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1 **Coupled non-equilibrium fluctuations in a polymeric ternary mixture**

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10  
11 **Abstract**

12 We investigate by dynamic shadowgraphy the non-equilibrium fluctuations at the steady state  
13 of a thermodiffusion experiment in a polymeric ternary mixture of polystyrene-toluene-n-  
14 hexane. The structure function of the refractive index reveals the existence of quite different  
15 decay times, thus requiring the analysis of a wide range of correlation times. This is related to  
16 the simultaneous presence of three distinct decay modes corresponding to (from fastest to  
17 slowest) relaxation of temperature fluctuations, of the concentration fluctuations of the mixed  
18 solvent, and of the concentration fluctuations of the polymer in the binary solvent. An  
19 investigation of the decay times at the corresponding diffusive regimes provides a measurement  
20 of the thermal diffusivity and the two eigenvalues of the mass diffusion matrix of the ternary  
21 mixture. Similar experiments were performed in the past but here, to suppress the confinement  
22 effect and obtain a more direct comparison with the theory, a thicker sample is studied.  
23 Moreover, also a faster camera is used allowing the experimental observation of faster modes,  
24 like the propagative ones. The experimental values of the decay times are eventually compared  
25 with those predicted by different available theories. Finally, we present a more complete  
26 theoretical model to describe the non-equilibrium fluctuations in the bulk of a ternary mixture  
27 at the steady state of a thermodiffusion experiment.

28 **Keywords:** Multicomponent mixtures, Polymer, Thermodiffusion, Shadowgraphy, Non-  
29 equilibrium, Fluctuations

30

## 31 **1. Introduction**

32 The majority of the fluids encountered in nature and industry are multicomponent mixtures.  
33 The knowledge of their transport properties is crucial for many different applications from both  
34 scientific and technological points of view. The efficiency of exploitation of the crude oil wells,  
35 as well as the environmental alternative focused on the CO<sub>2</sub> storage in deep brine aquifers, are  
36 some recent examples showing the interest of studying the transport properties of  
37 multicomponent mixtures subjected to non-equilibrium conditions [1, 2]. Complex fluids in  
38 non-equilibrium conditions exhibit giant fluctuations of the thermodynamic variables, the so-  
39 called non-equilibrium fluctuations (NEFs) [3-5]. By analysing NEFs through light scattering  
40 techniques, the transport properties of the fluid can be determined both at atmospheric [6] and  
41 at high pressure [7].

42 The non-equilibrium condition can be induced, for example, by applying a temperature gradient  
43 to a multicomponent fluid mixture, thus inducing a composition gradient within the fluid by  
44 means of the thermodiffusion, or Soret effect [8-10]. This transport process can be investigated  
45 by optical techniques and particularly by light scattering thanks to its ability to visualize NEFs  
46 without altering the intrinsic properties of the fluid. In this work, dynamic shadowgraphy has  
47 been adopted [11-13] to study the fluctuations of the refractive index as generated by the NEFs  
48 of the thermodynamic variables, like temperature and concentrations. By shadowgraphy, a large  
49 range of fluctuations sizes  $\lambda$  or, conversely, wave numbers  $q = 2\pi/\lambda$ , can be investigated at  
50 the same time. This approach, combined with statistical analysis, represents a powerful  
51 characterization technique able to provide simultaneous reliable measurements of different

52 transport properties, like mass diffusion coefficient or thermal diffusivity as well as Soret  
53 coefficient [6, 14, 15].

54 A suitable characterization of transport processes in complex mixtures requires a deep  
55 understanding of simpler fluids. So far, only binary mixtures [10, 16] have been extensively  
56 characterized. The extension of theories and experiments from binary to ternary mixtures  
57 requires further development due to the intrinsic and significant increase of difficulty with the  
58 number of components of the mixture. Currently, a great effort is devoted to investigate the  
59 transport phenomena in ternary mixtures, as performed in the present study. Thermodiffusion  
60 experiments in ternary mixtures are performed on ground, by using different optical techniques  
61 [10, 14, 17, 18], or in microgravity in order to avoid both convection and sedimentation. The  
62 thermodynamic characterization of ternary mixtures is one of the objectives of the following  
63 ESA projects: Diffusion Coefficient Measurements in ternary mIXtures (DCMIX) [18-23],  
64 Soret Coefficients in Crude Oil (SCCO) [1, 24-27] and Giant Fluctuations [28], as further  
65 elaborated in a recent colloquium paper [29].

66 As a benchmark ternary mixture, the tetraline, isobutylbenzene and n-dodecane sample has been  
67 studied by digital interferometry on ground and in microgravity within the DCMIX experiments  
68 [18, 19, 30-38]. In addition, Bataller et al. [17] investigated this mixture on ground by one-  
69 wavelength shadowgraphy. Since no other alternative was available at that time, Bataller et al.  
70 [17] compared their experimental results with the theory of concentration NEFs developed for  
71 ternary mixtures in the absence of gravity [39]. The two concentration modes related to the  
72 presence of the two independent components could not be distinguished experimentally, and  
73 only an average of the two eigenvalues of the mass diffusion matrix could be provided. This  
74 result is expected, as the mixture is composed of similar-size molecules, and consequently the  
75 two eigenvalues of the diffusion coefficient matrix are very similar to each other. The two  
76 eigenvalues  $\widehat{D}_1$  and  $\widehat{D}_2$  of the diffusion matrix  $\mathbf{D}$  need to be different enough to distinguish the

77 two concentration modes. An equivalent way to set this statement is to define a dimensionless  
78 number  $Dr = \widehat{D}_2/\widehat{D}_1$  ( $Dr$  for Diffusion eigenvalue Ratio and  $\widehat{D}_1$  representing the slowest  
79 diffusion mode) and require it to satisfy the relation  $Dr \gg 1$ . A ternary mixture containing a  
80 polymer dissolved in a binary mixed solvent is a good candidate for such measurement, due to  
81 the very different molecular size of its components and, correspondingly, a value of  $Dr \approx 10$ .  
82 This was experimentally proved for the diluted polymeric ternary mixture of polystyrene-  
83 toluene-n-hexane, as reported in [14], where a layer of  $L = 2 \text{ mm}$  thick was investigated by  
84 using one-wavelength shadowgraphy at a single image acquisition frequency of 28 Hz. By  
85 adopting the theoretical model of ternary mixtures in the absence of gravity, the dynamics of  
86 the NEFs could be analysed for large wave numbers [14]. From such analysis, it was only  
87 possible to determine the two eigenvalues of the mass diffusion matrix and the thermal  
88 diffusivity. Afterwards, the diffusion matrix was simplified by neglecting the off-diagonal  
89 elements and the result was utilised for obtaining an analytical relationship between the two  
90 Soret coefficients, without an independent measurement of them. More recently [40], we have  
91 further developed the theory of NEFs to include the effect of gravity, but not confinement so  
92 that a direct comparison with the data of Ref. [14] is impossible since fluid layer thickness of  
93 only 2 mm makes confinement effects important, as evidenced in related literature for binary  
94 mixtures [41, 42].

95 In the present study, we perform a new shadowgraph experiment on a similar ternary mixture,  
96 but in this case a thicker sample with vertical extension of  $L = 5 \text{ mm}$  is analysed in order to  
97 avoid the confinement effect, and be able to compare the experimental results with the theory  
98 of NEFs including gravity [40]. The present measurements are also carried out with a faster  
99 camera, allowing a more accurate characterization of thermal fluctuations and, thus, a better  
100 separation of them from concentration ones. Additionally, a new procedure of image acquisition  
101 combined with the concatenation of the structure functions allows us to investigate a wider

102 range of correlation times, as required for a complete analysis of this mixture that has a wide  
103 range of decay times. The experimental results are thus compared for the first time with the  
104 theoretical model developed for ternary mixtures in the presence of gravity [40], as well as with  
105 the recently developed theory that includes the coupling of velocity, thermal and solutal NEFs  
106 in the case of binary mixtures [43]. These comparisons suggest that a further development of  
107 the theory is required, in particular to include the coupling between the different NEFs in the  
108 case of the ternary mixture. As part of the contents of this paper we present such a development  
109 and compare with the experimental data.

110

## 111 **2. Experimental procedure**

### 112 *2.1 Polymeric solution preparation and characterization*

113 The sample is prepared by dissolving 2 wt% of polystyrene (PS,  $M_w = 4730 \text{ g/mol}$ , DIN-  
114 Poly(styrene) 4730 DA – PDI 1.03 by PSS-polymer) in 49 wt% toluene (Sigma-Aldrich,  
115 24,451-1, 99.8%) and 49 wt% n-hexane (Sigma-Aldrich, 13,938-6, >99%) at ambient  
116 temperature by using a magnetic stirrer. The thermophysical properties of the mixture, such as  
117 density, viscosity and both thermal and mass expansion coefficients are determined.

