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Modeling the interplay between Solvent Evaporation and Phase Separation Dynamics during Membrane Preparation

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Abstract

Keywords: Phase-field simulation, Cahn-Hilliard model, mobility, membranes, evaporation process

1. Introduction

Phase separation processes are widely used in industry for manufacturing various types of products, from usual metals to polymer solutions. Preparation of polymeric membrane is one of these applications of great interest [1, 2]. In the last four decades, research has been dedicated to the polymeric membrane formation mechanisms in order to better control the final membrane morphology [3, 4]. Starting from a homogeneous polymeric solution composed of a polymer dissolved in a good solvent, a thermodynamic demixing process is induced by a temperature change (Temperature Induced Phase Separation or TIPS process) [5–8] or by the intrusion of a non-solvent of the polymer (Non-solvent Phase Separation or NIPS process) [9, 10]. Starting

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12 from a ternary system composed of a polymer, a good solvent and a small
13 amount of a non-solvent of the polymer, a faster evaporation rate of the sol-
14 vent comparing to that of non-solvent can also induce the phase inversion
15 (Dry-casting process)[11]. During the demixing process, two phases will be
16 created: a polymer-rich phase mainly composed of polymer and a polymer-
17 lean phase mainly composed of solvent (and/or non-solvent depending on the
18 process). The polymer-rich phase form the membrane matrix after extraction
19 of the polymer-lean phase which will form membrane pores.

20 One of most important challenges in membrane manufacturing concerns
21 the control of the final morphology that will strongly affect the membrane
22 performances towards the targeted applications. For instance, asymmetric
23 structures characterized by a pore structure that gradually changes from very
24 large pores to very fine pores at the membrane surface [2], will be targeted
25 for pressure driven membrane processes (filtration in water treatment appli-
26 cations for example). The upper selective layer, responsible for membrane
27 selectivity, should be as thin as possible, while the pore size strongly in-
28 creases beneath this selective layer to maximize the filtration flux through the
29 membrane. On the contrary, symmetric membranes with uniform structures
30 through the entire membrane thickness could be interesting for applications
31 such as dialysis and electrodialysis, but also microfiltration [12].

32 Controlling the whole membrane structure is therefore the key point in
33 membrane preparation, but it still remains a goal hard to achieve since the
34 membrane formation mechanisms are quite complex and particularly difficult
35 to simulate, and hence to predict. Phase separation can be described using
36 the equations of Cahn and Hilliard [13] for polymeric systems, where the free

37 energy of mixing of the polymeric system is derived from Flory Huggins the-
38 ory [14] and the mobility term has to be described using a specific equation.
39 In a recent paper, Manzanarez et al. (2017) [15] investigated the influence
40 of this mobility term on the phase separation dynamics for a closed binary
41 polymeric system [16, 17].

42 However, additional features have to be described to simulate the mem-
43 brane formation since the phase separation is coupled with transfer phenom-
44 ena occurring at membrane interfaces. Indeed, mass exchanges often occurs
45 between the membrane and the external environment simultaneously with
46 phase separation. For instance, solvent extraction and non-solvent intake
47 occur during NIPS process [18, 19], while solvent and non-solvent evapora-
48 tion will be involved during dry-casting process. Recently, we also exhibited
49 how the phase inversion performed by LCST-TIPS process for water solu-
50 ble polymer systems was coupled with solvent evaporation [20]. Focusing on
51 the modeling of TIPS process, a wide literature exists and various types of
52 models have been developed during the last 30 years (phase field methods,
53 dissipative particle dynamics methods, Coarse grain simulation, Monte-Carlo
54 simulation...). Caneba and Song [5] were one of the first to develop a 1D
55 phase field model to simulate the TIPS process. They used Cahn-Hilliard
56 equations for spinodal decomposition, Flory-Huggins for thermodynamics
57 and Vrentas models for the description of the mobility terms. Later, Barton
58 and Mc Hugh [16, 21] added a temperature gradient due to heat transport to
59 simulate the droplets growth during demixing process, in 1D geometry yet.
60 Using phase field methods, the impact of a temperature gradient was also
61 investigated by Lee and coworkers [22] in 2D geometry and by Chan [23] in

