversal confinement on the steady-state species separation in thermogravitational columns	96
Scientific Committee	98

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Organizing Committee

99

Programme

Day 1 (Monday, 9 Ju	ne 2025)
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Timetable	Speaker	Title
16:00 - 16:30	Organizing committee	Welcome desk
16:30 - 17:00		Inaugural session
17:00-18:00	Juan Felipe Torres	All-liquid thermal desalination and brine concentration via mul- tichannel thermodiffusion
18:00 - 19:30	Welcome cocktail	

Day 2 (Tuesday, 10 June 2025)

Timetable	Speaker	Title
09:00-09:30 09:30-10:00 10:00-10:30	S. Wiegand A. El Yazidi H. Bataller	What is the nature of the Soret effect in salt solutions? Solar seawater desalination using thermogravitation Diffusion layer convection of two superimposed brines: experimen- tal and theoretical approaches
10:30-11:00	Coffee break	
11:00-12:00	Roberto Cerbino	Hydrodynamic fluctuations in sedimenting colloids: following in Perrin's footsteps to the international space station
12:00-12:30	F. Bresme	Nanoparticle thermophoresis: the impact of internal degrees of freedom and interfacial thermal resistance
12:30-14:00	Lunch break	
14:00-14:30	B. Hafskjold	Thermodiffusion and thermo-osmosis in membrane systems
14:30-15:00	R. Gervasone	Optothermally-induced deformations in soft solids
15:00-15:30	A. Bhattacharyay	Transport by diffusion gradient
15:30 - 16:00	Coffee break	
16:00 - 18:00	Social event	

Day 3 (Wednesday, 11 June 2025)

Timetable	Speaker	Title
09:00-09:30	A. Mialdun	Transport properties of toluene-methanol-cyclohexane ternary mixture obtained in DCMIX space experiment
09:30-10:00	W. Köhler	Thermodiffusion of the ternary system polystyrene + toluene + cyclohexane
10:00-10:30	A. Errarte	Experimental analysis of absorption mechanisms in LiBr-H ₂ O solution
10:30-11:00	Coffee break	
11:00-12:00	Marco Braibanti	ESA's thermodiffusion experiments in Space: Insights from the past, current progress, and future opportunities
12:00-12:30	E. Dubois	Inversion of the themodiffusive properties of nanoparticle in mix- tures of ionic liquid and water
12:30-14:00	Lunch break	
14:00-15:30	Poster session	
15:30-16:00	Coffee break	
16:00 - 16:30	L. García-Fernández	Effects of membrane porous structure on the performance of non- isothermal separation process
16:30 - 17:00	P. Fruton	Anomalous behaviour in out-of-equilibrium CO_2
17:00-18:00	Meetings	
Evening	Gala dinner	

Timetable	Speaker	Title
09:00-09:30	E. Sondermann	Thermodiffusion in liquid $Ag_{60}Cu_{40}$
09:30-10:00	V. Shevtsova	Impact of the Soret effect on the Marangoni convection in the
10:00-10:30	G. Guevara-Carrión	Binary diffusion coefficients from non-equilibrium molecular dy- namics simulation
10:30-11:00	Coffee break	
11:00-12:00	Arantxa Alonso	Numerical insights into pattern formation in binary convection in cylinders
12:00-12:30	B. A. Rudani	Thermophoresis: the case of apomyoglobin
12:30-14:00	Lunch break	
14:00-14:30	H. Imuetinyan	Shadowgraphy study of transport properties in cyclohex- anol/Toluene binary mixtures
14:30-15:00	M. Bessega	Thermophoresis-driven aggressition of 2D colloidal quasicrystals
15:00-15:30	A. Arango-Restrepo	Self-phoretic mobility of active droplets
15:30-16:00	Coffee break	
16:00 - 16:30	S. Castellini	Taming the diffusiophoretic convective instability in colloidal sus- pensions
16:30 - 17:00	A. Sanjuan	Thermodiffusion coefficients in quartenary liquid mixtures
17:00-17:30	L. García-Fernández	Tribute to José M. Ortiz de Záraté
17 00 10 00	and F. Croccolo	
17:30-18:30	Meetings	

Day 4 (Thursday, 12 June 2025)

Day 5 (Friday, 12 June 2025)

Timetable	Speaker	Title
09:00-09:30	S. Villa	Molecular diffusion is is to a cartesian diver
09:30-10:00	M. Brizioli	Experimental investigation of non-equilibrium fluctuations under non-stationary conditions
10:00-10:30	B. Seta	Role of cross-diffusion on double diffusion in ternary system
10:30-11:00	Coffee break	
11:00-11:30	H. Badfar	Influence of magnetic Fields on n-Eicosane-Fe $_3O_4$ nanofluids: a novel investigations of thermophoresis, thermocapillarity, and natural convection
11:30-12:00	T. Lyubimova	Soret-induced convection in a layered porous medium simulating an anticlinal geological fold under the action of a geothermal tem- perature gradient
12:00-12:30	B. L. Smorodin	Convection of a binary fluid mixture in the Hele-Shaw cell with modulated heating
12:30-13:00	Closure	

Oral Communications Day 1

From Concept to Device: Engineering the Soret Effect for Scalable All-Liquid Thermal Separation

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Introduction

The Water–Food–Energy Nexus underscores the profound interdependence between water availability, food security, and energy generation. These systems are intricately linked—interventions in one often trigger cascading effects across the others. For instance, evaporation ponds used in lithium extraction—vital for the global transition to electrified transport—consume vast tracts of land and lead to substantial water loss through evaporation, thereby reducing agricultural land use and exacerbating water scarcity. New desalination technologies could provide water and food security without compromising energy security.

Membrane systems degrade over time, chemical treatments can be hazardous, and phase-change processes such as distillation are energy intensive. Despite more than six decades of commercial development, desalination today supplies less than 0. 5% of the global freshwater demand. With over a billion people affected by water scarcity, the need for new water treatment solutions that are both scalable and sustainable is urgent. But what would an ideal water treatment technology look like? It should: (1) Operate using low-cost or freely available energy, ideally waste heat below 80 °C; (2) Function entirely within the liquid phase, avoiding energy-intensive phase changes; (3) Eliminate the need for membranes or chemical additives, reducing cost and complexity; and (4) Be scalable and manufacturable using accessible technologies such as injection moulding or 3D printing.

In response to this challenge, we have developed multichannel thermodiffusion [1, 2]—the first thermal desalination technology that operates fully in the liquid phase. Using the Soret effect, i.e. the migration of solute species in response to temperature gradients, this method avoids evaporation, membranes, and chemical agents altogether. The process is simple, modular, energy-efficient, and inherently scalable. In recent work, we demonstrated laboratory-scale desalination devices processing 36 mL h^{-1} with a concentration drop of 2000 ppm. We are now scaling up to modular systems capable of handling over 100 mL h^{-1} , with brine concentration shifts exceeding $35\,000$ ppm. Our long-term goal is the deployment of fullscale systems processing up to $1000 \text{ m}^3 \text{ d}^{-1}$.

Thermodiffusion performs exceptionally well in a broad salinity range, from RO brine (about 70 000 ppm) to near saturation levels (exceeding 200 000 ppm). It outperforms evaporation ponds in both energy efficiency and cost effectiveness, even when powered by electricity. Unlike evaporation-based systems, which irreversibly lose water to the atmosphere, thermodiffusion retains it, enabling reuse of water in agriculture, industry, and beyond. The technology also holds promise for 6

resource recovery from brines and treatment of produced water in the oil and gas sector. When driven by low-grade or waste heat (e.g. that from data centres), its operational costs are significantly reduced, offering a viable and sustainable alternative to conventional methods.

a Single rectangular channel (side view)





This presentation outlines the concept and analysis of multichannel thermodiffusion and its translation to lab-scale devices and ultimately industrial prototypes that could transform water treatment and resource recovery.

Enhancing thermodiffusive separation

We are engineering several methods to enhance thermodiffusive desalination. In [1, 2], six methods of improvement for thermodiffusive separation are identified and analysed, as outlined in the following. (1) A large multichannel arrangement, known as the Burgers cascade [3, 4], amplifies modest thermodiffusive concentration differences through interconnected channels, increasing separation efficiency and yield. This scalable design overcomes single-channel limitations and was first demonstrated for gases by Saiki et al. [5] and for liquids by Xu et al. [2]. (2) Partial separation in a developing flow allows significant concentration changes within reduced residence times, increasing volumetric flow, and balancing efficiency with throughput. (3) Nonlinear vertical temperature profiles create quasi-uniform thermal zones that minimise stagnation-concentration coupling, improving yield and energy performance. (4) Optimal recovery rate balances yield and flow. The ideal values range from 50-60% for desalination and 20-30% for brine concentration, maximising efficiency. (5) Selective thermal insulation targets low-contribution regions in the Burgers cascade, cutting energy losses while maintaining yield, thus improving sustainability. (6) High-pressure operation enhances efficiency by raising the Soret coefficient at higher mean temperatures without boiling, making the process more competitive than evaporation.



Figure 2: Device evolution from tested lab-scale device to large-scale modular design of a liquid Burgers cascade.

Device manufacturing and testing

We recently built and tested a lab-scale liquid Burgers cascade (LBC) with a modest number of channel pairs of 4×4 (32 channels in total), as reported in [2] and shown in Fig. 2(a, left). We performed thermodiffusive separation using seawater at normal temperature [2] and, more recently, feedwater concentrations close to saturation level. For example, for a 7

mean concentration of 210 000 ppm, we achieved a separation exceeding 12000 ppm, as shown in Fig. 2(a, right). Furthermore, our modelling shows that for seawater brine, generally we need more than 20 rows to achieve concentration differences of impact in the industry. To do this, we designed the prototype shown in Fig. 2(b), which will soon be tested. The inset plot shows the expected concentration concentration along the brine concentration path (TDS or thermodiffusive salination) and the desalination path (TDD or thermodiffusive desalination). The aim of this prototype is to demonstrate the modularity of the LBC. A significant effort of our modelling is to calculate the specific energy consumption for this process. We have found that for feedwater concentrations exceeding 150 000 ppm, multichannel thermodiffusion is more efficient than evaporation, even without temperatures below 100 °C. We are now working towards testing and assessing new designs of the LBC, and using techno-economic analysis to understand their cost-effectiveness in real industrial-scale processes.

Conclusions

Multichannel thermodiffusion presents a promising new direction for sustainable water treatment, taking advantage of the Soret effect to achieve thermal separation of the liquid phase without evaporation, membranes or chemical additives. We have demonstrated the scalability of this approach through modular designs and enhanced separation techniques, including the LBC, partial separation strategies, and optimised thermal and hydraulic configurations. These innovations enable efficient operation across a wide salinity range and under lowgrade heat, making the technology particularly suitable for agricultural reuse, industrial applications, and resource recovery from brines. By integrating this process with emerging heat sources such as data centres, thermodiffusive desalination offers a viable, energy-efficient, and scalable solution to address the growing global challenges of water.

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Oral Communications Day 2

What is the nature of the Soret Effect in Salt Solutions?

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Introduction

In recent years, the existence of minima in the Soret coefficient as a function of concentration has been investigated by experiments for various aqueous salt solutions [1, 2, 3]. In the case of aqueous iodide solution, a hydration layer model has been proposed [2]. In this model, the salt molecules are assumed to be surrounded by a shell of more or less tightly bound water molecules, and it has been hypothesized that the minimum occurs when these hydration shells begin to overlap, i.e., when the hydrated spherical salt molecules are randomly closely packed. The application of the hydration model has a somewhat unsatisfactory aspect in that the position of the Soret minimum is imposed to be able to perform the analysis and is not independently represented by the procedure. For the iodides studied in our previous paper[2], this was not a problem since the data clearly indicated where the minimum was to be found. The data for aqueous lithium chloride (LiCl) solutions are clearly less conclusive, and the analysis runs the risk of emphasizing a minimum that may well be unphysical. To avoid such a risk, we decided to analyze the data by calculating the ratio of the Onsager coefficients and comparing it with recent simulations of binary (nonionic) Lennard-Jones mixtures. The simulations showed that L_{1q}'/L_{11} is independent of concentration, while a minimum occurs in the thermodynamic factor [4]. It was found that L_{1q}'/L_{11} for aqueous LiCl solutions can be expressed as a monotonous exponential function. The minimum of the Soret coefficient results from a minimum of the thermodynamic factor, which occurs at concentrations far below the experimental concentrations. Only after multiplication with the (negative) monotonic Onsager ratio did the minimum move into the experimental concentration window.

In this paper we will study the Onsager ratio L_{1q}'/L_{11} and the thermodynamic factor in relation to the hydration of salts. We will find that except for lithium salts, all other aqueous salt solutions that show a minimum of the Soret coefficient with concentration also exhibit a minimum of the Onsager ratio L_{1q}'/L_{11} , while the thermodynamic factor does not or barely does. This makes it clear that for aqueous salt solutions the minimum of the Soret coefficient with concentration cannot be explained by thermodynamics alone, but that kinetic contributions are mainly responsible. An indication that kinetic processes play an important role is the observation that the Soret coefficient for sodium and potassium increases monotonically with the hydrodynamic radii of the salt ions and not with their ionic radius.

In this paper we analyze the data of ten 1:1 electrolytes in water together with newly measured Soret coefficients for aqueous caesium iodide (CsI) solutions [5].

Results for caesium iodide

While the concentration dependence of the Soret coefficient for lithium, sodium, and potassium iodide as a function of concentration could be well described by the concept of overlapping hydration shells [2], this is not expected for CsI. According to recent terahertz spectroscopy experiments [6], tight hydration shells do not form around larger cations such as Cs. To better understand the relationship between the minimum of the Soret coefficients and the hydration of the cations, we extend the data set by providing results for CsI.



Figure 1: Soret coefficients of aqueous CsI solutions as a function of concentration for temperatures between 15° C and 45° C. The Bezier lines connecting the data points are a guide for the eye.

Fig. 1(a) shows the $S_{\rm T}$ of aqueous CsI solutions as a function of concentration for temperatures between 15°C and 45°C [5]. At the lowest measured temperature of 15°C, $S_{\rm T}$ increases monotonically with concentration. At higher temperatures ($T \gtrsim 30$ °C), however, $S_{\rm T}$ develops a non-monotonic dependence on concentration. Note that the minimum occurs at 1 m, the same concentration as for the other iodide salts.

Discussion of various salt systems

Along the lines of the theory of irreversible thermodynamics [7] Gittus and Bresme suggested to write the Soret coefficient as a product of two factors, one being purely thermodynamic and the other, the ratio of two Onsager coefficients $L_{1q'}/L_{11}$, being dynamic in principle [4]

$$S_{\rm T} = \frac{1}{RT^2} \frac{M_1}{\Gamma} \cdot \frac{L_{1q}'}{L_{11}}$$
(1)
$$\Gamma = \frac{m_1}{k_B T} \left(1 + \frac{m_1 M_1}{\Omega M_2} \right) \left(\frac{\partial \mu_1}{\partial m_1} \right)_{p,T},$$

and to investigate their relation to the minimum of the Soret coefficient separately. Here M_1 is the molar mass of the salt, m_1 its molality and μ_1 its chemical potential; M_2 is the molar mass of the solvent and Ω its molality. In the following we refer to $M_1/(RT^2\Gamma)$ as the thermodynamic factor. To calculate the thermodynamic factors we used thermodynamic data from the literature. The ratios of Onsager coefficients L_{1q}'/L_{11} are next obtained by dividing the experimental Soret coefficients by the corresponding thermodynamic factors.

Figure 2 shows the typical function shapes of the thermodynamic factor, L_{1q}'/L_{11} and $S_{\rm T}$ as a function of concentration for all analyzed salts except lithium. While L_{1q}'/L_{11} shows a clear minimum with concentration the thermodynamic factor does not [5]. Moreover, for the spherical sodium and potassium salts with the same anion, we find that the thermodynamic factors increase with increasing Pauling radii of the cations, while the Onsager ratios and the Soret coefficients increase monotonically with the radii of the hydrated cations. While empirical models exist to describe ion hydration thermodynamics, this phenomenon is not accounted for by classical thermodynamics [8].



Figure 2: Typical shape of $M_{\text{salt}}/(RT^2\Gamma)$, L_{1q}'/L_{11} and S_{T} as function of molality for various 1:1 salts.

Conclusions

Our measurements on aqueous CsI solutions support the conclusion of THZ spectroscopy that the water molecules surrounding small cations are not as tight bound, since we do not observe a minimum of $S_{\rm T}$ with concentration as observed for iodide salts with smaller cations. Puzzling is the development of a minimum at higher temperatures at the same concentration, where the other iodides show a minimum in $S_{\rm T}$ over the entire temperature range investigated. Further, we analyze the experimental data of ten aqueous salt solutions by expressing the Soret coefficients as products of two factors, one purely thermodynamic factor and one being the ratio of two Onsager coefficients. It turns out that the ratio of Onsager coefficients is the main responsible for the non-monotonic behavior of the Soret coefficients. In case L_{1q} and L_{11} have a common dynamic factor while otherwise being described by thermodynamic properties becomes a thermodynamic property. In the present paper it is shown that such is not the case for ionic salt solutions.

Acknowledgements

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Solar seawater desalination using thermogravitation

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Introduction

The species separation of a binary mixture from pure thermodiffusion between the top and bottom of a horizontal cavity heated from above was demonstrated by the work of the Brussels thermodynamics team led by Professor E. Prigogine [1]. The first measurements of the Soret coefficient for binary mixtures were obtained by the technique called flow cell method. Subsequently species separation and the measurement of thermodiffusion coefficients were conducted in vertical thermogravitation columns (TGC), [2]. We showed that it was possible to obtain these results under certain conditions in horizontal columns [3]. We then undertook various thermogravitational diffusion studies with the aim of improving the species separation using different geometric configurations and boundary conditions [4]. Very recently, Shuqi Xu et al. [5] proposed a technical procedure that employs pure thermodiffusion for seawater desalination. The electrical energy required for desalination through this process is less than 1% of the energy needed for conventional industrial methods (such as reverse osmosis, electrodialysis, etc.).

In this study, we consider an inclined porous parallelepipedic cavity subjected to a uniform solar radiative flux and cooled from below by circulating a flow of cold seawater (Figure 1). The inclination of the cavity is chosen to maximize the incident radiant flux. This inclination, combined with the imposed conditions, generates convection and thermodiffusion within the cavity. The interaction between convection and thermodiffusion, known as thermogravitation, enables the species separation of within the cell. The flow within the cell is controlled by three important parameters: the cell's angle of inclination, its thickness (which determines the intensity of convective flow), and the heat flux incident on the upper wall (which governs the extent of thermodiffusion).

Analytical and Numerical Results

By assuming a parallel flow approximation, we analytically determined the velocity, temperature, and concentration fields [4]. This approach yielded two distinct solutions: one that accounts for the" forgotten effect" and another that neglects it. Furthermore, we investigated the conditions required to achieve optimal separation. Through this analysis, we established the optimal relationship between cavity thickness and tilt angle to maximize separation efficiency. Finally, we identified the optimal values of the control parameter, ensuring max-



Figure 1: Inclined parallelepipedic cell containing a binary fluid in a porous medium.

imum separation in the studied binary mixture.

Unsteady numerical simulations were conducted to compare the results with the analytical findings. To this end, the conservation equations (mass, momentum, energy, and species) were solved numerically using appropriate boundary conditions and different initial values. These simulations were performed using the commercial software Comsol Multiphysics, which employs the finite element method. The simulations were conducted for a cavity with a thickness of $e = 6.10^{-3}$ m and a length of L = 1 m. A uniform heat flux and a constant temperature were imposed on the walls of the configuration. Additionally, a permeability of $K = 4.2.10^{-10}$ m, and a porosity of $\epsilon = 0.48$. were considered. The analytical and numerical results obtained in this study exhibit good agreement. The binary mixture was: seawater composed for a water (96.5 wt%) and NaCl(3.5wt%).

Figures (2-3-4) present the numerical (black dots) and analytical (solid lines) results for the case where the "forgotten effect" was taken into account and the case where it was not, respectively for the velocity, mass fraction, and mass fraction. The figures demonstrate that the analytical results are in very good agreement with the numerical ones.

Linear stability analysis

We analyzed the linear stability of the equilibrium solution obtained for a horizontal cavity heated from above with a con-



Figure 2: Velocity component U as a function of z for q = 250 $W \cdot m^{-2}$ and $\alpha = 30^{\circ}$, obtained analytically (continuous Line: black, forgotten effect, red without simplifying hypothesis) and using direct numerical simulation (dotted line).



Figure 3: Mass fraction obtained as a function of x for q = 250 $W \cdot m^{-2}$ and $\alpha = 30^{\circ}$, obtained analytically (continuous line) and using direct numerical simulation (dotted line).



Figure 4: Mass fraction gradient versus thickness e for q = 250 $W \cdot m^{-2}$ and $\alpha = 30^{\circ}$, obtained analytically (continuous line) and using direct numerical simulation (dotted line).

stant heat flux and for negative values of the separation factor. We will therefore study the stability of this flow to determine whether it remains stable for a Rayleigh number greater than the optimal Rayleigh number leading to maximum separation. To do this, we revisit the system of equations corresponding to the previous study, formulated in dimensionless form, with the appropriate boundary conditions and by introducing the associated perturbations. These equations were solved numerically using a MATLAB code based on the Chebyshev spectral Tau collocation method.



Figure 5: Linear stability curve: Ra function of k

Conclusions

We have studied the separation of a binary mixture in the case of a confined cell, examining the influence of the inclination angle, cavity thickness, and solar heat flux on the species separation within the mixture. The convective flow induced by the solar heat flux can lead to significant species separation within the cavity. The two important parameters controlling this process are the heat flux applied to the top wall and the cavity tilt angle. They determine the intensity of the convective flow and importance of the species separation. We have identified the optimal coupling between the cavity thickness and the tilt angle to achieve maximum separation. From this study, we deduced the optimal values of the control parameters that lead to maximum separation within the binary mixture. Additionally, we have highlighted a trade-off between separation, solar heat flux, and cell thickness: high separation is achieved for a smaller thickness and a higher heat flux, while a larger thickness requires a lower incident radiant flux. The analytical results are confirmed by direct 2D numerical simulations.

In the context of solar desalination using thermogravitation in a parallelepipedic cell, the cavity is heated from above. Under these conditions, if the thermodiffusion coefficient D_T is positive, the densest constituent migrates toward the cold wall at the bottom, resulting in an infinitely stable equilibrium solution. Conversely, if D_T is negative, the densest constituent moves toward the hot wall at the top, leading to a loss of infinite stability in the equilibrium solution.

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Diffusion Layer Convection of two superimposed brines: experimental and theoretical approaches

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Introduction

Understanding the impact of interactions and how they promote the growth of instabilities during the transport of heat and chemical species in multicomponent systems, is essential for accurately predicting and managing mixing processes in natural or industrial settings. In the particular case of CO_2 storage in deep saline aquifers, understanding the dynamics of CO_2 dissolution and diffusion of salts present in the system is essential for quantifying the injected flows and assessing the safety and sustainability of the process. Knowledge of the diffusion coefficients in the multicomponent systems is therefore essential.

In single-component solutions, diffusion stabilizes the system by limiting the growth rate of perturbations caused by density variations due to temperature or concentration gradients. However, in multicomponent systems, where density depends on multiple scalar quantities (e.g., heat and solute or two solutes), the interplay of these factors can lead to destabilization and the development of complex instabilities (Bratsun *et al.*, 2022).

A system with initially stable density stratification can become unstable over time if its components diffuse at different rates (Stern, 1960). When the unstably stratified solute diffuses slower than the stable one, double-diffusive convection (DDC) occurs, forming elongated convective cells called fingers. If the unstable solute diffuses faster, an oscillatory instability, known as diffusive convection (DC), develops. For a stepped density stratification with two mixed layers, monotonic instability forms near the diffusive interface, while the interface remains stable. This leads to diffusive-layer convection (DLC), where convective motion occurs above and below the mixing zone. These phenomena collectively fall under double-diffusive instability (Radko, 2013).

Methodology

Two characteristic salts of saline aquifers are considered in this work. We superimposed a layer of sodium chloride (NaCl) on a layer of sodium sulfate (Na₂SO₄), for different concentrations and in different concentration ratios. The cell was first filled with the less dense solution and then by slowly injecting the denser one from the cell bottom by means of syringe pumps. We utilized interferometry, a non-invasive optical technique, to track minute concentration changes through variations in refractive index. The sample cell was placed in a Mach-Zehnder interferometer, and refractive field was mapped over time.

For the interpretation of the experimental results, we first calculated at the experimental concentrations the ionic species diffusion coefficients present in the solutions, using the geochemical software PHREEQ-C (Parkhurst, & Appelo, 2013). The ionic activity coefficients for the computations have been calculated according to the Pitzer equations. Main and cross diffusion coefficients of the ternary mixture NaCl + Na₂SO₄ + H₂O have been calculated with equations deduced from the Nernst-Planck formalism of the ionic fluxes (Oko et al., 2024).

These coefficients have been used in the numerical model for ternary isothermal system. The mixtures are placed in a rectangular cell of length $L_x=20$ mm and height $L_y=20$ mm, with the y-axis oriented vertically against gravity. At the initial time of contact, t = 0, the mixtures are separated by a sharp boundary at $y = y_0$, and the density profile between two layers of solutions follows a step function.

At the macroscopic scale, the spatio-temporal dynamics of the diffusive system is described by the Navier-Stokes and mass transfer equations in the Boussinesq approximation. The mass transfer equations, written for each solution, include diffusion and cross-diffusion coefficients. The main diffusion coefficients describe the flow of solute due to its own concentration gradient, and the cross-term diffusion coefficients describe the flow of solute due to a gradient of another salt. The Boussinesq approximation assumes that the density fluctuations that occur with the onset of fluid motion are caused solely by concentration effects. All variations in fluid properties other than density are neglected. Furthermore, this approximation ignores density differences except where they appear in the terms responsible for the convective buoyancy force.

In addition to non-linear simulations, we suggested the theoretical approach predicting the instability patterns for the given set of diffusion coefficients (Šeta, 2020).

Results

After the NaCl-water and Na₂SO₄-water solutions are brought into contact, diffusion processes alter the density profile, leading to unstable conditions. In our research, we analyze six different combinations of the salts concentrations. In all cases, system was initially stable. Here, we present one example, where a 3.026 mol/L (or 15.2% wt) NaCl solution is superimposed on a 1.7 mol/L (or 19.2 % wt) Na₂SO₄ solution.



Figure 1: The spatio-temporal evolution of the double diffusion instability in the form of the Diffusion Convection Layer (DLC) when the upper layer is composed of the NaCl-H2O solution and the bottom layer is composed of the Na2SO4-H2O solution. The series of snapshots at the top represent experimental results and the series at the bottom show numerical results.

The experimental and numerical results are presented in Figure 1. It should be noted that the numerical results show the mass fraction, while the experimental data show the variation of the refractive index in terms of the unwrapped phase. Another difference is that the numerical results present the pattern in the whole cell, while the experimental results show the results in the field of view corresponding to the central part of the cell. For this reason, we show four snapshots from experiments and three from the computer simulations.

Both sources in Figure 1 clearly demonstrate the instability in the form of DLC: the interface between the two mixtures remains undisturbed, despite active convection occurring both above and below the interface. Additionally, the series of snapshots from the experiment and simulations show similar evolutions of the convective patterns. The numerical simulations reveal that, at the very beginning (not shown), the instability emerges as a set of small plumes with a welldefined wavelength along the interface on both sides of the interface. The subsequent development is more pronounced in the NaCl-H₂O (top) solution compared to the Na₂SO₄-H₂O (bottom) solution.

The plumes at the upper solute grow rapidly, moving from left to right and merging, as clearly shown in snapshot #3 from the experiment or in (a) of the numerical results. As they approach the upper wall, the structure of their mushroomshaped heads begins to dissipate and diffuse, as seen in snapshot (b) of the numerical results. At this point, a new plume forms near the interface between the decaying ones, as shown in snapshot (c) of the numerical results. This new plume then grows, catches up with the advancing one, and merges, as depicted in snapshot #4.

In the lower layer, the temporal dynamics is somewhat similar, but the convective cells are much larger and plumes motion is slower.