118 The kinematic viscosity  $\nu$  is measured at 25°C by a capillary viscometer (Ubbelohde  
119 SCHOTT). The thermal and mass expansion coefficients,  $\alpha$  and  $\beta_i$ , respectively, are defined as  
120 follows:

$$121 \quad \alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_{\omega, p}, \quad (1)$$

$$122 \quad \beta_i = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial \omega_i} \right)_{T, p}, \quad (2)$$

123 where  $\rho$  is the mixture density,  $T$  is the temperature and  $\omega_i$  is the concentration of component  
124  $i$  in mass fraction. Following a common notation, components are ordered according to their

125 (pure) density, hence, in this study 1 corresponds to PS, 2 corresponds to toluene and 3  
126 corresponds to n-hexane.

127 The coefficients  $\alpha$  and  $\beta_i$  are indirectly determined from measurements of the mixture density  
128 performed at different conditions through a Density Meter (ANTON PAAR, DMA 5000). For  
129 the thermal expansion coefficient, the density is measured at different temperatures (from 23 to  
130 27°C), while keeping the concentrations constant at  $\omega_1 = 0.02$  and  $\omega_2 = 0.49$ . The mass  
131 expansion coefficients are obtained after measuring the density at different concentrations while  
132 keeping the temperature constant at 25°C. To obtain the mass expansion coefficient of the  
133 polymer in the mixed solvent,  $\beta_1$ , the concentration of the polystyrene is changed from  $\omega_1 =$   
134 0.000 to  $\omega_1 = 0.035$ , keeping  $\omega_2 = \omega_3$ . For the mass expansion coefficient of the mixed  
135 solvent,  $\beta_2$ , the composition of the mixed solvent is modified from  $\omega_2 = 0.47$  to  $\omega_2 = 0.51$ ,  
136 keeping  $\omega_1 = 0.02$  constant. Measured values of  $\rho$ ,  $\nu$ ,  $\alpha$  and  $\beta_i$  are summarized in Table 1. The  
137 values of  $\rho$ ,  $\nu$ ,  $\alpha$  and  $\beta_2$  are consistent with those reported in [44], determined for the equi-  
138 massic toluene-n-hexane binary mixture at  $T_{mean} = 25$  °C. The measurements of viscosity and  
139 density are repeated at least three times for each sample. The values reported in Table 1 are  
140 calculated as the average of the three measurements and the corresponding uncertainties are the  
141 standard deviations. The parameter  $\alpha$  is determined through Eq. 1, i.e. dividing the slope of the  
142 density vs. temperature by the density of the sample at the nominal temperature. Similarly,  $\beta_i$   
143 are calculated through Eq. 2, i.e. dividing the slope of the density vs. concentration by the  
144 density of the sample at the nominal concentration.

145

146 ***Table 1: Thermophysical properties of the polystyrene-toluene-n-hexane mixture***

Parameter	Value
$\rho$	$(750.0 \pm 0.4) \times 10^{-3} \text{ g/cm}^3$
$\nu$	$(5.24 \pm 0.01) \times 10^{-3} \text{ cm}^2/\text{s}$

$\alpha$	$(9.1 \pm 0.7) \times 10^{-4}/\text{K}$
$\beta_1$	$(3.1 \pm 0.1) \times 10^{-1}$
$\beta_2$	$(2.6 \pm 0.1) \times 10^{-1}$

147

## 148 2.2 Thermodiffusion experiment

149 The experimental set-up is quite similar to the one used in previous studies and a more detailed  
150 description can be found elsewhere [6, 7]. Before filling our thermodiffusion cell, its interior is  
151 evacuated by using a vacuum pump for more than four hours in order to evaporate all the  
152 residual fluids. Subsequently, the mixture is injected into the cell. The sample is sandwiched  
153 between two square sapphire windows of 8 mm thick, mechanically separated to provide a  
154 vertical thickness of the fluid layer of  $L = (5.0 \pm 0.1) \text{ mm}$ . Two thermoelectric (TEC) Peltier  
155 devices are used to apply the temperature gradient to the fluid mixture. Both TECs are  
156 independently connected to two proportional-integral-derivative (PID) temperature controllers  
157 (Wavelength Electronics, MODEL LFI - 3751), being able to set the temperatures of the two  
158 sides of the fluid slab with an absolute accuracy of 0.01 K and a relative RMS stability of 1 mK  
159 over 24 hours. The temperature gradient is applied in the  $z$  direction, and the sample is always  
160 heated from above in order to avoid convection, since both Soret coefficients are expected to  
161 be positive [44-46]. When applying a temperature gradient, the two TECs actually act as heat  
162 pumps in the same direction, thus a heat exchanger flushed with water coming from a thermostat  
163 (HUBER, ministate 125) removes the excess heat from the external side of the Peltier elements.  
164 The thermodiffusion experiments are performed by imposing temperature differences of  $\Delta T =$   
165 10, 15 and 20 K over the vertical extension of the sample cell. After imposing the temperature  
166 gradient, and before starting the image acquisition through the shadowgraph setup, it is  
167 necessary that the sample reaches the stationary state where the Soret effect is completely  
168 balanced by Fickian diffusion. In our experimental conditions, the diffusion time  $\tau = L^2/D$  is



169 of the order of  $8.3 \times 10^4$  s, i.e. about 23 hours. This value is obtained from the diffusion  
170 coefficient of the polymer in a typical solvent, like toluene  $D \approx 3 \times 10^{-6}$   $cm^2/s$  [45].

171 Density fluctuations  $\delta\rho$  generated by both temperature fluctuations  $\delta T$  and concentration  
172 fluctuations  $\delta\omega_i$  give rise to refractive index fluctuations  $\delta n = \delta T(\partial n/\partial T) +$   
173  $\sum_i \delta\omega_i(\partial n/\partial\omega_i)$ , which can be detected by optical techniques, as described in the literature  
174 [11, 13, 47]. In general, velocity fluctuations are not supposed to induce fluctuations of the  
175 density or of the refractive index.

176 In our optical setup, a super-luminous diode (Superlum, SLD-MS-261-MP2-SM) with a  
177 wavelength of  $\lambda = (675 \pm 13)$  nm acts as the light source, illuminating the sample parallel to  
178 the temperature gradient. The light is provided out of a monomode optical fibre and the beam  
179 is collimated by an achromatic doublet lens with focal length  $f = 150$  mm and placed at its  
180 focal distance from the fibre output. After the collimating lens, a linear polariser is positioned  
181 before the sample and a second linear polariser (analyser) after it, providing a control of the  
182 light intensity independent of the integration time of the detector. Finally, the light beam  
183 impinges onto a scientific-CMOS camera (Hamamatsu Digital Camera C13440, ORCA - Flash  
184 4.0) whose detector size is  $s = 1.33$  cm, placed in the near field, i.e. at a distance  $z =$   
185  $(200 \pm 5)$  mm from the sample midplane. The s-CMOS camera allows a ‘fast’ image  
186 acquisition frequency up to 100Hz at full frame ( $2048 \times 2048$  pixels), thus enabling a fruitful  
187 characterization of the temperature fluctuations in the observable wave number range. The  
188 shadowgraph signal is the result of the interference of the transmitted beam with the ones  
189 scattered by the sample refractive index fluctuations. In our experiment series of  $N = 2500$   
190 images of  $2048 \times 2048$  pixels, corresponding to  $q_{min} = 2\pi/s = 4.72/cm$ , are recorded for  
191 three different frequencies of  $f = 100, 10, 1$  Hz, corresponding to minimum correlation times  
192 of  $dt_{min} = 0.01, 0.1, 1$  s. The recorded images are eventually analysed by the Differential  
193 Dynamic Algorithm (DDA) briefly described in the following section [48].

