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Interfacial hydrodynamic instabilities driven by cross-diffusion in reverse

microemulsions 2

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When two microemulsions are put in contact in the gravity field along a horizontal contact line, cross-diffusion 11 can trigger the transport of one species in presence of a gradient in concentration of another species. We show 12 here theoretically that such cross-diffusion effects can induce buoyancy-driven convective instabilities at the 13 interface between two solutions of different compositions even when initially the less dense solution lies on 14 top of the denser one. Two different sources of convective modes are identified depending whether positive 15 or negative cross-diffusion is involved. We evidence the two predicted cross-diffusion driven instabilities 16 experimentally using a two-layer stratification of Aerosol-OT (AOT) water-in-oil microemulsions solutions 17 with different water or AOT composition. 18

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Cross-diffusion, Multi-components systems 21

Aerosol-OT (AOT) microemulsions have been 44 I. INTRODUCTION 22

well studied in the context of reaction-diffusion 23

24 patterns in particular when the reactants of the oscillatory Belousov-Zhabotinsly reaction are dis- 45 25 solved in it. Recently, such microemulsions have 46 26 also proved to be good model systems to study, 47 27 in absence of any reaction, convective instabili-48 28 ties driven in the gravity field by cross-diffusion 49 29 effects when gradients in a salt concentration trig- 50 30 gers co-flow of water and AOT. Here we show 51 31 that even in a simpler three components water- 52 32 AOT-octane system, cross-diffusion can trigger 53 33 buovancy-driven motions when a gradient of ei- 54 34 ther water or AOT is imposed to an initially ⁵⁵ 35 statically stable stratification of two different mi- 56 36 croemulsions. This paves the way to future un- 57 37 derstanding of cross-diffusion driven hydrody- 58 38 namic instabilities and to studies of more complex 59 39 reaction-diffusion-convection patterns where con- 60 40 vective effects could be induced by gradients in 61 41 concentration inherent to reaction-diffusion pat- 62 42 terns. 63 43

New dynamical properties arising from the interplay of dissipative physico-chemical systems with dispersed media and soft matter are being studied since many years. The dynamics of the well known Belousov-Zhabotinsky $(BZ)^{1,2}$ chemical oscillator, in particular, has been studied with many self-assembled matrices³ and structured media⁴ including gels and hydrogels⁵⁻⁸, micelles⁹⁻¹⁴, polymers¹⁵⁻¹⁸ and lipid vesicles and aggregates¹⁹⁻²⁴. Particularly important from the pattern formation viewpoint, the AOT water-in-oil reverse microemulsions (ME), are probably the most thoroughly studied system in combination with the BZ reaction. Microemulsions can be defined as optically clear, thermodynamically stable and isotropic liquid mixtures of an organic component (more commonly termed *oil*), water and surfactant (see the sketch in Figure 1a for the structure). In particular, in a reverse ME the hydrophilic BZ reagents can be solubilized in water AOT-coated nano-droplets to create a great amount of coupled nano-oscillators. Early works dealt with the temporal behavior of the BZ reaction when dissolved in the $ME^{25,26}$. When the Brandeis group evidenced for the first time Turing structures and other exotic patterns in ME loaded with reactants of the BZ system in a spatially extended reactor $^{27-30}$, the system attracted much more interest. The Brandeis group found that transport phenomena played a key role in the generation of the large amount of patterns observed in ME. Specifically, microemulsions induce two different diffusion modes for the BZ intermediates: slow diffusion for the hydrophilic activator, which can only move together with the droplets, and fast diffusion of the hydrophobic

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inhibitor, free to move alone into the oil phase with a134 76 diffusion coefficient two orders of magnitude larger than₁₃₅ 77 that of the activator. In order to generalize the modelling₁₃₆ 78 of the related pattern formation, cross-diffusion terms,137 79 *i.e.* the phenomenon by which a flux of a given species₁₃₈ 80 entrains the diffusive transport of another species³¹, were₁₃₉ 81 introduced in reaction-diffusion equations. In their semi-140 82 nal paper³², Vanag and Epstein introduce cross-diffusion₁₄₁ 83 phenomena in reaction-diffusion models, an aspect gen-142 84 erally neglected in chemo-physical systems. In this con-143 85 text, the Brandeis group developed a new method to144 86 exploit the Taylor dispersion technique (TDT, see sec-145 87 tion IB), in order to measure the diffusion matrix up₁₄₆ 88 to a 5-component microemulsion systems $(H_2O + AOT_{147})$ 89 + 2 BZ reagents in octane as the oil phase)^{33–35} and $_{148}$ 90 study the effect of cross-diffusion on the onset of Turing149 91 instabilities 35 . 150 92

Besides these breakthroughs in reaction-diffusion (RD)₁₅₁ 93 systems, I.R. Epstein has also pioneered the studies of₁₅₂ 94 reaction-diffusion-convection (RDC) patterns in autocat-153 95 alytic systems when convection develops around traveling₁₅₄ 96 fronts in solutions because of density gradients due to the155 97 exothermicity of the reaction and/or volume changes be-156 98 tween reactants and products.^{36–39}. 157 ٩q With the idea that RD patterns and convective effects₁₅₈ 100

should be able to interact in microemulsions to give rise159 101 to a wealth of possible new RDC patterns and instabil-160 102 ities, we recently⁴⁰ started investigating hydrodynamic₁₆₁ 103 convective patterns triggered by cross-diffusion in mi-162 104 croemulsions in the absence of any reaction. The objec-163 105 tive is twofold: first, the ME system is a perfect model 106 system to explore new convective modes related to the 107 introduction of cross-diffusion effects in the analysis of¹⁶⁴ 108 hydrodynamic instabilities of miscible two-layer systems. 109