62 1D geometry to better understand the formation of anisotropic morphologies
63 by TIPS process. Later the Cahn-Hilliard equations were solved in 3D geom-
64 etry for modeling TIPS process [17]. Using different modeling method, He
65 et al. [24], Tang and coworkers simulated the TIPS process by Dissipative
66 Particle Dynamics simulation (DPD) (2013, 2015, 2016) [25–27]. Even more
67 recently, Tang and coworkers [28] used DPD and Coarse Grain methods to
68 simulate the coupling between phase separation and mass transfer when the
69 UCST-TIPS process is conducted by immersing a hot polymer solution into
70 a cold water bath. In the latter case, mass exchanges are expected to be very
71 rapid since they occur in liquid phase. However, the coupling between mass
72 exchanges by solvent evaporation and phase separation was less investigated.
73 Mino et al. [17] only considered in their simulations an initial concentra-
74 tion gradient that could be due to an initial solvent evaporation but their
75 simulations did not involve the direct coupling between both phenomena.
76 However, for LCST-TIPS process the coupling between solvent evaporation
77 and phase separation dynamics is crucial since both dynamics are slowed and
78 concomitant [20, 29]. Whatever the process aforementioned, it is of prime
79 importance to elucidate how the mass exchanges affect the phase separation
80 dynamics, and hence the final membrane morphology. Surprisingly, to the
81 best of our knowledge, few theoretical studies have considered this coupling
82 [30].

83 This paper focuses on the coupling between the phase separation induced
84 by TIPS process and mass transfer phenomena for a simplified binary poly-
85 mer/solvent system. More specifically, the solvent evaporation occurring at
86 the upper membrane interface will be simulated and its interplay with the

87 phase separation dynamics will be investigated.

88 In the first part of the paper, the coupling between phase separation
89 and solvent evaporation will be simulated and discussed in a horizontal 2D
90 plan, and then in the second part, the simulations will be performed in a 2D
91 vertical cross-section of the membrane in order to investigate the possible
92 formation of concentration gradients.

93 *Theory*

94 The diffusion equation that describes the phase separation is a modified
95 time-dependent Ginzburg-Landau theory for a conserved order parameter.

$$\frac{\partial\phi(\mathbf{r},t)}{\partial t} = \nabla \cdot \left[\Lambda(\phi, \mathbf{r}) \nabla \frac{\delta F}{\delta\phi(\mathbf{r})} \right] + \sigma(\phi, \mathbf{r}) \quad (1)$$

96 where $\phi(\mathbf{r}, t)$ is the volume fraction of the polymer, $\Lambda(\phi, \mathbf{r})$ the mobility term
97 and F is the free energy functional of the system can thus be expressed as
98 [13] :

$$F[\phi(\mathbf{r}, t)] = \int dr \left[f(\phi) + \frac{C}{2} |\nabla\phi|^2 \right] \quad (2)$$

99 where $f(\phi)$ is the free energy of mixing per lattice site for polymer solutions
100 described by the Flory-Huggins theory [14]:

$$f(\phi) = \frac{k_B T}{v_0} \left[\frac{\phi}{N} \ln\phi + (1 - \phi) \ln(1 - \phi) + \chi\phi(1 - \phi) \right] \quad (3)$$

101 were the degree of polymerization $N = 150$, v_0 is the volume of the monomer
102 and χ is the interaction parameter. This parameter is supposed to be here
103 an inverse function of temperature. All quenches studied here are made at a
104 constant χ and are consequently isothermal. $C|\nabla\phi|^2/2$ is the gradient energy
105 contribution which describes the cost of an interface between the two phases

106 resulting from the phase separation. The gradient parameter C follow here
 107 the Debye approximation [31]:

$$C(\phi) \approx \frac{k_B T}{v_0} \frac{\chi}{3} R_g^2 \quad (4)$$

108 R_g is the radius of gyration of the polymer ($R_g^2 \approx a^2 N/6$ where a is the Kuhn
 109 length and N the degree of polymerization). The term C can be related to the
 110 polymer chain length and the surface tension. Thus, from a purely numerical
 111 point of view, this parameter imposes a space discretization (typically a mesh
 112 must be lower than C) which makes it possible to determine the final size of
 113 the simulated field ($L = 250 C$). Finally, the source term $\sigma(\phi, \mathbf{r})$ is added to
 114 the continuity equation in order to add evaporative transfers at the interface
 115 between the system and the outside.