194

### 195 *2.3 Dynamic shadowgraphy*

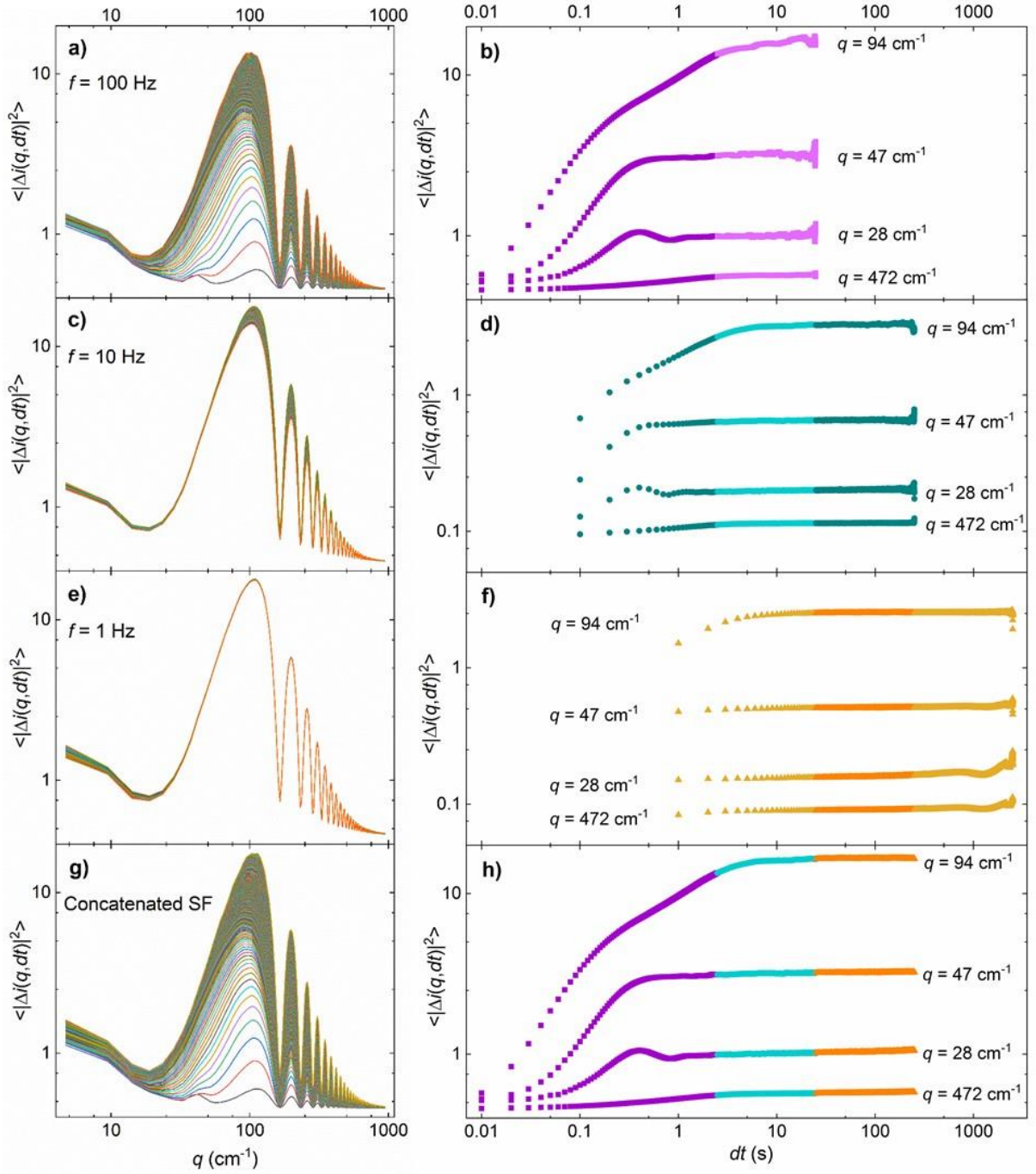
196 The DDA analysis consists of the following steps: images are recorded at different times as bi-  
197 dimensional intensity maps  $I(\vec{x}, t)$  and are 2D-Fourier transformed and normalized to get  
198  $i(\vec{q}, t) = I(\vec{q}, t)/I(0, t)$ . Then, differences between pairs of normalised Fast Fourier  
199 Transforms (FFTs) are calculated and their square moduli are determined  $|\Delta i(\vec{q}, t, dt)|^2 =$   
200  $|i(\vec{q}, t) - i(\vec{q}, t + dt)|^2$ . These quantities are computed for all possible delay times  $dt$ ,  
201 multiples of the  $dt_{min}$  set by the acquisition frequency of the detector. Finally, the results are  
202 averaged first over time  $\langle |\Delta i(\vec{q}, dt)|^2 \rangle = \langle |\Delta i(\vec{q}, t, dt)|^2 \rangle_t$  and second over the modulus of the  
203 wave vector  $\vec{q}$ ,  $\langle |\Delta i(q, dt)|^2 \rangle = \langle |\Delta i(\vec{q}, dt)|^2 \rangle_{|\vec{q}|}$ . The resultant function is the so-called  
204 Structure Function (SF)  $\langle |\Delta i(q, dt)|^2 \rangle$ . All these calculations are performed by a custom  
205 software running on a graphic card and taking advantage of the massive parallelization of the  
206 Graphic Processing Unit (GPU), thus requiring about one hour of computational time for each  
207 experiment, i.e. the three series of 2500 images of  $2048 \times 2048$  pixels [49].

208

### 209 *2.4 Concatenation of the experimental structure function*

210 As mentioned above, in the experiments reported in this study, sets of images of  $2048 \times 2048$   
211 pixels have been recorded at three different acquisition frequencies at the steady state of the  
212 thermodiffusion process. Then, the experimental SF is determined by analysing each stack of  
213 images acquired at a specific frequency. Examples of  $\langle |\Delta i(q, dt)|^2 \rangle$  are shown in Fig. 1, as a  
214 function of the wave number (Fig. 1a, 1c, 1e) and as a function of the correlation time  $dt$  for  
215 different wave numbers (Fig. 1b, 1d, 1f). The SFs obtained at three different frequencies are  
216 then merged in order to form a single concatenated SF, or c-SF (Fig. 1g), that covers a large  
217 range of correlation times of about four orders of magnitude, as shown in Fig. 1h.

218 As stated above, the c-SF is the result of merging the SFs determined at three different  
219 frequencies (from left to right in Fig. 1h): the first points correspond to the data acquired at 100  
220 Hz (from Fig. 1b, dark purple squares at short  $dt$ ), the second ones to 10 Hz (from Fig. 1d, light  
221 cyan circles at intermediate  $dt$ ) and the third ones to 1 Hz (from Fig. 1f, dark orange triangles  
222 at large  $dt$ ). The concatenation procedure is made by simply selecting the relevant part of the  
223 SFs as shown in Fig. 1. About the 10% of the delay times of each data set are used for the  
224 concatenation, disregarding those that are already included in the slower frequency slot. This  
225 means that from the fastest acquisition set only delay times in the range 0.01-2.5 s are taken,  
226 from the intermediate one the selected range is 2.5-25 s and from the slowest one 25-250 s. The  
227 concatenation procedure has been already applied in our precedent work [43], but here it is  
228 described in more detail. We point out that this scheme becomes useful whenever it is necessary  
229 to investigate NEFs with quite different decay times and that it is similar to the multi-tau  
230 approach utilised in dynamic light scattering [50].



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**Figure 1: Structure function of the thermodiffusion experiment carried out at temperature difference of 20 K for a series of images of  $2048 \times 2048$  pixels at 100, 10 and 1 Hz, as a function of the wave number (a, c, e, respectively) and as a function of correlation time (b, d, f, respectively). Concatenated structure function as a function of the wave number (g) and as a function of time (h). Purple squares, cyan circles and orange triangles correspond to the data acquired at 100, 10 and 1 Hz, respectively.**

238

## 239 2.5 Analysis of experimental signals

240 After the DDA and the concatenation process one gets the c-SF; it represents the raw  
241 experimental signals, obtained only from the acquired image series. For the analysis of these  
242 concatenated  $\langle |\Delta i(q, dt)|^2 \rangle$ , the physical optics theory of shadowgraph proposes the following  
243 expression [12, 48]:

$$244 \quad \langle |\Delta i(q, dt)|^2 \rangle = 2\{T(q)S(q)[1 - I_{SF}(q, dt)] + B(q)\}, \quad (3)$$

245 where  $T(q)$  is the shadowgraph optical transfer function [11],  $S(q)$  is the static power spectrum,  
246  $B(q)$  is the background and  $I_{SF}(q, dt)$  is the intermediate scattering function, that usually is  
247 described as a sum of exponential decays:  $I_{SF}(q, dt) = \sum_i a_i \exp(-dt/\tau_i(q))$ , where  $a_i$  are  
248 the amplitudes of the different modes (with  $\sum_i a_i = 1$ ) and  $\tau_i(q)$  the wave-number dependent  
249 relaxation times.

250 A simple observation of Fig. 1h, without any calculation, shows that, depending on the wave  
251 number range, up to three different decay times can be distinguished in the c-SF. In some cases,  
252 these decay times differ by more than one order of magnitude. In addition, and also depending  
253 on the wave number range, one can observe in Fig. 1h damped oscillations in  $\langle |\Delta i(q, dt)|^2 \rangle$ .  
254 This oscillating (propagating) phenomenon means that at least two of the relaxation times  $\tau_i(q)$   
255 present in the  $I_{SF}(q, dt)$  of Eq. 3 (and their associated amplitudes) form a pair of complex  
256 conjugate numbers. We conclude that a complex scenario of NEFs with different decay times  
257 is present in the case of a ternary mixture with large  $Le$  and  $Dr$  numbers, and a key question is  
258 the selection of the number of modes in the  $I_{SF}(q, dt)$  of Eq. 3 and whether they are purely  
259 diffusive (monotonically decaying) or propagating (oscillating). A rational choice needs to be  
260 guided by the available theoretical models for NEFs in ternary mixtures, which we review next.