Even though some early works have started addressing₁₆₅ 110 this problem in polymers^{41,42}, cross-diffusion driven con-₁₆₆ 111 vective instabilities in absence of any reaction are still₁₆₇ 112 poorly understood. The second objective is to under-168 113 stand which convective modes can be observed in mi-169 114 croemulsions before starting to add the complexity of RD_{170} 115 patterning to construct new RDC patterns. In this con-171 116 text, we first studied⁴⁰ fingered convective motions de-172 117 veloping at the interface between two identical $AOT-ME_{173}$ 118 in a gravitational field, when the lower denser solution $_{174}$ 119 contains a simple water-soluble molecule (NaBrO₃) free₁₇₅ 120 to diffuse towards the upper less dense layer and gen-176 121 erate by cross diffusion a positive co-flux of both water₁₇₇ 122 and AOT. In detail, when NaBrO₃ diffused from the bot-₁₇₈ 123 tom to the upper layer, it dragged along both H_2O and 124 AOT molecules thus generating a non-monotonic den-179 125 sity distribution around the contact line, destabilizing¹⁸⁰ 126 convectively an initially stable system. By means of a¹⁸¹ 127 diffusion model, we explained the dependence of the hy-182 128 drodynamic patterns upon [NaBrO₃] cross-diffusion and¹⁸³ 129 we opened a new path to study the coupling between 130 pattern formation due to RD and RDC interactions in^{184} 131 microemulsions systems.

In this paper, we show that cross-diffusion drives $\operatorname{con-}^{^{186}}$ 133 187

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vective instabilities in an initial statically stable stratification between two microemulsions (without any added salt) in a Hele-Shaw cell by just imposing a gradient in water or AOT concentration. By using the TDT we characterise the diffusion matrix of the Water/AOT mixture and show how ME represent a convenient model to study cross-diffusion-driven convection. On the basis of Fick's equations including cross-diffusion coefficients, we predict two different possible convective instability scenarios based on the sign of the cross-diffusion terms. We use these results to devise experiments where the species free to diffuse from one layer to the other present either positive or negative cross-diffusion coefficients. We demonstrate experimentally the difference in convective patterns for the two predicted instability scenarios and compare the properties of the obtained convective patterns.

The paper is structured as follows, in section IA we briefly sketch transport properties of a microemulsion system. In section IB the main features of the Taylor dispersion method are described. The experimental methods and setup are presented in section II while results are discussed in section III. In particular, in section III A the diffusion matrices of the Water/AOT systems investigated are characterised. In sections III B 1 and III B 2 we introduce a theoretical approach to cross-diffusion-driven convection and, by analyzing the shape of the density profiles, we characterize two classes of instability scenarios that are next demonstrated experimentally in section III C. Finally, conclusions are drawn in section IV.

Α. Transport processes in microemulsions

Sodium bis(2-ethylhexyl) sulfosuccinate, usually referred to as Aerosol-OT, or simply AOT, is able to feature stable reverse microemulsions in a simple threecomponent system for a broad range of compositions. The geometry of the dispersed domains may range from spherical or elongated droplets to lamellar phases, through interconnected channels of various length and local topology. The exact shape of the water and oil pseudophases depends upon a number of factors, such as chemical nature and concentration of the microemulsion components, temperature and pressure. However, at fixed temperature and pressure, the structural properties of AOT reverse microemulsions can be basically described by two parameters²⁷:

- the water to AOT molar concentration ratio ω $= [H_2O]/[AOT]$ which, in the case of droplets, gives an estimation of the water core radius, expressed in nanometers, according to the relation³⁰ $R_w \simeq 0.17 \omega$.
- the volume fraction of the dispersed phase $\phi_d =$ $\phi_{\rm H_2O} + \phi_{\rm AOT}$ which can be used as an indicator of the interactions among water domains. In fact, higher values of ϕ_d result in clusters formation and

eventually in the onset of a continuous aqueous²³⁹ phase (percolation threshold^{30,43} $\phi_d \sim 0.5 - 0.6$). ²⁴⁰

In a ternary system like ME (H_2O (Species 1) / AOT 190 (Species 2) + Octane as the solvent), the diffusion ma-191 trix consists of 4 elements: 2 diagonal main diffusion 192 coefficients $(D_{11} \text{ and } D_{22})$, which account for the mo-193 tion of water and AOT in octane respectively, according $_{242}$ 194 to their own concentration gradient and 2 off $diagonal_{243}$ 195 cross-diffusion coefficients $(D_{12} \text{ and } D_{21})$, related to the₂₄₄ 196 motion of water generated by a gradient of AOT and 197 vice versa. Diffusion is therefore described by a set of 198 two equations and four diffusion coefficients as 199