Conclusions

during the evolution of Diffusion Layer Convection in a system where a NaCl layer is superimposed on a Na₂SO₄ layer. The main and cross diffusion coefficients of the ternary mixture $NaCl + Na_2SO_4 + H_2O$ have been calculated using equations based on the Nernst-Planck formalism for ionic fluxes. The non-linear simulations provide insight into the observed instabilities. The good agreement between the simulations and experiments validates our method for calculating the main and cross diffusion coefficients of the ternary mixture and demonstrates the applicability of the experimental technique for studying double diffusive instabilities.

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The optical technique of Mach-Zehnder interferometry has been successfully applied to visualize the convective patterns 15

Hydrodynamic Fluctuations in Sedimenting Colloids: Following in Perrin's Footsteps to the International Space Station

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Introduction

In 1926, Perrin was awarded the Nobel Prize in Physics for his seminal investigations of the interplay between gravitational settling and Brownian motion in colloidal suspensions (Perrin 1909). His meticulous measurements of the particle number at different heights within sedimented suspensions confirmed the exponential concentration profiles predicted by Boltzmann statistics. Moreover, his precise determination of diffusion coefficients of Brownian particles at fixed heights validated Einstein's theory (Einstein 1905). These pioneering quantitative microscopy experiments provided definitive empirical evidence for the discrete nature of matter, thereby confirming the existence of atoms and molecules (Cerbino 2018).

Interestingly, Einstein's theory strictly applies only to very dilute colloidal suspensions. However, concentrations in sedimented colloidal samples may become sufficiently high that a clear distinction between two types of diffusion is necessary: self-diffusion, which describes the random motion of individual particles relative to their initial positions independently of other particles; and collective diffusion, which characterizes the cooperative motion of multiple particles manifesting as relaxation of concentration fluctuations and resulting in the net transport of particles driven by concentration gradients.

While self-diffusion coefficients can be measured with particle tracking experiments similar to the ones of Perrin, the determination of collective diffusion typically requires probing the relaxation of sample concentration Fourier modes characterized by wave-vector q in the limit $q \rightarrow 0$. This type of measurement is done with Dynamic Light Scattering (DLS), an ensemble method that relies on detecting scattered light intensity fluctuations arising from particle movements within the sample. However, while particle tracking in three dimensions can be performed with modern microscopy approaches such as confocal microscopy or digital holographic microscopy, using DLS to obtain depth-resolved information is technically very challenging due to the large size of the scattering volume compared to the required axial resolution. Probably due to these challenges, a complete picture of the spontaneous relaxation dynamics of sedimented colloidal samples is currently not available, not even for the simplest case of a well-established equilibrium sedimentation profile.

equilibrium process through which colloidal particles settle under gravity from an initially homogeneous state. Already in the simplest case of large, non-Brownian particles, theoretical treatments of sedimentation kinetics face fundamental difficulties, exemplified by the Luke-Caflisch paradox (Guazzelli 2011, Segre 2016). Due to long-range hydrodynamic interactions, the velocity fluctuations of sedimenting particles are theoretically expected to diverge as the container size increases. Experimental observations, however, consistently show that velocity fluctuations remain finite and do not scale indefinitely with the system size. A possible explanation involves the spontaneous formation of correlated particle clusters (swirls) that effectively suppress long-range interactions (Guazzelli 2011, Segre 2016). A recent theoretical analysis alternatively proposes that explicitly incorporating particle inertia, previously neglected at low Reynolds numbers, may effectively resolve this paradox by damping high-frequency velocity fluctuations, thereby naturally limiting their magnitude in large systems (Wolgemuth 2024). Only very recently have experiments with smaller Brownian particles been performed, suggesting an even more complex scenario (Hirano 2024) and demonstrating the urgent need for novel experimental techniques to independently and accurately quantify self and collective diffusion dynamics in sedimenting suspensions.

Results

To address these challenges, we employed Differential Dynamic Microscopy (DDM), an advanced imaging technique that exploits sequences of microscopy images to obtain dynamic scattering information analogous to that provided by Dynamic Light Scattering (DLS) (Cerbino 2008). Specifically, DDM analyzes the temporal fluctuations of Fourier transforms of microscopy images, extracting information about the relaxation dynamics of concentration Fourier modes in a wide range of wave-vectors q. Unlike traditional DLS, DDM allows depth-resolved measurements in sedimented samples, overcoming the technical limitations inherent in standard scattering approaches. Therefore, our experiments focused on characterizing the relaxation behavior at different heights within sedimented colloidal suspensions. For large q, the measured dynamics closely matched those observed in uniform suspensions at identical concentrations, primarily reflecting classical diffusive behavior influenced by direct and hydrodynamic particle interactions (Pusey 1991). However, for small q, we observed an unexpected anomaly: the relaxation of

interactions between equilibrium velocity fluctuations and sedimentation-induced macroscopic concentration gradients. Remarkably, this behavior closely resembles phenomena previously observed in non-equilibrium systems subjected to macroscopic concentration gradients generated by thermophoresis (Ortiz de Zarate 2006), despite our sedimented samples being ostensibly at equilibrium. Motivated by this analogy and by the observation that in non-equilibrium systems, finite-size effects become relevant at even smaller q (Giraudet 2015), we performed further experiments involving systematic variation of sample thickness. Our experiments confirm that at even lower wavevectors, diffusive-like relaxation dynamics re-emerge, albeit with an enhanced effective diffusion coefficient compared to higher-q dynamics.

Conclusions and perspectives

Our study highlights surprising parallels between equilibrium sedimentation profiles and non-equilibrium thermophoretic systems, shedding new light on the underlying mechanisms driving relaxation dynamics in colloidal suspensions. Given the intriguing parallels between sedimentation-induced buoyancy effects and thermophoretic gradients, a promising next step would be to study sedimentation kinetics directly from an initially homogeneous colloidal state. Theoretical models predict that during this transient process, the system would genuinely be out of equilibrium, with large-scale concentration fluctuations significantly suppressed (Vailati 1998) thus providing a simple, quantitative and verifiable resolution to the Luke-Caflisch paradox. Experimentally verifying these predictions on Earth is technically challenging due to the constant influence of gravity and difficulties distinguishing genuine gravity-driven phenomena from experimental artifacts. To overcome these limitations, the SEDIMENTING COLLOIDS ESA experiment, scheduled for execution aboard the International Space Station (ISS) in 2027-2028, will provide an unparalleled opportunity. Using the FLUMIAS facility-a microscope coupled to a centrifuge that enables precise control of effective gravitythis space-based research aims to rigorously investigate sedimentation kinetics under conditions free from terrestrial constraints.

Acknowledgements

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Nanoparticle thermophoresis: the impact of internal degrees of freedom and interfacial thermal resistance

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Introduction

The manipulation of nanoparticles and molecules through thermal fields has emerged as a promising avenue for tailoring the behaviour of soft matter systems (D. Niether, S. Wiegand, 2019). Heterogeneous nanoparticles have gained prominence due to their potential as fundamental units in self-assembling materials with unique properties. In this study, we employ non-equilibrium molecular dynamics simulations and theory to explore the thermophoretic responses of nanoparticles subjected to thermal fields. We focus on understanding how the heterogeneous structures of these particles influence their Soret coefficient, S_T , and thermal orientation.

We examined a variety of heterogeneous nanoparticles, each characterised by distinct internal structures, mass distributions, and particle-solvent interactions, to uncover their thermophoretic response in liquids, supercritical states and near-critical conditions. We find a significant enhancement of the Soret coefficient and the thermal orientation of anisotropic nanoparticles near the critical point. We quantify the role of mass anisotropy on the thermal orientation of heterogeneous nanoparticles. (F. Bresme et al. 2022) and demonstrate that this response can be modelled using the Langevin function,

$$< \cos \theta > = \mathcal{L}(\kappa) = \coth(\kappa) - \frac{1}{\kappa}$$

where κ determines the strength of the thermal orientation,

$$\kappa = -S_T \mu \nabla T$$

where $\mu = |\vec{r}_{com} - \vec{r}_{cog}|$, "com" and "cog" are the centre of mass and centre of geometry of the nanoparticle and ∇T is the thermal gradient and θ is the angle between the mass dipole and the heat flux direction.

Additionally, we investigated the microscopic mechanisms responsible for nanoparticle thermophoresis. Traditional theoretical models link the Soret coefficient to interfacial effects (Duhr, Braun 2006) and changes in interfacial tension surrounding the colloid, where gradients in surface tension induce fluid flow (Wurger, 2007; Arango-Restrepo, Rubi, 2019; Giddings 1995; Gaspard 2019). A novel aspect of our work is introducing a theoretical approach that explicitly incorporates the effects of Kapitza resistance, a critical factor in interfacial heat transport. Our formulation allows for precisely monitoring thermophoresis as a function of the Kapitza resistance. We derive an equation for the Soret coefficient that includes thermal transport properties: the thermal conductivity of the nanoparticle and solvent, as well as the Kapitza resistance:

$$S_T = \frac{4\pi R^2 (1+\alpha')}{3K_B T} \gamma_T + \frac{1}{T}$$

where *R* is the nanoparticle radius, $\gamma_T = \frac{d\gamma}{dT}$ is the derivative of the interfacial tension, and α' quantifies the impact of the nanoparticle and solvent thermal conductivities, and the Kapitza resistances of the nanoparticle-solvent interface, on the Soret coefficient.

We validate our approach using a nonequilibrium molecular dynamics model of a colloid suspended in a solvent and demonstrate the Kapitza (Olarte-Plata, Bresme, 2024). This investigation enhances our theoretical understanding of nanoparticle behaviour in thermal fields and offers a framework for future experimental exploration.

Conclusions

We investigated the thermophoretic response of heterogeneous nanoparticles (internal mass gradient and interaction gradients). We found a coupling effect between the nanoparticle internal mass distribution and the heat flux, which results in thermal orientation. This coupling effect influences the Soret coefficients. We quantified and verified the coupling effect in both liquid and supercritical suspensions. Our simulations show a significant enhancement of thermophoresis and thermal orientation near a critical point.

We extended previous theories of the Soret effect, which modelled the thermophoretic force in terms of Marangoni flows around colloids. Our new approach incorporates the Kapitza resistance of nanoparticle-solvent interfaces and provides a link between this property and the Soret coefficient. The thermophoretic force observed in the nanoparticle models investigated here aligns with the development of velocity fields around the nanoparticle-fluid interface that propels the nanoparticle away from the heat sources.

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Thermodiffusion and thermo-osmosis in membrane systems

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Introduction

Diffusion and osmosis in membrane systems have several important applications' such as water purification [1], waste heat utilization [2], and in biohysics [3]. In thermo-osmosis, which can occur in pure systems as well as mixtures, the driving force is a temperature difference across the membrane. The microscopic mechanism is related to the temperature difference across the membrane [4, 5]. Thermodiffusion occurs in mixtures with or without a membrane [6]. Both processes have been extensively studied experimentally, especially in search of suitable membranes (thermo-osmosis) [1, 7], and separation efficiency (thermodiffusion). Understanding the microscopic mechanisms and theory development have been supported by computer simulations.

It is known that a porous medium has an impact on thermodiffusion [8–10], but previous studies have focused on systems with larger pores (larger permeability) than those studied here. In this work, we focus on the role of the membrane when both thermodiffusion and thermo-osmosis occur simultaneously. We have simulated a two-component fluid system with a nano-porous membrane that separates a hot and a cold fluid compartment. The fluid is a Lennard-Jones/spline model. The potential parameters ϵ and σ control the interactions between the two fluid components and between the fluid and the membrane.

We want to determine the effect of a membrane on the separation efficiency in a binary fluid mixture. To quantify efficiency, we use the difference in composition between the cold and the hot zones in the fluid, whic is related to the Soret coefficient [11].

Theory

Separation of components in a bulk fluid mixture subject to a temperature gradient (thermodiffusion) can be quantified as the Soret coefficient [12]. When a membrane is introduced, transport mechanisms will be different in the bulk and across the membrane. We use non-equilibrium thermodynamics (NET) for heterogeneous systems [13] to describe the membrane's contribution to the separation. The total difference in composition between the cold and hot zones in the system, $\Delta x_1 = x_{1,C} - x_{1,H}$, is the sum of three terms, Δx_1 (hot bulk), Δx_1 (membrane), and Δx_1 (cold bulk). The membrane has two surfaces and pores, all of which may contribute to driving forces for mass transport.

The result of thermo-osmosis is a pressure difference $\Delta P = P_{\rm C} - P_{\rm H}$. Since the pressure in each of the bulk zones is con-

stant, the only contribution to ΔP comes from the membrane. The Δx_1 and ΔP will be determined at zero mass fluxes, $J_1 = J_2 = 0.$

The results were interpreted in terms of NET leading to quantified transport coefficient. For a more detailed description of the theory, please see references [10, 12, 13].

Simulations



Figure 1: MD box with two slit-pore membranes. The upper right panel shows the box with the fluid, component 1 in red and component 2 in blue.

Molecular dynamics simulations were performed with a Lennard-Jones/spline model, N = 13,824 particles in a box with aspect ratio L_x : L_y : $L_z = 2$: 1: 1. The MD box had two slit-pore membranes as illustrated in Figure 1 and two fluid components. The box was organized in 64 layers of equal thickness and normal to the x-direction. One layer at each end of the box (the hot zone) was thermostated to a high temperature $T_{\rm H}$ and two layers in the center (the cold zone) to a low temperature $T_{\rm C}$. This created temperature gradients in the system. The role of the interactions between the fluid and the membrane was investigated by systematically varying the potential parameter $0.5 < \varepsilon_{2m} < 2.0$, where subscript "2m" represents fluid component 2 and membrane component m. The mass ratio between the two fluid components was also varied, $0.1 < m_2/m_1 < 10.0$. All the other other potential parameters were kept constant at value 1.0. This gave combinations of seven values of both ε_{2m} and m_2/m_1 , altogether 49 combinations.

The membrane structure was kept fixed with eight slit pores in each membrane as illustrated in Figure 1. This means that the membrane was a perfect thermal insulator. The width of each slit was $2.68\sigma_{11}$ *i.e.* 2.68 in Lennard-Jones units, which will be used from here on. This is a nanoporous membrane. In all cases, the thermostat set points were $T_{\rm H} = 4.0$ and $T_{\rm C} = 2.0$.

Results

The results include Δx_1 and ΔP as function of ε_{2m} and m_2/m_1 . In addition, the three contributions to Δx_1 from the two bulk zones and the membrane were determined. As an example, we show in Figure 2 selected results for Δx_1 . Note that $\Delta T = T_{\rm C} - T_{\rm H} = -2.0$ in all cases. This is the total temperature drop, the contributions from the three zones are not necessarily the same in all cases.

It is clear that the fluid-membrane interaction has an impact on the separation effect. Note in particular that for $m_2/m_1 =$ 1.0, there would have been no separation had it not been for the membrane.



Figure 2: The mole-fraction difference for component 1, $\Delta x_1 = x_{1,\text{C}} - x_{1,\text{H}}$, as function of the potential parameter $\varepsilon_{2\text{m}}$ between fluid component 2 and the membrane for three selected mass ratios. The circles are results from simulations without the membrane.

Conclusions

The primary objectives of this study were the effects of fluid-membrane interactions on thermodiffusion and thermoosmosis, and the coupling between them. We have found that a nanoporous membrane can have a significant impact on the Soret effect. If the properties of the fluid components are identical except for the adsorption preference for the membrane, there will still be a Soret effect caused by this preference. The membrane strengthens/reduces the Soret effect if the lighter/heavier component adsorbs more strongly on the membrane. In other words, the separation efficiency increases if the lighter component is more strongly attracted to the membrane. The combined effects of thermodiffusion and thermo-osmosis in nanoporous membranes can be used for simultaneous generation of separation and pressure differences, using temperature gradients as the only driving force.

Acknowledgements

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Optothermally-Induced Deformations in Soft Solids

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Introduction

The development of new non-invasive techniques for weakly perturbing soft materials is a fundamental requirement in characterizing their rheological and mechanical properties. In this work, we present a novel technique based on an optothermal approach capable of exerting localized strains in soft solids as a consequence of an inhomogeneous temperature profile induced by a weakly absorbed near-IfraRed laser beam.

Setup and Materials

The experimental apparatus combines a 90° Photon Correlation Imaging (PCI) [1] along with a thermal lensing setup where a pump IR (λ =980nm, weakly absorbed by water) gaussian laser beam, allows for slightly heating the sample in a localized and controllable fashion. Responses from the materials are therefore detected both by capturing images of the intensity scattered by a λ =532nm probe laser beam and by observing the self-induced lensing effect on the IR beam.

The work considers both the case of a reversible, thermoresponsive physical gel of biomedical and technological interest (Mebiol®), and the case of a weak and non-thermoresponsive chemical gel made by irreversible aggregation of polystyrene colloidal particles.

The thermoresponsive gel ultimately consists of a block copolymer composed of poly(N-isopropylacrylamide) (pNI-PAAM, a thermosensitive moiety, phase separating at high T) and polyethylene glycol (PEG) blocks; PEG being hydrophilic hinders the phase separation resulting in a transparent, reversible gelling polymer whose properties are easily tuned by temperature [2].



Figure 1: Transmitted IR intensity pattern across a gelling $(9\% \text{ w/v}, T=30^{\circ}\text{C})$ Mebiol® sample, taken at different times. Image (a) is taken after 1 minute since turning on IR, image (b) after 10 minutes, while image (c) is taken after 60 minutes of IR exposure.



Figure 2: Size of the transmitted IR pattern as a function of time for different temperatures of a thermosensitive Mebiol® gel.

Results

By studying the thermoresponsive gel (where crosslinks are transient, and thus a spontaneous dynamics is exhibited), we were able to induce a localized thermally-driven mass flux taking place on unexpectedly long time-scales, resulting in a long-lasting deformation pattern. This is clearly seen by observing the self-defocusing effect by the IR laser beam as it travels through the sample. While the temperature profile builds up in the order of a second, the defocusing effect develops on orders-of-magnitude-longer timescales (see figure 1). Being the sample thermoresponsive, the magnitude of such effect is strongly affected by temperature (figure 2). By observing the lensing effect, refractive index variations within the sample can be reconstructed, and different timescales allow for easily separating the effects of 'pure thermal lensing' from those due to heat-induced mass-flow.

Most remarkably, such deformations are only partially recovered, on timescales even larger than the ones required to induce them. This paves the way for on-demand printing a longlasting stress pattern into thermoresponsive soft solids.

We then show how, also in the weak non-thermoresponsive sample, we are able to induce strains as a consequence of localized optothermal heating. Local heating results in a displacement pattern which can be observed and quantified by performing a velocimetry analysis (see figure 3), where opposite-directed deformation patterns arise when the sample is heated and cooled back. Strains are thus partially recovered by removing the temperature gradient, highlighting an elastic behavior; the difference in magnitude between the strain build-up and recovery processes, allow for quantifying



Figure 3: Displacement field induced on a non-termosensitive polystyrene gel by a localized IR heating. Laser path is along the horizontal direction. Displacement fields are reconstructed through speckle image velocimetry and color-mapped based on the orentation of local displacement field. (a) refers to the effect of IR laser being turned on, (b) refers to the same sample when the laser is turned off.

unrecovered strains. The extent of such elastic regime as well as the role of 'plastic' strains is shown to depend upon the magnitude and time scales of the applied thermal stress.

Deformation of such non-thermoresponsive soft gel can be ascribed to convective flows arising within the surrounding water. This translates into a dependence of strains from water's thermal expansivity, with deformations becoming weaker and weaker as temperature is decreased (see figure 4), allowing for a fine tuning of the optothermally induced strains. This allows for mechanically stressing in a locally-controlled and reversible fashion (without breaking or permanently damaging the sample) a material so soft it can barely stand its own weight.



Figure 4: Displacement magnitude (arbitrary units) observed while optothermally straining polystyrene gel at different temperatures (°C). On x-axis the first derivative of water density with respect to temperature is reported.

Conclusions

We present a non-invasive method for testing mechanical properties of very soft materials by exploiting weak heating arising from localized electromagnetic radiation absorption.

We show how this allows for stressing in a measurable yet nondamaging fashion weak samples, as well as for encoding complex semi-permanent stress patterns upon more advanced thermosensitive gels.

The same optothermal excitation method is exploited on the COLIS setup, an advanced light-scattering apparatus recently uploaded onboard the International Space Station to investigate soft matter [3]. On the ground, preliminary experiments with pulsating NIR excitation showed that the dynamics of thermoresponsive glassy samples can be significantly accelerated through swelling-deswelling cycles, paving the way for investigating the yielding transition in an original driving mode, complementary to the extensively studied mechanical shear.

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Transport by diffusion gradient

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Introduction

Thermodiffusion happens in the presence of temperature gradient. The temperature gradient creates a diffusion gradient resulting in broken isotropy of space which gives rise to transport. However, existence of diffusion gradient does not necessarily need existence of a temperature gradient. Diffusion gradients can exist near interfaces even in constant temperatures. I would present some consequences of diffusion gradients at constant temperature on transport of single Brownian particle.

Section 1

The Langevin dynamics of single Brownian particle at viscous limit in presence of diffusion gradient is an Itô process. The Itô process is consistent with fluctuation dissipation theorem. Fluctuation dissipation theorem ensures fast local relaxation of the heat-bath resulting in existence of a mesoscopic local time-scale for the relaxation of a Brownian particle. This scenario allows existence of coordinate dependence of diffusion near interfaces.

The broken homogeneity of space in presence of diffusion gradients gives rise to existence of diffusivity dependent density of state resulting in additional entropy. This is an interesting entropy which increases near interfaces or constricted regions where interfaces are nearby. The effect of existence of this entropy is additional transport over space which can drive particles along diffusion gradients. Moreover, such circumstances can result in uniformly moving steady states of structurally symmetry broken small systems in a thermal environment. I would present these results in my talk.

Conclusions

Results I like to present in this talk are counter-intuitive, in a line not much explored so far, however, perfectly consistent physical consequences based on Langevin dynamics in thermal environment.

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Oral Communications Day 3

Transport properties of toluene-methanol-cyclohexane ternary mixture obtained in DCMIX space experiment

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Introduction

The separation of mixtures driven by a temperature gradient, known as thermodiffusion or the Soret effect, is a second-order phenomenon with relatively small magnitude in ordinary liquid mixtures. However, it has practical applications in cases where conventional separation techniques are inefficient, such as isotope separation. Additionally, it plays a significant role in large-scale, long-duration geophysical processes by influencing species distribution. These aspects contribute to the ongoing interest in thermodiffusion and motivate the extension of studies from binary solutions to more realistic multicomponent mixtures (Köhler et al., 2015). The study of multicomponent mixtures adds complexity but provides a better representation of real-world technological and natural systems.

This is exactly the case for the ternary mixture of toluenemethanol-cyclohexane (Tol-Meth-Ch), where two latter components form the couple with a large miscibility gap, while the former one facilitates mixing between them. There exist some scarce studies revealing an anomalous behaviour of both diffusion and thermodiffusion near demixing zone (Giglio et al., 1975), thus the use of the easily accessible and relatively well characterized Tol-Meth-Ch mixture for extending the studies was a natural option.

However, the extension of thermodiffusion measurements from binary to ternary mixtures is not so simple. The presence of two characteristic diffusion times and different possible separation signs make ternary mixtures easily susceptible to gravitational instabilities that develop even in the lowprofile Soret cells that can ensure the stability of binary mixtures. To overcome this problem, the DCMIX (Diffusion Coefficients Measurement In ternary miXtures) experiment was implemented on the International Space Station (ISS) by the European Space Agency (ESA), in collaboration with the Canadian Space Agency and Roskosmos. Taking advantage of the modular design of the Selectable Optical Diagnostics Instrument (SODI) specifically developed for this experiment, the DCMIX experiment evolved in several campaigns, each dedicated to the measurement of a particular ternary mixture. Each campaign required the replacement of the instrument's single module, the cell array, which typically contained five cells with ternary mixtures and one companion cell with the reference binary mixture, allowing a total of six different state points of a selected ternary system to be evaluated. The Tol-Meth-Ch was the target of the second campaign. DCMIX-2. and due to its partial success, three state points of the mixture were also investigated in the fourth campaign, DCMIX-4.

Experiment

The diagnostic chosen in SODI for the detection and resolution of two independent concentrations is two-color (2wavelength) interferometry. A typical experimental cell has been designed as a Soret cell (see Fig.1a for the core part of the cell), which allows the observation of the compositional separation of the mixture evolving in response to the thermal gradient applied between two metallic caps. The instrument is suitable for continuous *in situ* monitoring of the concentration evolution in the volume of the cell and is able to provide both the non-isothermal mass transport (thermodiffusion) coefficients according to the steady-state separation magnitude and the isothermal mass transport (diffusion) properties following the kinetics of the process.

More details on the hardware, typical experimental schedule, and data extraction approaches and algorithms can be found elsewhere (Mialdun et al., 2018).



Figure 1: Soret cell of DCMIX experiment. (a) Scheme of the core part of the cell with glass frame and expansion compensation volume. (b) Result of the compatibility test with demixing and vapor bubble formation.

It is worth noting that the ground preparation for the campaign, which led to the selection of particular state points for the space experiment, included several important independent studies:

• Measurement of the optical properties of the mixture in the full concentration range to define the regions with better resolvability of two independent concentrations by the wavelengths selected for SODI (Sechenvh et al., 2012).

- Assessment of the regions of gravitationally unstable separation, where the mixture can certainly not be measured on the ground (Shevtsova et al., 2014).
- Compatibility of mixtures and individual solvents with seals (Santos et al., 2016).

In the latter study it was found that the ability of long-term storage of cells filled with liquid samples, indispensable in the preparation of space experiments, is compromised by the permeation of solvents through the designed rubber seals. With the small working volume of the liquid sample, the escape of even a small percentage of the mixture can result in a dramatic change of the liquid state inside the cell (see for example Fig.1b), which blocks the ability to measure the transport properties. It has also been found that permeation is not uniform, with one solvent permeating more easily than another, making the expected concentration shift of the liquid sample with time difficult to predict. Despite some measures taken in the last steps of the DCMIX-2 experiment preparation, the concentration shift developed during the campaign. It forced a modification of the cell array design for subsequent campaigns by changing the material of the seals to a more resistant one. Moreover, this problem inspired the decision to repeat experiments with three state points of Tol-Meth-Ch mixture in the DCMIX-4 campaign.

Results

Analysis of the results of the DCMIX-2 experiment explicitly confirmed the presence of the concentration shift, as shown in the left panel of Fig.2. Both the kinetics and the steady-state separation in the same cell are significantly different with time passed. At the same time, the repeatability of the separation in the DCMIX-4 experiment is excellent, demonstrating the absence of solvent permeation and the resulting concentration shift.



Figure 2: Comparison of separation curves in DCMIX-2 and DCMIX-4 experiments, obtained by repeating the experiments in the same cell, with a time interval of one month between the repetitions.

The fact of concentration drift in the DCMIX-2 experiment poses an interesting challenge: the possibility of attributing the measured mixture to a particular state point in concentration space on the basis of determined transport properties. We try to address this challenge in this work. Apart from this interesting, albeit side study, we have estimated the separation and diffusion kinetics along the isoconcentration line of cyclohexane $w_{ch} = 0.40 \text{ mass}$ fraction, and the iso-concentration line of methanol, $w_{meth} = 0.25 \text{ mass}$ fraction, as the miscibility gap is approached. These results clearly support the basic hypothesis by demonstrating a substantial increase in separation as the miscibility gap is approached, accompanied by a decrease in the magnitude of the minor eigenvalue of the diffusion matrix near the demixing zone.

Conclusions

The results of the DCMIX space experiment improved the understanding of mass transport behavior in such strongly nonideal systems as toluene-methanol-cyclohexane. These findings facilitated the formulation of conclusions regarding the specificity of transport properties behavior in states close to the miscibility gap, including the slowing down of diffusion kinetics and the divergence of Soret separation.

Acknowledgements

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Thermodiffusion of the ternary system polystyrene + toluene + cyclohexane

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Introduction

Experiments on semidilute and concentrated polymer solutions with temperature gradients are scarce and polymer thermodiffusion, in particular at finite concentrations, has remained an intriguing and controversial problem that touches very fundamental questions of polymer dynamics. While collective diffusion is sped up in the semidilute regime, as predicted by the blob model, thermodiffusion is not affected by chain overlap and entanglements and the Soret effect is not sensitive to the glass transition at high polymer concentrations.