261

## 262 3. Theoretical framework

263 *3.1 Thermodiffusion in ternary mixtures*

264 In a ternary mixture, the mass concentrations of the three components are related by:  $\omega_1 +$   
 265  $\omega_2 + \omega_3 = 1$ , which means that only two concentrations, e.g.  $\omega_1$  and  $\omega_2$ , are independent. The  
 266 corresponding diffusion fluxes  $J_1$  and  $J_2$  in the centre-of-mass frame of reference have  
 267 thermodiffusion and Fickian components, as expressed by [51]:

$$268 \quad \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = -\rho \left[ \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \begin{pmatrix} \nabla\omega_1 \\ \nabla\omega_2 \end{pmatrix} + \begin{pmatrix} \omega_1(1-\omega_1) & -\omega_1\omega_2 \\ -\omega_1\omega_2 & \omega_2(1-\omega_2) \end{pmatrix} \begin{pmatrix} D_{T1} \\ D_{T2} \end{pmatrix} \nabla T \right], \quad (4)$$

269 where  $\rho$  is the density of the mixture,  $D_{ij}$  are the components of the centre-of-mass diffusion  
 270 matrix,  $\nabla\omega_i$  are the concentration gradients,  $D_{T_i}$  are the invariant thermodiffusion coefficients  
 271 and  $\nabla T$  is the applied temperature gradient.

272 At the stationary state, the diffusion fluxes become zero and, following Ortiz de Zárate [51],  
 273 the Soret coefficients  $S_{T_i}$  can be expressed by:

$$274 \quad \begin{pmatrix} \omega_1(1-\omega_1) & -\omega_1\omega_2 \\ -\omega_1\omega_2 & \omega_2(1-\omega_2) \end{pmatrix} \begin{pmatrix} S_{T1} \\ S_{T2} \end{pmatrix} \nabla T = - \begin{pmatrix} \nabla\omega_1 \\ \nabla\omega_2 \end{pmatrix}, \quad (5)$$

275 The introduction of the matrix concentration pre-factors in Eqs. 4 and 5 forces the  
 276 thermodiffusion coefficients  $D_{T_i}$  and the Soret coefficients  $S_{T_i}$  to display the same frame-  
 277 invariance properties of the single  $D_T$  or  $S_T$  of a binary mixture, that is, they are numerically  
 278 the same irrespective of whether mass fractions or mole fractions are used to express the  
 279 composition [51]. Here, for simplicity, we display the equations only in the mass fraction  
 280 framework.

281 Fluctuating Hydrodynamics (FHD) has been recently extended to ternary mixtures first  
 282 considering equilibrium fluctuations [52] and then non-equilibrium fluctuations [39, 40]. The  
 283 first NE theory [39] neglected the effects of gravity and confinement. In that case, there is no  
 284 mixing between the decay rates of the four hydrodynamic modes (fluctuations of velocity,  
 285 temperature and two concentrations) which continue to decay with their well-known  
 286 equilibrium values given by kinematic viscosity, thermal diffusivity and the two eigenvalues

287  $\widehat{D}_i$  of the diffusion matrix  $\mathbf{D}$ . These  $\widehat{D}_i$ , are always real and positive, and can be related to the  
 288 four components  $D_{ij}$  of Eq. 4 by [39, 40]:

$$289 \quad \widehat{D}_{1,2} = \frac{1}{2} \left[ D_{11} + D_{22} \mp \sqrt{(D_{11} - D_{22})^2 - 4D_{12}D_{21}} \right]. \quad (6)$$

290 In accordance with the aforementioned common notation (i.e. 1 for PS, 2 for toluene and 3 for  
 291 n-hexane),  $\widehat{D}_1 < \widehat{D}_2$  since  $\widehat{D}_1$  represents the slowest diffusion mode essentially related to the  
 292 diffusion of the polystyrene in the binary solvent.

293 Since refractive index does not depend on fluid velocity, only three of the four hydrodynamic  
 294 modes are directly observable by optical techniques. Hence, within the approximations of Ref.  
 295 [39] (no gravity and no confinement) we conclude that for a thermodiffusion experiment in a  
 296 ternary mixture, a suitable expression for the  $I_{SF}(q, dt)$  can be provided by the sum of three  
 297 exponential decays given by two concentration modes, plus one mode for temperature  
 298 fluctuations:

$$299 \quad I_{SF}(q, dt) = a_1 \exp[-dt/\tau_1(q)] + a_2 \exp[-dt/\tau_2(q)] + (1 - a_1 - a_2) \exp[-dt/\tau_3(q)], \quad (7)$$

300  
 301 where  $a_i$  are the normalised amplitudes of the different modes and  $\tau_i(q)$  the corresponding  
 302 relaxation times.

303

### 304 *3.2 Concentration NEFs in ternary mixtures including gravity effects*

305 For NEFs, first the theory was developed in the absence of gravity force [39]; while gravity  
 306 effects were incorporated by Martínez Pancorbo et al. [40]. Both of these papers adopted the  
 307 so-called large Lewis number approximation that uncouples temperature fluctuations from  
 308 concentration fluctuations. Next, we briefly summarize the main results of Ref. [40] and recall  
 309 the expressions useful for the experimental data analysis.

310 The presence of gravity causes a mix between the two concentrations NEFs. The corresponding  
 311 decay times can be described as  $\tau_i(q) = 1/[\gamma_i(q)q^2]$ , where the diffusivities  $\gamma_i(q)$  in  
 312 dimensionless form, are given by the following equation [40]:

$$313 \quad \gamma_i(\tilde{q}) = \frac{1}{2} \left( \widehat{D}_1 + \widehat{D}_2 - \frac{Ra_i \widehat{D}_i}{\tilde{q}^4} \right) \times \left[ 1 \mp \sqrt{1 - \frac{\frac{4\widehat{D}_1\widehat{D}_2}{(\widehat{D}_1+\widehat{D}_2)^2} \left[ 1 - \frac{Ra_{S,ter}}{\tilde{q}^4} \right]}{\left[ 1 - \frac{Ra_i\widehat{D}_i}{\tilde{q}^4(\widehat{D}_1+\widehat{D}_2)} \right]^2}} \right], \quad (8)$$

314 where  $\tilde{q} = qL$  is the dimensionless wave number, and  $Ra_i$  are the two solutal Rayleigh numbers  
 315 defined for ternary mixtures by:

$$316 \quad Ra_i = \frac{gL^4}{\nu\widehat{D}_i} \beta'_i \nabla \omega'_i, \quad (9)$$

$$317 \quad Ra_i \widehat{D}_i = Ra_1 \widehat{D}_1 + Ra_2 \widehat{D}_2, \quad (10)$$

$$318 \quad Ra_{S,ter} = Ra_1 + Ra_2, \quad (11)$$

319 In Eq. 9, the primes indicate the concentrations (mass fractions) in which the diffusion matrix  
 320 is diagonal, for a generic diffusion matrix [53]:

$$321 \quad \begin{pmatrix} \omega'_1 \\ \omega'_2 \end{pmatrix} = \begin{pmatrix} 1 & \frac{D_{22}-\widehat{D}_2}{D_{21}} \\ \frac{D_{11}-\widehat{D}_1}{D_{12}} & 1 \end{pmatrix} \begin{pmatrix} \omega_1 \\ \omega_2 \end{pmatrix}. \quad (12)$$

322 The use of “diagonal” concentrations simplifies the theory but, as we shall see, somewhat  
 323 complicates the interpretation of experimental results. In general, they differ from the  
 324 measurable mass fractions.

325 In summary, in this model [40] the two concentration modes couple, while temperature  
 326 fluctuations remain uncoupled, keeping their equilibrium decay rate unaltered. Since for typical  
 327 values of  $Ra_i$  the two decay times of Eq. 8 are real numbers, this theory [40] suggests to still  
 328 use Eq. 7 for the  $I_{SF}(q, dt)$ . We note that the notation of Eqs. 9-11 implies that, for a ternary  
 329 mixture, two Lewis numbers ( $Le_1$  and  $Le_2$ ) can be defined as  $Le_i = a_T/\widehat{D}_i$ .

330

### 331 3.3 Coupling of concentration and temperature NEFs in binary mixtures



332 In the simplest case of binary mixtures, most of the available literature on concentration and  
 333 temperature NEFs makes use of the simplification that the two modes are always decoupled.  
 334 This is essentially true whenever the large Lewis number approximation is valid, that is the case  
 335 of ordinary liquid mixtures whose mass diffusion coefficient is much smaller than the thermal  
 336 diffusivity. However, the decoupling assumption fails to be valid for very large fluctuations,  
 337 i.e. for small wave numbers, as recently demonstrated both experimentally and theoretically  
 338 [43]. In particular, only the full coupling of velocity, temperature and concentration NEFs in  
 339 the bulk fluid can explain the appearance of propagating modes giving rise to a  $I_{SF}(q, dt)$  that  
 340 includes oscillations at very small wave numbers. This mechanism also induces a slowing-down  
 341 of the non-propagating concentration NEFs similar to that caused by the confinement effect  
 342 [41, 42].

343 This theory of full coupling between NE velocity, temperature and concentrations fluctuations  
 344 has been published only for binary mixtures. We briefly recall here the main steps of the  
 345 theoretical framework, while for details we address the reader to the literature [43].