$$J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \tag{1}_{24}$$

$$J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \tag{2)^{246}}$$

where J_i is the flux of the *i* species and C_1 and C_2 are₂₄₈ 200 the concentrations of H₂O and AOT, respectively. 201 249 The cross-diffusion coefficients were found to be neces-250 202 sary to describe in details ME systems, in particular a 203 flux of AOT generates a large co-flux of water $(D_{12}$ pos-204 itive), while the flux of H₂O generates a counter-flux of 205 AOT $(D_{21} \text{ negative})^{44-46}$. The presence of solutes in ME 206 also generates large cross-diffusion effects, which where 207 measured up to a 5 components system^{33–35}. Excluded²⁵¹ 208 volume effects, are the most important mechanisms in $^{292}_{253}$ 209 generating cross diffusion in ME, because the motion of $^{253}_{254}$ 210 AOT or H_2O changes the size of the droplets' water core 211 influencing the actual concentration of the two species. $\frac{25}{256}$ 212 Further mechanisms related with the size of the water 213 droplets are, however, at $play^{34,45}$. 214 258

215 B. The Taylor dispersion technique

262 The Taylor dispersion technique $(TDT)^{47-50}$ is a_{263} 216 fast and reliable method for measuring the diffu-217 sion coefficients of solutes in one- or multi-component 218 solutions $^{33-35,45,51,52}$. The TDT is based on the diffusive 219 spreading of a drop of solution injected into a laminarly 220 flowing stream of the same mixture but with slightly dif-221 ferent concentrations. A small volume of the perturbing $_{265}$ 222 solution is injected into the flowing eluent at the entrance $\frac{1}{266}$ 223 of a long capillary tube having a radius R_0 . As it moves 224 267 along the tube at a constant speed u_0 (cm/s), the injected 225 sample is deformed by the flow and by radial diffusion. If 226 the flow has a parabolic velocity profile, the drop spreads 227 out into a shape that can be fitted by a combination of n228 Gaussian functions for an (n + 1)-component system (n 229 solutes + 1 solvent). The eluted peak is monitored by a 230 suitable detector, chosen according to the composition of²⁶⁸ 231 the analyzed samples. The diffusion coefficients are cal-232 culated from the parameters of the Gaussian functions²⁶⁹ 233

that fit the eluted peak.

Taylor demonstrated that if the elution process is $slow_{270}$ enough, the radial variation of the sample concentration₂₇₁ is small relative to the axial variation and the concen-₂₇₂ tration profile of the *i*-th species (c_i) in a *n*-component₂₇₃ system can be described with a one-dimensional equation $(c_i \text{ is averaged over the cross section of the tube})$ taking the form^{33,47}

$$\frac{\partial c_i}{\partial t} = \sum_{j=1}^n F_{ij} \frac{\partial^2 c_j}{\partial z^2} \tag{3}$$

where F_{ij} are called dispersion coefficients. They have the same units as the molecular diffusion coefficients D_{ij} (cm² s⁻¹) and are related to them through the relation

$$F_{ij} = \frac{R_0^2 u_0^2}{48 \det(\mathbf{D})} \det(\mathbf{M}_{Dji}) (-1)^{(i+j)}$$
(4)

det(**D**) is the determinant of the $n \times n$ diffusion matrix **D** and det(**M**_{Dji}) is the determinant of the minor associated with element D_{ji} of **D**.

The F_{ij} can be obtained from the experimentally found parameters characterizing the Gaussian fit to eluted peaks: $P_{i,exp}$, K_i , and σ_i through the following equation

$$l_0^{-1} \sum_{i=1}^n \sigma_i P_{i,\exp} = \sum_{j=1}^n c_{j0} \sum_{i=1}^n K_i F_{ij}$$
(5)

where l_0 (cm) is the length of the capillary occupied by the sample injected at the initial time $(l_0^{-1} = \pi R_0^2/V_0, V_0$ is the injected volume), $P_{i,exp}$ are the pre-exponential parts of the Gaussian, σ_i are the dispersions of the Gaussian functions which are equal to the eigenvalues of the dispersion matrix \mathbf{F} , c_{i0} is the difference between the concentration of component *i* in the injected sample and in the carrier stream, K_i is the instrumental sensitivity with respect to that component (typically linear in the concentration). The experimentally measurable quantities $P_{i,exp}$, K_i , and σ_i can be found by fitting all the experimental peak curves v(t) (generated with injections of different compositions) according to

$$v(t) = \sum_{i=1}^{n} \frac{P_{i,\exp}}{\sqrt{4\pi\sigma_i t}} \exp\left[-\frac{u_0^2(t-t_0)^2}{4\sigma_i t}\right]$$
(6)

where u_0 is the mean velocity of the carrier stream and t_0 is the retention time. The coefficients K_i can be found by analyzing different experiments involving injections with only one $c_{i0} \neq 0$ as

$$K_i = l_0^{-1} (\sum_{j=1}^n P_{j, \exp_i}) / c_{i0} \qquad i = 1...n$$
 (7)

II. EXPERIMENTAL SETUPS

A. Taylor Dispersion setup

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In all experiments a 15 m silica glass dispersion capillary (inner radius $R_0 = (0.016 \pm 0.002)$ cm) was placed between the injector and the cell of the differential flowthrough thermostated refractive index detector, RID In

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 $\rho_{\rm B} > \rho_{\rm T}$