So far, thermodiffusion research on polymers has been concerned mainly with binary systems, i.e., a polymer dissolved in a pure solvent. Only few works on ternary systems exist with a dilute polymer in a mixed solvent. Here, we report on experiments on polystyrene (PS) in the mixed solvent toluene (Tol) + cyclohexane (cHex) over the entire composition range of the solvent and for polymer concentrations up to $c_1 = 0.1$ mass fractions. We circumvent the contrast factor matrix inversion problem by resorting to reasonable a priori assumptions about the directions of the eigenvectors of the diffusion matrix following a procedure developed in a previous publication (Sommermann et al., 2022) and reported at IMT15.

Experimental

PS with molar masses of $M_w = 4.88$ kg/mol and $M_w = 17.90$ kg/mol was dissolved in mixtures of Tol and cHex. Measurements were performed by means of multi-color optical beam deflection (OBD) in a Soret cell of h = 1.2 mm height. The thermal and solutal optical contrast factors were measured interferometrically and refractometrically, respectively.

1 Results

Fast and slow mode Due to the poor condition number, the usual two-color data evaluation technique based on the inversion of the solutal contrast factor matrix results in an unfavorably large error amplification. In order to circumvent this problem, we have resorted to a reasonable assumption about the direction of the diffusion eigenvectors demonstrated in Ref. (Sommermann et al., 2022) for the limit of dilute polymer solutions. In this work, we extend the model towards higher polymer concentrations up to the semidilute regime. The OBD signals are characterized by a fast and a slow mode (Fig. 1). We attribute the former to the solvent-solvent interdiffusion and the latter to the diffusion of the polymer with respect to the solvent at fixed solvent composition.



Figure 1: Solutal contribution to the normalized OBD signal for a symmetric solvent with equal mass fractions of Tol and cHex for different polymer concentrations c_1 . The fast mode with a negative amplitude and the slow mode with a positive amplitude are clearly discernible. From Ref. (Sommermann et al., 2023).



Figure 2: Left: amplitude M_{12} of the slow mode as a function of PS concentration c_1 for different solvent compositions Tol:cHex. Right: amplitude M_11 of the fast mode as a function of the Tol concentration c_2 for different polymer concentrations c_1 . From Ref. (Sommermann et al., 2023).

Fig. 2 (left) shows that the amplitude of the slow mode increases with increasing polymer concentration. The increase becomes steeper for higher cHex content of the solvent. This reflects the poorer solvent quality of the theta solvent cHex in comparison to the good solvent Tol. A higher cHex content brings the sample closer to the critical point, where the Soret coefficient is known to diverge. In agreement with our assign-

ment of the fast mode, its amplitude in Fig. 2 (right) vanishes in the two limits of vanishing concentration of either one of the two solvents. The maximum is reached for approximately symmetric solvent compositions, as expected from the c(1-c)term in the thermodiffusion equation of a binary mixture. In contrast to the slow mode, the amplitude of the fast mode is almost independent of polymer concentration.

Signs of the transport coefficients A detailed analysis of the amplitudes in combination with the optical contrast factors reveals positive Soret and thermodiffusion coefficients for the polymer PS and negative ones for Tol. An intriguing situation arises for the solvent cHex. Immediately after the application of a temperature gradient to the homogeneous mixture, cHex migrates to the cold side during the fast mode. Then, when the slow mode sets in, cHex reverses its migration direction and now migrates towards the warm side. This leads to a positive thermodiffusion coefficient but a negative Soret coefficient of cHex. Different signs of Soret and thermodiffusion coefficients have also been reported for the DCMIX2-system toluene/methanol/cyclohexane (Berin et al., 2023). They are a consequence of cross diffusion terms in the thermodiffusion equation and can only be observed in ternary (or higher) mixtures, but not in binaries.

Universal thermophoretic velocity The assignment of the slow mode to the (thermo)diffusion of the polymer with respect to the mixed solvent of constant composition suggests a comparison with other properties of binary polymer solutions.



Figure 3: Thermodiffusion coefficient of PS during the slow mode (left). Scaled with the viscosity of the mixed solvent (right). From Ref. (Sommermann et al., 2023).

A remarkable observation is the universality of the thermophoretic velocity of polymers with sufficiently large Kuhn segments, which depends only on the solvent viscosity and, of course, the temperature gradient. When multiplied with the solvent viscosity η , the frictional contribution is scaled out and the product ηD_T assumes the universal value $\eta D_T \approx$ $6 \times 10^{-15} \text{ m}^2 \text{K}^{-1}$ Pa (Stadelmaier et al., 2009). Fig. 3 shows that the identical universal value is observed for PS in the mixed solvent, independent of its Tol:cHex-composition.

2 Conclusion

We have investigated thermodiffusion in a ternary system consisting of a polymer in a mixed solvent. The solvent composition was varied over the entire composition range and the polymer concentration was up to $c_1 = 0.1$. We have found that it is possible to avoid the difficult and error-prone inversion of the optical contrast factor matrix by reasonable assumptions about the directions of the diffusion eigenvectors in the ternary composition space.

The thermodiffusion dynamics shows bimodal time dependence with two distinct modes. A consistent picture is obtained for the system PS/Tol/cHex by attributing the slow mode to the polymer diffusion with respect to the mixed solvent and the fast mode to the interdiffusion of the two solvents. Remarkable features of polymer thermodiffusion, such as the universal thermophoretic velocity, are recovered in the ternary mixture. Even the surprising observation of different signs of the thermodiffusion and the Soret coefficient of one of the solvents finds a natural interpretation by cross diffusion combined with the time scale separation of the diffusion eigenmodes. The method should be applicable to other polymeric systems and also to colloids in mixed solvents. Whether it is still applicable to, e.g., strongly polar and hydrogen bonding systems with very asymmetric interactions between the species is a priori not clear and requires further investigations.

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Experimental analysis of absorption mechanisms in LiBr-H₂O solution

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Introduction

The exploitation of renewable energy in heating and cooling production has a key role in emissions reduction, and absorption technology could play a crucial role (R. Nikbakhti et al. 2020). However, even today, main applications require increased capabilities, opening up avenues of research in terms of improved heat and mass transfer (S. Sehgal et al. 2021). The absorber is the most critical component of any absorption systems (J. D. Killion et al. 2003), and the performance is critically dependent upon the thermodynamic properties of the working liquid-pair (J. Sun et al. 2012), known as refrigerant (the one which changes phase) and the absorbent (Perez-Blanco 1984). During absorption process, temperature, concentration and surface tension gradients are induced, therefore the Soret and Marangoni effects are present in the process (P. F. Arroiabe et al. 2019). Many studies have been conducted to understand and improve the absorption process between the vapor refrigerant and the solution, in order to intensify the heat and mass transfer. Three main approaches are used (C. Amaris et al. 2014): i) Improve the wetting area between the absorber surface and the solution. ii) Add surfactants to decrease the surface tension of the mixture, where heat and mass transfer is increased by the Marangoni convection (F. Ziegler et al. 1996), and iii) Nanoparticles can be added to increase the thermal conductivity and therefore the heat and mass transfer (Y. T. Kang et al. 2008). This study examines experimentally the absorption performance of LiBr-H₂O solution, considering the mixture itself and the effects of n-Octanol surfactant and nanoparticles (W. Jiang et al. 2022; C. W. Park et al. 2004), addressing gaps in the understanding of underlying transport mechanisms. Convective instabilities in LiBr-H $_2O$ mixture have been investigated by numerical simulations (P. F. Arroiabe et al. 2024a, 2024b), but there is a lack of experimental validation. Therefore, an experimental setup has been developed, including an absorption cell, an evaporator and a vacuum pump, and Optical Digital Interferometry technique is used to track both heat and mass transfer within the absorber mixture (A. Mialdun et al. 2008). Therefore, this research provides insights into additive-induced transport phenomena, advancing performance of LiBr-H₂O absorption technology.

Experimental setup

The experimental setup (Figure 1) consists of two main parts, the evaporator-absorber system and the interferometer. The setup consists of four elements: the vapor generator, absorption cell, vacuum pump, and data acquisition system, all connected via stainless-steel tubes and valves. The steam generator, a 25-liter aluminum vessel, is heated by an external thermostatic bath, where pressure is controlled by a WIKA S-11 vacuum sensor and temperature by two T thermocouples. The absorption cell, where the LiBr-H₂O mixture absorbs water vapor, is the system's core. It is designed with a 70 mm wide, 20 mm deep, and 20 mm high volume. The stainlesssteel structure has a central cavity, with sapphire windows at the front and back to visualize the process. The system is sealed with O-rings and pressure is measured with a WIKA S-11 sensor. Eleven thermocouples are also inserted through a feed-through to monitor the mixture. The optical system consists of a single-laser Mach-Zehnder interferometer. It uses a polarized He-Ne red laser (632.8 nm) with a spatial filter and collimating lens to expand the beam. A mirror deflects the beam 90° before entering the interferometer, where a beam



Figure 1: Evaporator-absorber experimental setup, with optical digital interferometry used to track absorption process.

splitter divides it into reference and test beams. The test beam passes through the cell, placed on top of a cold plate. After recombination, the interference pattern is captured by a Manta G-505B CCD camera. To start running an experiment, the evaporator is filled with double-distilled water and stabilized at the target temperature. The system is then evacuated with a vacuum pump, reducing the evaporator pressure to near the water's saturation pressure, while the cell pressure remains slightly lower. Image acquisition starts at a frequency adjusted based on the mixture's properties. The vacuum is then used to fill the cell by opening a bottom valve until the liquid reaches a height of 10 mm, after which the valve is closed to prevent further vapor absorption. Equilibration of the system is considered once the interferogram fringes align vertically, perpendicular to the interface. Finally, the evaporator and cell are connected by opening the valves, and the vacuum pump is isolated.

Results

In all the tests, the LiBr-H₂O mixture used for the experiments contained 0.55 mass fraction of LiBr (Merck Millipore REF: 213225). As surfactant, n-Octanol (Merck Millipore, REF: 8.20931) between 0-150 ppm was used. Figure 2 compares the results obtained in an experiment with and without surfactant under close experimental conditions after six minutes of experiment. From top to bottom the figures shows the interference pattern, the wrapped phase map and the vertical profiles of the refractive index in liquid. In the case of the experiment without surfactant, temperature and pressure of the evaporator were $T_{evap} = 9.58^{\circ} C$ and $P_{evap} = 1.55 \ kPa$, and in the cell were $T_{cell} = 28.7^{\circ} C$ and $P_{cell} = 0.6 \ kPa$. In the case of



Figure 2: Top to bottom: interference patterns, wrapped optical phase maps, and vertical profiles of the refractive index in liquid. Case without surfactant (left) and with surfactant (right).

surfactant, however, temperature and pressure of the evaporator were $T_{evap} = 9.53^{\circ} C$ and $P_{evap} = 1.65 kPa$, and in the cell were $T_{cell} = 25.4^{\circ} C$ and $P_{cell} = 0.47 kPa$.

Experiments without surfactant show stable stratification, almost homogeneous liquid volume far from the interface, and strong, optically unresolvable gradient in close proximity to the interface. On the other hand, the experiment with surfactant shows strong convective flow, therefore mixing of the sample and highly inhomogeneous liquid bulk.

Conclusions

We have experimentally examined the absorption dynamics in the LiBr-H₂O binary mixture without and with the addition of n-Octanol surfactant. Uniform absorption was observed for pure LiBr-H₂O mixture, where after contact with water vapour, a purely diffusive regime is observed. In the case of surfactant added mixture, Marangoni convection is initially emerged, followed by buoyant convection. The findings highlight that Marangoni convection induced by additives enhances mixing, thereby improving the overall absorption process. The advantage of the optical diagnostics for identification and characterization of convective/diffusive mass transfer regimes in absorption system is effectively demonstrated.

Acknowledgements

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Inversion of the thermodiffusive properties of nanoparticles in mixtures of ionic liquid and water

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Introduction

The thermodiffusion of nanoparticles (NPs) dispersed in a liquid has been shown to depend on the composition of the interface between NPs and solvent, for example playing on the nature of the counterions that compensate the charge of the NPs (Lopes Filomeno et al, 2017) or playing on the solvent keeping the same counterions (Sarkar et al, 2019). In the present study, the solvent is varied from water to pure ionic liquid, thus from a dilute electrolyte to pure salt (Fiuza et al, 2024). The Soret coefficient is measured on the whole range of composition as a function of temperature.

Samples

The nanoparticles of iron oxide of diameter 6.9 nm are coated with sodium citrate ligands and dispersed in water at neutral pH. Their negative surface charge is thus compensated by sodium counterions. Water can be exchanged by the ionic liquid, here ethylammnium nitrate (EAN), by adding EAN and pumping water. The mixtures are then produced by mixing the colloidal dispersion in water with the one in EAN, at the same volume fractions, here 1 vol% or 3 vol%. This system provides stable colloidal dispersions on the whole range of composition, i.e. whatever the salt concentration. This has been validated by Dynamic Light Scattering, that provides a diffusion coefficient, and Small Angle Neutron Scattering, that provides information on the interactions between the NPs. Interparticle repulsion is repulsive in pure and nearly pure solvents and changes to weakly attractive in the intermediate range of compositions.

Thermodiffusion measurements

Forced Rayleigh Scattering (FRS) measurements have been performed with a home made device previously described (Sarkar et al, 2019). In summary, the sample is sealed in a 25 microns thickness glass cell. The image of a grid of spatial wavelength of the order of 100 microns is focused in the sample. The solution is heated in the lighted stripes by the highpower white lamp and thanks to the high absorption of the NPs. The created temperature gradients. ∇T . and the Soret-induced concentration gradients, $\nabla \Phi$, are probed by the diffraction of a non-absorbing He-Ne laser beam. In the stationary state, the Soret coefficient S_T is defined by:

$$\overrightarrow{\nabla}\Phi = -\Phi S_T \overrightarrow{\nabla}T.$$
 (1)

The concentration and temperature gradients are separated thanks to the few Hz modulation of the high power lamp because in our case the temperature gradient relaxes 10^3 quicker than the concentration gradient.



Figure 1: Soret coefficient determined for the colloidal dispersions at 1vol% as a function of the weight fraction w_{EAN} in the mixtures water/EAN at different temperatures.

The Soret coefficient S_T obtained for the samples at 1vol% of nanoparticles and at various temperatures, is shown in Figure 1 as a function of the weight fraction $w_{\rm EAN}$ of EAN in the mixtures. S_T is negative in water. It first increases towards zero while adding EAN and then becomes positive. At room T this sign reversal occurs at $w_{\rm EAN}$ ranging between 0.03 and 0.2. The same evolution occurs for all temperatures between room temperature and 80°C. However a clear sign inversion of $\Delta S_T/\Delta T$ is observed around $w_{\rm EAN} \sim 0.55 \pm 0.15$ whatever T and Φ . This quantity $\Delta S_T/\Delta T$ has been shown to be correlated to the hydrophilicity/ hydrophobicity of the solute, looking at proteins in water (Niether et al. 2018). Therefore the surface of the NPs is hydrophilic below $w_{\rm EAN}\sim 0.55$, where $\Delta S_{\rm T}/\Delta T>0$, and hydrophobic above $w_{\rm EAN}\sim 0.55$, where $\Delta S_{\rm T}/\Delta T<0.$

Conclusions

These results are associated to the change of the nature of the NPs' counterions and to the change of the solvent organization at the NP/ solvent interface. The pure EAN/water mixtures are heterogeneous (Hayes et al, 2011) due to the alkyl chains of the cations that tend to associate and evolve from EAN islands in water to water islands in EAN as $w_{\rm EAN}$ increases. The transition is around $w_{\rm EAN} \sim 0.55$. The solid interface of NPs in the mixtures follows this evolution thus moving from hydrophilic in water to hydrophobic in EAN.

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Effects of membrane porous structure on the performance of non-isothermal separation process

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Introduction

Advancements in water treatment technologies play a crucial role in addressing water scarcity, a persistent global challenge. Among these technologies, membrane distillation (MD) has gained special attention as an emerging nonisothermal process due to its eco-friendly nature and ability to treat highly saline water. MD operates under a temperature gradient across a porous hydrophobic membrane, inducing a water vapor pressure difference that drives the separation process (Khayet and Matsuura 2011). Most of the membranes are polymeric prepared by the nonsolvent-induced phase separation (NIPS) technique. Both flat-sheet and hollow fiber membrane configurations can be prepared by NIPS technique (García-Fernández et al. 2024). If highly porous membranes are required, electrospun nanofibrous polymeric membranes are preferred since the porosity (i.e., void volume fraction) can achieve values higher than 90% resulting in high permeate flux and thermal efficiency (i.e, very low heat transfer by conduction through this type of membranes). In general, membranes with different morphological structures can be prepared to maximize the MD performance (L. García-Fernández et al., 2015). However, conventional membrane fabrication often involves toxic solvents, raising environmental concerns due to solvent wastewater containing and air pollution, especially during the formation of hollow fiber membranes. To overcome this issue, researchers are actively looking for sustainable alternatives, such as the use of green solvents and nonsolvents in membrane engineering (Wang et al. 2019, Prat et al. 2016).

In this study, polymeric flat-sheet, hollow fiber and electrospun nanofibrous membranes were prepared using environmentally friendly solvents for desalination by MD.

Experimental methodology

The copolymer poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP) was dissolved in different green solvents including Triethyl phosphate (TEP), Dimethyl sulfoxide (DMSO), Ethyl acetate (ETAC) or Acetone and their mixtures. The prepared homogenous thermodynamics of the phase inversion process were analyzed. The obtained results allow to predict the resultant membrane morphological structure. The flat-sheet membranes were prepared via NIPS using a casting machine. The effect of the solvent type on the membrane characteristics was studied. The best mixed solvent was chosen to prepare hollow fiber membranes via NIPS using dry/wet or wet/wet spinning methodologies. In this case, different green aqueous mixtures were employed as coagulants (water and 40 wt% tetraethylenglycol (TetraEt40)). The coagulant power effect of this weak and viscous coagulant on the membrane surface morphology was studied. In order to enhance the membrane porosity, nanofibrous membranes were prepared using electrospinning and a polymeric solution prepared with a solvent mixture containing a highly volatile green solvent. Finally, all prepared membranes were characterized by different techniques and applied in desalination by MD.

Results and discussion

Flat-sheet membranes

Different flat-sheet membranes were prepared via NIPS using DMSO (100 wt%), DMSO/TEP and DMSO/ETAC (60/40 wt%) as solvents, and water as nonsolvent. Scanning Electron Microscopy (SEM) images of the membrane cross-sections are shown in Fig. 1. It was observed that the use of mixed solvents induced the formation of more spongy structures (Fig. 1b and c) due to slower phase inversion processes. The membrane prepared with DMSO/TEP as solvent mixture exhibited the best MD performance.


Hollow fiber membranes

Green hollow fiber membranes were prepared via wet/wet spinning technique using DMSO/TEP as mixed solvent and different both internal and external coagulants. The viscous coagulant (TetraEt40) slightly reduced the membrane thickness and increased the surface porosity (Fig. 2). This nonsolvent effect on the membrane structure resulted in an improvement of the MD permeate flux and separation factor.



Fig. 2. SEM images of the cross-section morphology and the inner and outer surfaces of the hollow fiber membranes prepared with different coagulants: a) water and b) TetraEt40.

Electrospun nanofibrous membranes

The preparation of green electrospun nanofibrous membranes for MD applications represents a novel membrane engineering research line. This fabrication technique requires that one of the green solvents of the mixture exhibits a high degree of volatility. Therefore, DMSO was mixed with ETAC or Acetone (60/40 wt%) for preparing the electrospinning membranes. The use of acetone in the solvent mixture induced the formation of rougher fibers (Fig. 3), which could act as micro-turbulence promoters. Compared with the membranes prepared via NIPS, the nanofibrous membranes exhibited significantly higher MD permeate fluxes due to the high intrinsic porosity of these structures. However, the mechanical properties and wettability of these membranes must be improved in order to use them for long-term applications without compromising the MD separation factor.



Fig. 3. SEM surface images of the electrospun nanofibrous membranes prepared with different solvent mixtures: a) DMSO/Acetone and b) DMSO/ETAC.

Conclusions

Both green flat-sheet and hollow fiber polymeric membranes were successfully prepared by the NIPS technique. These membranes exhibited suitable properties for MD desalination. Electrospun nanofibrous membranes prepared with green solvents also showed promising results for this application. However, further research is needed to perform successful long-term desalination experiments with these highly porous membrane structures. The adopted green methodologies proved to be suitable for MD membranes preparation.

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Anomalous behaviour in out-of-equilibrium supercritical CO₂

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Introduction

The supercritical state is defined as the (p-T)-region beyond the critical plait point where thermophysical properties at equilibrium vary continuously. Thus, no clear distinction between a gas and a liquid occurs around this region. However, recent studies have shown that there is a specific (p,T)-region, starting from the critical plait point, where the response function of thermophysical properties is maximum (Gallo et al., 2014) and shows a critical enhancement (Giraudet et al., 2016). The (p,T)-line forming the Widom line represents the transition from a gas-like to a liquid-like behavior demarked by notable changes in the network-like structure at the molecular scale (Simeoni et al., 2010). Notably, in this region, a small perturbation of the equilibrium state induced by a temperature gradient implies a huge density gradient, and thus, the emergence of large-intensity nonequilibrium fluctuations (NEFs).

NEFs can be used as a probing tool for the simultaneous determination of several thermophysical properties (Croccolo et al., 2012; Wu et al., 2020) as well as the effect of confinement (Giraudet et al., 2015) and propagating waves (Croccolo et al., 2019). A deep analysis of the behavior of NEFs across the Widom line could provide useful information about the determination of gas-like and liquid-like phases.

In the present work, we investigate the behavior of pure CO_2 stressed by various thermal gradients both around and far from the Widom line, inducing symmetric and asymmetric density gradients (cf. Figure 1).

Materials

A shadowgraph apparatus is used to record series of images related to the density fluctuations within the system. The optical setup consists of a superluminescent diode and a lens providing a collimated quasi-monochromatic beam at a wavelength of 670 ± 10 nm, and a s-CMOS camera. The sample is maintained in a cell in which pressure is controlled at various values up to 20 MPa. More than 20 thermal gradients are applied by two Peltier modules regulated by a control module. For further information on the setup and sample cell, see Ref. (Giraudet et al., 2014). All measurements were repeated several times using different acquisition frequencies to provide optimal accuracy.



Figure 1: Density map of pure CO₂ around the critical plait point ($T_c = 304.21$ K, $p_c = 7.37$ MPa, $\rho_c = 469.03$ kg·m⁻³). The boiling line (continuous dark line) and the critical isochore assimilated to the Widom line (Fomin et al., 2015) near the critical plait point (dotted line) are represented. Various temperature differences applied to the 5 mm thick sample of pure CO₂ and the corresponding density differences are displayed by the lines terminated by open circles (symmetric density gradient) and open squares (asymmetric density gradient).

Analysis and discussion

Using a differential dynamic algorithm implemented in custom software (Cerchiari et al., 2012; Norouzisadeh et al., 2021), we determined the structure functions (SFs) of the density fluctuations characterizing their evolution both in space (the reciprocal Fourier space) and time. In Figure 2, various temporal SFs at various wave number and for two thermodynamic experimental conditions are reported.

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When the fluid temperatures are set far from the Widom region (top), all SFs can be described by a single exponential growth, combined with a single oscillation Brunt–Väisälä frequency typical of propagating waves already observed in literature (Croccolo et al. 2019; Carpineti et al. 2021). The single oscillation can be reconducted to the presence of a pure liquid in a single phase. In contrast, when the temperatures cross the critical isochore (bottom), we observe the sum of

two exponential growths with two interfering oscillations corresponding to two propagating waves at different Brunt– Väisälä frequencies. The presence of two distinct Brunt– Väisälä frequencies denotes two derivatives of the density gradient over the vertical axis, and therefore two quasi-phases in the sample.

The non-equilibrium condition provided by the temperature gradient and the presence of gravity, makes the fluid stratified according to its density. Thus, we can assimilate the fluid to a two-quasi-phase system with distinct diffusivities and compressibilities that can be derived from the dynamics of NEFs and the density derivative can be obtained from the oscillation frequency of the propagating modes. We discuss both the characterization of the continuous transition between the two assimilated phases and the influence of the thermodynamic parameters of the system on the fluid properties.

This study has a fundamental interest in a better understanding of the thermodynamics of supercritical fluids in non-equilibrium conditions. Besides this, this study hasindustrial implcations, notably in the storage of CO_2 in geological sites. Further studies will be performed in the future by means of molecular dynamic smulations to confirm this behavior from a microscale point of view.



Figure 2: Normalized autocorrelation functions of density NEFs for several wavenumbers when 1 (top: p = 15 MPa, T = 313.15 K, $\Delta T = 44$ K, $\Delta \rho = 330.59$ kg.m⁻³) or 2 (bottom: p = 7.4 MPa, T = 304.25 K, $\Delta T = 2$ K, $\Delta \rho = 331.49$ kg.m⁻³) quasi-phases are detected.

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Oral Communications Day 4

Thermodiffusion in liquid Ag₆₀Cu₄₀

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Introduction

Thermodiffusion in liquid alloys influences the homogeneity of doped semiconductors and grown crystals as well as the microstructure formation during solidification. The calculation of thermodiffusion by molecular dynamic simulation can be very sensitive to the specific potential (Levchenko et al. 2016). There exist several theoretical models attempting to predict binary thermodiffusion, but there is still no comprehensive model able to predict the Soret coefficient for a wider range of systems, as recently shown by (Hoang et al. 2022).

Copper and silver are used together with tin in ternary Sn–Ag–Cu (SAC) alloys for soldering, in efforts to replace the toxic lead based solders. The thermodiffusion in liquid Ag–Cu was modeled by Sarder et al. (Sarder et al. 2019), using molecular dynamics (MD) simulations. They found silver to migrate to the cold side, with a Soret coefficient of $1.8 \times 10^{-3} \text{ K}^{-1}$ for liquid Ag_{62.5}Cu_{37.5} at a temperature of 1100 K.

It is the goal of this work to measure the Soret effect in liquid $Ag_{60}Cu_{40}$ using a specialized shear cell furnace, and compare the measured value with the results from simulations.

Method

For binary alloys with sufficient contrast in x-ray absorption x-ray radiography can be used for in-situ measurement of thermodiffusion (Sondermann et al. 2019). This technique excludes disturbances by solidification and reveals possible error sources as e.g. free surfaces. For multicomponent alloys and alloys with insufficient contrast in x-ray absorption, a specialized shear cell furnace is used.

The setup for these measurements is very similar to the setup described in (Krüger et al. 2023). The samples have the form of a cylinder with 1.3 mm in diameter and 10 mm in height. The crucible that holds the samples is made of boron-nitrite. It can be separated into six parts of 1.5 mm height each. The furnace is shown in Fig. 1. For the measurement it is surrounded by heat insulation and placed inside a vacuum chamber.

During an experiment, the Cu-Ag samples in the furnace are heated up to an average temperature of 1123 K. After annealing for more then four hours the liquid alloy is separated into six parts and then cooled down to room temperature. The solidified parts are subsequently removed from the crucible and analyzed by energy dispersive X-ray spectroscopy (EDS).



Figure 1: Furnace for measurements of thermodiffusion in liquid alloys. The white parts are made of boron-nitrite, while the metallic parts are made of high-melting niobium and tungsten.

Results and discussion

The annealing time was chosen taking into account the interdiffusion in liquid Cu-Ag measured previously and the length of the sample. The measured Soret coefficient for $Ag_{60}Cu_{40}$ suggests that silver is migrating to the cold side as it was also predicted by MD simulation. However, the measured effect is only slightly larger than the measurement uncertainty. If there is any thermodiffusion in liquid $Ag_{60}Cu_{40}$, it is at least on a much smaller order than other similar liquid alloys, like Ag–Al and Al–Cu.

Conclusions

For liquid Ag–Cu, only a barely significant migration of silver towards the cold side was observed. This is the same direction as found in earlier published MD simulations, although much weaker than the simulated results. From the comparison of other parameters of the simulations with earlier measurements on those parameters, it is argued that only a qualitative match in such a sensitive cross-effect as thermodiffusion can be expected.