346 In order to take into account a more complete description of the behaviour of NEFs within a  
 347 thermodiffusion experiment, one should write the evolution equations of the fluctuations of  
 348 velocity  $v_z$ , temperature and concentration of the single independent component:

$$349 \quad \frac{\partial}{\partial t} \begin{bmatrix} \delta v_z(q, t) \\ \delta T(q, t) \\ \delta \omega(q, t) \end{bmatrix} = -\mathbf{G}(q) \begin{bmatrix} \delta v_z(q, t) \\ \delta T(q, t) \\ \delta \omega(q, t) \end{bmatrix}, \quad (13)$$

350 where the inverse linear response matrix in its dimensionless form can be written as:

$$351 \quad \mathbf{G}(\tilde{q}) = \begin{bmatrix} PrLe\tilde{q}^2 & -1 & 1 \\ -Ra_sPrLe/\psi & Le\tilde{q}^2 & 0 \\ Ra_sPrLe & \psi\tilde{q}^2 & \tilde{q}^2 \end{bmatrix}, \quad (14)$$

352 In the previous equation the well-known dimensionless numbers appear, namely the Lewis  
 353 number  $Le = a_T/D$ , where  $a_T$  is the thermal diffusivity; the Prandtl number  $Pr = \nu/a_T$ ; the

354 separation ratio  $\psi = c_0(1 - c_0)S_T\beta/\alpha$ ; and the solutal Rayleigh number  $Ra_S =$   
 355  $[\beta g \nabla \omega / (\nu D)] L^4$ .

356 The solution of Eqs. 13 and 14 requires the computation of the eigenvalues and eigenvectors of  
 357 the matrix  $\mathbf{G}(\tilde{q})$ :

$$358 \quad \det[\mathbf{G}(\tilde{q}) - \lambda \mathbf{1}] = [\Gamma_{v_z}(\tilde{q}) - \lambda][\Gamma_T(\tilde{q}) - \lambda][\Gamma_\omega(\tilde{q}) - \lambda], \quad (15)$$

359 with NE fluctuations dimensionless decay times given by  $\tau_i(\tilde{q}) = 1/[\Gamma_i(\tilde{q})]$ . Although Eq. 15  
 360 can be solved analytically, the resulting expressions of the roots as a function of  $q$  are so  
 361 complicated that, in practice, it is more useful to have a numerical solution for fixed values of  
 362 the parameters  $Pr$ ,  $Le$ ,  $Ra_S$  and  $\psi$ , in the whole range of  $q$ .

363 Depending on the parameter values and on the wave number  $q$ , Eq. 15 may have a pair of  
 364 complex conjugate solutions, which typically happens at small  $q$  values. The resulting  
 365  $I_{SF}(q, dt)$  function in those cases shows a sinusoidal term:

$$366 \quad I_{SF}(q, dt) = a_1 \exp[-dt/\tau_1(q)] + \left\{ \frac{1 - a_1}{\cos[\phi(q)]} \right\} \cos[\Omega(q)dt + \phi(q)] \exp[-dt/\tau_2(q)]$$

367 , (16)

368 where  $\Omega(q)$  is the oscillation frequency and  $\phi(q)$  a phase term.

369

### 370 *3.4 Coupling of concentration and temperature NEFs in ternary mixtures*

371 The next step in the development of FHD is to include all the couplings among the fluctuating  
 372 modes for a ternary mixture. Of course, in that case one needs to consider the evolution of  
 373 fluctuations in velocity  $\delta v_z$ , temperature and concentration of the two independent components:

$$374 \quad \frac{\partial}{\partial t} \begin{bmatrix} \delta v_z(q, t) \\ \delta T(q, t) \\ \delta \omega_1(q, t) \\ \delta \omega_2(q, t) \end{bmatrix} = -\mathbf{G}_t(q) \begin{bmatrix} \delta v_z(q, t) \\ \delta T(q, t) \\ \delta \omega_1(q, t) \\ \delta \omega_2(q, t) \end{bmatrix}, \quad (17)$$

375 where the inverse linear response matrix for “diagonal” concentrations can be written in  
 376 dimensionless form as:

$$\mathbf{G}_t(\tilde{q}) = \begin{bmatrix} PrLe_t\tilde{q}^2 & -1 & 1 & 1 \\ -PrLe_t^2Ra & Le_t\tilde{q}^2 & 0 & 0 \\ PrLe_t^2Ra\psi'_1 & \psi'_1\tilde{q}^2 & \tilde{q}^2 & 0 \\ PrLe_t^2Ra\psi'_2 & Dr\psi'_2\tilde{q}^2 & 0 & Dr\tilde{q}^2 \end{bmatrix}. \quad (18)$$

378 To make dimensionless Eqs. 17 and 18,  $L$  is used as unit of length and  $L^2/\widehat{D}_1$  as unit of time;  
379 consequently,  $\tilde{q} = qL$  for wave numbers, and  $L/\widehat{D}_1$  is the unit of velocity. Hence, everything is  
380 made dimensionless with respect to the slower diffusive mode. Other dimensionless parameters  
381 in Eq. 18 are: one (unique) ternary Lewis number  $Le_t = a_T/\widehat{D}_1$ , the Diffusion eigenvalue Ratio  
382  $Dr = \widehat{D}_2/\widehat{D}_1$ , the thermal Rayleigh number  $Ra = -\alpha gL^4 \nabla T/(va_T)$  and the ‘‘diagonal’’  
383 separation ratios  $\psi'_i = D_{T,i}^{\omega'}\beta'_i/(\widehat{D}_i\alpha)$ , with  $D_{T,i}^{\omega'}$  being the (diagonal) thermodiffusion  
384 coefficients as defined in Ref. [18]. We point out that this approach is different from the one  
385 used in our previous publication [40] and reported in section 3.2, where two Lewis numbers  
386 were introduced.

387 As in the case of binary mixtures, the solution of Eq. 17 requires to numerically evaluate the  
388 dimensionless decay rates  $\Gamma_i(\tilde{q})$  as the four eigenvalues of the matrix  $\mathbf{G}_t(\tilde{q})$ , namely:

$$\det[\mathbf{G}_t(\tilde{q}) - \lambda\mathbf{1}] = [\Gamma_{v_z}(\tilde{q}) - \lambda][\Gamma_T(\tilde{q}) - \lambda][\Gamma_{\omega_1}(\tilde{q}) - \lambda][\Gamma_{\omega_2}(\tilde{q}) - \lambda]. \quad (19)$$

390 A more detailed explanation of the full-coupling theory for ternary mixtures is outside the scope  
391 of the present publication and will be the subject of a future paper. We simply mention that,  
392 depending on  $q$ , complex solutions of Eq. 19 may exist. As was the case with binaries, for  
393 parameter values typical of ternary liquid mixtures, these propagating modes do appear as a  
394 mixing between the temperature and the viscous (velocity) modes. The consequence is an  
395 oscillatory  $I_{SF}(q, dt)$  such as the one expressed in Eq. 16, but with an additional exponential  
396 term to represent the extra concentration mode.

397

#### 398 4. Results

399

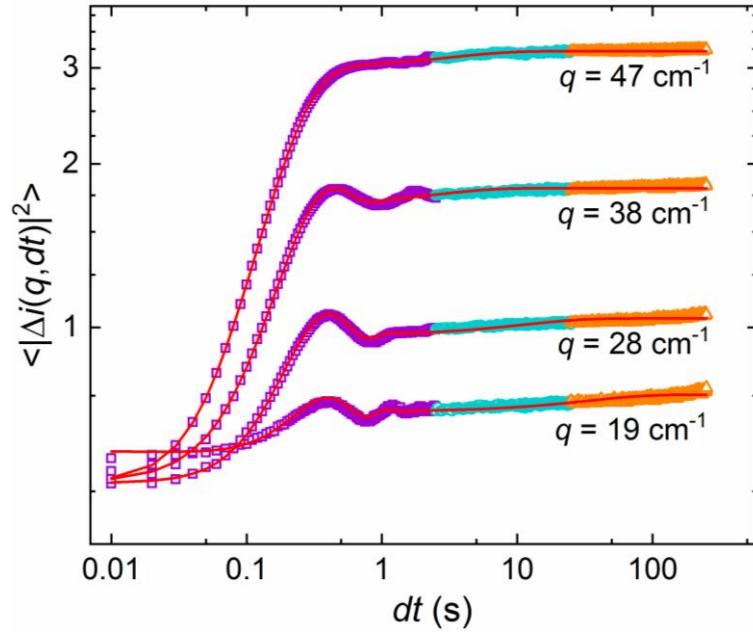
#### 400 4.1 Intermediate scattering function analysis

401 As mentioned in section 2.5, for most wave numbers the  $I_{SF}(q, dt)$  of Eq. 3 is usually defined  
402 as a sum of exponential decays. However, a preliminary analysis of the experimental SF is  
403 required to check the suitability of this model. As it can be seen in the c-SF shown in Fig. 1h  
404 for  $q = 94/cm$ , three exponential decays can be detected, corresponding (from left to right) to  
405 the relaxation of the temperature and concentration (faster and slower mass modes) NEFs.  
406 Then, the  $I_{SF}(q, dt)$  can be modelled for most wave numbers by a sum of three exponential  
407 decays, as defined in section 3.1 by Eq. 7 for a system including one thermal mode plus two  
408 solutal, well separated, modes. In the studied system, the corresponding three exponential  
409 decays represent the following three modes: long decay times for the two concentration modes,  
410 slower for mass diffusion of the denser component (PS in the binary solvent), and faster for  
411 mass diffusion of the two components of the solvent mixture (toluene and n-hexane); and the  
412 shortest decay time corresponds to the thermal diffusivity of the overall mixture.