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(Agilent G1362A). The RID measures the difference be-³³¹ 274 tween the refractive index of the eluent which is present³³² 275 in a reference cell and the refractive index of the flowing³³³ 276 solution containing the sample, which passes through a³³⁴ 277 measuring cell. The refractive index is, in fact, depen-335 278 dent on the composition of the system and, for dilute₃₃₆ 279 solutions, it is a linear combination of the refractive in-337 280 dex of each component weighted by its concentration. 338 281 In order to eliminate small bubbles from the solutions,₃₃₉ 282 an inline ion exchange resin based de-gasser (Agilent₃₄₀ 283 G1322A) was placed between the eluent reservoir and₃₄₁ 284 the pump. 342 285

- The tubing was coiled in a 30 cm diameter helix and im_{-343}
- ²⁸⁷ mersed in a thermostated water-bath (Julabo ME-16G), ³⁴⁴ ²⁸⁸ kept at 25 °C. The eluent flow was kept steady and con-
- kept at 25 °C. The eluent flow was kept steady and constant at 0.015 mL/min by using an isocratic pump (Agi-
- lent G1310B). A 2 μ L sample loop was used for samples
- ²⁹¹ injection. The detector was connected to a personal com-²⁹² puter for data acquisition.
- ²⁹³ Solutions were prepared by using bidistilled water, AOT³⁴⁶
- ²⁹⁴ (Aldrich) was of analytical grade and used as received.
- Octane (Sigma) was further purified by mixing with con-347
 centrated sulfuric acid for seven days.
 Samples were injected every 60 min to avoid the overlap-349
 ping of the peaks. Experimental peaks generated with350
 different injections were simultaneously fitted, by using351
 the Levenberg-Marquardt algorithm⁵³, to equation (6).352
- ³⁰¹ In order to correct the instrumental drift, a baseline of ³⁵³ ³⁰² the form (a + bt) was previously subtracted from the ³⁵⁴
- ³⁰³ recorded signals with the help of a suitable software. ³⁵⁵

B. Hele-Shaw cell

The experimental reactor used to study convective dynamics at the interface between two MEs of different compositions consists of a vertically oriented Hele-Shaw cell, composed of two borosilicate glasses separated by a spacer of 0.10 mm (Figure 1(a))⁵⁴. Two different water-in-oil (W/O) reverse microemulsions were filled in the reactor through the inlet ports positioned at the top and the bottom of the cell ("In" arrows in Fig. 1(a)). The excess of the solutions is pumped out through the cell's outlets ("Out" arrows in Fig. 1(a)) until a flat interface between the two liquids is obtained. Each of the two microemulsions having different composition initially occupies half of the reactor height. The top and bottom solutions are prepared at room temperature $(\sim 21^{\circ}C)$ by means of distilled water and of a 1.5 M AOT in octane stock solution, conveniently diluted until the desired ϕ_d (0.16 – 0.20) is reached. The top and bottom microemulsions are prepared at slightly different droplet size ($\omega = 8 - 14$), with the bottom solution always denser than the top one. Different ω ratios are obtained by varying the amount of H_2O (AOT) while keeping the amount of AOT (H_2O) constant.

The dynamics of the interface is tracked by using the Schlieren technique^{40,55}, which allows to observe the gradients in the refractive index between both microemulsions, due to their density differences and, therefore, monitor the convective motions in solutions without the presence of dyes.

The solutal expansion coefficient of each *i*-component ($i = H_2O$, AOT) was determined according to $\alpha_i = \frac{1}{\rho_0} \frac{\partial \rho}{\partial C_i}$ where ρ_0 is the density of the solvent (octane) and C_i the molar concentration of the i-th species. In order to measure these coefficients the volume of both the solvent and of one of the components was fixed, while the concentration of the other was gradually increased. The densities were measured by using an Anton Paar densimeter and it was found that the solutal expansion coefficients were 0.0051 M⁻¹ for H₂O and 0.154 M⁻¹ for AOT.

III. RESULTS

A. Diffusion matrices

In order to characterize the diffusion matrix of the microemulsions used for the Hele-Shaw experiments, three systems below the percolation limit were investigated; namely, microemulsions with the smallest and the largest value for the concentration ratio, ω , and the volume fraction, ϕ_d , (8.15; 0.165) and (14; 0.2), respectively and one composition in the middle of the interval, (11.84; 0.18). Several experiments were performed by injecting samples with an excess of one (H₂O or AOT) or two



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components. All Taylor dispersion peaks obtained were 356 then simultaneously fitted using eq. (6) with i = 1, 2 to 357 extract the experimental parameters $(P_{i,exp}, \sigma_i)$. As an 358 example, figure 2 shows the peaks obtained by injecting 359 samples with an excess of only AOT (\blacktriangle) or only H₂O 360 (\blacksquare) into a carrier stream of microemulsion with $\omega = 14$ 361 and $\phi_d = 0.2$. The sensitivity coefficients K_i were found 362 by introducing the fitted parameters in eq. (7). By using 363 eq. (5), we find the dispersion coefficients F_{ij} and finally, 364 by using eq. (4) we transform F_{ij} to diffusion coefficients 365 D_{ij} . The complete procedure to fine-tune the diffusion 366 matrix values is reported elsewhere 33 . 367

Table I. Ternary Diffusion Coefficients (in $10^{-6} \text{ cm}^2/\text{s}$) for the H₂O (i=1)/AOT (i=2)/Octane systems at different ω and ϕ_d .