116 In a recent paper, we investigated the influence of the mobility term on the
 117 phase separation dynamics [15] using Fourier transforms and Minkowski de-
 118 scriptors. Fast, Slow and Vrentas model were compared for various conditions
 119 of initial quenching with a polymeric system described by the Flory-Huggins
 120 theory. For binary systems, those models were shown to give somewhat dif-
 121 ferent results in terms of growth law. Experimental data found in literature
 122 however shown to mostly validate the Fast model [32, 33]. This model was
 123 consequently chosen here and writes as:

$$\Lambda(\phi, \mathbf{r}) = \phi(1 - \phi) [\phi D_s + (1 - \phi) N D_p] \quad (5)$$

124 In this study, constant values are taken to estimate the tracer diffusion
 125 of the solvent D_s and the polymer $D_p = D_s/N$.

126 To describe the solvent evaporation during phase inversion process, a
 127 solvent flux was added at the upper interface, from the polymeric system to

128 the external environment:

$$J_{evap}(\phi, \mathbf{r}_{\text{upper}}) = k\Delta g(\phi) \quad (6)$$

129 where $\Delta g(\phi) = a_s^i(T^i) - a_s^\infty(T^\infty)$ is the difference in activities between the
130 upper polymer solution at the interface and the solvent in the external en-
131 vironment [34–37]. The solvent activity at the upper interface was calculated
132 using the mathematical description of the free energy of mixing, herein the
133 Flory-Huggins theory:

$$a_s = \exp\left[\frac{1}{k_B T} \left(\frac{\partial \Delta G_m}{\partial n_s}\right)\right] \quad (7)$$

134 In equation (6), k represents the mass transfer coefficient that mainly
135 depends on the hydrodynamic conditions in the air above the interface and
136 can be calculated using semi-empirical correlations. The evaporation regime
137 are described by the convective Biot number:

$$Bi = \frac{k}{D_0} l(t=0) \quad (8)$$

138 For the simulations of this work, a simplified approach was used and four
139 different values of k were chosen for testing different regime of evaporation:
140 $Bi = 0.01, 0.1$ and 0.5 . The solvent activity in the external environment was
141 assumed to be null.

142 It must be noted that the simplified model of evaporation used here
143 is based on the assumption that diffusion of species is the limiting factor
144 of evaporation [38]. This model can be complemented by taking into ac-
145 count the gelification of the polymer in the evaporating crust [34, 39, 40],
146 a phenomenon which is ignored here. Moreover, another approach, alter-
147 native to diffusion-limited models, was recently proposed for dealing with
148 non-equilibrium situations [41].

149 *Methods*

150 The non-dimensional system of partial differential equations was nu-
151 merically solved in two dimensions using finite element software: COMSOL
152 Multiphysics 5.4 with the scaling parameters $L_0 = l_x = 1[\mu m]$, $t_0 = L_0^2/D_0$
153 and the Biot number (equation 8).

154 A structured moving mesh was used with 64x64 nodes and it was refined
155 until no change in the numerical result was obtained. A variable time step
156 was used to improve the numerical resolution. For the results in the YZ plane,
157 the resolution of mass transfers process induces a displacement of the upper
158 domain boundary that smoothly displaces the mesh nodes at the surface and
159 inside the bulk of the domain.

160 The images resulting from phase separation-evaporation simulation were
161 analyzed using Fast Fourier Transform (FFT) performed by Image J (NIST),
162 as well as by calculating the Minkowski descriptors for estimating the topo-
163 logical indicators such as the volume fraction, the connectivity, and the Euler
164 characteristics. More details on the procedure to obtain such data, can be
165 found in our previous paper [15]. For all pictures, the FFT returned a recipro-
166 cal space image exhibiting a ring, confirming the existence of a characteristic
167 size of phase separation $L_m(t)$. For determining this size with precision,
168 these rings were radially averaged to provide a $I(q)$ curve-also called struc-
169 ture factor- where I is proportional to the square of the Fourier transform
170 of concentration correlations and q is the wavevector of reciprocal space.
171 These structure factors were compared at different distances (see below) of
172 the evaporating surface for assessing the phase separation homogeneity.