413 Nevertheless, for small wave numbers such as  $q = 28/cm$ , oscillations are detected in the c-  
414 SF (see Fig. 1h), indicating the presence of propagating modes [43]. Fig. 2 shows the  
415 oscillations in the experimental c-SF for several wave numbers in the range  $19/cm < q <$   
416  $47/cm$ . These need to be taken into account by using a proper  $I_{SF}(q, dt)$  function, such as the  
417 one described in section 3.3 by Eq. 16. The latter equation is defined for a binary mixture, and  
418 includes one solutal mode, i.e. the exponential decay, and a coupled thermo-viscous mode, i.e.  
419 the damped oscillation. For analysing ternary mixtures, one should supplement Eq. 16 with an  
420 additional exponential term, representing the second solutal mode. However, after carrying out  
421 a careful comparison of the corresponding fitting output, we have found that the addition of this  
422 term gives more scattered results due to the increase in the number of fitting parameters. For  
423 that reason, Eq. 16 has been used to fit the raw data in the wave number range where oscillations

424 are detected in the c-SF. The slower concentration mode is, thus, unobservable in this wave  
 425 number range.

426



427

428 **Figure 2: Concatenated structure function of the thermodiffusion experiment carried out at**  
 429 **temperature difference of 20 K for a series of images of  $2048 \times 2048$  as a function of time**  
 430 **for different small wave numbers. Purple squares, cyan circles and orange triangles**  
 431 **correspond to the data acquired at 100, 10 and 1 Hz, respectively, and the red curves to the**  
 432 **fitting functions through Eqs. 3 and 16.**

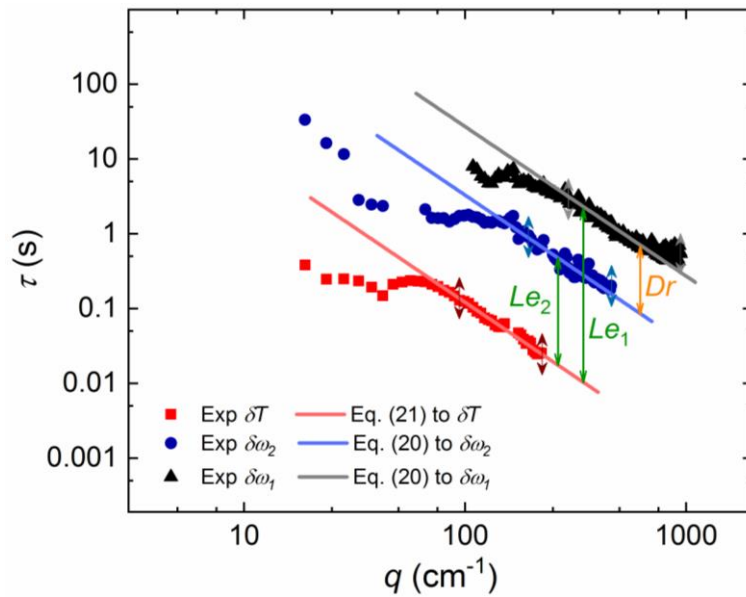
433

434 Generally, the quality of these fittings is good, as demonstrated in Fig. 2, with an average  $R^2$  of  
 435 about 0.99, which translates into a 3% mean relative uncertainty for the decay times determined  
 436 by these fittings. However, both  $R^2$  and the relative uncertainty of the decay times depend on  
 437 the wave number. The best accuracy is obtained for intermediate wave numbers where the  
 438 signal-to-noise ratio of the c-SF is the largest (see Fig. 1g). Decay times with a relative  
 439 uncertainty larger than 10% have been disregarded for the further analysis.

440

441 *4.2 Decay times of the NEFs*

442 Figure 3 shows the decay times of the different fluctuating modes as resulting from the  
 443 modelling of the experimental c-SF by using Eqs. 3 and Eq. 7 or Eq. 16 depending on the  
 444 analysed  $q$ . Three decay times are easily distinguished (from top to bottom): the slowest mode  
 445 (black symbols) describes the concentration mode of the polymer into the binary solvent; the  
 446 intermediate one (blue symbols) the concentration mode of the binary solvent mixture; and the  
 447 fastest one (red symbols) the temperature mode. These decay times cover a span of about three  
 448 orders of magnitude, which is quite impressive for an imaging technique. This justifies the  
 449 necessity of performing measurements at different acquisition frequencies and of carrying out  
 450 the concatenation procedure adopted here. Besides decay times, when the Eq. 16 is used, the  
 451 fitting procedure also gives the oscillation frequency  $\Omega(q)$  of the propagating modes appearing  
 452 in Fig. 2 for wave numbers  $q < 47/cm$ .



453

454 ***Figure 3: Decay times of NEFs on the ternary mixture of PS-toluene-n-hexane in a***  
 455 ***thermodiffusion experiment performed at temperature difference of 20 K, as a function of***  
 456 ***the wave number  $q$ . Lines represent fitting functions through Eqs. 20-21 over the diffusive***  
 457 ***wave number range, as indicated in the text.***

458

459 The experimental decay times shown in Fig. 3 are to be discussed first in the diffusive regime  
460 only (for large enough wave numbers), where the three decay times are well-separated. As  
461 elucidated at the end of section 3.1, in this region of large wave numbers the effect of gravity  
462 is negligible for both concentration modes, and the decay times of the two concentration modes  
463 are given by the eigenvalues of the diffusion matrix:

$$464 \quad \tau_i(q) = 1/(\widehat{D}_i q^2). \quad (20)$$

465 By fitting the experimental decay times in the diffusive regime ( $q > 290/cm$  for the  
466 concentration NEFs, c-NEFs, of component 1 and  $q > 190/cm$  for the c-NEFs of component  
467 2) to Eq. 20, the eigenvalues of the diffusion matrix can be determined. The diffusion coefficient  
468  $\widehat{D}_1$  obtained from the slowest concentration mode represents the mass diffusion eigenvalue of  
469 the polymer in the binary solvent mixture.  $\widehat{D}_2$  calculated from the intermediate decay times  
470 (i.e. faster concentration mode) represents the mass diffusion eigenvalue of toluene in n-hexane  
471 (i.e. interdiffusion of the solvents in the solvent mixture). The resulting two eigenvalues  $\widehat{D}_1$  and  
472  $\widehat{D}_2$  are reported in Table 2. These values in Table 2 are calculated by averaging the fitting results  
473 of the experiments performed at three temperature differences, 20, 15 and 10 K, and the  
474 uncertainties are the corresponding standard deviations. These values are comparable with those  
475 obtained in our previous study [14] for a similar polymeric mixture prepared with the same  
476 components of this study but a slightly different polymer molecular weight, and with those  
477 reported in [43, 45] for the diluted binary mixture of PS-toluene and in [44, 46] for the binary  
478 solvent mixture of toluene-n-hexane. Furthermore, the value of the  $Dr$  number can be  
479 determined as the ratio between the two eigenvalues, resulting in  $Dr = 8.4$  (see Table 2). This  
480 value totally justifies the selection of the polymeric mixture as a suitable sample for  
481 experimentally studying well-separated concentration modes.

482 In a similar way, in order to get information about the thermal diffusivity  $a_T$  of the ternary  
483 mixture, one can try to fit the data points of the thermal mode with the theoretical predictions

484 for thermal NEFs only. In the diffusive regime, the decay time of the thermal mode can be  
 485 expressed as [54]:

$$486 \quad \tau_{th}(q) = 1/(a_T q^2), \quad (21)$$

487 and the fitting of temperature NEFs for  $q > 90/cm$  in Fig. 3 provides the thermal diffusivity  
 488 value reported in Table 2. This result is again comparable with the one obtained in previous  
 489 studies for a similar polymeric mixture [14] as well as with that reported in [46] for the equi-  
 490 molar toluene-n-hexane binary solvent mixture.

491 From the two diffusion eigenvalues and the thermal diffusivity, the  $Le_i$  numbers can be  
 492 determined, which are also listed in Table 2.