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Impact of the Soret effect on the Marangoni convection in the absorption process

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Introduction

Absorption technology is attracting significant attention due to its potential for sustainable and energy-efficient heating and cooling. More broadly, gas absorption by fluids plays a critical role in a wide range of applications, including environmental control, chemical engineering, and space technology. In the ideal case, when the interface is flat and there are no temperature or concentration perturbations, absorption occurs through a diffusion process. In practice, however, small perturbations are always present, which alter the surface tension locally and cause thermal and solutal Marangoni convection (Arroiabe et al. 2024, 2025). In addition, the LiBr-water binary mixture exhibits a Soret effect. The Soret effect (also known as thermodiffusion) describes the formation of a composition gradient in a multicomponent mixture subjected to a temperature gradient. The Soret coefficient was recently measured in our laboratory and the results revealed that the Soret coefficient is negative.

There are several studies on Marangoni convection with Soret effect (Kim et al., 2004, Morozov et al., 2013). In the evaporation problem (Zhang et al., 2007), where both types of Marangoni convection are present, the solutal convection was driven by the Soret effect. It was reported that evaporation primarily influenced pattern formation in the early stages, while the Soret effect became more significant at later stages. These studies were focused on the onset of convection.

The focus of our study is on the absorption of vapor by the LiBr-water binary mixture, which is widely used in absorbers. Although LiBr dissociates in water, it is treated as a single component in this investigation. This approach is justified by considering the macroscopic motion of the LiBr solution as a whole, characterized by macroscopic quantities measured for this solution. Local equilibrium between the concentrations of ions with opposite electrical charges is maintained by the condition of zero macroscopic bulk charge density.

Problem formulation

During the absorption process, the water is absorbed from the gaseous medium in contact with the solution, while LiBr is neither consumed nor added to the solution. The binary LiBr-H2O mixture where the absorbent (LiBr) is non-volatile (vanishing vapor pressure). Denoting the mass fraction of LiBr by w, its diffusive flux will be written as

$$J_1 = -\rho(D\nabla w + D'_T \nabla T) \tag{1}$$

where D are the Fick diffusion coefficients and D'_T are the thermodiffusion coefficients (here $D'_{Ti} = w(1 - w)D_T$). The problem of absorption which is shown in Fig. 1 is described by the Navier–Stokes, heat, and mass transfer equation (Arroiabe et al. 2024, 2025). The temperature and concentration at the interface are continuously related by equilibrium conditions:

$$w_e(T, P_0) = w_{e0}^* + w_T^*(T - T_0)$$
⁽²⁾

where w_{e0}^* is the equilibrium concentration at the reference state, and $w_T^* = \partial w / \partial T$ is the linear concentration coefficient, both depending on pressure.



Figure 1: Sketch of diffusion/absorption process.

A small perturbation in absorption at the centre of the interface (as shown in Fig 1) disturbs the equilibrium, generating surface tension gradients that drive Marangoni flows. The surface tension of the the LiBr-water mixture depends on temperature and composition. The interplay of solutal, thermal, and buoyant convection in the presence of absorption is a rather complex problem, and the Soret effect adds further complexity. We can formulate a very general question - does the Soret effect make a significant impact on the Marangoni convection? The previous studies were aimed on the onset of convection.

Results

Initially, when the bulk solution is far from equilibrium, the absorption process occurs particularly rapidly and then slows down. This can be attributed to the fact that thermodynamic equilibrium is reached immediately at the interface during absorption. Then, the diffusion of LiBr from the interior of the solution to the interface occurs at a rate comparable to that of water vapor absorption. The composition perturbation is imposed 10 s after the absorption process commences, with an instantaneous and singular effect. Until quite late times, the flow is symmetric with respect to the cell center, and we consider below only half of the cavity. The flow pattern is rather complex and let us start from the temperature shown in Fig.2.

Figure 2 shows temperature change due to convection with (solid curves) and without (dashed curves) the Soret effect.



Figure 2: The vertical temperature distribution at different cell positions at t=40 s. Only the temperature change after introducing perturbation is shown, i.e., the ΔT produced by convection. The solid and dashed curves of the same color show ΔT with and without Soret effect.

The general trend up to $z/H \approx 0.8$ is that the interface temperature is lower than the interior temperature. Below $z/H \approx 0.8$ the temperature decreases. It suggests the possibility of two regimes for the action of the Soret effect: at the subsurface on the short time scale and at the lower part on the long time scale. The patterns in the upper part are primarily affected by Marangoni convection.

Figure 3 shows the variation of the mass fraction caused by the Soret effect. We draw the reader attention, that the vertical scale starts at z/H = 0.7. It clearly indicates that the compositional variation occurs close to the interface and its sign depends on the positions along the cell, i.e., on the flow pattern. The largest influence of the Soret is observed at x/L=0.6and x/L=0.7. As shown in the lower graph, the role of convection is weaker at these positions than at neighboring positions.

Conclusions

This study investigates the evolution of a convective instability in a LiBr-water binary mixture. The instability is driven by thermal and solutal Marangoni stresses in presence of absorption and modified by the Soret effect. These effects are investigated through numerical simulations. The results of the preliminary study demonstrate that on a time scale of one minute, the role of the Soret effect on mass transfer can be important locally in the subsurface.

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Figure 3: (top) The variation of mass fraction due to Soret effect across the cell at different horizontal positions at t=40 s. (bottom) The pattern indicating flow structure and composition (by redish colors). The vertical lines indicate positions at which curves $(w - w(S_T = 0))$ are shown. The horizontal green dashed line shows z/H = 0.85.

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Binary Diffusion Coefficients from Non-Equilibrium Molecular Dynamics Simulation

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Introduction

Diffusion processes play a fundamental role in nature and various industrial applications, such as distillation, absorption, and extraction. The design, operation, and optimization of these processes with rate-based (non-equilibrium) methods rely on precise diffusion coefficient data. However, due to the inherently slow nature of diffusion in liquid-like systems, experimental measurements are often laborious, time-consuming, and expensive, making comprehensive data acquisition challenging.

In contrast, molecular dynamics simulations have emerged as a powerful tool for investigating diffusion processes, benefiting from advances in computational power and continuous improvements of simulation algorithms. Today, molecular dynamics simulations are widely used to understand, model, and predict diffusion processes in both scientific and engineering applications. They have been shown to provide reliable diffusion coefficient data and offer insights into microscopic transport mechanisms that are inaccessible by experiments.

Traditionally, the Fick diffusion coefficient is determined through equilibrium molecular dynamics (EMD) simulations by computing the Maxwell-Stefan diffusion coefficient and the thermodynamic factor, typically using the Green-Kubo or Einstein formalism and Kirkwood-Buff integration. Although Non-Equilibrium Molecular Dynamics (NEMD) methods are commonly used to sample other transport properties, such as shear viscosity and thermal conductivity, they are rarely applied to calculate diffusion coefficients of bulk fluid mixtures. This is mainly due to the limitations of conventional NEMD algorithms, which often require large concentration gradients, making them less accurate and impractical for capturing the concentration dependence of Fick diffusion coefficients (Liu et al., 2012).

In this work, we explore the application of NEMD for determining the Fick diffusion coefficient with an approach that is analogous to experimental techniques, employing a methodology similar to the gradient relaxation molecular dynamics (GRMD) approach proposed by Maginn et al. (Maginn et al., 1993) for the diffusion of methane in silicalites. In this approach, an initial concentration inhomogeneity is allowed to relax over time, enabling the determination of the mutual diffusion coefficient by applying Fick's diffusion equation.

1 Theory

Fick's law describes the relationship between the diffusive flux of a component and its molar density gradient. For a binary mixture, the diffusive molar flux of component 1 J_1 , relative to an averaged mixture velocity u_o is given by

$$J_1 = c_1 \left(u_1 - u_0 \right) = -D_{11} \nabla c_1, \tag{1}$$

where u_1 is the diffusion velocity of component 1 with respect to a stationary coordinate reference frame, c_1 the molar density of component 1 and D_{11} is the Fick diffusion coefficient.

In Maxwell-Stefan theory, the chemical potential gradient $\nabla \mu$ is assumed to be balanced by the friction forces acting between the components that are proportional to their relative velocity $u_1 - u_2$. For a binary mixture, it reads

$$\frac{1}{RT}\nabla\mu_1 = -\frac{x_2\left(u_1 - u_2\right)}{D_{12}},\tag{2}$$

where R the ideal gas constant, T the temperature and D_{12} the Maxwell-Stefan diffusion coefficient. D_{12} is commonly obtained from EMD simulations.

Since Fick's law and Maxwell-Stefan theory describe the same physical phenomenon, the two diffusion coefficients are related by

$$D_{11} = \Gamma_{11} \cdot D_{12}.$$
 (3)

where Γ_{11} is the thermodynamic factor of the mixture. Consequently, in EMD methods, both the Maxwell-Stefan diffusion coefficient and the thermodynamic factor must be sampled to determine the Fick diffusion coefficient.

2 NEMD Method

Although NEMD is the natural approach for sampling transport properties, as these are inherently addressing nonequilibrium phenomena, equilibrium methods relying on statistical fluctuations are more commonly employed in the literature to determine diffusion coefficients. Here, we propose a NEMD method in which two pure fluids at the desired temperature and pressure conditions are initially brought into physical contact and allowed to relax over time, mimicking a macroscopic experiment. During simulation, the evolution of partial densities and component velocities is sampled in a spatially resolved manner. This allows for the characterization of the system for a large number of instantaneous states. Since the complete information required to compute the Fick diffusion coefficient is contained in the partial density and velocity distributions, spatially and temporally resolved Fick diffusion coefficients can be obtained using equation (1). Consequently, this method relies only on Fick's definition of the diffusion processes.

To test the proposed NEMD method, we studied the diffusion of symmetric Lennard-Jones mixtures. The unlike interactions between the identical, but distinguishable Lennard-Jones particles ($\sigma_1 = \sigma_2 and \varepsilon_1 = \varepsilon_2$) were defined using the modified Lorentz-Berthelot combining rules: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = 0.9 \cdot \sqrt{\varepsilon_i \varepsilon_j}$. The simulation were executed for 3×10^5 time steps and involved a total of 5×10^8 Lennard-Jones particles. Figures 1 and 2 show the temporal and spatial evolution of the partial density and velocity profiles of the studied Lennard-Jones mixture during simulation.



Figure 1: Temporal and spatial evolution of the partial density of both components along the z axis of the studied Lennard-Jones mixture at $k_{\rm B}T/\varepsilon_1 = 0.97$ and $\rho\sigma_1^3/\varepsilon_1 = 0.6708$.



Figure 2: Temporal and spatial evolution of the velocity of both components along the *z* axis of the studied Lennard-Jones mixture at $k_{\rm B}T/\varepsilon_1 = 0.97$ and $\rho\sigma_1^3/\varepsilon_1 = 0.6708$.

Using this method, the Fick diffusion coefficient was determined across the entire composition range from a single simulation run. Diffusion coefficient data obtained during the last 1000 time steps of the simulation showed excellent agreement with results from EMD simulations based on the Green-Kubo formalism and Kirkwood-Buff integration, as illustrated in Figure 3. Note that due to the large number of particles in the simulation volume, system size effects do not need to be accounted for.

To further validate the proposed methodology, it was successfully applied to determine the Fick diffusion coefficient of a real fluid mixture consisting of supercritical carbon dioxide and methane.



Figure 3: Composition dependence of the Fick diffusion coefficient for the studied Lennard-Jones mixture at $k_{\rm B}T/\varepsilon_1 = 0.97$ and $\rho \sigma_1^3/\varepsilon_1 = 0.6708$. Present NEMD results (blue bullets) are compared with EMD simulation results (black circles).

Conclusions

A simple inhomogeneous Non-Equilibrium Molecular Dynamics (NEMD) method was developed and validated for determining the Fick diffusion coefficient across the entire composition range from a single simulation run. These coefficients were obtained by mimicking macroscopic experiments, allowing the relaxation of partial densities and velocities from an initially imposed step-function profile. The results from NEMD simulations show an excellent agreement with those obtained from equilibrium methods based on the Green-Kubo formalism and Kirkwood-Buff integration. The method was validated using a symmetric Lennard-Jones mixtures as well as a real fluid mixture of supercritical carbon dioxide and methane, demonstrating its accuracy and applicability.

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Numerical insights into pattern formation in binary convection in cylinders

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Introduction

Binary mixture convection exhibits a wide range of dynamical behaviours driven by the interplay of thermal, solutal, and shear gradients. These depend on both the mixture properties and the geometric configuration and boundary conditions.

The onset of convection is strongly influenced by the Soret coefficient. Mixtures with a negative Soret coefficient often display oscillatory instabilities and time-dependent patterns, including dispersive chaos near criticality. Primary and secondary bifurcations can be subcritical, leading to temporal complexity. In contrast, mixtures with a positive Soret coefficient typically develop stationary patterns near onset, as observed in early experiments in cylindrical cells (Le Gal et al., 1985; Moses et al. 1986). However, numerical studies suggest that oscillatory instabilities can also arise under specific conditions (Weggler et al., 2010; Hu et al., 2021).

We use in-house numerical tools to solve the Navier-Stokes equations for binary convection in cylindrical geometries. Most results come from a three-dimensional time-stepping spectral code (Mercadet et al., 2010) that captures stable patterns. Additionally, a Newton-Krylov solver enables to compute stable and unstable steady states, while continuation techniques and Arnoldi iteration allow tracking solution branches and analyzing their stability. Although we have extensively applied the Newton-Krylov solver to two-dimensional cases, solving the corresponding three-dimensional systems remained computationally prohibitive until now.

Results

We analyze convective patterns near the onset of convection in binary mixtures with both negative and positive Soret coefficients. We consider non-inclined cylindrical cells with aspect ratios ranging from 1 to 12 and introduce a slight inclination in some cases.

Figure 1 presents convective patterns in a $\Gamma \approx 11$ cell for water-ethanol mixtures (S = -0.09, $\sigma = 24$, $\tau = 0.008$). Experiments (Lerman et al.,1999) and numerical results (Mercader et al., 2008) reveal that such mixtures tend to develop localized structures in medium-to-large aspect ratio cells, where coherent structures combining patches of travelling waves and quasi-steady convection are observed. As heating increases, convection intensifies, forming travelling-wave regions that expand from the cell center until reaching a high-amplitude state. A persistent localized state, not reported in those experiments, has been identified numerically.

Figure 2 shows several convective patterns in smaller aspect

(a) $^{134.4}$ $^{153.3}$ $^{152.9}$ $^{132.9}$ $^{146.9}$ 146

Figure 1: Pattern formation in a non-inclined $\Gamma = 11$ cell for a water-ethanol binary mixture with S = -0.09, $\sigma = 24$, and $\tau = 0.008$. (a) Experimental observations (Lerman et al.,1999). (b) Numerical results (Mercader et al., 2008).

ratio cells ($\Gamma = 0.25, 1, 2, 3$) for a mixture with S = -0.1, $\sigma = 10$, and $\tau = 0.001$. Despite the oscillatory nature of the primary instability, in highly confined geometries ($\Gamma \leq 2.5$), only purely thermal stationary modes persist after long transients. For $\Gamma = 3$, multistability emerges, with coexisting stationary and time-dependent patterns.



Figure 2: Pattern formation in non-inclined $\Gamma = 0.25, 1, 2, 3$ cells for a mixture with S = -0.1, $\sigma = 10$, and $\tau = 0.001$. Numerical results (Alonso et al., 2014).

Figure 3 illustrates stationary square convective patterns observed in the Soret regime for mixtures with S = 0.13, $\sigma = 16$, and $\tau = 0.011$. Experiments on cylindrical cells (Le Gal et al., 1985; Moses et al., 1986) revealed a transition from Soret-dominated motion near onset to thermal convection at higher heating, with complex time-dependent dynamics in the crossover region.

When a shear mechanism is introduced by slightly tilting the cavity, the interaction of shear and double-diffusive instability mechanisms, leads to new oscillatory patterns. Figure 4 presents the so-called superhighway convection (SHC) patterns, that were observed experimentally in $\Gamma = 10$ cells (Croccolo et al., 2013) and obtained numerically in $\Gamma = 5$ cells (Alonso et al., 2018). A detailed analysis revals that SHC convective patterns reveals can be not only time-periodic but also



Figure 3: Square patterns in a non-inclined large aspect ratio cell for a binary mixture with S = 0.13, $\sigma = 16$, and $\tau = 0.011$. (a) Experimental observations (Le Gal et al., 1985). (b) Numerical results (Alonso et al., 2025).

quasiperiodic, multi-frequency modulated, and even chaotic (Alonso et al., 2025). Investigating smaller cells is a promising direction. Identifying the so-called Minimal Flow Unit capable of sustaining SHC oscillations would reduce spatio-temporal complexity, simplify phase space topology, and provide deeper insight into the fundamental instability mechanisms.



Figure 4: Superhighway convection patterns in a slightly inclined cell ($\alpha = 24 \text{ mrad}$) for a binary mixture with S = 0.13, $\sigma = 16$, and $\tau = 0.011$. (a) Experimental observations (Croccolo et al., 2013). (b) Numerical results (Alonso et al., 2018).

Conclusions

The use of cylindrical cells to study binary mixture convection is highly convenient, as they enable controlled experiments that facilitate direct comparison with numerical simulations. While three-dimensional time integration of the Navier-Stokes equations is computationally expensive, particularly with realistic binary mixture parameters, it provides a detailed characterization of convective patterns, complementing experimental measurements. Numerical simulations, for instance, offer precise insights into temperature, concentration, and velocity fields, enhancing both qualitative and quantitave understanding of flow structures.

Beyond time-steppers, advanced numerical techniques provide deeper insights. Newton-Krylov solvers for steady and periodic orbits, combined with continuation methods, allow tracking solution branches and analyzing their stability. Obtaining the structure of these branches offers a comprehensive view of the system dynamics, and helps to interpret experimental results and to predict pattern selection and flow evolution.

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Thermophoresis: The case of apomyoglobin

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Introduction

This study investigates the thermodiffusive behavior of apomyoglobin (Apo-Mb) at different pH levels using the thermal diffusion forced Rayleigh scattering (TDFRS) technique, highlighting hydration changes associated with its conformational states. It is an extensively studied model system for understanding protein folding, the heme-free form of myoglobin. At near-neutral pH (~6), Apo-Mb adopts a compact, native structure; at slightly acidic pH (\sim 4-4.5), it shifts to a partially folded "molten globule" state; and at pH~2, it reaches an acidunfolded state. As the pH decreases, the net positive charge of the protein increases, leading to protein unfolding [1]. The predominantly α -helical conformation of Apo-Mb is stabilized by strong intramolecular hydrogen bonding, which enhances its structural stability and exhibits a hydrophilic character on the surface of the protein. In the unfolded state, hydrophobic exposure reduces electrostatic interactions and effective hydrophilicity, which decreases solvation stability and promotes aggregation because unfolded proteins minimize water contact [2]. In addition, anions interact preferentially with the positively charged regions of the protein and effectively shield the repulsive forces between positive charges by binding to them, thus reducing internal repulsion. In particular, anions with higher charge and affinity towards protein are more effective than anions with lower affinity in inducing the transition from unfolded to folded proteins [3]. The stability of intermediate states of Apo-Mb strongly depends on the net charge of the protein, emphasizing that loss of positively charged residues generally increases stability by reducing internal charge repulsion and vice versa [4].

For aqueous systems, the Soret coefficient $S_{\rm T}$ of the solute changes its sign from negative to positive with increasing temperature [5]. Previous studies on aqueous systems have shown that the temperature sensitivity of $S_{\rm T}$ (difference at two temperatures) $\Delta S_{\rm T}(\Delta T)$ decreases with increasing temperature which has been attributed to the disruption of hydrogen bonding at higher temperatures [5, 6]. Thus, a highly hydrophilic solute exhibits high temperature sensitivity compared to a hydrophobic one. However, the thermophoretic behavior of proteins is a complex interplay of surface properties, as the solvent-accessible surface area also depends on the ionic strength and surface charge[7].

Thermophoresis of Apomyoglobin

Figure 1 shows the temperature dependence of $S_{\rm T}$ for Apo-Mb solutions measured at different pH values with and without buffer. At lower temperatures, Apo-Mb is thermophilic at pH 2 and pH 6, but switches to thermophobic behavior when the temperature increases above ~20°C. In contrast, Apo-Mb remains thermophobic at pH 4 over the entire temperature range studied. However, the value of $S_{\rm T}$ increases with increasing temperature in all solution conditions [7]. Interestingly, in the presence of sodium phosphate buffer (NaP), the light scattering intensity increased exponentially at 45°C due to protein aggregation, obscuring the cuvette window and preventing data collection. According to the Hofmeister series, the phosphate anions in the buffer are very hydrophilic and act as strong water structure makers, resulting in a more compact protein structure and its aggregation [3, 8].



Figure 1: Temperature dependence of $S_{\rm T}$, measured for 7 mg/ml Apo-Mb with and without buffer at different pH values corresponding to the different folding states of Apo-Mb

Correlation between Circular Dichroism (CD) and TDFRS

Prior to TDFRS measurements, the secondary structure content and charge of Apo-Mb under different solution conditions were confirmed by CD. In absence of buffer, the α -helical content decreases progressively with decreasing pH. In case of buffers, NaP buffer stabilizes the α -helix at pH 6, whereas sodium acetate (NaAc) buffer at pH 4 promotes partial unfolding by decreasing the α -helix content. At pH2, a small fraction of the α -helical content is still retained in its unfolded state [1].



Figure 2: The plot shows a strong correlation between temperature sensitivity, $\Delta S_{\rm T}(\Delta T)$ and α -helix content.

Figure 2 shows a correlation between temperature sensitivity, $\Delta S_{\rm T}(\Delta T)$ and α -helix content. The α -helix content is a reliable indicator of the hydrophilicity of proteins. This is because in a α -helix conformation, the hydrophobic residues tend to be buried in the core of the protein, while the hydrophilic residues are exposed to the aqueous environment. Therefore, a higher α -helix content corresponds to a more hydrophilic protein. In addition, previous studies show that the α -helix content of a protein mainly determines the protein diffusion [1]. This correlation is also observed in our results. In particular, the temperature sensitivity of the thermodiffusive behavior, expressed by $\Delta S_{\rm T}(\Delta T)$, decreases in the following order as the hydrophilicity of Apo-Mb decreases (which is achieved by lowering the pH): $\Delta S_{\rm T}$ (pH 6) > $\Delta S_{\rm T}$ (pH 4) > $\Delta S_{\rm T}$ (pH 2). However, NaP buffer makes the protein more compact, resulting in increased hydrophilicity and a higher value of $\Delta S_{\rm T}(\Delta T)$ [8]. NaAc buffer enhanced protein solubilization at pH 4, reducing hydrophilicity by exposing hydrophobic regions. This resulted in a significantly lower $\Delta S_{\rm T}(\Delta T)$ value compared to the unbuffered acidic solution at the same pH [9]. At pH 2, the protein structure was largely disrupted, with a significant decrease in the α -helix content and an increase in the net positive charge. This perturbation led to a deviation from the observed trend between $\Delta S_{\rm T}(\Delta T)$ and α -helix content.

Conclusions

Our study investigates the influence of structural conformational changes on the thermodiffusion behavior of Apo-Mb using the TDFRS technique. We found that the α -helix content is strongly correlated with hydrophilicity and thus influences the thermodiffusion behavior. Reducing the α -helix content led to a decrease in hydrophilicity (pH6 > pH4 > pH2) and a decrease in the temperature sensitivity of $\Delta S_{\rm T}(\Delta T)$. $(\Delta S_{\rm T}(\Delta T)$ (pH6) > $\Delta S_{\rm T}(\Delta T)$ (pH4) > $\Delta S_{\rm T}(\Delta T)$ (pH2)). The type of buffer also plays a significant role in modulating the structural and diffusional properties of apo-Mb. At pH 6, NaP buffer preserves the α -helix but promotes aggregation of the protein due to electrostatic screening, as evidenced by a lower diffusion coefficient. Whereas acetate buffer at pH 4 decreases the α -helix content of the protein and the temperature sensitivity of $S_{\rm T}$ and increases the solubility of the protein in solution. Increasing the concentration of acetate buffer at pH 4 further decreases the temperature sensitivity of $S_{\rm T}$.

Overall, we observed a strong correlation between $\Delta S_{\rm T}(\Delta T)$ and α -helix content; $\Delta S_{\rm T}(\Delta T)$ increases steadily with increasing hydrophilicity and α -helix content of Apo-Mb. These results highlight the complex interplay between the structural state of Apo-Mb, pH, buffer composition and thermodiffusion behavior and provide valuable insights into protein hydration.

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Shadowgraphy Study of Transport Properties in Cyclohexanol/Toluene Binary Mixtures

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Introduction

One possible means of determining the transport properties of fluid mixtures, such as mass and thermal diffusion coefficients is to perform non-equilibrium experiments. A fluid in non-equilibrium is the result of applying a gradient of one or more intensive properties, particularly temperature (Groot and Mazur, 1984). A comprehensive understanding of nonequilibrium systems can be offered by the study of nonequilibrium fluctuations (NEFs), which differ from their equilibrium counterpart due to their long-range nature (Ortiz de Zárate, 2006 and Croccolo et al., 2016).

In a recent study, we examined the equilibrium properties of ternary mixtures of cyclohexanol, toluene and CO_2 in a pressure range up to 30 MPa (Imuetinyan et al., 2025). We now shift to the study of non-equilibrium properties of these mixtures, beginning with an analysis of binary liquid mixtures of cyclohexanol and toluene at atmospheric pressure. We investigate a thin layer of the binary fluid under a steady temperature gradient stabilising the system in the presence of gravity, focusing on concentration fluctuations around the stationary concentration gradient established by the Soret effect. In these conditions, we study the dynamics of these non-equilibrium concentration fluctuations (c-NEFs) in order to measure the mass diffusion coefficient.

The concentration gradient ∇c is obtained by applying a temperature gradient ∇T to the mixture

$$\nabla c = -c \left(1 - c\right) S_T \nabla T,\tag{1}$$

where S_T is the Soret coefficient.

Experimental methodology

A thermodiffusion (TD) cell is installed in the shadowgraph setup in Figure 1a including a superluminous diode (SLD) as a light source and a s-CMOS camera for imaging. The camera is positioned at $z = (20 \pm 1)$ cm from the cell without any collecting lens. Two polarisers are placed before and after the TD cell to control the beam intensity and prevent camera saturation, optimising image data retrieval. The s-CMOS camera (Hamamatsu Photonics ORCA Flash 4.0 series) features 2048 \times 2048 pixels of 6.5 \times 6.5 μ m. It can acquire images at up to 100 Hz full resolution, enabling access to correlation

times short enough for investigating temperature fluctuations, with a minimum wave vector $q_{\min} = 4.72 \text{ cm}^{-1}$.



Figure 1: Schematic of the Shadowgraph apparatus, (a) its optical elements, and (b) the thermodiffusion cell.

Figure 1b shows the thermodiffusion cell configuration (Croccolo et al., 2019). Three Delrin spacers and Viton Orings secure the sapphire windows, defining the vertical thickness of the sample fluid. This setup allows precise temperature control of the windows to within 0.5 mK using two Peltier elements with 12.5 mm central holes for light beam cross. Two thermistors annealed in two aluminum plates allow for precise measurement of the temperature and its control via PID devices. Two thick aluminum plates outside the Peltier elements, including water circulation from a thermal bath, dissipate the excess heat. We conducted a study on the mixture consisting of 70% cyclohexanol and 30% toluene (w/w), which transport properties were not present in the existing literature. We conducted thermodiffusion experiments in a TD cell of L = 1 mm with a temperature difference of 20 K, heating the mixture from the top. The average temperature of the experiment was 298.15 K. The solutal (β_c) and thermal (β_T) expansion coefficients are 0.12 and 9.07 × 10⁻⁴ K⁻¹, respectively. We collected data at the non-equilibrium steady state achieved after a time larger than the mass diffusion time, i.e. we waited 24 hours after applying the temperature gradient.

Results and discussions

The NEFs experiment involved capturing 3000 image sets at varying delay times of 10, 32, 64, 128, 256, 512, and 1024 ms. These images were examined using DIFFMICRO (DM), an advanced proprietary differential dynamic image analysis software. The DM analysis begins by normalising the images by their mean intensity and then calculating image differences at specified delay times to extract differential signals. The resulting difference images undergo a 2D-space-Fourier transformation in silico, separating the light scattering contributions at various wave vectors. A Differential Dynamic Algorithm (DDA) derives the structure function from the images of non-equilibrium concentration fluctuations within the binary liquid mixture. After a fitting procedure, this process ultimately yielded the experimental decay times τ_c .