1	ω	ϕ_d	D_{11}	D_{12}	D_{21}	D_{22}
ĺ	8.15	0.165	0.8 ± 0.1	3.6 ± 1.0	-0.0015 ± 0.0020	1.10 ± 0.01
	11.84	0.18	0.60 ± 0.04	7.8 ± 2.0	-0.010 ± 0.002	1.30 ± 0.04
	14	0.2	0.3 ± 0.1	1.1 ± 0.2	-0.005 ± 0.004	0.96 ± 0.01

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Table I reports the diffusion matrices of the investigated 370 systems, which span the whole range of the microemul-371 sions composition used for the Hele-Shaw cell experi-372 ments. Since both ω and ϕ_d have been varied simul-373 taneously, it is difficult to find a clear trend for the de-374 pendence of D_{ij} upon the system composition. However, 375 for the purpose of this work, we were more interested 402 376 in finding the nature and the order of magnitude of the $^{\rm 403}$ 377 cross-diffusion coefficients to be used in simulations (see⁴⁰⁴ 378 section IIIB). The results reported in Table I fit well with⁴⁰⁵ 379 literature data determined for other compositions of the⁴⁰⁶ 380 microemulsions $^{33-35,44,45}$, in particular we find that the 407 381 motion of AOT generates large co-fluxes of water ($D_{12^{408}}$ 382 large and positive) and the motion of water generates⁴⁰⁹ 383 small counter-fluxes of AOT $(D_{21} \text{ small and negative})^{410}$ 384 for all the parameters range explored in the Hele-Shaw⁴¹¹ 385 experiments. 412 380

388 B. Theoretical approach

389 1. Cross-Diffusion Model

The possible convective instabilities which take place 390 at the horizontal interface between two microemulsions₄₁₇ 391 in a vertical Hele-Shaw cell (see Figure 1a)), can be in-418 392 terpreted by studying the corresponding temporal evolu-419 393 tion of one-dimensional density profiles along the vertical⁴²⁰ 394 axis Z, where the gravitational acceleration \bar{g} is oriented₄₂₁ 395 downwards. The density profiles give qualitative infor-422 396 mation about the instabilities to be expected, as their₄₂₃ 397 morphology shows whether and where local regions of₄₂₄ 398 denser fluid overlying less dense zones may develop along₄₂₅ 399 the gravitational axis. 426 400

401 Consider a spatial domain of length L_Z where a solu-427



Figure 2. Taylor dispersion peaks for the system = H₂O/AOT/octane. (**▲**) Experimental peak for a sample containing an excess of AOT, Δ [AOT] = 0.1 M, Δ [H₂O] = 0 M. (**■**) Experimental peak for a sample containing an excess of H₂O, Δ [AOT] = 0 M, Δ [H₂O] = 2 M. The composition of the leuent is [H₂O] = 4.38 M, [AOT] = 0.31 M and [octane] = 5.14 M (ω = 14 and ϕ_d = 0.2), T = 25 °C. Solid lines are the best fit obtained with sum of two Gaussian curves with P_{1,exp} = 1.4 × 10⁷ R.I.U. × cm, P_{2,exp} = 1.7 × 10⁷ R.I.U. × cm (**▲**) and P_{1,exp} = -2 × 10⁵ R.I.U. × cm, P_{2,exp} = -7 × 10⁶ R.I.U. × cm (**■**). For both peaks, σ_1 = 6 cm²/s, σ_2 = 12 cm²/s, K_1 = -2.85 × 10⁶ R.I.U./M and K_2 = 1.07 × 10⁸ R.I.U./M.

tion T of density ρ^T , containing the solute 1 (H₂O) with the initial concentration $C_{1,0}^T$ and the solute 2 (AOT) with concentration $C_{2,0}^T$ is placed on top of the solution B, with concentration $C_{1,0}^B = C_{1,0}^T$, $C_{2,0}^B > C_{2,0}^T$ (or vice versa, depending on the type of cross-diffusion we are interested in). The density ρ^B is always larger than ρ^T in order to start from a stable configuration with regard to a Rayleigh-Taylor instability⁵⁶. Upon contact, the two miscible solutions, initially separated along the horizontal interface $z = L_Z/2$, start mixing by diffusion. The diffusion of each species is affected by concentration gradients in the other one and hence the spatio-temporal dynamics of the system obeys a set of fickian equations including the cross-diffusive terms of the diffusion matrix **D**:

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$$\partial_t C_1 = D_{11} \nabla^2 C_1 + D_{12} \nabla^2 C_2 \tag{8}$$

$$\partial_t C_2 = D_{21} \nabla^2 C_1 + D_{22} \nabla^2 C_2 \tag{9}$$

Although main (D_{ii}) and cross-diffusion coefficients $(D_{ij}, i \neq j)$ depend on the chemical composition of the system (see Table I), as a first approximation, we consider them here as constant^{35,40}.