493

494 ***Table 2: Diffusion coefficient eigenvalues,  $Le_i$  and  $Dr$  numbers of the polymeric ternary***  
 495 ***mixture***

Parameter	Value
$\hat{D}_1$	$(3.8 \pm 0.1) \times 10^{-6} \text{ cm}^2/\text{s}$
$\hat{D}_2$	$(3.1 \pm 0.1) \times 10^{-5} \text{ cm}^2/\text{s}$
$a_T$	$(8.5 \pm 0.2) \times 10^{-4} \text{ cm}^2/\text{s}$
$Le_1$	$227 \pm 12$
$Le_2$	$27 \pm 2$
$Dr$	$8.4 \pm 0.6$

496

## 497 **5. Discussion**

### 498 *Comparison between experimental and theoretical decay times*

499 As described in section 3.2, Martínez-Pancorbo et al. [40] presents the analysis of the  
 500 fluctuations of two independent concentrations together with the effect of buoyancy, but  
 501 considering neither the effect of confinement nor the presence of temperature and velocity

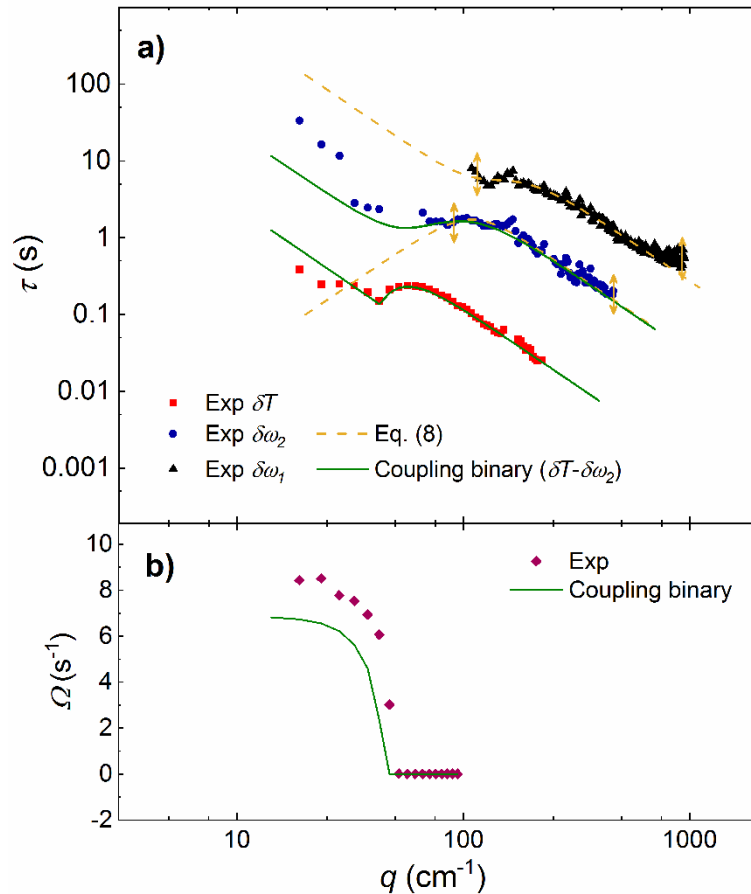


502 fluctuations. Consequently, the coupling between modes which is known to be important at  
503 small wave numbers, as demonstrated for binary mixtures [43], is not taken into account. In  
504 order to be insensitive to confinement effects the experiments reported here have been  
505 performed in a thick cell with vertical dimension of  $L = 5 \text{ mm}$ . In these conditions, the effect  
506 of confinement should not be visible in the investigated wave number range. In fact,  
507 confinement effects appear only at dimensionless wave numbers  $\tilde{q} = qL < 5$ , corresponding  
508 here to dimensional wave numbers  $q < 10/\text{cm}$ , at the very bottom of the investigated range of  
509  $q$  [41, 42].

510 Regarding coupling effects, it is mandatory to consider them whenever oscillations are visible  
511 in the experimental c-SF at small  $q$  (see Fig. 2). The complete FHD theory, including the  
512 presence of velocity and temperature fluctuations and the various couplings among all modes,  
513 has been previously published by us [43] for the case of binary mixtures, as summarised in  
514 section 3.3. The results of [43] can be very useful for discussing the impact of the velocity-  
515 temperature coupling on the measured decay times.

516 In the following, we compare the experimental values of decay times at different wave numbers  
517 (obtained by fitting the c-SF through Eqs. 3 and 7 or 16), with the two published models [40,  
518 43]. This allows to understand the impact of the different effects on the measured c-SF, and to  
519 evaluate if a more complete theoretical framework is needed or if on the contrary, the available  
520 theories can be simply applied in different wave number ranges in order to extract the transport  
521 properties of the investigated ternary mixture. As described in the previous section, at least the  
522 diffusion coefficients can be safely determined by fitting decay times at large wave numbers,  
523 where NEFs are dominated only by the diffusion phenomenon. The measurement of the Soret  
524 coefficient is more complicated as it requires the analysis of the effect of gravity [6], or other  
525 suitable analysis [55]. The simultaneous and independent characterization of the two Soret  
526 coefficients of a ternary mixture requires a complete knowledge of the diffusion matrix

527 including the cross-diffusivities. This has not been achieved yet by Shadowgraphy and is the  
 528 ultimate goal of our current research. Although we estimate that this can be done with one-  
 529 wavelength Shadowgraphy, a more precise information can be obtained with a two-wavelength  
 530 version of the technique. The two-wavelength Shadowgraphy is currently being developed in  
 531 our lab, also in relation to the future space experiments of the NEUF-DIX project [28].  
 532 Figure 4 shows the experimental decay times and the oscillation frequency obtained from the  
 533 c-SF (data points are the same as in Fig. 3), together with theoretical predictions provided either  
 534 by Eq. 8 (dashed yellow curves) or by numerically solving Eqs.14-15 (solid green curves).  
 535



536  
 537 **Figure 4:** a) Decay times and b) oscillation frequency of NEFs on the ternary mixture of PS-  
 538 toluene-n-hexane in a thermodiffusion experiment performed at temperature difference of  
 539 20 K, as a function of the wave number  $q$ . Experimental data are shown by points, while lines

540 *represent the numerical calculations of Eqs. 8 (dashed lines) and the theory developed for*  
541 *binary mixtures including the effect of propagating modes (solid lines).*

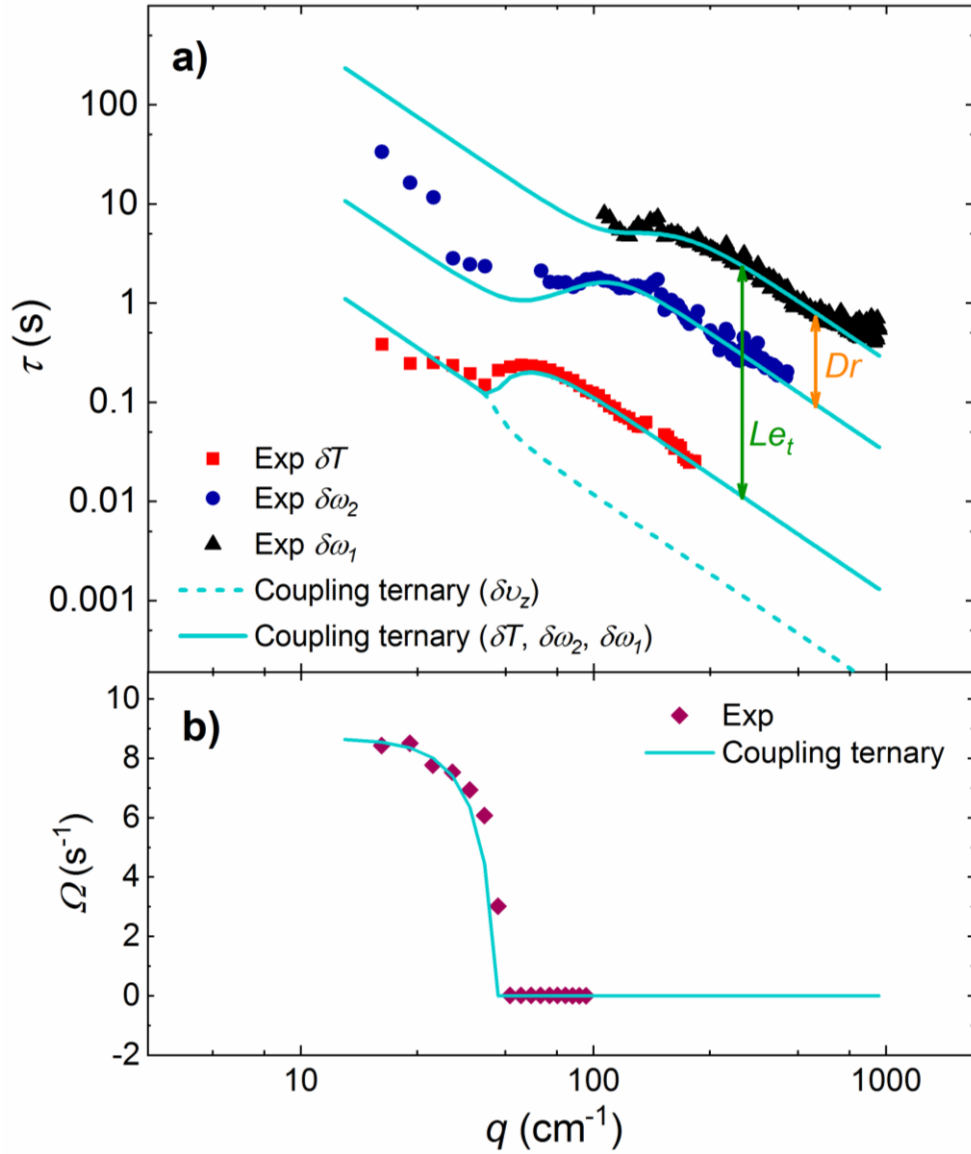
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543 The experimental data are fitted to Eq. 8 by fixing the diffusion matrix eigenvalues ( $\widehat{D}_1$  and  $\widehat{D}_2$ )  
544 to the corresponding values presented in Table 2. The parameters obtained from this fitting to  
545 Eq. 8 are:  $Ra_i \widehat{D}_i = (260 \pm 40) \text{ cm}^2/\text{s}$ , and  $Ra_{S,ter} = (4.6 \pm 1.0) \times 10^7$ . As visible in Fig. 4a,  
546 the experimental results suggest that the available theory for the ternary mixture reported by  
547 Martínez Pancorbo et al. [40] cannot describe the behaviour of c-NEFs in the present  
548 experiment for the whole range of wave numbers. The theory provides suitable predictions for  
549 intermediate and especially for large wave numbers, but fails in the limit of small  $q$  (in  
550 particular for the fastest concentration mode) where the effect of the coupling with temperature  
551 fluctuations, and the consequent appearance of propagating modes in the experimental structure  
552 function become significant (see section 3.3) [43]. Hence, investigation of the coupling with  
553 temperature fluctuations is required for a full understanding of the present experimental results.  
554 We proceed into two steps: first we compare with the published theory [43] for the binary  
555 mixture case (one concentration mode) as reviewed in section 3.3; second we compare with the  
556 theory for ternary mixtures (two concentration modes) as briefly presented here in section 3.4.  
557 This allows appreciating the features that are genuinely related to the ternary mixture case.