Figure 2: Experimental decay times as a function of the wave vector for $\Delta T = 20$ K. The red dashed line depicts the theoretical solution provided by Equation 2, considering gravity and diffusion only.

The c-NEFs in this system decay exponentially with decay time depending on the wave number q of the fluctuations, assuming confinement effects are ignored. The theoretical decay time can be written as:

$$\tau_c = \frac{1}{Dq^2 \left(1 + \left(\frac{q_{cs}}{q}\right)^4\right)},\tag{2}$$

where D is the mutual diffusion coefficient of the binary liquid mixture. Figure 2 shows the log-log plot of the experimental decay time as a function of the wave vector for a temperature gradient $\Delta T = 20$ K. The experimental data were fitted using Equation 2. Notably, the theoretical solution used to fit the experimental data did not consider confinement effects, which can explain the deviation at small q (Giraudet et al., 2016). The mutual diffusion coefficient of the binary mixture is determined to be 4.0×10^{-10} m²·s⁻¹ and the Soret coefficient (S_T) is estimated to be 8.0×10^{-4} K⁻¹.

Conclusions

In this study, we employed an experimental methodology based on shadowgraphy to determine the transport properties of a binary liquid mixture comprising 70 wt% cyclohexanol and 30 wt% toluene. Notably absent from the literature, the thermal diffusion and Soret coefficients were quantified using our analysis protocol. We intend to further this research by investigating thermal gradient-driven transport in ternary cyclohexanol + toluene + CO_2 mixtures.

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Thermophoresis-driven Aggregation of 2D Colloidal Quasicrystals

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Introduction

Thermophoresis, namely the motion of a colloidal particle in a fluid due to an imposed temperature gradient, is a wellestablished phenomenon, with many applications in the fields of biophysics, nanotechnology and environmental science. However, some of its aspects still require further clarification. In particular, a highly debated issue is the dependence of the thermophoretic velocity of colloidal particles on their size. From a theoretical point of view, it is possible to infer that, since thermophoresis is driven by interfacial effects, the resulting motion of the colloid should be independent of its radius [1]. On the other hand, some experimental studies argue that the thermophoretic velocity is directly proportional to the particle radius [2]. In this work, we confirm that the thermophoretic velocity is independent on the radius of colloidal hard spheres. This remarkable property is exploited to assemble high-density colloidal phases from a binary mixture, keeping a constant stoichiometry along the aggregate.

Experimental setup

The system under examination consists on a binary mixture of silica particles in a water solution confined inside a 5 μ m sample cell. Since silica is considerably denser than water, the particles are always sedimented on the bottom plane of the cell, resulting in an effective two-dimensional system of non-additive hard disks [3]. The thermophoretic motion of the particles is induced by a near-infrared laser beam that, being absorbed by water, creates a circularly symmetric temperature profile which drives the thermophilic silica colloids towards the beam center [4]. By tracing the particles through a camera aligned to the beam axis we obtain the radial velocity profile of the two colloidal species of the mixture, showing that the thermophoretic mobility does not depend on the particle radius (see Fig. 1) and is negligibly influenced by confinement.

Quasicrystal growth

After verifying the independence of the thermophoretic velocity from the colloid size, we exploited thermal forces to confine dense phases in which the stoichiometry of the binary mixture is constant across the whole aggregate. By changing the



Figure 1: Radial thermophoretic velocity profile induced by a gaussian laser beam for a binary mixture of silica colloids confined in an effective 2D setup (a). The mean radius of bigger particles (in red) is $2.3 \,\mu\text{m}$, while for the small one (in blue) is $1.5 \,\mu\text{m}$. The particles motion is captured with a camera, through which we obtained the track for each particle in the sample (b).

size ratios and the relative concentrations in the mixture, we managed to aggregate a 12-fold symmetric quasicrystal (see Fig. 2), representing the first experimental realization of predictions for non-additive hard-disk mixtures [5]. Notably, we found that thermophoretic accumulation is not suitable for the formation of quasicrystals with the 8-fold symmetry, which are predicted at higher concentrations of the smaller particles.

These outstanding results have also been confirmed by direct molecular dynamics simulations, where the aggregation of a hard-sphere binary mixture is driven by an external force akin to that induced by the heating laser in the experimental setup. Our method allowed to replicate the state diagram in Ref. [5], except again for the 8-fold quasicrystal, where the driving force hinders the system from reaching the equilibrium state. This behavior suggests that a different aggregation procedure is needed for this structure, as our method favors the formation of different metastable phases. Moreover, the comparison between simulations and experimental results allows us to discuss the role of particle accumulation in the formation of ordered and glassy phases, serving as a powerful tool for investigating the emergence of quasicrystals.



Figure 2: Structure factor of the big particles calculated from an experimental image (inset) of the effective 2-dimensional system of non-additive hard disks. The structure shows a 12fold symmetry, the same predicted through molecular dynamics simulations. The size ratio of the mixture is about 0.43, while the small particles fraction is 0.4.

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Self-Phoretic Mobility of Active Droplets

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Introduction

Active nanoemulsions are systems in which the droplets exhibit induced mobility as a result of internal chemical reactions. These reactions generate concentration and temperature gradients at the droplets' surfaces, triggering two key phenomena: self-thermophoresis and self-diffusiophoresis. Both mechanisms are coupled when the reaction is either endothermic or exothermic. In the case of a significantly high reaction heat, self-thermophoresis becomes the dominant driving force, as the temperature gradient induces a strong thermophoretic motion of the droplets. These dynamic behaviors are essential for understanding transport processes in active nanoemulsions, offering insights into their potential applications in various fields, including drug delivery and materials science.

In this work, we aim to compute the self-phoretic velocities and coefficients for spherical Janus active nanodroplets within nanoemulsions and to determine the modified diffusivities for homogeneous active nanodroplets due to self-phoretic phenomena (Arango-Restrepo et al., 2024). These analyses provide a deeper understanding of transport processes in active nanoemulsions.

Spherical Janus active droplets

We examine a spherical Janus active droplet with a portion of its surface acting as a catalyst, driving an irreversible first order chemical reaction in which a substrate A is converted to products B. This reaction takes place in a medium with no external flow, charged species or interparticle interactions. At the interface (*i*) between the droplet (*d*) and the surrounding fluid (*b*), all chemical species are present. Fig. (1) illustrates the Spherical Janus active droplet and its surroundings.

The dimensionless substrate and product concentration at the droplet interface are given by:

$$0 = \frac{\partial^2 \hat{C}_A}{\partial \phi^2} - \alpha^2 \hat{C}_A \Theta(\phi_0 - \phi) - \beta^2 (\hat{C}_A - \hat{C}_A^{(b)})$$
(1)

where $\alpha^2 = k_r R^2 / D_s$ and $\beta^2 = U R^2 / D_s$ are the dimensionless numbers summarising the effect of the reaction and adsorption on the interface.

$$0 = \frac{\partial^2 \hat{C}_B}{\partial \phi^2} + \alpha^2 \hat{C}_A \Theta(\phi_0 - \phi) - \beta^2 \hat{C}_B$$
(2)

in which we have assumed that the product concentration at the interface greatly exceeds its concentration in the bulk.

On the other hand, the dimensionless temperature at the interface is:

$$0 = \frac{\partial^2 \hat{T}}{\partial \phi^2} + \Theta(\phi_0 - \phi) \lambda^2 \hat{C}_A - \omega^2 (\hat{T} - \hat{T}^{(b)})$$
(3)

in which for an exothermic reaction, $\lambda^2 = \frac{R^2 |\Delta H_r| k_r C_0}{kT_0}$ and $\omega^2 = \frac{U_q R}{k}$. These 2 dimensionless numbers account for the heat generated and cooling effect respectively in the particle interface.

According to the Faxén theorem, variations in surface tension along the interface induce hydrodynamic stresses, leading to a slip velocity on the surface (Bafaluy et al., 1995). Consequently, both, the droplet and the surrounding fluid are propelled. This force is known as the phoretic force and can be expressed as:

$$\mathbf{F}_{ph} = \int_{s} \nabla_{s} \gamma ds = \int_{s} (\gamma_{C_{A}} \nabla_{s} C_{A} + \gamma_{C_{B}} \nabla_{s} C_{B} + \gamma_{T} \nabla_{s} T) ds \quad (4)$$

In the presence of an imposed fluid field or concentration field, the droplet aligns with the respective field. By solving Eqs. (1-3) and substituting the solutions into Eq. (4), it is possible to determine the self-diffusiophoretic velocity and the self-thermophoretic velocity.

$$v_{sd} = -\frac{1}{6\pi\eta_0} \left(-4\gamma_{C_A} \frac{1 - \sqrt{(\alpha/\beta)^2 + 1}}{1 + \sqrt{(\alpha/\beta)^2 + 1}} + \frac{1}{2}\gamma_{C_B}\alpha^2 \left(1 + \frac{\alpha^2}{\alpha^2 + \beta^2} \right) \right) \Delta z$$

$$v_{st} = -\frac{2D_A}{3\pi\eta_0 k_s} \gamma_T \alpha^2 \frac{\alpha^2 + 2\beta^2}{\omega^2} \left(1 + \sqrt{(\alpha/\beta)^2 + 1}^3 \right)^{-1} \Delta Q_r$$
(6)

(6) in which the fugacity difference $\Delta z = C_0 \frac{\beta^2}{\alpha^2 + \beta^2}$ and generated heat potential $\Delta Q_r = \Delta z |\Delta H_r|$ are the thermodynamic forces. Velocities are shown in Fig. 2. Notice that we can write the

Homogeneous active droplet

velocities as $v_{sd} = \mathscr{D}_z \Delta z$ and $v_{st} = \mathscr{D}_Q \Delta Q_r$.

In this case, the orientation dynamic is completely random. Thus we write the original Langevin equation of the particle velocity considering two noises that are independent and not correlated

$$m\dot{\mathbf{v}} = -\xi_t \mathbf{v} + \mathbf{F}_{ph} + \mathbf{F}_R \tag{7}$$

in which $\mathbf{v} = d\mathbf{x}/dt$, *m* is the active droplet mass. The phoretic random force considering a random orientation of the particle fulfills the fluctuation-dissipation theorem $\langle \mathbf{F}_R(t)\mathbf{F}_R(t')\rangle =$



Figure 1: Illustration of a Janus active droplet undergoing a first-order reaction at its interface, where substrate A is converted into product B inducing a surface gradient of the surface tension $\nabla_s \gamma$. Here, the droplet is depicted with a defined orientation **n**, extending from the catalytic (golden color) to the non-catalytic side (blue color). The interface region *i* is located between the inner section of the droplet *d* and the mass of the surrounding fluid *b*.



Figure 2: Self-phoretic velocities in m/s as a function of the ratio between dimensionless numbers accounting for the relation reactionadsorption (α^2/β^2) and heat generated-cooling (λ^2/ω^2) . a) Selfdiffusio-phoretic v_{sd} , b) Self-thermophoretic v_{st} velocities. The spherical Janus active droplet has a radius of 100nm.

 $2D_0\delta(t-t')$ and $\langle \mathbf{F}_{ph}(t)\mathbf{F}_{ph}(t')\rangle = 2D_{ph}\delta(t-t')$, with D_0 the passive diffusivity and D_{ph} the phoretic diffusion coefficient.

Solving the Langevin equation for long times and taking the average we can obtain the modified diffusivity

$$D = \frac{k_B T}{\xi_t} + \frac{E_s^{(e)}}{\xi_t} = D_0 + D_{ph} = D_0 \left(1 + \frac{E_s^{(e)}}{k_B T}\right)$$
(8)

in which then $D_{ph} = E_s^{(e)}/\xi_t$ with $E_s^{(e)}$ the surface excess energy of the droplet defined as

$$E_{s}^{(e)} = \int_{A} e_{s}^{(e)} dA = -\gamma_{T} \int_{A} (T - T_{0}) dA - \sum_{i} \gamma_{Ci} \int_{A} (C_{i} - C_{i,eq}) dA$$
(9)

in which γ_i are the partial derivative of the surface tension as a function of the concentration of the ith compound and γ_T the partial derivative of the surface tension as a function of the temperature.

Conclusions

In this study, we calculate the self-phoretic velocities and coefficients for spherical Janus active droplets and determine the modified diffusivities for homogeneous active droplets. These results highlight the transport processes driven by selfthermophoresis and self-diffusiophoresis. They provide a framework for understanding the interplay of chemical reactions, concentration gradients, and temperature gradients in active nanoemulsions, which could potentially be applied in targeted drug delivery.

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Taming the diffusiophoretic convective instability in colloidal suspensions

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Introduction

A colloidal suspension with a stabilizing density gradient is, in principle, expected to remain convectively stable. However, recent experiments demonstrated that a vertical solute gradient can trigger a *diffusiophoretic convective instability* (DCI), even under stable density stratification (Anzivino et al., 2024). This instability arises from the upward motion of colloidal particles in response to solute gradients, leading to spontaneous flow patterns. In this work, we explore how initial conditions and



Figure 1: Phase diagram of DCI in the (c_0, ϕ_0) parameter space, where c_0 is initial glycerol concentration and ϕ_0 is initial colloid volume fraction. (Castellini et al., 2025)

stratification details influence the onset of DCI (Fig. 1). In contrast to previous configurations where colloids were uniformly distributed, we investigate a setup where both colloids and solute are initially localized in the lower half of the sample.

Diffusiophoretic Instability Control

We experimentally show that in the confined setup, the onset of convection occurs only when the glycerol concentration exceeds a threshold value of approximately 0.3 w/w. Below this threshold, the system remains quiescent despite the presence of solute gradients.

Numerical simulations based on nonlinear double-diffusion equations with diffusiophoretic coupling confirm the experi-

mental observations and explain the emergence of the threshold. These results also confirm that interparticle interactions are not significant in triggering the instability.



Figure 2: a) Top view and b) side view of diffusiophoretic flow. The red lines in b) highlight the convection region.

Side-View Imaging and 2D Modeling

We also report observations from Hele-Shaw cell experiments with lateral visualization (Fig. 2 b). This quasi-2D geometry enables precise measurement of the structure and wavelength of convective rolls, revealing highly ordered flow patterns at the interface between stratified layers.

This configuration allows for direct comparison with 2D numerical models, leading to improved characterization of flow regimes and instability development in confined systems.

Conclusions

We demonstrate that the diffusiophoretic convective instability can be suppressed by tailoring the initial solute and colloid distributions. Side-view visualization provides insights into the interface dynamics and enhances the comparison with simulations, offering a robust platform for studying DCI.

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Thermodiffusion coefficients in quaternary liquid mixtures

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Introduction

Mass transport driven by temperature gradients, known as Soret effect, has been observed in liquid and gaseous mixtures as well as in solids. Thus, this complex phenomenon is not linked to a specific application but is fundamental in various fields for multiple purposes (W. Köhler et al. 2016).

The Soret coefficient (S_T) is the quantity that relates the thermodiffusion coefficient (D_T) to the molecular diffusion coefficient (D) and can be either positive or negative (W. Köhler et al. 2023). Early research analyzed binary mixtures, leading to the first benchmarking study aimed at determining the mass transport properties of binary liquid systems using various laboratory techniques (J. K. Platten et al. 2003). In this international effort, the traditional thermogravitational column technique (TGC) was the main method to determine the D_T coefficient of the mixtures via sample extraction.

However, most systems involved in natural and industrial processes consist of more than two species. Consequently, in recent years, scientific interest has shifted toward the study of ternary systems, which represents the simplest case of a multicomponent mixture. Despite initial discrepancies in laboratory results, several systems have been successfully investigated to date as benchmarks in ternary mixtures (M. M. Bou-Ali et al., 2015), as well as polymers, aqueous mixtures, and nanofluids. Moreover, these mixtures have been analyzed under both terrestrial and microgravity conditions as part of the Diffusion and Thermodiffusion Coefficients in Ternary MIXtures (DCMIX) work (M. Braibanti et al. 2019).

Considering the advancements achieved in the analysis of ternary systems, current research aims to extend the study to quaternary liquid mixtures. In such systems, the complexity increases further, as these mixtures are composed of nine molecular diffusion coefficients (three pure and six crosscoefficients) and four thermodiffusion coefficients. To date, it has been observed that, in general, the study of quaternary systems remains scarce. M. Eslamian et al. 2010 employed the principles of nonequilibrium thermodynamics in order to predict D_T coefficients in such systems. They concluded that their complex model was only capable of estimating the sign of the D_T coefficient of each component of the mixture. However, no experimental studies have been suggested for validation purposes. G. Guevara-Carrion et al. 2020 studied the molecular diffusion coefficient matrix in a quaternary system via molecular dynamics simulations. They considered a liquid mixture made up of water, methanol, ethanol and isopropanol. Regarding experimental studies, C. Peters et al. 2020 measured the pure and cross-diffusion coefficients of the quaternary system composed of toluene, cyclohexane, methanol and acetone in a microfluidic channel, employing Raman spectroscopy for analysis. However, as this is a novel technique, it would be beneficial to validate its application beforehand using the reference binary or ternary systems (J. K. Platten et al. 2003 and M. M. Bou-Ali et al. 2015).

Thus, the motivation of this work is to determine, for the first time, the thermodiffusion coefficients of each component in a quaternary mixture using the traditional TGC technique. Considering the steps previously followed in the study of binary and ternary systems (M. M. Bou-Ali et al. 2005 and A. Leahy-Dios et al. 2005), the objective of this work is to develop a new experimental methodology to determine the phenomenological thermodiffusion coefficients (D'_T) of each component in a quaternary mixture using the TGC method. In this context, we considered the following mixture composed of 1-methylnaphthalene (MN), 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB) and dodecane (C12) in an equal mass fraction (0.25|0.25|0.25|0.25) and at an average working temperature of $t_0 = 25^{\circ}$ C.

Methodology

The development of a new approach for analyzing a quaternary system is based on the works of M. M. Bou-Ali et al. 2005 and A. Leahy-Dios et al. 2005, who first established a detailed methodology for determining the D'_T coefficient in ternary mixtures via the traditional extraction TGC technique. Unlike a ternary mixture, quaternary systems are composed of four independent components (c_1, c_2, c_3, c_4) . Hence, measuring the change in density (ρ) and refractive index (n) alone is insufficient to determine the mass fraction of each species in the TGC. In this work we apply the speed of sound (c_s) as a calibration property to determine the composition changes within the quaternary mixture together with the density and refractive index. In this manner, ρ , n and c_s can be expressed as linear functions for small composition changes, allowing the definition of the following calibration equations:

$$\rho = a + bc_1 + dc_2 + ec_3 \tag{1}$$

$$n = a' + b'c_1 + d'c_2 + e'c_3 \tag{2}$$

$$c_s = a'' + b''c_1 + d''c_2 + e''c_3 \tag{3}$$

In Eqs. (1), (2) and (3), a, b, d, e, a', b', d', e', a'', b'', d'' and e'' are the calibration constants for ρ , n and c_s . Knowing the



Figure 1: Quaternary mixture thermodiffusion experiment in the new two-meter TGC: variation of ρ , n and c_s along the column height.

above-mentioned constants, it is possible to determine the concentrations $(c_1, c_2 \text{ and } c_3)$ from the measurements of the thermophysical properties ρ , n and c_s . The mass fraction of the fourth species is obtained from $c_4 = 1 - c_1 - c_2 - c_3$. As presented in Eqs. (1), (2) and (3), for a quaternary mixture, three calibration hyperplanes are required

Methodology

We consider the traditional TGC technique. The six samples are extracted at different heights of the column, and properties ρ , n and c_s are measured (see Figure 1) and converted into concentrations using calibration constants from Eqs. (1), (2) and (3). This results in a linear concentration gradient of each species (c_i) as a function of the column height (L_z), enabling the direct determination of the slope $\frac{partialc_i}{\partial L_z}$ and therefore D'_T of each component ($D'_{T,i}$) (see Eq. (4)).

 L_x refers to the gap of the cavity, α is the thermal expansion coefficient, μ the dynamic viscosity and g the gravitational force. We used the following Anton Paar equipment for sample characterization: DSA 5000 M (ρ , α and c_s), AMVn (μ) and Abbemat MW (n). In this work, n was measured for a



Figure 2: Fluid Mechanics Group laboratory traditional TGCs.

wavelength of $\lambda = 435.8$ nm.

$$D_{T,i}^{'} = -\frac{L_x^4}{504} \frac{\alpha g \rho}{\mu} \frac{\partial c_i}{\partial L_z}$$
(4)

The Fluid Mechanics Group at Mondragon Unibertsitatea has two different traditional TGCs ($L_z = 980$ mm, thickness $L_y =$ 50 ± 1 mm and $L_x = 1.02 \pm 0.005$ mm and $L_z = 500$ mm, $L_y = 50 \pm 1$ mm and $L_x = 1.00 \pm 0.005$ mm). In this work, we designed and fabricated a new traditional TGC with the same gap but a total length of two meters. This new TGC doubles the steady-state species separation compared to the one-meter column, enhancing precision for quaternary mixtures. Figure 2 shows the three TGCs of our laboratory.

Preliminary results

We illustrate the ρ , the n and the c_s variation of the quaternary mixture MN|THN|IBB|C12 in the new two-meter TGC after reaching stationary-state regime. The results of the ρ , the n and the c_s for the 6 samples taken along the height of the column show a linear regression (Figure 1). Thus, by means of the calibration constants, the concentration distribution of each component and therefore its thermodiffusion coefficient can be determined via Eq. (4).

Conclusions

In this work, we developed a new methodology adapted to the traditional TGC technique to experimentally determine, for the first time, the D'_T coefficients of each component in a quaternary mixture.

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Oral Communications Day 5

Molecular diffusion investigated with a cartesian diver

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It is known that students often struggle with hydrodynamics, to the point that they find it difficult to clearly distinguish between concepts like pressure and force. It is evident that teaching in a more engaging way, e.g. using simple experiments that help students to visualize the theoretical concepts, is very effective for enhancing students understanding.

We propose an engaging experiment that can be carried out using common household items and allows for the introduction of fundamental physics concepts such as hydrostatics, harmonic oscillations, and molecular diffusion. The experiment, suitable for both university and high school students, is a variant of the classic Cartesian diver experiment. In this version, the body is initially in equilibrium at the interface between two miscible liquids of different densities, rather than in a liquid of uniform density. Eventually, a pressure impulse is applied to the sealed container causing an increase in the diver density. Thus, an elastic restoring force is generated, setting the diver into oscillation at the Brunt–Väisälä frequency that depends on the density gradient. This setup allows for monitoring the evolution of the density gradient over time thus obtaining a quantitative comparison between the experimental data and theoretical predictions obtained from the numerical solution of the diffusion equation.

Experimental investigation of non-equilibrium fluctuations under non-stationary conditions

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Introduction

Quantitative shadowgraph experiments has been extensively used to in studying phoretic phenomena under stationary conditions, particularly for investigating non-equilibrium fluctuations in binary mixtures [1, 2]. Recently, there has been a growing interest in the investigation of non-equilibrium systems under non-stationary conditions, as many technological and industrial processes occur under these conditions. A major practical limitation to the investigation of transport phenomena under non-stationary conditions is set by the stability of the experimental apparatus. These instabilities (often triggered by time-dependent temperature differences) can have optical signatures that superimpose on the genuine signal of nonequilibrium fluctuations, encoded in the so-called image structure functions $D(q, \Delta t)$, leading to spurious contributions. One of those contributions, recently reported in different studies on binary mixtures subject to an imposed temperature gradient [3, 4], consists of an additive drift term in the image structure function with a quadratic dependence on the time delay Δt . In our work, we derive a model to account for this contribution and elucidate the mechanisms underlying its occurrence. Specifically, we find that this effect is due to the imperfect alignment of the sample cell with respect to gravity, which leads to a nonzero horizontal component of the refractive index gradient inside the sample. This component induces a time-dependent deflection of the illumination beam as a concentration gradient, generated by the Soret effect by an imposed temperature difference, builds up or relaxes, resulting in a slow, rigid translation of the entire image. This translation turns out to be the cause of the drift observed in the image structure function [5]. Correcting this artifact allows for accurate investigation of nonequilibrium fluctuations even in non-stationary conditions.

Materials and Methods

The experiments have been performed on a binary mixture of polystyrene polymer and toluene, with a polystyrene concentration c = 2.0% w/w. The sample is loaded in a thermal gradient cell of thickness h = 1.30 mm, coupled with a shadowgraph diagnostic apparatus. At the beginning of each experiment,

the sample is in a stationary nonequilibrium state, characterized by a linear concentration profile, generated through thermophoresis by applying a steady temperature gradient (heating from above). The temperature gradient is applied at least 4000 s before the beginning of the experiment. We perform measurements both under stationary and non-stationary (transient) conditions. Fluctuations in stationary conditions are investigated by maintaining the imposed temperature difference for the whole duration of the observation. The temperature gradient is then suddenly removed, and the fluctuations occurring under isothermal, non-stationary conditions are monitored. In this last condition, the amplitude of temperature fluctuations is negligibly small, allowing us to study the concentration nonequilibrium fluctuations during the relaxation towards equilibrium of the concentration profile. We repeated these experiments multiple times with different temperature differences ΔT (4 K, 8 K, and 17 K) and for different tilt angles θ , defined as the angle between the gravity direction and the normal to the cell plates.

To investigate non-equilibrium fluctuations, we used Dynamic Shadography[6]. Illumination is provided by a superluminescent diode (Superlum, SLD-MS-261-MP2-SM) with a wavelength of $\lambda = (675 \pm 13)nm$, placed at the focal distance f = 200 mm of an achromatic doublet. Images are recorded exploiting a sCMOS camera (PCO.panda), specifically for each experiments we acquired a series of 60000 images at a frame rate of 30Hz with a resolution of 512×512 pixels and an effective pixel size of $d_{eff} = 26 \ \mu$ m. Image sequences are then analyzed using a Fourier-based differential method known as Differential Dynamic Analysis (DDA).

Modeling a slow uniform drift in the images

Shadowgraph images typically present a strong image background, on top of which faint sample fluctuations may be visible. This strong background can be ascribed to the diffraction pattern produced by dust particles, scratches, or imperfections on the cell windows. Usually, under stationary conditions, this background contribution is generally effectively removed by DDA analysis. However, in the transient regime, image differences reveal the presence of a residual pattern similar to the

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static background, with increasing contrast as a function of the delay time. This observation suggests the presence of a uniform, rigid drift occurring during the transient state.

To account for this, we define a "moving" image intensity distribution $I_M(\mathbf{x}, t)$, expressed as

$$I_M(\mathbf{x},t) = I(\mathbf{x} + \mathbf{v}_0 t, t), \tag{1}$$

where $I(\mathbf{x}, t)$ is the stationary intensity distribution and v_0 is the velocity of the image translation. In Fourier space, this expression becomes

$$\hat{I}_M(\mathbf{q},t) = e^{-j\mathbf{q}\cdot\mathbf{v}_0t}\hat{I}(\mathbf{q},t).$$
(2)

Using this result, and decomposing the image intensity distribution as

$$I(\mathbf{x},t) = \delta I(\mathbf{x},t) + I_0(\mathbf{x}) + I_N(\mathbf{x},t), \qquad (3)$$

where $\delta I(\mathbf{x}, t)$ represents intensity fluctuations arising from refractive index fluctuations within the sample, $I_0(\mathbf{x})$ corresponds to the static background intensity, and $I_N(\mathbf{x}, t)$ denotes the detection noise, the image structure function $D(q, \Delta t)$ obtained from DDA can be written, under the assumption of small displacements and single-exponential dynamics, as

$$D(q,\Delta t) \simeq A(q) \left(1 - e^{-\Gamma(q)\Delta t}\right) + \alpha(q)\Delta t^2 + B(q), \quad (4)$$

with

$$\alpha(q) = \frac{1}{2}q^2 v_0^2 |\hat{I}_0(q)|^2.$$
(5)

Comparing Eq. 4 with the expression obtained from the stationary case $D(q, \Delta t) \simeq A(q) (1 - e^{-\Gamma(q)\Delta t}) + B(q)$, we can observe the presence of and additive term, quadratic in the delay time Δt , whose amplitude depends on the velocity v_0 and the spectrum of the background intensity $|\hat{I}_0(q)|^2$ at each wave vector q.