We solve eqs (8)-(9) with a constant concentration of either water or AOT and a jump in the concentration of the other specie centered around $z = L_Z/2$. No-flux boundary conditions are imposed at the borders of the spatial domain. We obtain numerically the concentration profiles $C_1(x,t)$ and $C_2(x,t)$ which are next used to reconstruct the related density profiles according to the

state equation: 428

$$\rho(C_1, C_2) = \rho^T \left(1 + \alpha_1 (C_1 - C_{1,0}^T) + \alpha_2 (C_2 - C_{2,0}^T) \right) (10)$$

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This expansion relies on the assumption that con-430 centrations slightly change with respect to the initial 431 composition of the reference top solution with density 432 ρ^T and we can then admit a linear dependence of the 433 global density ρ upon the solute concentration. In eq. (10), $\alpha_i = \frac{1}{\rho^T} \frac{\partial \rho}{\partial C_i}$ is the solutal expansion coefficient of 434 435 the i-th species. 436

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Density profiles analysis 2. 438

The double-layer initial condition represents a key 439 specificity of the cross-diffusion problem under study. 440 Depending upon the starting concentration profile of the 441 two species, we can "select" a specific cross-diffusion path 442 and, in turn, the related convective dynamics. For in-443 stance, when a concentration jump is initially imposed 444 to AOT at constant water content, this induces a dif-445 fusive motion in the initially homogeneous distribution 446 of H_2O via the cross-diffusion term D_{12} , while the other 447 cross-diffusion term (D_{21}) plays a negligible influence. 448 In particular, species 2 (AOT) generates a co-flux of the 449 species 1 (water) since D_{12} is positive. Vice versa, when 450 the initial concentration jump is imposed on water at 451 constant AOT, cross-diffusion effects, triggered by the 452 propagation of water towards the upper layer, influence 453 the evolution of AOT as controlled by D_{21} . In this case 454 the diffusion of H₂O generates a counter-flux of AOT. 456

These mechanisms are shown in Fig.3. Both panels₄₇₇ 457 (a) and (b) describe in the first two graphs the spatio- $_{478}$ 458 temporal evolution of the species concentration starting $_{479}$ 459 from one of the two initial configurations under analysis; $_{\!\scriptscriptstyle 480}$ 460 the third graph displays the resulting density profiles. $_{431}$ 461 The concentration profiles are obtained by solving in one $_{_{482}}$ 462 spatial dimension (Z) the diffusion equations with the 463 characteristic diffusion matrix of the ME (see sec. III A): $_{434}$ 464

$$\boldsymbol{D} = \begin{pmatrix} 0.6 & 7.8 \\ -0.01 & 1.3 \end{pmatrix} \times 10^{-6} \text{cm}^2 \text{ s}^{-1}, \qquad (11)^{486}_{487}$$

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$$= \begin{pmatrix} 0.00 & 1.0\\ -0.01 & 1.3 \end{pmatrix} \times 10^{-6} \text{cm}^2 \text{ s}^{-1}, \qquad (11)_{486}$$

while the density distribution is found according to eq.489 466 (10), using the solutal expansion coefficients measured₄₉₀ 467 experimentally (see sec. II): $\alpha_{H_2O} = 0.0051 \text{ M}^{-1} \text{ and}_{_{491}}$ $\alpha_{AOT} = 0.154 \text{ M}^{-1}$. Fig.3.a illustrates how the diffusion₄₉₂ 468 469 of species 1, featuring an initial concentration jump, gen-493 470 erates a counter-flux of species 2 ruled by the negative₄₉₄ 471 cross-diffusivity $D_{21} = -0.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. In the con-495 centration profile $C_2(Z, t)$ this induces a local depletion496 472 473 area in the upper layer and a symmetric accumulation497 474 475 of species 2 just below the initial interface $L_Z/2$. By₄₉₈ contrast, when the initial concentration jump is imposed₄₉₉ 476



Figure 3. Spatio-temporal evolution of the concentration profiles $C_1(Z,t)$, $C_2(Z,t)$ and of the density excess $(\rho - \rho^T(z))$. In each graph we show with black lines the initial distribution of the variables, while red and blue profiles depict the spatial concentration and density at intermediate and long times, respectively. a) NCC mechanism due to the negative cross-diffusion term (D_{21}) and induced by means of a concentration jump in the species 1 (water). b) PCC scenario with positive cross-diffusion (D_{12}) triggered by the upwards diffusion of the species 2 (AOT).

to the AOT (species 2) (Fig.3.b), its diffusion from the bottom to the upper layer promotes a co-flux of the water (species 1), quantified by the positive cross-diffusivity $D_{12} = 7.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. As a result, the concentration profile $C_1(Z,t)$ develops a non-monotonic shape with a local maximum and a minimum symmetrically located above and below the initial interface, respectively. We clearly observe an inversion in the morphology of the nonmonotonic density profiles depending whether the initial jump is imposed on species 1 (water) or species 2 (AOT), as this activates different cross-diffusion terms with opposite sign.

Non-monotonic density profiles will develop because of cross-diffusion effects provided a sufficient influence of the non-monotonic concentration to the global density. In the first case (Fig.3.a), though the small negative crossdiffusion D_{21} drives the formation of concentration extrema of small amplitude in $C_2(Z, t)$, the AOT has a large weight (α_{AOT}) to the density and we can identify a minimum and a maximum above and below the interface. respectively. This profile is reminiscent of typical density profiles characterizing Diffusive Layer Convection (DLC) scenarios^{56,57} and we can expect that, starting from an

initial constant AOT concentration and a jump in H₂O,555 500 convective modes will grow in the upper and the lower 501 laver, without deforming the initial contact line between 502 the two stratified solutions. We will refer to this scenario 503 as Negative Cross-diffusion-driven Convection (NCC). 504 Analogous considerations can be drawn for the opposite 505 initial configuration shown in Fig.3.b. Here the cross-506 diffusion term responsible for the non-monotonic evolu-507 tion of $C_1(Z,t)$, D_{12} , is positive and large. This means 508 that $C_1(Z,t)$ can develop concentration extrema but, 509 since H_2O presents a small relative contribution to the 510 system density, the smoothing of the initial AOT gradi-511 ent must be waited to observe the influence of H_2O in the 512 density evolution. Fig.3.b (third panel), allows to appre-513 ciate how, starting from an initial condition in which the 514 density increases downwards the gravitational axis, the 515 density profile changes in time into a monotonically de-516 creasing profile. In real experiments this results in a fin-517 gered deformation of the initial interface and hereunder 518 we refer to this scenario as Positive Cross-diffusion-driven 519 Convection (PCC). 520