558 As already mentioned, Fig. 4 shows, superposed on the experimental data, the theoretical  
559 predictions (green solid lines) of the theory [43] with one concentration mode. The theoretical  
560 curves have been obtained numerically (solving Eqs. 14 and 15) by keeping constant the Lewis  
561 number  $Le = 27$  to the same value of  $Le_2$  shown in Table 2, and varying the values of  $Pr$  and  
562  $\psi$  to best fit the data. The solutal Rayleigh number  $Ra_{S,2} = -(q_{S,2}^* L)^4$  is also kept constant at  
563  $-5.8 \times 10^6$ , after evaluating the value of the solutal rolloff wave number  $q_{S,2}^*$ . This value  
564 represents the wave number where the fluctuation  $\delta\omega_2$  behaviour changes from diffusive to

565 gravitational [6]. The resulting values for the free fitting parameters are the following:  $Pr =$   
566  $9.0$  and  $\psi = 0.9$ . As it can be observed in Fig. 4a, the decay times provided by the numerical  
567 solution agree very well with the experimental decay times of the temperature NEFs in the  
568 whole range of wave numbers. However, for the diffusion mass mode, at the smallest wave  
569 number range, the agreement is not as good as for the temperature, and a slowing-down of the  
570 experimental decay times is visible in comparison to the corresponding numerical solution  
571 (green solid line). The theoretical results of the oscillation frequency are likewise similar to the  
572 experimental data (see Fig. 4b). This last comparison between the experimental and theoretical  
573 decay times shows the importance of including temperature fluctuations in the theoretical  
574 analysis.

575 Next, we finally take into account the more complete theory of NEFs, which includes the  
576 coupling of thermal and viscous fluctuations to the two independent concentration modes  
577 present in a ternary mixture, as briefly described in section 3.4. The comparison between  
578 experimental and theoretical decay times is shown in Fig. 5. The effect of considering the two  
579 concentration modes and the associated couplings is evident by comparing Fig. 4 and 5.



580

581

582 *Figure 5: a) Decay times and b) oscillation frequency of NEFs on the ternary mixture of PS-*  
 583 *toluene-n-hexane in a thermodiffusion experiment performed at temperature difference of*  
 584 *20 K, as a function of the wave number  $q$ . Experimental data are shown by points, while lines*  
 585 *represent the theory developed for ternary mixtures including the effect of propagating*  
 586 *modes.*

587 The theoretical curves shown in Fig. 5 have been obtained numerically (solving Eqs. 18 and  
 588 19) by keeping constant  $Le_t = 227$  and  $Dr = 8.4$  (the  $Le_1$  and  $Dr$  values shown in Table 2),  
 589 and varying the values of  $Pr$ ,  $\psi'_1$  and  $\psi'_2$  to best fit the data. Additionally, the term  $PrLe_t^2Ra =$

590  $\alpha g L^4 \nabla T / \widehat{D}_1^2$  appearing in the matrix  $G_t(\tilde{q})$  of Eq. 18 is also kept fix at  $1.6 \times 10^{11}$ , considering  
591 for this number the  $\alpha$  value of Table 1, the  $\widehat{D}_1$  value of Table 2, and the applied temperature  
592 gradient. The resulting values for the free fitting parameters are the following:  $Pr = 10$ ,  $\psi'_1 =$   
593  $0.7$  and  $\psi'_2 = 0.4$ . The theoretical results show that for large wave numbers ( $q \geq 47 \text{ cm}^{-1}$ ), four  
594 real solutions are obtained, demonstrating that all the modes are decoupled in this wave number  
595 range. The velocity mode cannot be observed experimentally, as it does not give rise to  
596 refractive index fluctuations. For small wave numbers ( $q < 47 \text{ cm}^{-1}$ ), two real solutions and a  
597 pair of complex conjugate ones are obtained numerically, indicating that velocity and  
598 temperature fluctuations are mixed at small  $q$ . This mixing induces the appearance of  
599 propagating modes, observed in the experimental c-SF of Fig. 2 as oscillations at small  $q$ .

600 Applying the full theory of section 3.4, we found a reasonable agreement between the  
601 experimental and the theoretical data for the three modes, especially for large and intermediate  
602 wave numbers. However, we would like to point out that the numerical values of  $Pr$ ,  $\psi'_1$  and  
603  $\psi'_2$  must be taken into account with caution as the fitting procedure is not robust. The focus here  
604 is mainly on the qualitative understanding of the behaviour of the different modes in a ternary  
605 mixture when the coupling among them is included.

606 One relevant point is the slowing-down of the two concentration modes and their consequent  
607 diffusive-like behaviours at very small wave numbers (see Fig. 5a). In addition, it is worth  
608 noting the good agreement obtained for the frequency of the propagating mode, as can be seen  
609 in Fig. 5b. It clearly improves the results of the binary model shown in Fig. 4b.

610 Of course, the effect of confinement should be also included in the theory if one wants to  
611 describe layers of ternary mixtures of any vertical thickness. Unfortunately, this additional  
612 development requires more effort and no analytical solution can be obtained.

613

## 614 **6. Conclusions**

615 The concentration and temperature NEFs in a thermodiffusion experiment of a ternary mixture  
616 composed of polystyrene, toluene and n-hexane are characterized by dynamic shadowgraphy.  
617 The decay times of the NEFs are determined and three modes are clearly distinguished. The  
618 fastest decay times are associated to the temperature NEFs, the intermediate ones to the  
619 concentration NEFs of the molecular solvent and the slowest ones to the concentration NEFs  
620 of the polymer. To encompass the very different decay times (i.e. large range of correlation  
621 times), images are acquired at various frequencies, and the corresponding SFs are merged into  
622 the so-called c-SF by following the described concatenation procedure.

623 In order to exploit the obtained decay times, first, they are fitted with a simple diffusive model  
624 at large wave numbers to obtain the diffusion eigenvalues  $\hat{D}_1$  and  $\hat{D}_2$  and the thermal diffusivity  
625  $a_T$ . Secondly, the theory developed for the two concentration modes of a ternary mixture in the  
626 presence of gravity is compared with the experimental results for the first time. The  
627 experimental decay times of the concentration modes at intermediate and large wave numbers  
628 appear to be in good agreement with this theoretical model. However, for smaller wave  
629 numbers, a slowing-down of the experimental decay times of NEFs is detected with respect to  
630 the predictions of that theory. Due to the large thickness of the thermodiffusion cell,  
631 confinement effects cannot be considered as the origin of such discrepancy. In addition,  
632 evidence of propagating modes on the structure function suggests that the aforementioned  
633 slowing-down could be originated by the coupling of the temperature and viscous modes to the  
634 concentration ones. Comparison with the decay times from the theory developed to describe  
635 such coupling in a binary mixture shows a better agreement for the thermal and the faster  
636 concentration modes at intermediate wave numbers. This positive outcome lead us to further  
637 develop the theory of NEFs in the case of ternary mixtures, by including the coupling of  
638 velocity, temperature and the two concentration modes under strong gravitational stabilization

639 and for large size fluctuations (small wave numbers). A better qualitative agreement is found  
640 between the new theoretical development and the experimental data points.

641

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648

## 649 **Authors contribution statement**

650

651 The experimental measurements and data analysis were performed by L. García-Fernández, H.  
652 Bataller and F. Croccolo. P. Fruton contributed to the concatenation procedure of the Structure  
653 Function. J.M. Ortiz de Zárate and L. García-Fernández focused on the new theoretical  
654 development presented in section 3.4. All the authors contributed to the discussion of the results  
655 and in writing the manuscript.

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