Transient state: relaxation towards equilibrium of the non-equilibrium fluctuations

To test our model and understand the physical origin of this effect, we focus on the transient states corresponding to the sudden removal of the imposed temperature difference across the mixture previously under steady thermal stress. In this case, since the temperature is uniform, thermal fluctuations are negligible, and non-linear effects, mainly due to the temperature dependence of the physical constant, are minimized. Exploiting Eq.4 and Eq.5, we find that for different times \bar{t} after switching off the temperature gradient, the velocity slows down, presenting a strong dependence on the imposed temperature difference ΔT increasing with it (Fig.1.a). Moreover, we perform experiments by tilting the gradient cell with respect the gravity, nominally $\theta = 1.3 \times 10^{-2}$ rad, 0 rad and -1.3×10^{-2} rad. As shown in Fig.1.b, we observe that the velocity is significantly



Figure 1: Drift velocity during transient-state measurements (a) estimated from the same inclination angle θ and different temperature differences ($\Delta T = 4$, K (black squares), $\Delta T = 8$, K (dark gray triangles), and $\Delta T = 17$, K (light gray circles)) and (b) for different inclination angles θ of the gradient cell with respect to gravity and fixed $\Delta T = 17K$. Circles indicate the velocity estimated from Differential Dynamic Analysis, while squares correspond to the velocity obtained via realspace tracking of the global image displacement. Colors represent different inclination angles: $\theta = -1.3 \times 10^{-2}$, rad (green), $\theta = +1.3 \times 10^{-2}$, rad (red), and $\theta = 0$, rad (blue).Image adapted from [5]

larger for $\theta = \pm 1.3 \times 10^{-2}$ rad than for $\theta = 0$ rad.

These findings point to the emergence of a refractive index component Δn parallel to the cell plates when the cell is tilted relative to gravity. In the absence of gravity, the concentration profile builds perfectly parallel to the temperature gradient, perpendicular to the plates. On the other hand, in the presence of gravity, a small misalignment of the cell with respect to it, leads to the formation of isoconcentration surfaces orthogonal to gravity, determining an angular deflection $\delta \theta = \theta \Delta n$ to the collimated beam. In the stationary case, since the concentration profile is stable, this beam deflection remains constant over



Figure 2: Transient-state measurements during relaxation towards equilibrium state after suddenly switching to zero the temperature difference ($\Delta T = 17K$). (a) Representative normalized image structure functions NISF at different time \bar{t} =300s, 675s and 1800s after switching off the thermal gradient, from black to light blue, for q=1.3×10² cm⁻¹ (left panel) and q=2.85×10² cm⁻¹ (right panel). The continuous lines are the best fitting curves to NIFs with Eq.??. (b) Relaxation rates $\Gamma(q)$ and mean squared amplitude A(q) in time from black to light blue. Continuous lines represent the best-fit curves to the filled circles considering Eq.7 and 8, respectively. (c) Time evolution of the dynamic and static roll-off wave vector during the relaxation of the concentration profile. In the inset, the diffusion coefficient estimated from the fit to $\Gamma(q)$. (d) Ratio of the static and dynamic roll-off wave vector in time. Inset, ratio of the two q_{ro} for initial temperature difference $\Delta T = 4K$ (triangles) $\Delta T = 8K$ (squares).

time. Conversely, a in the transient regime, the evolving concentration profile leads to a time-dependent deflection, which results in a time-dependent displacement with velocity

$$v_0 \propto \theta \frac{\partial n}{\partial c} \frac{d}{dt} \Delta c.$$
 (6)

To assess the efficacy of our correction, we fit Eq.4 to the data during the transient state for different times \bar{t} after switching off the temperature gradient (continuous lines in Fig.2.a). From the fits, we can estimate the rate $\Gamma(q)$ and amplitude A(q) of the solutal mode (Fig.2.b). The continuous lines in Fig.2.b represent the best fitting curves to the data using the theoretical expressions of the linearized hydrodynamic framework [2]

$$\Gamma(q) = D_0 q^2 \left[1 + \left(\frac{q_{ro}^{dy}}{q}\right)^4 \right],\tag{7}$$

$$A(q) = T(q) \left[\frac{a}{1 + (q/q_{ro}^{st})^4} \right].$$
 (8)

As can be observed by the time evolution of the static and dynamic roll-off wavevectors (2.c) obtained from eq. 7 and 8, respectively, no significant deviation can be observed between them, since their ratio is compatible with unity at all times \bar{t} (Fig.2.d).

This experimental condition, which, to the best of our knowledge, has never been exploited before in this kind of study, turns out to be particularly convenient as it enables observing Soret-induced concentration fluctuations in isothermal conditions, completely decoupling purely thermal effects.

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Role of cross-diffusion on double diffusion in ternary system

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Introduction

Buoyancy can result from multiple factors acting together, such as temperature differences, concentration variations, or differences in how substances diffuse within a mixture. When these density changes cause fluid movement, the process is known as double-diffusive convection. This phenomenon is common in natural systems, like ocean mixing through salt fingers, and also appears in laboratory experiments that measure diffusion coefficients. It is often observed in setups with sharp interfaces, such as Hele-Shaw cells or sliding symmetric tubes (Seta et al., 2019). In such experiments, doublediffusive convection is typically considered a disturbance that can affect the accuracy of diffusion measurements. To minimize its influence, it is essential to understand its causes, different forms, and impact on diffusion and mixing processes. Moreover, a thorough understanding of convective instabilities in multicomponent systems can provide valuable insights into unresolved phenomena, such as the formation of thermohaline staircases. These layered structures, observed in oceanic and astrophysical contexts, result from complex interactions between diffusion and convection. By studying how instabilities develop under different conditions, we can better explain their emergence and improve predictive models for similar natural and industrial processes.

Historically, several assumptions were made regarding instabilities in ternary systems. One key assumption was the existence of two distinct types: Diffusion-Layer Convection (DLC), also known as overstability, and Double-Diffusive (DD) convection, often referred to as fingering. These instabilities have fundamentally different origins. DLC develops symmetrically at the edges of the boundary, forming on both sides while remaining separated by a stable diffusive layer around the interface. In contrast, DD emerges from the center, also symmetrically, but it disrupts the entire layer interface.

The development of instabilities depends on both main diffusion and cross-diffusion coefficients. Cross-diffusion coefficients are often neglected, either due to the difficulty of determining them accurately or because they are sometimes several orders of magnitude smaller than the main diffusion coefficients. However, to fully understand their impact, one must start with the analytical solution for diffusion in ternary systems.

By carefully analyzing this solution, it is possible to identify the conditions under which density inversion occurs. This can be done by tracking the sign of the first derivative of the diffusion equation solution. The complete analytical solution and the equations required to generate the stability diagram are presented elsewhere (Seta et al., 2019).

Numerical model

To analyze instabilities, we implemented the governing equations in the open-source finite volume software OpenFOAM. The spatio-temporal dynamics of the system are described by the Navier-Stokes equations coupled with mass transfer equations under the Boussinesq approximation. These equations have been formulated and solved within the OpenFOAM framework (Seta et al., 2019), allowing for detailed numerical simulations of the instability mechanisms in multicomponent systems:

$$\operatorname{div} \vec{V} = 0, \tag{1}$$

$$\frac{\partial V}{\partial t} + \vec{V} \cdot \nabla \vec{V} = -\frac{1}{\rho_r} \nabla p + \nu \Delta \vec{V} + \vec{g} \rho^*$$
(2)

$$\frac{\partial c_1}{\partial t} + \vec{V} \cdot \nabla c_1 = \nabla (D_{11} \nabla c_1) + \nabla (D_{12} \nabla c_2) \tag{3}$$

$$\frac{\partial c_2}{\partial t} + \vec{V} \cdot \nabla c_2 = \nabla (D_{21} \nabla c_1) + \nabla (D_{22} \nabla c_2) \tag{4}$$

Here \vec{V} is the velocity; p is the difference between total and hydrodynamic pressure; ν is the kinematic viscosity and $\rho^* = \rho - \rho_r$. Hereafter, the notations D_{ij} and D_{ii} will be used for the full set and the main terms of the diffusion matrix, respectively. The mixture analyzed in this study was the DCMIX2 system, consisting of Toluene-Methanol-Cyclohexane, with 0.62-0.31-0.07 composition.

Case	D_{11}	D_{12}	D_{21}	D_{22}
1	2.244	1.337	-0.226	0.551
2	2.244	0	0	0.551
3	2.244	0	-0.226	0.551
4	2.244	1.337	0	0.551

Table 1: Diffusion coefficients $D_{ij} \times 10^{-9} \text{m}^2/\text{s}$ in four cases

Results

We consider four cases with representative diffusion coefficients, which are listed in Table 1. The main diffusion coefficients remains unchanged in all cases, while the cross-



Figure 1: Four different cases, depending whether cross-diffusion coefficients are neglected or not.

diffusion coefficients are different. The theoretical treatment (Seta et al., 2020) of the system with constant diffusion coefficients provides four possible states: gravitationally unstable, gravitationally stable, DD, and DLC. The top raw in Fig. 1 identifies these states for the set of coefficients from Table 1. In each panel, below the red line is an unstable state in the form of a Rayleigh-Taylor instability when the heavier liquid is above the lighter one. The remaining three states lie above the red line, indicating that they are initially stable. However, once diffusion begins, the experiments marked in yellow (DD) or blue (DLC) will develop convective motion over time.

To ensure a direct comparison, the initial conditions for all four cases were set at the same position, meaning they share the same concentration values, denoted by "x" in Fig. 1 (upper panel). The specific initial conditions were: $c_{1,top} = 0.64$, $c_{2,top} = 0.345$, $c_{2,bot} = 0.275$, which results in concentration differences of $\Delta c_1 = 0.04$ and $\Delta c_2 = -0.07$.

Case 1, where all four diffusion coefficients are included, exhibits DLC behavior, characterized by oscillatory plumes moving from right to left once convection begins. In Case 2, where cross-diffusion is neglected, the system develops fingerlike (DD) motion, emphasizing the importance of considering cross-diffusion coefficients.

In Case 3, where only $D_{12} = 0$, the behavior remains similar to Case 2. This is because, in this particular system, D_{12} plays a dominant role among the two cross-diffusion coefficients due to its magnitude. In Case 4, where only $D_{21} = 0$, the behavior is similar to Case 1 but with slightly more stable conditions. This suggests that in this system, D_{21} has a destabilizing effect, enlarging the DLC region in Case 1 compared to Case 4. As a result, the initial experimental conditions in Case 1 are positioned deeper within the DLC region.

Conclusions

We have demonstrated the importance of cross-diffusion coefficients in ternary mixtures for accurately predicting doublediffusive convection instabilities. In this particular system, neglecting cross-diffusion coefficients led to completely opposite and incorrect behavior, where DD convection appeared instead of DLC.

Future work will focus on incorporating more complex and accurate assumptions, such as concentration-dependent diffusion coefficients, which may give rise to new, previously unobserved behaviors.

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Influence of Magnetic Fields on n-Eicosane $-Fe_3O_4$ Nanofluids: A Novel Investigation of Thermophoresis, Thermocapillarity, and Natural Convection

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Introduction

The present work analyses the effects generated by the application of magnetic fields in fluid systems of n-Eicosane (C20), with homogeneously dispersed ferromagnetic Fe_3O_4 nanoparticles. Thermophoresis and thermocapillary together with the natural convection have been the onset of driving forces acting in the above-mentioned C20- Fe_3O_4 nanofluid. The novelty and relevance of the present study lies in the fact that there are no publications combining all three effects in this type of fluid systems. In addition, the investigation of the magnetic effect on the dynamics of the PCM systems might be interesting to look into. The literature reports that, applying non-uniform magnetic fields on nano-enhanced phase change materials (NEPCMs) lead to an increment in convection and a decrement in the size of the transition liquid-solid regions (Zhuang et al. 2023; Mousavi et al. 2024).

Governing Equations:

Assuming that, the present nanofluid is Newtonian and incompressible the governing equations include the continuity, momentum, and energy equations, nanoparticles' transport equations, Brownian D_B and Thermophoretic D_T Diffusion Coefficients, Marangoni equation, and as well the equation of the magnetic grains flux in a ferrofluid, as follows (Dubert et al. 2024; Aminfar et al. 2013):

$$\nabla \cdot \vec{V} = 0,$$

$$\rho_{nf} \vec{V} \cdot \nabla \vec{V} = -\nabla p - \frac{\mu_{nf}}{K} \vec{V} + \nabla \cdot (\mu_{nf} \nabla \vec{V}) + (\rho \beta)_{nf} (T - T_c) \vec{g}$$

$$(\rho C_p)_{nf} \vec{V} \cdot \nabla T = \nabla \cdot (k_{nf} \nabla T) - \varepsilon C_{p,p} \vec{J_p} \cdot \nabla T,$$

$$\rho_p \vec{V} \cdot \nabla \phi = \nabla \cdot (\rho_p D_B \nabla \phi) + \nabla \cdot (\rho_p D_T \nabla T),$$

$$D_B = \frac{k_B T}{3\pi \mu_f d_p}, \quad D_T = 0.26 \frac{k_f}{2k_f + k_p} \frac{\mu_f}{\rho_f T} \phi,$$

$$\mu \nabla_n \mathbf{u}_t = -\gamma \nabla_t T,$$

$$\mathbf{j} = -D \nabla \phi + S_T \nabla T - \frac{\phi H}{\mu_0} \xi L(\xi) \nabla H.$$
(1)

Where \vec{V} the velocity vector, p the pressure, T the temperature, ϕ volume fraction of nanoparticles, S_T Soret coefficient, H magnetic field strength, ξ Langevin parameter, and $L(\xi)$ Langevin function. The thermophysical properties of the nanofluid, including density, specific heat, thermal expansion coefficient. viscosity. and thermal conductivity. can be determined by the following equations (Aminfar et al. 2013):

$$\begin{split} \rho_{nf} &= (1-\phi)\rho_f + \phi\rho_p, \\ (\rho C_p)_{nf} &= (1-\phi)(\rho C_p)_f + \phi(\rho C_p)_p, \\ (\rho\beta)_{nf} &= (1-\phi)(\rho\beta)_f + \phi(\rho\beta)_p, \\ \mu_{nf} &= \mu_f \left(1 - 34.87 \left(\frac{d_p}{d_f}\right)^{-0.3} \phi^{1.03}\right), \\ k_{nf} &= k_f \left(1 + 4.4 \operatorname{Re}_B^{0.4} \operatorname{Pr}^{0.66} \left(\frac{T}{T_f}\right)^{10} \left(\frac{k_p}{k_f}\right)^{0.03} \phi^{0.66}\right) \end{split}$$

A rectangular domain of Aspect Ratio (length/height) 2.25 has been considered here as a computational domain. The boundary conditions and physical properties of the liquid and nanoparticles used are shown in Figure 1 and Table 1. The magnetic field is produced by a constant electrical current through a wire located at the middle top of the domain. The direction of the current might be entering the domain (clokwise magnetic field) or getting out the domain (counter-clokwise magnetic field). The initial conditions used were zero velocity and a uniform thermal field across the domain, with a temperature of T = $28.5^{\circ}C$ and a temperature difference between the hot and cold walls of $\Delta T = 45^{\circ}C$.



Figure 1: Boundary Condition; by u we refer to the vector velocity

Table 1: Physical properties of C20 and Nanoparticle (Fe_3O_4)

Property	Symbol	C20 / <i>Fe</i> ₃ <i>O</i> ₄
Density (kg m ⁻³)	$ ho_f/ ho_p$	778/5200
Dynamic viscosity (kg m ^{-1} s ^{-1})	μ_f	0.0032
Thermal conductivity (W m ^{-1} K ^{-1})	κ_f/κ_p	0.15/6.0
Specific heat $(J kg^{-1} K^{-1})$	$c_{p,f}/c_{p,p}$	2280/670
Thermal expansion coefficient (K ⁻¹)	β_f/β_p	$9 \times 10^{-4} / 1.3 \times 10^{-5}$
Surface tension gradient (N m ^{-1} K ^{-1})	σ_{f}	-8.44×10^{-5}

The OpenFoam package was selected to simulate the whole flow characteristics. The PIMPLE algorithm was used to solve simultaneously the momentum and continuity equations, and to assure a correct coupling between the pressure and velocity fields. The temperature was calculated in each PIMPLE iteration. The final system of linear equations (for pressure, velocity and temperature fields) was solved by using the Geometric-Algebraic MultiGrid (GAMG) solver method.

Results

Figure 2 compares the streamlines at t=500s for four different fluid systems. The first one contains pure C20, the second C20 with nanaoparticles without applying any magnetic field, and last two represent the mixture under magnetic field imposed both clockwise (CMF) and counterclockwise (CCMF) directions. It can be seen that adding Marangoni to the previous cases, helped improve the heat transfer distribution through the whole cavity which lead to uniform distribution of the temperature. Figure 3, plots the evolution of the velocity along the length for all the studied cases. It can be seen that, just by adding nanoparticles the velocity doubled, though imposing the magnetic field this velocity increased more. As expected, when the magnetic field is applied counterclockwise, in the same direction as Marangoni acts, the velocity increased compared to the case when the magnetic field was applied in the clockwise direction.



Figure 2: Snapshot of streamlines at t=500s for four different conditions: a) Pure C20, b) C20 with nanoparticles, c) C20 with nanoparticle under CMF effect, d) C20 with nanoparticles under CCMF effect.



Milano (Italy), June 2025



Figure 3: Horizontal velocity profiles along the line (0, 90%H, 0) to (L, 90%H, 0) under the four conditions.

Conclusions

The addition of ferromagnetic nanoparticles to the molten C20 introduces a new driving force which, by appropriate external control, can greatly modify the bulk flow patterns. Thus, a correct combined action of thermocapillary and magnetic effects can significantly increase the heat exchange between both hot and cold sides and thus increase their heat transfer rate.

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Soret-induced convection in a layered porous medium simulating an anticlinal geological fold under the action of a geothermal temperature gradient

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Introduction

In this paper we study Soret-induced convection in a layered porous medium simulating an anticlinal geological fold under the action of a geothermal temperature gradient. Geological structures are layered formations of rocks different in porosity and permeability. When layers of rock undergo plastic deformation, they become folded. Saturated with liquids, such natural underground reservoirs become the systems for natural convective processes.

Problem formulation

Soret-induced convection of a binary mixture of tetralin (50%) and dodecane (50%) in a porous medium is studied. The lighter component tetralin is taken as a solute and the heavier component dodecane as a solvent. It is assumed that the mixture density linearly depends on temperature and solute concentration. The transport and viscosity coefficients are assumed to be constant. The influence of the Dufour effect and barodiffusion is neglected. A system of three fluid-saturated porous layers with a bend imitating an anticlinal geological fold is considered. The length of the calculation domain is 200 m, the width is 100 m, the height of each layer is 25 m. Such dimensions are typical for the formations, the fold angle is nearly 152 degrees.

The modeling is carried out within the framework of the Darcy-Boussinesq equations taking into account the Soret effect. We consider heating from below with a temperature gradient equal to $3 \cdot 10^{-2}$ K/m, which corresponds to the average geothermal gradient. The temperature value $T_0 =$ 353.5 K used in the calculations is the average temperature at an oil depth of $2 \cdot 10^3$ m at an average geothermal gradient. At the external boundaries, the impermeability condition and the absence of diffusion flux of the solute are set. The temperatures at the top and bottom boundaries correspond to a strictly vertical geothermal gradient, and zero heat flux is imposed on the vertical ones. At the boundaries between the layers, the continuity of pressure, thermal and diffusion fluxes, as well as the continuity of the vertical component of velocity, temperature and concentration are set. The porosity of all the layers are assumed to be the same and equal to 0.1. The permeabilities of the top and bottom layers are taken equal and always lower than the permeability of inner layer. The calculations are carried out for the permeabilities of layers ranging from

 $2 \cdot 10^{-11} m^2$ to $10^{-14} m^2$. Such properties are typical for fine-grained sand, clayey sands, siltstones, micro-fractured limestones, sandstone and shale.

Linear stability problem

We first investigated linear stability of a convectionless state considering an infinite porous layer, saturated with a binary fluid, tilted at an angle α to the vertical. The layer is subjected to the gravity field. The boundaries of the layer are rigid, impermeable for the solute and perfectly thermally conductive. The temperature distribution specified at the boundaries corresponds to a strictly vertical temperature gradient. The study was carried out for fixed values of the separation ratio and Lewis number corresponding to a mixture of tetralin (50%) and dodecane (50%): $\psi = 0.694$, Le = 150. The other parameters were varied.

It is found that at the considered value of the separation ratio the longitudinal rolls are the most dangerous type of disturbances over the entire range of layer tilt angles. Besides, over the entire range of layer inclination angles, these disturbances have a finite-wavelength structure. At layer inclination angles smaller than 41°, the presence of the solute increases the stability of the system, and at larger angles the stability of the system is greatly reduced due to the presence of the solute.

Three-dimensional calculations

In three-dimensional numerical calculations for full nonlinear non-stationary problem for the configuration imitating an anticlinal fold (Fig.1), to be more close to the linear stability problem, the permeability values in the upper and lower layers were fixed below the threshold value and only the permeability of the middle layer was changed.



Fig.1. 3D calculation domain.
It follows from the solution of linear stability problem that at the layer inclination angle equal to 76 degrees the critical Rayleigh number is $Ra_c = 6.956$ and the most dangerous disturbances are the convective rolls with axes parallel to Xaxis (longitudinal rolls). Besides, the wavenumber of these disturbances in z-direction is $k \approx 1.66$. For the geometry considered in nonlinear calculations this means that the permeability value at which the convection can be expected should be higher than $8.5 \cdot 10^{-13} m^2$. Thus, the case when the permeabilities of the top and bottom layers are equal to $10^{-14} m^2$ well corresponds to the configuration considered in the linear stability problem. For this case, calculations were carried out for the permeability values of the middle layer from $2 \cdot 10^{-14} m^2$ and higher.

The calculations show that at permeabilities of the middle layer $K_2 = 2 \cdot 10^{-13} m^2$ and lower, a symmetrical two-vortex flow, which structure corresponds to the longwave mode, is realized. The vortices are located inside the fold wings with a symmetry axis coinciding with the fold axis. At $K_2 = 2 \cdot 10^{-13} m^2$ the flow is localized in the middle layer and practically does not penetrate into less permeable upper and lower layers. With the decrease of permeability of the middle layer, the flow intensity is such low that it does not affect the distribution of the solute concentration in the middle layer, the solute concentration is observed, but this is associated with the geometry of the domain. In plane C, the solute is distributed linearly in height.

When the permeability of the middle layer increases to the value $K_2 = 10^{-12} m^2$ or higher, the flow takes the structure of longitudinal rolls. For the permeability of the middle layer equal to $K_2 = 10^{-12} m^2$, the longitudinal rolls appear along the middle layer, which in our calculations simulates a carbon layer. In the plane A, these rolls look like a vortex flow, similar to that realized at lower permeabilities. In the plane B, the rolls are visible along the layer with thickenings at the fold bend, and in the plane D, the cells are observed across the rolls. This flow is localized in the middle layer. In this case the maximum value of the vertical velocity component is an order of magnitude higher than at lower permeabilities. The flow structure in the plane B corresponds to that obtained in linear stability analysis.

Analysis of the concentration distribution when the longitudinal rolls mode is realized show that in plane A, the flow is weak, so the concentration isolines are deformed only due to the geometry of the cavity, as in the case of low permeabilities of the middle layer. However, along the layer, along the rolls, as well as across it in the vertical cross-section, significant deformation of the concentration isolines is observed. In the axial plane of the fold and in other planes parallel to it, the isolines are deformed by the flow, therefore, in the region of the middle layer their deformation is significant, and in the outer layers the concentration distribution is close to linear in vertical direction.

At the permeability of the middle layer equal to $K_2 = 2 \cdot 10^{-12} m^2$, first a longwave regime appears in the cavity. The two-vortex flow occupies the volume of the middle layer. This structure exists for about $2.5 \cdot 10^3$ years. After this, an asymmetrical structure appears, consisting of five

longitudinal rolls. At a time of about $8 \cdot 10^3$ years, the next structure transformation occurs, and the flow becomes symmetrical four-vortex.

An increase in the permeability of the middle layer accelerates the development of flow. At $K_2 = 10^{-11}m^2$, the longwave regime is observed until about 10^3 years. At time $t = 1.5 \cdot 10^3$ years, the flow already has a six-vortex longitudinal structure. The second transformation of the structure occurs around $2 \cdot 10^3$ years: a merger of two vortices is observed, the structure becomes asymmetrical, five vortices have different sizes in the plane D. The third transformation is observed at $t \approx 3.5 \cdot 10^3$ years. Here the sizes of the vortices are equalized. Further modeling carried out up to 10^4 years does not show subsequent changes in the flow structure. A further increase in permeability K_2 leads to a highly nonlinear behavior of the flow intensity.

Conclusions

Three-dimensional Soret-induced convection in a three-layer porous system imitating an anticlinal geological fold, under the influence of a geothermal temperature gradient has been studied. The layer porosities are the same and the permeabilities are different. The mixture of tetralin and dodecane is considered as a fluid saturating the porous medium. Investigation of the linear stability of the motionless state of a binary mixture in an inclined porous layer under the vertical temperature gradient has shown that at any laver inclination angles, the most dangerous disturbances are longitudinal rolls with finite wave numbers in perpendicular direction. For the system parameters under consideration, the presence of a solute can change the convection threshold in both directions depending on the layer inclination angle. The threshold change can reach 26%. Full 3D nonlinear calculations have been performed for fixed permeabilities of the external layers, lower than the threshold value according to the linear theory. The calculations have shown that, after a long period of time from the beginning of the process, a flow arises. The development of a steady flow occurs over a long period of up to 6000 years. It is found that at small permeabilities of all layers, arising flow has a longwave character. With the increase of permeability of the middle layer (higher than $K_2 = 2 \cdot 10^{-13} m^2$, the flow in the plane of a geological fold limbs takes the form of longitudinal rolls and in the perpendicular direction the flow structure becomes multicellular, this flow structure well corresponds to the linear stability results. The flow is localized in the middle layer and significantly influences the concentration field.

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Convection of a Binary Fluid Mixture in the Hele-Shaw Cell with Modulated Heating

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Introduction

Modulated heating with a frequency that is large compared to the traveling wave (TW) frequencies under stationary driving was investigated in horizontal layer (B.L. Smorodin et al. 2009). Depending on parameters, the following response behavior was found: (i) quasiperiodic TWs and (ii) frequency locked subharmonic standing wave (SW) that get stabilized by the modulation



Figure 1: Temperature modulation on the lower boundary

Modulated heating in the Hele-Shaw cell

Instability and nonlinear convective flows in a vertical Hele-Shaw cell filled with a binary mixture are analyzed under the influence of temperature modulation. We consider the ethanol-water mixture with the Lewis number L = 0.01, the Prandtl number Pr = 10, and the separation ratio $\psi = 0.25$. Finite difference numerical simulations are performed for realistic boundary conditions.

Two types of harmonic modulation of the temperature difference at narrow horizontal boundaries of the Hele-Shaw cell with an amplitude a = 1 and a dimensionless frequency Ω are analyzed. 1) Temperature modulations at the boundaries are in antiphase; 2) the temperature of the upper boundary is kept at some fixed temperature, and the temperature of the lower boundary varies around the average value. In these cases, the symmetry properties relative to the midpoint of the layer height for thermal and concentration waves in a quiescent fluid are different. In case 1) the temperature and concentration distributions are even functions relative to the midpoint; in case 2) the distributions do not have a definite parity.

The instability of the binary fluid mixture in the Hele-Shaw cell is associated with oscillatory perturbations. Depending on the frequency, it can occur either as a result of forward bifurcation (SW in Fig.1, $\Omega = 0.06$) or backward bifurcation (TW in Fig. 1, $\Omega = 0, 0.08, 0.1$).

The bifurcation maps of the solutions (Fig.2) depend on the type of modulation. The differences are as follows. The threshold for oscillatory convection in the case of temperature modulation at the lower boundary with $R_{osc} = 0.42$ is slightly lower than it is in the case with antiphase modulation at $R_{osc} = 0.45$.