521 C. Hele-Shaw results

In order to confirm the theoretical predictions, we per-522 formed experiments in a Hele-Shaw cell by stratifying 523 two microemulsions with different initial concentrations 524 of water and AOT. In all experiments, we start from an 525 initial statically stable stratification, *i.e.* the microemul-526 sion located in the bottom is denser than the one on 527 the top. We explore two different scenarios to analyze 528 the negative (NCC) and positive (PCC) cross-diffusive-529 driven instabilities. In the negative cross-diffusive case 530 (Fig.3.a) the AOT concentration is initially constant ev-531 erywhere while the microemulsion on the top has less 532 water than that placed below, as depicted in Figure 4(a). 533 When the difference in water concentration is relatively 534 small ($\Delta [\rm H_2O]_{\rm bottom-top}<0.75$ M) we do not observe any buoyant instability. This can be understood as a 535 536 limitation of our experimental device in discerning small 537 gradients in the refractive index. However, for larger gra-558 538 dients (0.75 M $<\Delta [{\rm H_2O}]_{\rm bottom-top}<1.75$ M) the ini-559 tially stable configuration becomes unstable after 5 – 6560 539 540 minutes exhibiting convective vortices at symmetric dis-561 541 tances above and below the unperturbed interface (see 562 542 Figures 4(b) - (d), features that compare favorably with₅₆₃ 543 the classification given in sec. IIIB for the same ini-564 544 tial configuration (NCC scenario). We recover the typi-565 545 cal nonlinear dynamics of DLC modes where convective566 546 vortices develop at symmetric distances around an un-567 547 perturbed interface 56,57. We track the evolution of the 568 548 mixing zone, defined as the distance between the most₅₆₉ 549 upwards and downwards tip of the fingers. Figure 5570 550 demonstrates that the larger the initial jump in water571 551 concentration the slower the mixing of the microemul-572 552 sions. This is expected as the cross-diffusion effects have 573 553 then to overcome a larger stabilizing density jump to pro-574 554

mote convection.



Figure 4. Experimental negative cross-diffusive instability. a) Sketch of the experimental initial conditions required to achieve negative cross-diffusion. b)-d) Three snapshots showing the evolution of the DLC mode obtained with $\Delta H_2 O_{bottom-top} = 1.15$ M taken at t = 0, 700 and 1200 s. ME_T $\omega = 8.15$, $\phi_d = 0.16$; ME_B $\omega = 12.2$, $\phi_d = 0.185$. Frame sizes (b) – (d) = 11.45 mm × 8.9 mm



Figure 5. Temporal evolution of mixing length for different values of the initial water concentration jump.

In order to analyze the positive cross-diffusive (PCC) driven convective instability, we start with a jump on the AOT surfactant concentration between both microemulsions at a homogeneous amount of water, as sketched in Figure 6(a). By imposing a surfactant jump in the range $0.02M < AOT_{bottom-top} < 0.06$ M, the initial contact line deforms into equally separated fingers that grow vertically with time at the interface (Figures 6(b) – (d)). These structures are successfully predicted by the analysis of the density profile obtained from the cross-diffusion model in analogous conditions (PCC scenario) and can be better perceived by performing spatio-temporal plots along the horizontal and vertical axis (Figure 7). Horizontally, along the initial contact line between both microemulsions (dashed line in Figure 7(a)), we observe

how convective fingers (vertically oriented white stripes 575 in Figure 7(c) have a characteristic hydrodynamic wave-576 length. This feature, defined as the average distance 577 between consecutive convective fingers, has been calcu-578 lated before being altered due to the appearance of lateral 579 flows in the system. Analysis at different density jumps 580 between both microemulsions show that the larger the 581 initial jump in AOT concentration the smaller the wave-582 length as reported in Figure 7(d). The vertical space-583 time plot (Figure 7(b)) accounts for the induction pe-584 riod, defined as the interval of time that convective fin-585 gers require to develop. This characteristic time is short-586 ened as the initial jump in AOT concentration is reduced 587 (Figure 7(e)). Furthermore, Figure 7(b) gives us infor-588 mation about the asymmetric growth rate of convective 589 fingers (90 μ m/min for ascending fingers in contrast to 590 75 μ m/min for the descending ones). 591



Figure 6. Experimental positive cross-diffusive instability. a)₆₀₆ Sketch of the experimental initial concentration of a jump of₆₀₇ AOT between both microemulsions while the water concen-₆₀₈ tration is constant. (b) – (d) Three snapshots taken at t = 0, 700 and 1250 s displaying the evolution of double diffusive modes obtained with $\Delta AOT_{bottom-top} = 0.06$ M. ME_T $\omega = {}^{610}_{612}$ 11.95, $\phi_d = 0.19$; ME_B $\omega = 9.8$, $\phi_d = 0.2$. Frame sizes (b) $-{}^{611}_{612}$ (d) = 11.45 mm × 8.9 mm.