The loss of stability of the extended traveling wave and

the transition to the conductive state (saddle-node bifurcation) with a decrease in the Rayleigh number to the subcritical region occurs at the point $Ra_{TW}^S = 0.44$ (downward arrow in Fig. 2). The spectrum of the traveling wave at the point Ra_{TW}^S has the frequency of the TW ω_{TW} and its combination with the external frequency $\Omega \pm \omega_{TW}$.

TW is stable over a wide range of Rayleigh numbers R if temperature is modulated on the lower boundary. TW is destroyed at some critical value of the Rayleigh number and the stable standing wave (SW) is formed when the boundary temperatures are modulated in antiphase: The intensity of convection in the SW is lower than that in the TW.



Figure 2: The dependencies of the Nusselt number on the Rayleigh number: Ω =0.1. Temperature modulation on the lower boundary (blue circles) and temperature modulations in antiphase (orange circles)

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Enhancing Species Separation in a Two Sided Lid-Driven Horizontal Cavity

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Introduction

The coupling between shear-driven convection and thermodiffusion is a complex phenomenon due to the interactions between the different forces acting on the binary mixture. Until now, the species separation obtained in vertical columns has been limited (Platten et al. 2003). The convective flow velocity depends on temperature difference, ΔT maintained on the vertical surfaces of the column and the thickness H separating these two surfaces. For a given thickness, increasing ΔT enhances thermodiffusion but also increases convective velocity, which reduces species separation. For a fixed ΔT value, optimum separation occurs in a vertical column with a thickness of less than one millimeter, (Seta et al. 2019).

In this study, we propose a novel approach that decouples fluid flow driving species separation from the imposed temperature difference between the parallel surfaces of the column. Furthermore, we explore boundary conditions that maximize ΔT without inducing natural convection, regardless of the sign of the Soret coefficient (Mojtabi et al., 2019).

Physical consideration and analytical solution

We consider a rectangular cavity with large aspect ratio B = L/H, where H is the cavity height along the y axis and L is the length along the x axis. The cavity is filled with a binary mixture with density ρ and dynamic viscosity μ . The two vertical walls x = 0 and x = L are adiabatic and impermeable, while the horizontal walls y = 0 and y = H are maintained at constant and uniform temperatures T_{lo} , and T_{up} , moving at two opposite but constant imposed velocities $(fU_P \vec{e}_x, U_P \vec{e}_x)$ (see Fig. 1).

We assume that the variations of the mass fraction in the vicinity of C_0 remain small.

For the cavity under study, filled with a binary fluid with $D_T > 0$ or $D_T < 0$, three configurations permit a forced convection regime, $U_p < 10^{-5} m/s$. Indeed for $D_T > 0$ and cell heated from below, $T_{lo} > T_{up}$, natural convection begins for a critical Rayleigh number lower than that associated with the Rayleigh Bénard problem $Ra_c = 1708$.



Figure 1: Cell diagram

It follows that natural convection, which is added to forced convection, appears for a small temperature difference no longer ensuring notable species separation. For positive thermodiffusion coefficient ($T_{lo} < T_{up}$, horizontal cell heated from above). The denser constituent migrates towards the bottom wall, the convective solution in the horizontal layer remains infinitely stable, allowing significant species separation for a wider range of ΔT and H.

For negative thermodiffusion coefficient, two configurations could lead to a forced convection regime for moderate values of $|T_{lo} - T_{up}|$:

 $*T_{lo} - T_{up} > 0$ (horizontal cell heated from below). the denser constituent moves downward. The convective solution, loses stability for a critical Rayleigh number Ra_c s greater than $Ra_c = 1708$.

 $*T_{lo} - T_{up} < 0$ (horizontal cell heated from above), the denser constituent migrates to upper wall. This thermally stable configuration may lose stability for of Ra > 1708 leading to a mass instability.

To keep only forced convection and prevent the birth of mixed convection, the two published studies (Mojtabi, 2020 and Mojtabi et al.2023) demonstrated the possibility of significantly enhancing separation in microgravity, facilitating the measurement of thermodiffusion coefficients in binary and ternary mixtures.

Velocity field structure in forced convection

For a shallow cavity $A \gg 1$, the parallel flow approximation holds. The streamlines remain parallel to the x direction except for the vicinity of the insulated walls x = 0 and x = L, which gives:

$$\vec{V}_b = U_b(y)\mathbf{e}_x, \ T_b = bx + g(y), \ C_b = mx + f(y)$$
 (1)

The constants b and m respectively represent the temperature and mass fraction gradients along the x direction. The constant b is zero due to imposed constant temperature on the walls y = 0, H. Thus for a fixed value of y_0 , the species separation between x = 0 and x = L is given by $\Delta C = mL$.

Maximum species separation occurs for f = -1, leading to basic velocity field:

$$U_{b} = (2y - H) \left(\frac{mg\beta_{C}}{\nu} Hy^{2} - \frac{mg\beta_{C}}{\nu} H^{2}y + 12U_{P} \right) / 12H.$$
(2)

This velocity is zero at y = H/2 and at two symmetrical real values of y, if the associated quadratic equation's discriminant $\left(\frac{mg\beta_C}{\nu}H^2\right)^2 - 48\frac{mg\beta_CHU_p}{\nu}$ is positive. This condition leads to a three-cell convective structure, as shown in Figures 2 and 3 for a Water-Ethanol mixture ($\Delta T = 20^{\circ}C$). The two extreme convective cells rotate clockwise and the central one rotates counter clockwise at lower velocity than the two other ones. The central convective cell leads to species separation between the two ends of the cavity, x = 0 and x = L opposite to the two others cells Cf. Figure 3. Otherwise, y = H/2 is the only real root; This condition leads to a unicellular convective structure (Cf.Figure4).



Figure 2: The horizontal velocity component, $U_b(y)$: analytical, solid line, numerical, black dots



Figure 3: Streamlines for Water-Ethanol ($\Delta T = 20^{\circ}C$)



Figure 4: The horizontal velocity component, $U_b(y)$: analytical, solid line, numerical, black dots

Mass fraction field in forced convection

Once the temperature and velocity fields are calculated, we deduce the following mass fraction field:

$$C = mx + \frac{m}{D} \left(Pmy^3 \frac{10H^2 - 15Hy + 6y^2}{720} + U_p y^2 \frac{-6H^2 + 4Hy}{12H^2} + \frac{H^2 U_p}{12} - \frac{H^5 Pm}{1440} - \frac{LD}{D2} \right) + \frac{C_0 (1 - C_0) (T_b - T_{lo}) (H - 2y)}{2DH}$$
(3)

The mass fraction gradient, m, is derived by ensuring mass flux conservation across any cross-section perpendicular to the x-axis: $\int_0^H (U_b C - D \frac{\partial C_b}{\partial x} dy = 0)$. This equation leads to an algebraic equation of the third degree having as solutions the gradient of mass fraction, m:

$$H^{8}P^{2}m^{3} - 216H^{5}PU_{b}m^{2} + (12096)H^{2}U_{p}^{2} - 504H^{3}PD_{T}(T_{up} - T_{lo})C_{0}(1 - C_{0}) + 362880D^{2})m + 60480D_{T}(T_{up} - T_{lo})C_{0}(1 - C_{0})U_{p} = 0 \quad (4)$$

Numerical simulations confirm the validity of our simplifying assumptions, as shown in Figure 5.



Figure 5: Mass fraction field C(x) analytical, solid line, numerical, black dots

Optimization of the species separation

The species separation of binary mixture is defined as the difference in mass fraction, C, of the denser component between the two ends of the cavity, $\Delta C = C(x = L) - C(x = 0) =$ mL. For a given binary mixture, the mass fraction gradient, m, depends on the fluid properties, cavity geometry (H), imposed temperature difference (ΔT), and wall velocity (U_b). Optimal separation conditions were identified for the four analysed configurations

Conclusions

We demonstrate the potential for significantly improving species separation in a binary mixture using a novel configuration. This approach achieves greater separation than conventional thermogravitational columns (TGCs). From the measurement of the mass fraction gradient m, for a fixed U_p and $-U_p$ velocity imposed on the horizontal walls, it is possible to access the measurement of the thermodiffusion coefficient D_T of the binary mixture in a terrestrial laboratory. This method applies to both positive and negative D_T thermal diffusion coefficient unlike TGCs

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Comprehensive Analysis of PCM Melting Dynamics: Thermogravitational convection and Marangoni Flows

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Introduction

Energy demand is continuously growing due to the rapid developments in the industry and technology, and higher living standards of customers. Depletion of non-renewable energy sources causes global warming, leading researchers to focus on cleaner, sustainable alternatives (Irfan Lone and Jilte 2021). Phase Change Materials (PCMs) absorbs, stores and releases thermal energy in form of latent heat of phase transition, melting or freezing, and are becoming a promising solution for energy storage due to their low cost, environmentally friendly nature, and safety in thermal energy applications (Du et al. 2018). The efficacy of phase change materials for energy storage is largely contingent upon their heat of fusion, which determines the quantity of thermal energy absorbed during melting and released upon solidification (Ezquerro et al. 2019; Porter et al. 2023). It is therefore essential to maximize this heat of fusion. Several studies suggest adding metallic particles to PCMs; being the thermal conductivity of metallic solids higher than that of PCMs would increase the energy transfer capacity (Fernandes et al. 2012; Zhang et al. 2022). Under terrestrial conditions, convective motions within the liquid phase of the PCM can help solve the problem of low conductivity. Convective motions driven by density gradients induced by temperature differences can enhance the heat transfer rate by an order of magnitude (over conduction heat transfer) (Madruga and Mendoza 2017). However, that strategy is not applicable in microgravity, since natural convection does not occur in absence of gravity. Therefore, a way to improve PCM heat transfer in microgravity is to benefit from the Marangoni flow induced by the thermal gradients of the surface tension at the boundary between two fluids (Dubert et al. 2024; Šeta et al. 2021). Given the growing interest, this work aims to provide a new, non-intrusive technique to study melting processes in paraffin waxes with metallic particles, for both Earth and microgravity studies. The effect of viscosity is evaluated (in term of particle concentration) over both thermogravitational and Marangoni convection, measuring both the melting rate, and convection flows by Event-Based imaging Velocimetry (EBV).

Experimental setup

EBV relies on imaging small particles illuminated by a continuous laser light-sheet (Willert and Klinner 2022). Moving particles generate continuous time-stamped events on the detector, later used to infer their velocity. The system records changes of image intensity on the pixel level (positive event for increasing and negative for decreasing change) (Willert and Klinner 2022). Maps of the evolving flow-field can then be obtained from the event-tracks produced by particles. In this case, the Metavision® EVK4 - HD kit has been used for PCM melting experiments. The cell to monitor the melting process consists of two aluminium walls an adiabatic bottom and two methacrylate windows. The temperature gradients are generated by water circulation controlled by thermostatic baths. In order to induce Marangoni convection, the upper part is left free, as the convective flow is driven by the balance between viscous and thermocapillary forces acting on the interface. For the analysis of the thermogravitational convection, the upper surface is covered so that it is in direct contact with the PCM. Paraffin PCMs as n-octadecane, n-nonadecane, n-eicosane



Figure 1: Setup consisting of the Metavision® EVK4 – HD camera, the PCM melting cell and the backlight.

are considered due to the significant latent heat of fusion, negligible overcooling, low vapour pressure at fusion and chemical stability (Chebli and Mechighel 2025). As tracing particle, magnetite (Fe₃O₄, 50-100 nm) and Iron (Fe, 4.5-5.2 μ m) are selected to increase heat transfer rate.

Preliminary results

Preliminary results are shown for the case where top surface is free. Tracing particles are initially trapped in solid PCM. When the temperature gradient is turned on, the PCM starts melting from the hot wall causing the Marangoni convection, and particles rotate with the flow. Given the small size of the



Figure 2: Melting process of *n*-Octadecane with magnetite particles inside the PCM induced by a 20° C temperature difference.

particles, the event-based camera is focused in a small region of the cell. Once the melting starts, the backlight illuminates the melted region and the flow is captured by the EVK4 – HD camera, following the events created by the movement of particles. Figure 3 shows the capture and processing of the flow in the upper right region of the cell during the beginning of the melting process.



Figure 3: Capture of right upper part of the cell during the beginning of melting, segmentation of corresponding elements, determination of changes in particle position from the events and the colormap of the velocity flow.

Conclusions

Preliminary results show the ability of EVK-4HD and the Event Based Method to capture the motion to track particle movements and therefore determine the flow. As expected, convective flows promote the melting process of PCM. Work on improving the data acquisition and post-processing procedure is currently under development.

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Dynamic Differential Microscopy: Investigating Transport Phenomena in the Fourier Space

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Introduction

Differential Dynamic Microscopy (DDM) is an optical method for characterizing complex fluids (Cerbino et al. 2008), increasingly used to study particle dynamics of a wide variety of samples undergoing diffusion (Zhang et al. 2023). In this work, we provide an overview of the DDM technique, highlighting its advantages over traditional methods for diffusion analysis such as Dynamic Light Scattering (DLS) and Particle Tracking (PT). Based on these results, we discuss the experimental feasibility of extending the method to the study of a sample stressed by a macroscopic temperature gradient and its potential benefits for the study of thermodiffusion.

Overview

DDM was originally developed to study the Brownian motion of nanoparticles in a fluid at equilibrium conditions. It has subsequently been used in a wide range of applications, including the analysis of bacterial motility (Wilson et al. 2011), the study of the viscoelastic behaviour of soft matter (Bayles et al. 2017) and the measurement of the size of proteins in solution (Guidolin et al. 2023).

The DDM technique is based on the analysis of a long sequence of images acquired by microscopy at a given time interval (Fig. 1A). The analysis of images differences highlights the general movement of the particles over time and thus their dynamics. (Fig. 1B, left column). When bi-dimensional Fourier transform is applied to the image differences, one obtains the so-called structure functions in the form of spectral images (Fig. 1B, right column), each pixel corresponding to a single wave vector, i.e. a single spatial scale within the system.

DDM presents several advantages over traditional methods for measuring particle size and diffusion coefficients. Unlike DLS, it can effectively analyse heterogeneous and viscous samples, even in the presence of dust and optical imperfections. It also operates with cost-effective microscopic equipment and allows precise spatial selection of the region of interest. Moreover, DDM does not require individual particle labelling, enabling a more robust statistical analysis compared to PT methods.

Image processing relies on the Differential Dynamic Algorithm (DDA) (Croccolo et al. 2006; Cerchiari, et al. 2012; Norouzisadeh et al. 2021). A version of this algorithm has led to the development of the DIFFMICRO 2.0 software, which is currently available for free online (Norouzisadeh et al. 2021). A modified version maximizing GPU performance and memory management, allowing the analysis of thousands of images within seconds has recently been developed and protected. The new version is working on GPU only and is at least one order of magnitude faster than the published one.



Figure 1: Principle of the DDM method, (A) Acquisition of the time sequence of images and (B) Image processing. The image side is 0.67 mm, the Fourier space contains wave vectors from 94.4 cm⁻¹ to about 5×104^{-1} . Time differences are expressed as multiples of the acquisition time of 0.05 s. The sample is a dispersion of polystyrene fluorescent particles of 1 μ m-diameter in water.

Mass Diffusion Experiments

In order to show the efficiency of DDM to calculate the size of microscopic particles dispersed in a fluid, we performed measurements of the diffusion coefficient on known samples (polystyrene particles diluted in water), using two microscopy techniques (bright field and fluorescence). The results validate the method and show that it is possible to obtain additional qualitative information of the fluid by studying its structure functions.

Future needs

The multi-scale analysis obtained by using the DDM method enables the measurement of particle motion across different spatial and temporal resolutions, providing a means to investigate the impact of different conditions on their mobility. One interesting case would be the presence of temperature gradients. In the latter case, the DDM method allows for the observation of transient effects on a large number of particles over time, which is particularly advantageous for studying viscous or highly concentrated samples. However, implementing this approach presents several challenges.





Figure 2: Microscopic images of samples in (A) fluorescent and (B) bright fields. The image side is 0.67 mm. The sample is a dispersion of polystyrene fluorescent particles of 1 μ m-diameter in water.

From an experimental perspective, precise control of sample geometry, pressure and differential temperature is essential to ensure the stability of the thermal gradient applied to the sample. The system must be compatible with microscopic imaging and allow unobstructed light transmission. Additionally, convective flows within the fluid must be minimized. Developing a thermostated cell for DDM would help meet these requirements, ensuring optimal conditions for image acquisition.

From an analytical perspective, the interpretation of the results requires a thorough investigation, as the influence of temperature gradients on diffusion is complex and governed by multiple physical parameters. In the field of diffusion studies, the development of AI-based tools has already contributed to simplifying data interpretation, with the help of

standardized samples. However, under the experimental conditions considered here, curve fitting and data analysis present additional challenges. A clear distinction must be established between the respective contributions of thermodiffusion, conventional diffusive processes, and other potential effects such as gravitational influences. Consequently, further efforts are required to enhance result reliability and to establish DDM as a helpful tool for the thermodiffusion research community.

Conclusion

DDM is a powerful technique for studying diffusion, enabling the recalculation of key parameters, similar to traditional methods, while providing significantly richer information through the analysis of a broad spectrum of wave vectors. It facilitates the development of advanced experimental and computational approaches in the diffusive regime, which may be adapted for the study of thermodiffusion. Its advantages, including multi-scale analysis, high spatial and temporal resolution, and compatibility with a wide range of samples, make it a robust method. However, its application remains to be fully established and requires further methodological developments, both in measurement instrumentation and data post-processing, to evaluate its feasibility and potential contributions to the field.

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Polymer Thermophoresis by Mesoscale Simulations

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Introduction

Thermophoresis is known as the directed motion of colloids, polymers, and molecules in a solution with applied temperature gradient. For sufficiently small temperature gradients ∇T , the so-called thermophoretic velocity \mathbf{v}_{T} , i.e. the average velocity of particles in a temperature gradient, is linearly related to ∇T ,

$$\mathbf{v}_{\mathrm{T}} = -D_{\mathrm{T}} \boldsymbol{\nabla} T, \qquad (1)$$

through the thermophoretic mobility (or thermodiffusion coefficient) $D_{\rm T}$, which can be determined experimentally or in simulations, and depends on particle and solvent properties (Köhler and Morozov, 2016; Wiegand, 2004).

We employ mesoscopic simulations to study the thermophoretic motion of polymers in a solvent via multiparticle collision dynamics (MPCD). So far, MPCD had been applied to the thermophoresis of thermophobic and thermophilic colloids (Lüsebrink et al., 2012; Tan et al., 2017). It had been demonstrated that the specific colloid-solvent interaction in the presence of a temperature gradient determines thermophoretic behavior (Lüsebrink et al., 2012). Here, we propose a new method to simulate the thermophoresis of homopolymers as well as block copolymers using the MPCD method. Our work demonstrates that the specific monomer-solvent interaction plays a major role in determining both magnitude and sign of the thermophoretic mobility. Our simulation results match well with experimental results by de Gans et al., 2003, as we can reproduce both a sign change of $D_{\rm T}$ induced by changing the solute-solvent interactions, and the decoupling of solvent quality and thermophoretic motion.

Methods

The MPCD solvent with temperature gradient

The multi-particle collision dynamics (MPCD) algorithm models the solvent as point particles. The algorithm alternates between ballistic movement, in which particles $\{i\}$ are propagated using

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t) \tag{2}$$

with time step size h, and (multi-particle) collision. For the collision, the simulation box is divided into cubic cells of side length a, within which the relative velocities of the particles, w.r.t. the center-of-mass velocity in the cell \mathbf{v}_{cm} , are rotated by angle α using the rotation operator $\hat{D}(\alpha)$ via

$$\mathbf{v}_i(t+h) = \mathbf{v}_{\rm cm}(t) + \hat{D}(\alpha) \cdot (\mathbf{v}_i(t) - \mathbf{v}_{\rm cm}(t)).$$
(3)

Two slabs within the box are thermostatted - one at the beginning and one at the center of the box - to T_1 and T_2 , respectively (Lüsebrink and Ripoll, 2012), to obatin a linear temperature profile that is alternating in direction. As a result, the density $\rho(\mathbf{r})$ adjusts to an inverse profile, as given by $\rho(\mathbf{r})T(\mathbf{r}) = \text{const.}$

The polymer chain

The polymer is simulated using molecular dynamics on a monomer resolved level. Between all monomer-monomer pairs, we apply purely repulsive interactions via the WCA potential $U_{\rm WCA}$ for excluded volume effects,

$$U_{\text{WCA}}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^6 \right] + \varepsilon, & \text{if } r \le 2^{1/6}, \\ 0, & \text{if } r > 2^{1/6}. \end{cases}$$
(4)

An additional FENE potential U_{FENE} acts on neighboring monomers to simulate chemical bonds,

$$U_{\text{FENE}}(r) = -\frac{K}{2}r_{\text{max}}^2 \log\left[1 - \left(\frac{r}{r_{\text{max}}}\right)^2\right].$$
 (5)

Results

Thermophoresis when coupling via MPC

One possible method of coupling the polymer with the solvent is by letting monomers participate in the multi-particle collision step of the solvent. That way, monomers and solvent particles can exchange momentum and therefore interact. Using that method, it turns out that the polymer exhibits no significant thermophoretic motion.

Thermophoresis when coupling via pairpotentials

Another possible method of coupling the polymer with the solvent is by employing a pair potential between monomer and solvent particle $U_{\rm ms}$. We chose to use a WCA-like potential by adding an attractive part, scaled by λ (Huissmann et al., 2009).

$$U_{\rm ms}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{24} - \left(\frac{\sigma}{r}\right)^{12} \right] + (1-\lambda)\varepsilon, & \text{if } r \le 2^{1/12}, \\ 4\lambda\varepsilon \left[\left(\frac{\sigma}{r}\right)^{24} - \left(\frac{\sigma}{r}\right)^{12} \right], & \text{if } r > 2^{1/12}. \end{cases}$$
(6)

We set the interaction length scale $\sigma = a/2$. As it turns out, λ is a parameter that lets us control both, the radius of gyration

 $R_{\rm G}$ and thermophoretic mobility $D_{\rm T}$ of the polymer (Fig. 1). Additionally, $D_{\rm T}$ results to be independent of polymer size N.



Figure 1: The thermophoretic mobility $D_{\rm T}$ is shown for different interaction parameters λ . $\lambda \leq 0$ represent purely repulsive monomer-solvent interactions and lead to thermophilic polymer behavior (red region). As we add attraction to the monomer-solvent interaction ($\lambda > 0$), the polymer shifts from being thermophilic to thermophobic (blue region).

Thermophoresis of block-copolymers

To investigate the thermophoretic behavior of blockcopolymers, we combine two parts A and B, consisting of N_A and N_B monomers, respectively, that only differ in λ . It turns out that the thermophoretic motion of a block-copolymer behaves simply like an interpolation between the two homopolymers from which it is built.

Conclusions

We found that in MPCD computer simulations, thermophoresis of polymers is achieved only when monomer-solvent potentials are accounted for explicitly. Therefore, we have introduced a new type of pair potential in the form of a generalized Lennard-Jones potential that is characterized by the interaction parameter λ and governs both the solvent quality and the thermophoretic mobility of the polymer. We found that thermophilic behavior of the polymer is induced by predominantly repulsive monomer-solvent interactions, whereas thermophobic behavior is observed when attractive interactions dominate. The temperature preference of the polymer agrees well with results by Lüsebrink et al., 2012, qualitatively, where they studied colloids in a temperature gradient via computer simulation using similar potentials. Our findings further agree well with experimental research on PEO in a water/ethanol mixture, which exhibited similar thermophoretic behavior (de Gans et al., 2003; Kita et al., 2004). By comparing simulations of polymers with different degree of polymerization, N = 20and N = 50, we could show that the thermophoretic mobility is independent of N, suggesting that thermophoresis is a monomer property. This is in agreement with what many experiments have also shown (Wiegand, 2004). Regarding the thermophoretic behavior of diblock copolymers it turned out that the thermophoretic mobility results as a linear interpolation between the two corresponding homopolymers, depending only on the fractional number of monomers in each of the two blocks.

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Photothermal membrane distillation: harnessing solar energy for clean water production and desalination

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Introduction

Solar energy is a powerful natural and renewable resource that can be harnessed in various applications. While most current solar energy systems focus on photovoltaics, thermal energy from solar irradiation holds great potential for future technologies. Membrane distillation (MD) is a nonisothermal technology of emerging interest for water treatment, particularly useful for desalination due to its ability to treat high-salinity water up to saturation and its near 100% rejection of non-volatile solutes [1]. MD relies on establishing a temperature difference placed between the hot feed side and the cold permeate side as a driving force for vapor transport through membrane pores. The membrane plays a crucial role in MD performance and thermal efficiency. It should exhibit high hydrophobic character to prevent pore wetting, high porosity to increase membrane permeability, optimized thickness, low thermal conductivity for enhanced thermal efficiency (i.e. reduce the heat transfer by conduction through the membrane matrix that is considered heat lost in MD), and high chemical resistance and good thermal stability for longterm performance [2-3].

Recently, photothermal membrane distillation (PMD) has emerged as an innovative approach to efficiently harness solar energy. PMD localizes heating at the membrane-feed water interface via photothermal effects, improving MD performance. The PMD process enhances the thermal efficiency of MD since heating is localized on the membrane surface reducing the temperature polarization at the feed/membrane side [4].

As can be seen in Fig. 1, in conventional MD, the membrane's feed surface temperature is lower than the bulk feed solution, and the opposite happens in the permeate side. This temperature difference between the bulk feed solution and the permeate and the transmembrane temperature difference is known as temperature polarization, which reduces the effective driving force decreasing water production rate (i.e., permeate flux). In contrast, in PMD the temperature polarization effect is reversed at the feed membrane side, by increasing the feed surface temperature above that of the bulk feed solution [4].

In this study, we propose a photothermal membrane using a polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) nanofibrous substrate coated with a PVDF-HFP-graphite as a photothermal active layer. The prepared membranes were characterized by different techniques and tested in both conventional MD and PMD configurations to evaluate its performance.



Photothermal membrane (PMD)

Figure 1: Schematic illustration showing the effect on temperature polarization of conventional MD compared to PMD.

Experimental section

Hydrophobic nanofibrous PVDF-HFP support membranes were prepared using the electrospinning technique. Three different coatings techniques (electrospinning, electrospraying and spray-coating) were used to prepare the photothermal active layer as shown in Fig. 2:

1. *Electrospinning* permits to obtain a nanofibrous membrane using a high-voltage up to 30 kV to stretch the electrified polymer jet formed at the tip of the metallic needle (Taylor cone)

2. *Electrospraying* uses a high-voltage atomization of a low-concentration polymer solution to produce nanoparticles or polymer droplets coating.

3. *Spray-coating* employs compressed gas or airbrush to form a thin coating layer on a support.



Figure 2: Photothermal coating techniques: electrospinning, electrospraying and spray-coating.

To fully understand membrane properties, a thorough characterization was conducted, focusing on the photothermal surface. Several key parameters were measured to evaluate the membrane performance and its thermal efficiency, such as the thickness of both the support and the photoactive layer, the liquid entry pressure (LEP), the inter-fiber space of the photothermal membrane and its distribution, and the water contact angle to assess the membrane hydrophobicity. The inter-fiber space (i.e. maximum, mean and minimum size) of the photothermal active membranes was determined following the wet/dry method using the porometry system following the procedure detailed in [5]. The liquid entry pressure (LEP) of water was measured as detailed elsewhere [5]. The optical properties of the PMD membranes were studied by measuring the membrane surface reflectance, transmittance, and absorbance efficiency. Scanning electron microscope (SEM) images provide morphological insights, including nanofiber diameter and its distribution as well as the surface structure. These characterizations help optimize membrane design for enhanced photothermal-driven desalination performance.

PMD experiments were performed using distilled water and NaCl aqueous solutions (30 g/L) as feed. The feed solution was brought into contact with the membrane's photoactive layer, while the permeate side was maintained in contact with cold water in a direct contact membrane distillation (DCMD) configuration. To investigate the impact of localized heating, two experiments were conducted: first without solar illumination, and then, under 1 sun illumination (i.e., with solar irradiation). Both experiments were conducted at a constant feed inlet temperature of 40°C and a constant permeate inlet temperature 20°C. In the PMD experiment, 88

due to the photothermal effect, the feed surface temperature was higher than that of the bulk feed

Compared to the conventional DCMD results, the PMD results show an improved permeate flux due to the mitigation of the temperature polarization effect and an enhanced thermal efficiency. Comparison between the different coated photothermal layers on the PVDF-HFP nanofibrous support are carried out in this study and an optimized PMD membrane is proposed.