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595 IV. CONCLUDING DISCUSSION

To conclude, through a combined experimental and₆₁₉ 596 theoretical study, we have demonstrated that ME are620 597 a simple and ideal model system where different convec-622 598 tive instabilities driven by 2-component cross-diffusion623 599 can be induced. Thanks to the TDT method we have₆₂₄ 600 first characterized the AOT-H₂O diffusion matrix of the625 601 microemulsion solutions for the concentrations used in $_{626}$ 602 the HS cell convective experiments. These measurements₆₂₇ 603 show that the diffusion matrix consists of a positive $D_{12^{628}}$ 604 and a negative D_{21} cross-diffusion term and that there 629 605



Figure 7. Analysis of positive cross-diffusive driven instability. (a) Initial frame (1.45 mm × 8.9 mm) displaying the horizontal contact line between two microemulsions carried out at ϕ_d = 0.18 and $\Delta AOT_{bottom-top} = 0.06M$. (b) Spatio-temporal dynamics obtained along the vertical red dotted line v showing the deformation of the contact line along the gravitational axis. Frame size = 8.9 mm × 2000 s. (c) Spatio-temporal plot constructed along the horizontal line h demonstrating the emergence of fingers at different locations of the interface and their temporal evolution. Frame size = 11.45 mm × 2000 s. Variation of wavelength (d) and induction time (e) for different initial jumps in the AOT concentration between the bottom and top microemulsions. A solid line was drawn in (d) and (e) to help the reader following the data trend.

is a suitable concentration range where H_2O and AOT can be varied without changing dramatically the actual values of the diffusion coefficients. With this information and knowing the solutal expansion coefficients of the two species, we could theoretically predict two possible cross-diffusion driven convective scenarios, depending upon which species features the initial concentration jump in the starting statically stable stratification. When the initial concentration jump is imposed on the water concentration, DLC-type convective patterns grow driven by the negative cross-diffusivity D_{21} (NCC). On the contrary DD-type of instabilities can develop in time in presence of an initial concentration jump introduced in AOT when the cross-diffusion dynamics is controlled by the positive D_{12} (PCC).

The positive and negative cross-diffusion-driven convective scenarios have been described on the basis of onedimensional density profiles directly constructed using experimental data. By studying the spatial dependence of these density profiles we can also interpret some features obtained from the analysis of experimental data. For instance, in our simulations we find that the time needed to form the monotonically decreasing profile in



Figure 8. Dependence upon Δ [AOT] of the maximal density⁶⁷⁷ jump ($\Delta \rho$) between the top and the bottom layer in the mono-⁶⁷⁸ tonically decreasing profile developing in the PCC scenario.

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the PCC (featuring a denser fluid over a less dense683 630 medium, like the blue profile in Fig.3.b (third panel))⁶⁸⁴ 631 is independent of the initial concentration jump imposed 632 to the AOT. By contrast, the related density jump, $\Delta \rho_{,_{687}}^{,_{687}}$ 633 which measures the maximal density difference between₆₈₈ 634 the top and the bottom layer as $max(\{\frac{\rho(L_z,t)-\rho(0,t)}{\rho(0,t)}\} \forall t),_{_{690}}^{_{690}}$ 635 , 690 slightly increases with Δ [AOT] (see Fig.8). Consider-636 ing the experimental error, these features are substan-692 637 tially recovered in the characterization of the experiments⁶⁹³ 638 shown in Fig.7.d and Fig.7.e. Here, we cannot recognise⁶⁹⁴ 639 any significant trend in the onset time of the instabil- $^{695}_{696}$ 640 ity (the average value is almost constant) while, the de_{-697} 641 creasing drifting of the pattern wavelength with Δ [AOT]₆₉₈ 642 can be ascribed to the increasing magnitude of $\Delta \rho$. The⁶⁹⁹ 643 larger this initial density jump, the more intense the re- 700 644 sulting convective dynamics and, in turn, the shorter the $_{702}$ 645 characteristic wavelengths to be expected. 646 Our results can be generalised to any multi-component⁷⁰⁴ 647 system showing either positive or negative cross-diffusion⁷⁰⁵ 648

terms in the diffusion matrix **D**. Similar results have $\frac{706}{707}$ 649 been found for polymer-sugar systems⁴¹ and polymer- $\frac{707}{708}$ 650 polyelectrolytes systems⁵⁸, both showing positive cross-651 diffusion terms due to an excluded volume mechanism.⁷¹⁰ 652 Microemulsions allowed us to investigate, for the first⁷¹¹ 653 time, the effect of negative cross-diffusion on the de 712 654 velopment of hydrodynamic instabilities and we found $_{714}$ 655 that the sign of the cross-diffusion coefficients is impor-715 656 tant to select the type of instability. These results also⁷¹⁶ 657 show that microemulsions will be a suitable experimental⁷¹⁷ 658 model to investigate the coupling among reaction-driven $^{\prime 10}_{719}$ 659 and diffusion-driven hydrodynamic instabilities. 660 720

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