Conclusions

Photothermal membrane distillation (PMD) enhances both the thermal efficiency and the permeate flux of the conventional membrane distillation by utilizing localized solar heating.

This promising achievement paves the way for future implementation of this technology in desalination and the treatment of brines. Further research is still necessary.

Acknowledgements

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Giant Fluctuations in complex mixtures on the International Space Station

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Introduction

Transport phenomena occur in any thermodynamic system out of equilibrium. Under these conditions, the variables of complex fluids systems exhibit non-equilibrium fluctuations (NEFs) which allow to determine the transport properties of the fluid (Croccolo et al. 2012, Ortiz de Zárate et al. 2006).

In a thermodiffusion experiment performed on Earth, both convection (driven by thermal or solutal expansion) and sedimentation effects are present in the multi-component mixture. Furthermore, on Earth gravity suppresses long-wavelength NEFs, whereas in microgravity these fluctuations fully develop, becoming Giant Fluctuations (GFs). Therefore, the study of GFs under microgravity conditions is essential for a deeper understanding of transport processes in complex fluids (Vailati et al. 2011).

The shadowgraph technique is a powerful optical tool for simultaneously and reliably measuring the refractive index fluctuations associated with NEFs in thermodynamic variables at multiple scales. By using the differential dynamic algorithm (Croccolo et al. 2006, Croccolo et al. 2012, Cerchiari et al. 2012, Norouzisadeh et al. 2021) on shadowgraph images, various transport properties can be determined. To accurately characterize multi-component complex fluids, the Giant Fluctuations space project adopts a two-wavelength shadowgraph setup. This approach allows for the independent determination of the thermodynamic behaviour of each component in ternary mixtures.

Theoretical models based on linearized fluctuating hydrodynamics accurately describe the static and dynamic properties of these GFs under ideal conditions, such as small gradients and stationary states. However, the Giant Fluctuations project aims to investigate NEFs in complex liquids under conditions that challenge theoretical models, including transient diffusion, concentrated samples, and large gradients (Baaske et al. 2016).

Scientific objectives

The Giant Fluctuations project involves applicative and fundamental objectives. A novel diagnostic tool based on

NEFs (two-wavelength shadowgraphy) has been designed and developed, being able to quantify the transport properties of complex fluids. Large gradients, time dependent processes as well as concentrated samples are planned to be studied through this setup using multi-component complex fluids, including polymeric mixtures and colloids, and evaluating the NEFs behaviour under confinement. The main goals of this project can be summarized as follows (Baaske et al. 2016):

- NEFs in a complex mixture including a polymer. Polymer dissolved in two solvents is chosen as a model ternary system due to the well separated diffusion time scales of its components, which facilitates the GFs analysis.
- Glass transition in a ternary mixture including a polymer. Both mechanisms, glass transition and chain entanglement slow down dynamics in a concentrated polymeric solution. These effects on temperature and concentration NEFs will be evaluated.
- Critical Casimir forces in equilibrium and out of equilibrium. Confinement effect analysis on the spatially long-range fluctuations.
- Transient fluctuations during thermodiffusion separation. To understand the behaviour of the fluctuations during the transient until the steady concentration gradient is reached in a complex mixture.
- Dense colloidal suspensions. Useful for experimental verification of NE Casimir forces, as well as promising research field to explore non-ideal conditions of practical relevance.
- Biological samples. Reach a deeper understanding of how NE conditions affect the interactions between proteins.

Experiment description

Thermodiffusion experiment analysis by two-wavelength shadowgraphy

The experimental device includes a thermodiffusion cell array composed of four samples, each one subjected to independent thermal gradient, and illuminated by two combined and collimated red and violet Superluminous Light Emitting Diodes (SLEDs) (Vailati et al. 2020). Light is scattered by temperature and concentration fluctuations of the sample and the corresponding shadowgraph images are captured by the sensor of a CCD camera. Images can be acquired with continuous-wave red source (CW-R), continuous-wave violet source (CW-V) and strobed red/violet sources. The selection of multiple optical lines allows a strict alignment of optical components due to the absence of moving parts. RedWire Space and Lambda-X have fabricated the experimental breadboard, following the design concept and all scientific requirements described by the science team of the Giant Fluctuations project. Based on the results of the scientific campaigns carried out on the experimental breadboard, optical calibrations as well as new shadowgraph diagnostics algorithm have been developed (Vailati et al. 2020). This technology offers several advantages for practical implementation, as it is a non-destructive, versatile technique suitable for studying different types of samples under various experimental conditions without altering the fluid's intrinsic properties (Croccolo et al. 2012).

Space missions and list of samples

The Giant Fluctuations project is currently scheduled for flight in 2025-2026 on-board the ISS. A full development of the Giant Fluctuations project will involve four or five space missions, each one with one cell array of four samples. The first mission is expected for April 2026, and the samples to be investigated during this campaign are detailed in Table 1. According to the results of the first flight campaign, the next missions will be completely defined. The main colloid experiments based on samples of Ludox and water at different concentrations are planned to be studied during the second mission. For future missions, the possibly to study pure fluids is also envisioned to analyze temperature NEFs in isolation. Glass transition experiments will also be conducted on ternary polymeric mixtures, and different ternary mixtures, such as those with similar-size molecules will be further analyzed. The effects of the lifetime of the samples as well as the temperature and the cell inclination on the experiment's performance are studied for all the samples.

	Sample	Concentration	Experiment
	Polystyrene +	2-98 wt%;	Transients
	toluene	9 ± 1 kg/mol	
	Polystyrene +	2-39-59 wt%	Ternary
	toluene +	$5 + 1 \ln \alpha / m a^{-1}$	Ternary
	cyclohexane	3 ± 1 kg/mol	mixtures
	Polystyrene +	50-50 wt%;	Glass
	toluene	5 ± 1 kg/mol	transition
		20 mg/ml-	
	Lysozyme +	20 mM sodium	Biological sample
	aqueous buffer	acetate pH 5,	
	(H_2O)	Sodium azide 0.05%	
		(w/v)	

Table 1. Fluid samples selected for the first flig	ht mission.
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Operation principles of the experiment

The operation conditions and the methodology required for suitable performing these thermodiffusion experiments must include the following steps:

- 1. Homogenization of the sample temperature
- 2. Application of the temperature gradient
- 3. Building-up the concentration profile
- 4. Steady concentration profile
- 5. Removal of the temperature gradient

6. Disappearance of the concentration profile

Image acquisition and downlinking protocols are specifically designed for each experiment, considering the dynamics of each sample, the experimental requirements of each step as well as the total mission duration and the available data storage capacity. For example, stroboscopic illumination is chosen for the image acquisition during the transient phases.

Conclusions

The transport properties of several complex fluids will be characterized through different thermodiffusion experiments performed on the ISS starting from 2026. The twowavelength shadowgraph instrument developed to be used under microgravity conditions will allow a comprehensive analysis of the behaviour of the NEFs even under no ideal conditions.

Acknowledgements

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Measurement of salt diffusion coefficient as a function of concentration in a free-diffusion cell by interferometry

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Introduction

The Fickian diffusion coefficient describes how molecules in a solution move collectively in response to a concentration gradient. In a concentrated solution, the diffusion coefficient accounts for interactions between particles, thus representing an essential tool for understanding mass transport in natural or industrial processes. In the particular case of CO_2 storage in deep saline aquifers, understanding Fickian mass diffusion of electrolytic aqueous solutions requires the knowledge of diffusion coefficients as a function of salt concentration and for wide concentration ranges up to saturation. For binary mixtures of salts in water, the imposed concentrations gradients in free-diffusion experiments are usually small, assuming that the diffusion coefficient remains constant and the position of the interface between solutions is stable over time (Ambrosini *et al.*, 2008).

In such a way, multiple experiments are required to obtain multiple values of the diffusion coefficient at different mean concentration. In this work, we show how in a free-diffusion experiment in the presence of a strong concentration gradient, it is possible to extract the diffusion coefficient as a function of the concentration in the range between the minimum and the maximum concentration imposed in the column.

Methodology

In this study, we utilize interferometry, a non-invasive optical technique, to track minute concentration changes in saline solutions through variations in the refractive index. A sample free-diffusion cell containing the solution was placed in a Mach-Zehnder interferometer, and concentration fields were mapped over time. The initial concentration gradient was generated by layering a less dense solution above a denser one. This condition is achieved by, first, filling the cell with the less dense fluid and then by slowly injecting the denser one from the cell bottom by means of syringe pumps. As the solutions come into contact, fringe density changes appear at their interface, while interferograms are recorded and saved as raw 8-bit grayscale images of size $2048 \times 2048 pix^2$ in real-time at a frequency f = 1 Hz. The interferograms are then post-processed to extract the phase information and the refractive index field, Δn , from the relation:

$$\Delta n = \frac{\lambda}{2\pi L} \Delta \varphi \tag{1}$$

Where $\lambda = 632.8 nm$, is light source wavelength, $L = 1.05 \pm 0.02$, is the optical path length, and $\Delta \varphi$ is computed phase difference between the test (measurement) and the reference beams. Under isothermal conditions, Δn relates to the concentration field, Δc by:

$$\Delta n = \frac{\partial n}{\partial c} \Delta c \tag{2}$$

Where the ratio $\partial n/\partial c$ (optical factor contrast) couples the optical measurements with the concentration field. This ratio was independently characterized using a refractometer.

As a reference value, we take the refractive index at the top of the column, which corresponds to the smallest value of the imposed concentration. The concentration profile is then calculated until the bottom of the column. The analysis of the profiles is done once the position of the interface is stabilized and as long as the free-diffusion takes place in the recorded field of view. The diffusion is governed by Fick's Second Law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left(D(c) \frac{\partial c}{\partial z} \right) \tag{3}$$

Where c(z,t) is the local concentration of molecules at position z and time t, D(c) is the concentration-dependent mass diffusion coefficient. Following (Sobac *et al.*, 2020), D(c) is numerically computed from c(z,t) by the relation;

$$D(c) = \frac{\partial \psi(z,t)}{\partial t} / \frac{\partial c}{\partial z}$$
(4)

Where $\psi(z,t) = \int_{z_{min}}^{z} c(z,t) dz$.

Results

Figure 1 shows the concentration dependent diffusion coefficients D(c) obtained from one single experiment where we have placed two solutions of NaCl with a mean concentration of 2.70 mol/L and a concentration difference of 2.00 mol/L. The D(c) values are estimated at several z positions in the experimental concentration profiles (at intervals of 0.05 mol/L) using eqn. (4). The error bars for D(c) represent standard deviations, calculated based on the mean value of D(c) computed at each position z. Our measurements are in good agreement with the reference measurements in the literature and reproduce well the evolution of the diffusion coefficient as a function of the concentration range of 2 mol/L we manage to extract the values of D over more than half of the range.



Figure 1: Concentration dependent diffusion coefficient of NaCl obtained from a single experiment on a solution with mean concentration of 2.70 mol/L and concentration difference of 2.00 mol/L, estimated from the measurements of c(z, t) using eqn. 4. The literature values are from (Guo et al., 1999; Nimdeo et al., 2014; Rard & Miller, 1979; Torres et al., 2012; Vitagliano & Lyons, 1956).

Conclusions

In this work, we employed Mach-Zehnder interferometry to investigate mass transport in saline solutions. Our setup enables precise measurements of concentration profiles in solutions with large initial gradients, allowing us to extract precise values of the diffusion coefficient D(c) over a wide concentration range (c = 2.00 - 3.30 mol/L) from a single experiment.

This approach offers a significant advantage over traditional methods in the literature, where diffusion coefficients are typically measured only at a single mean concentration per experiment.

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Stability of quasi-equilibrium of a binary fluid-inclined layer under the action of high-frequency vibrations

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Introduction

The linear stability of quasi-equilibrium states of an inclined binary fluid layer subjected to the gravity field and highfrequency small-amplitude vibrations is investigated. The study is conducted in the average approach. The conditions for quasi-equilibrium state existence are found and the linear stability of these states to the longwave and finite-wavelength perturbations is investigated. The results of the linear stability analysis are confirmed by the nonlinear modelling, which is carried out by the finite difference method.

Problem formulation

We consider the behavior of an inclined layer of a binary fluid subjected to the gravity field, linearly polarized translational high frequency vibrations and the prescribed temperature and concentration gradients parallel to each other. To describe the behavior of a fluid, we use the equations for natural convection of a binary mixture in the Boussinesq approximation written in the reference frame associated with an oscillating cavity. The average approach is used, which means that we decompose all the fields into the slowly varying average components and quickly oscillating pulsational components and apply the averaging over vibration period. We consider a typical liquid media with the Prandtl number Pr = 7, the Lewis number Le = 130 and small values of the buoyancy ratio $K \sim 10^{-2}-10^{-3}$.

Quasi-equilibrium states

The conditions for the existence of the quasi-equilibrium states are found, which binds the relations between the Rayleigh number, Ra, and the vibrational Rayleigh number, Ra_V These relations show that the quasi-equilibrium is possible when the density gradient is parallel to the gravity force and one of three conditions is satisfied: 1) the layer is horizontal; 2) the vibrations are orthogonal to the layer; 3) the vibration direction is parallel to the gravity force and the density gradient. In the current research, we study cases 1 and 2.

Numerical calculations

Using the shooting method, we obtain the stability maps in the plane (Ra, Ra_V). For a horizontal layer, the transverse vibrations increase the stability of the system, while the

stability is being lost with the change in vibration angle; the least stable configuration occurs with the longitudinal vibrations. For a single-component fluid (K = 0), the instability occurs only at finite wavelengths. However, when K > 0, a transition to longwave instability emerges once Ra_V exceeds a certain threshold. As an example, for the case of transverse vibrations and K = 0.001, the transition to the longwave instability occurs at $Ra_V = 60000$. For stronger concentration gradients the longwave instability occurs earlier, for K = 0.003 the transition already occurs at $Ra_V =$ 6000. In all cases, vibrations have a tendency to reduce a critical wave number. For the inclined layer under the action of transverse vibrations, the most stable configuration is achieved for the horizontal layer and most unstable, accordingly, for the vertical layer. Transverse vibrations in the inclined layer also lead to the increase in stability, however the inclination of the layer reduces the influence of the vibrations. In the limiting case of the vertical layer, the longwave instability is observed and vibrations do not change the threshold of this longwave instability, but the stabilizing effect takes place for finite wave numbers. The nonlinear problem was solved by the finite difference method using the stream function - vorticity formulation. A layer cell with periodic boundary conditions was set as the geometry configuration, where the cell length was chosen according to the wave length of the most dangerous perturbations. The direct numerical simulation confirms the thresholds obtained from the linear theory with an accuracy <1%. We obtained the concentrations and temperatures fields, which clearly showed us different mechanisms of the convection excitation under different parameters.

Conclusions

In the present work, we have studied quasi-equilibrium states of the binary fluid in the inclined layer subjected to frequency vibrations. The relation between the Rayleigh and vibrational Rayleigh numbers have been found analytically, which shows when the quasi-equilibrium can exist. The stability maps have been obtained for the horizontal layer with vibrations of arbitrary inclinations and for the inclined layer with transverse vibrations. In the limiting case of long-wave instability, the numerical results agree well with the longwave expansion. The direct numerical simulation was also carried out, which confirmed the result of the linear theory.

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On the thermocapillary and melting processes in PCM devices under terrestrial and microgravitatory environments

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Introduction

In liquid free surfaces subjected to thermal gradients, thermocapillary convection is the responsible mechanism to draws fluid from warmer areas of low surface tension to cooler ones of higher surface tension. This means that thermocapillary is gravity independent and, thus, the only space native convection. This peculiar characteristic has been used to increase the heat extraction rate in space Phasse Change Materials(PCM) devices [1]. However, even without gravity, the dynamics of all these phase change devices is very complex because the combined effect of, by one side, a continuous change of the volume of the liquid domain over time and, by the other, the own thermocapillary instabilities (steady multicellular structures, hydrothermal traveling waves, oscillatory standing waves, ...). Recent results suggest that the competition between thermocapillary and natural convection in PCM systems can get to eliminate flow instabilities in case of Earth laboratories. This means that the results in Earth laboratories can only help to validate the algorithm. These preliminary results indicate that PCM results on Earth laboratories can only be used to validate the algorithm but space predictions could not be checked experimentally, except in appropriate environments such as the International Space Station (ISS).

The present work will focus on the interaction thermocapillarynatural convection in Earth laboratories, comparatively analyzing the melting process in a cuboidal cell, where a temperature gradient is applied in the direction perpendicular to the gravitational field. A correct experimental-numerical comparison of this system will allow the numerical algorithm a reasonable prediction of microgravity results under the same conditions. At this respect, it must be not forgotten that the knowledge of these predictions is extremely valuable due to the high cost of any kind of experiments in space environments.

Experimental and numerical methodologies: The melting process is analysed in a parallelepiped cell, where a heat source or a temperature gradient is applied in the direction perpendicular to the gravitational field. To achieve this, the lower wall must be adiabatic, while the upper one is a free surface where Marangoni convection is induced. The cell $(22.5(L) \times 15.0(W) \times 15.0(H) \text{ mm}^3)$ is built of two aluminium sidewalls, a 3D printed base part and a front and rear window. all tightened by full-width screws. Water flowing in-

side the aluminium walls allow to keep constant pre-set temperature throughout the experiment, while the methacrylate windows allow to track and record the melting process. The n-octadecane was first melted and then the desired amount of PCM was added to the cell using the Gram VXI-310 highprecision balance. The sample was then solidified by placing it in the refrigerator for at least three hours. After verifying that all the PCM is in a solid state, the cell is tempered to a temperature slightly below the melting point of n-octadecane (28 °C). Then, the temperature of one of the walls is increased by 20 °C to initiate the melting process, which is recorded with a video camera. The numerical method used here utilizes a phase-change model based on the Enthalpy-Porosity formulation of the Navier-Stokes equations. Under this approach the mass, momentum and energy are linked by a temperature dependent scalar called liquid fraction ranging from zero in the solid phase to one in the liquid. Details about a complete mathematical formulation of the model can be consulted in the literature [2].

A rectangular domain of Aspect Ratio 1.5 [Length(22.5 mm)/Heigh(15 mm)] has been considered to mimic the cuboidal cell used experimentally. This means that, for calculations, the upper liquid/air interface has been considered perfectly flat avoiding the consideration of any modification in the geometry produced by the thermal expansion occurring during the melting process. Thermocapillary flow has been considered in this free surface while that no-slip conditions have been used in the rest of the solid boundaries. Concerning thermal boundary conditions, the bottom wall has been considered adiabatic and the lateral sides of the domain at fixed temperatures. A temperature gradient, ΔT , is applied between both left and right sides. The free surface has been considered to actively exchange heat with the surroundings. To close the numerical model, a complete characterization of the different thermophysical properties of the n-Octadecane, used here as PCM material, was first of all performed [2].

The finite volume OpenFOAM package was chosen to quantitatively process the melting process. The mesh used was made of rectangular regular elementary cells of $(0.8 \times 0.375) \times 10^{-1}$ mm². The PIMPLE algorithm was used to solve simultaneously the momentum and continuity equations in each one of the different elementary cells. The final system of lin-

ear equations (for pressure, velocity and temperature fields) was solved by using the preconditioned bi-conjugate gradient, PBiCG, method. The time step, initially set to one millisecond, could be automatically reduced if the Courant-Friedrich-Levy number exceeded the value of 0.5 [2].



Figure 1: Matching between experimental and numerical results: Snapshot of experimental and 2D numerical results for $\Delta T = 20^{\circ}$ C at t = 1800 s

Fig. 1 shows a snapshot of both experimental and numerical results of the PCM melting process in case of the abovementioned cuboidal cell with an external thermal gradient of 20°C. The numerical result shows a reasonable similarity with the visualization also enabling the obtaining of additional bulk flow details for, if necessary, further additional comparisons. Mention also that the results obtained with the present computational algorithm agree well with other similar results reported in the literature [3].

Results

Figure 2 shows two simultaneous flow snapshots under the same boundary conditions but with and without gravity (Earth and ISS labeled environments). The appreciably differences in



Figure 2: Snapshot results for temperature in two different places (point 1 (10%L, 90%H, 0), and point 2 (90%L, 90%H, 0)) and snapshot results of streamlines for ISS (no gravity), and Earth condition for ΔT =20°C at t=1800 s.

bulk flow patterns, and interface shapes, are a natural consequence of the strong natural convection developed in the Earth case. The absence of this convection generates a conductive flow region in the lower left part of the computational domain. Also, in the upper part, thermocapillary flow is dominant generating a unique strong vortical structure near the hot wall. This vortical structure is, in case of gravity, pushed toward the free surface by another small one of natural convective origin. In addition, the same Fig. 2 shows a time evolution of the thermal field in two different representative points under both ISS and gravity conditions. The addition of gravity appreciably increases the value of temperature as a consequence of the intense convective movement generated by the action of the gravitational field.

Conclusions

Melting starts close to the heated wall. The solid PCM in direct contact with the free surface melts faster than the paraffin adjacent to the adiabatic wall. This behaviour is attributed to the presence of Marangoni and thermogravitational convection, which significantly enhances heat transfer. Numerical simulations performed under the same conditions as the Earth ones, showed comparable PCM melting dynamics as the observed experimentally. Further predictions under microgravity conditions shows a strong thermocapillary convection near the free surface of the computational domain. All these results reasonable agrees with other works previously reported in the literature [4].

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Impact of the transversal confinement on the steady-state species separation in thermogravitational columns

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Introduction

In recent years, different experimental techniques have been developed to characterize liquid mixtures. The Thermogravitational Column Technique (TGC) is the main convective method used for the determination of the thermodiffusion coefficient. It consists of a cavity formed by two walls and the fluid injected into the column is subjected to a temperature gradient perpendicular to the gravitational field. This configuration induces the thermodiffusion effect, generating a horizontal concentration gradient. The created species separation activates the phenomenon of molecular diffusion, trying to homogenize the mentioned concentration gradient. Simultaneously, a convective flow arises due to the horizontal density gradient, further separating the species in the upward direction (Köhler et al., 2023). In 1939, W. H. Furry, R. C. Jones, and L. Onsager obtained an analytical solution for the steady-state separation of components in a binary system, by considering, among other assumptions, a two-dimensional rectangular cavity and that the system's density depends solely on temperature variation (the forgotten effect). Under these hypotheses, $\triangle c_{F,IO}^{*} = c^{*}(z^{*} = L_{z}) - c^{*}(z^{*} = 0)$ is given by FJO theory (W. H. Furry et al., 1939):

$$\triangle c_{FJO}^* = -504 \ c_0 (1 - c_0) \ \frac{L_z \ \nu}{e^4 \ \beta_T \ g} \ D_T \tag{1}$$

In Eq. (1), g refers to the gravity force and ν and β_T are the kinematic viscosity and the thermal expansion coefficient of the system. c_0 is the initial mass fraction of the densest component. Additionally, e and L_z are the cavity gap width and the analyzed height in the column. The analytical expression Eq. (1) shows that it is possible to determine the thermodiffusion coefficient D_T of the mixture, by measuring the steady-state species separation $\triangle c^*_{FJO}$ between two points in the column and considering the thermophysical properties of the system along with the cavity dimensions (Köhler et al., 2023).

Nevertheless, the analytical solution, Eq. (1), derived under the FJO hypotheses, lacks generality and is therefore not always applicable. Thus, the primary motivation of this work is to evaluate the validity of the FJO theory analytically, numerically and experimentally focusing exclusively on the transverse confinement effect, third dimension, which is not considered in Eq. (1).

Theoretical, Numerical and Experimental study

Valencia et al., 2002 showed that the parallel flow approximation used in the FJO theory Eq. (1) without the forgotten effect is valid provided that the condition $\frac{RaLe}{A} \leq 1000$, where $A = \frac{H}{e}$ is the vertical aspect ratio of the cavity and Le Ra is the product of Rayleigh number and Lewis number. *H* refers to the total height of the cavity. Here, we suppose that this condition is satisfied. By using the parallel flow approximation, one may dismiss the horizontal components of the velocity vector:

$$\vec{u} = (u = 0, v = 0, w) \tag{2}$$

In addition we look for dimensionless solutions in the form,

$$w = w(x, y), \quad c = c(x, y, z) = \gamma A z + \varphi(x, y), \quad T = T(x)$$
(3)

where γ is the dimensionless vertical mass gradient $\frac{1}{A} \frac{\partial c}{\partial z}$. After long and tedious algebra, not developed in the present contribution, we determine the fields w = w(x, y) and c(x, y, z) with T(x) = x. Finally by imposing the condition of zero mass flux through any horizontal section of the cavity perpendicular to the z axis we obtain the expression of the three-dimensional species separation, written in dimensional form, Δc_{3D}^* ,

$$\frac{\Delta c_{3D}^*}{\Delta c_{FJO}^*} = \frac{a_{\psi}(B)}{\frac{9!}{(Le\,Ra)^2} + a_c(B)} \tag{4}$$

with the solution of $\triangle c_{FJO}^*$ is given by Eq. (1) and $a_{\psi}(B)$ and $a_{\psi}(B)$ are functions of the transversal aspect ratio $B = \frac{b}{e}$ involving integrals of some series that we do not write their explicit expressions here for brevity. b represents the third dimension of the column, corresponding to the depth perpendicular to the direction of the applied temperature difference.

We emphasize that, in addition to the transversal aspect ratio B, the ratio $\frac{\Delta c_{3D}^*}{\Delta c_{FJO}^*}$ given by Eq. (4) depends, on a second parameter $Ra \ Le$.

The theoretical variation of the ratio $\frac{\triangle c_{3D}^*}{\triangle c_{FJO}^*}$ as a function of the transversal aspect ratio *B* is shown in Figure 1 by red dots with *B* ranging from 1 to 8.5 and for RaLe = 11588. As shown in this figure, the ratio $\frac{\triangle c_{3D}^*}{\triangle c_{FJO}^*}$ increases as *B* decreases, and the discrepancy may exceed 40% for a square cavity

(i.e. B = 1). In other words, in comparison with the species separation as predicted by two-dimensional FJO theory (strictly valid for infinite *B*), the transversal confinement of the cavity increases the separation between components along the cavity height. In Figure 1, we also present by a solid black line the fitting curve of the three-dimensional numerical results, obtained via Ansys Fluent 2022 R1[®] software within the species transport model. The inset of this figure compares the three-dimensional theoretical and numerical solutions, revealing that the discrepancies between them are less than 0.1%.

Figure 1: Ratio $\frac{\triangle c^*}{\triangle c^*_{FJO}}$ versus *B* for RaLe = 11588. The theoretical results (dots) are compared to the fit of the numerical ones (solid line).

Using optical digital interferometry (refer to A. Errarte et al., 2024 for experimental methodology and data processing), thermodiffusion experiments in microcolumns with aspect ratios B = 5.88 and B = 1.69 (the last microcolumn is designed and fabricated specifically for this work) are conducted for the well-known benchmark mixtures THN|C12 and THN|IBB (0.50|0.50 mass fraction) (J. K. Platten et al., 2003). Three distinct temperature differences between the vertical walls are imposed for each mixture. Thus, it is found that when the transversal aspect ratio of the cavity B is reduced from 5.88 to 1.69, the species separation increases significantly. In this context, and in comparison with the stationary-state components separation predicted via FJO theory, experimental results confirm that $\frac{\Delta c_{Exp}^*}{\Delta c_{FJO}^*}$ increases in average from 1.5% to 18.8% for THN $|C_{12}$ system and from 2.3% to 19.6% for THN|IBBmixture (B is decreased from 5.88 to 1.69). Therefore, and considering the experimental error associated with laboratory experiments, the increase in component separation is of the same order of magnitude for both systems. In addition, a good agreement between the experimental and theoretical results is observed with the maximum deviation being less than 2%(B = 5.88) and 1% (B = 1.69), thus confirming the validation of the three-dimensional theoretical and numerical models.

Conclusions

Three-dimensional theory under parallel flow assumption revealed that the transversal confinement of thermogravitational columns increases significantly the steady-state species separation. Numerical and experimental results strongly support this conclusion. A correlation law of the components separation as a function of the relevant parameters is found as an alternative to the FJO theory and can be used with confidence to determine the thermodiffusion coefficient in binary systems from steady-state components separation measurements.

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