173 The thresholding method transforms the grayscale image to black/white

174 images by sweeping all thresholds. Then, three topological descriptors are
175 extracted from those images: F is the ratio of the area occupied by the white
176 pixels divided by the total pixel number, U is the interface density obtained
177 by counting the pixel number of black/white neighbors and E_c is the Euler
178 characteristic which can be assimilated in this work to the difference between
179 the number of black non-connected domains and the number of white non-
180 connected domains. All images were normalized in size before analysis to
181 ensure a clear comparison from one image to another

182 *Results*

183 Two sets of results are presented herein: in a first part, simulations were
184 carried out in a 2D XY plane (horizontal plane) as reported in Figure 1. In a
185 second part, simulations in a 2D vertical YZ plane are presented to simulate
186 the phase separation in the membrane cross-section.

187 *Evaporation simulations in a horizontal XY 2D plane*

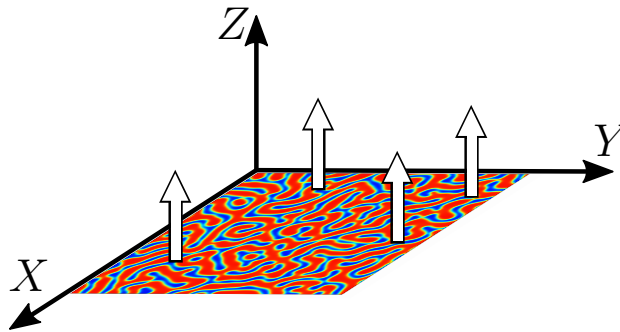


Figure 1: Schematic representation of the evaporation process in the XY plane

188 These first sets of simulations in the horizontal XY plane aimed at testing
189 a solvent loss in a 2D domain of $1 [\mu m] \times 1 [\mu m]$ where each point of the sim-

190 ulation domain was affected by the solvent loss (Figure 1). This 2D domain
 191 could conceptually correspond to the upper interface of a membrane exposed
 192 to air, as if the membrane would have null thickness. In this respect, bulk
 193 phenomena occurring deeper in the membrane were not taken into account
 194 for those first sets of simulations.

195 Considering the boundary conditions, the solvent activity in the air was
 196 considered to be null, assuming continuous ventilation in the external envi-
 197 ronment above the polymer solution, hence maximizing the driving force for
 198 solvent evaporation.

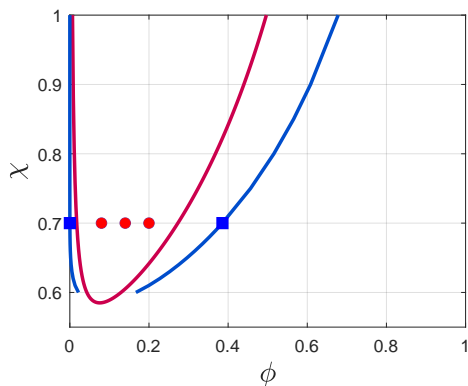


Figure 2: Phase diagram for a asymmetrical system ($N = 150$). The blue and red curves represent the binodal and the spinodal curve, respectively. The red point represent the initial composition tested in this study. The blue square gives the binodal phase composition equilibrium. In any spatial point of the phase field, The composition path goes from a red circle to $\phi = 1$. For separation in the XY plane, the leftmost red point was chosen as the quenching point ($\phi = 0.08$).

199 Both binodal and spinodal curves were calculated and represented in Fig-
 200 ure 2.a. The quenching point was chosen in the spinodal region of the phase
 201 diagram in such a way that $\chi = 0.7$. The initial polymer concentration at

202 this quenching point was $\phi_{init} = 0.08$ for this separation in the XY plane.

203 Starting from this phase diagram (Figure 2) and this quenching point, in
204 a closed system the phase separation would lead to the formation of a con-
205 tinuous polymer-lean phase and a disperse polymer-rich phase. At equilib-
206 rium, each phase would be expected to tend to its equilibrium concentration:
207 $\phi_a = 1.4 \cdot 10^{-4}$ for the polymer-lean phase and $\phi_b = 0.386$ for the polymer-
208 rich phase (cf. Figure 2). In absence of evaporation, the global polymer
209 volume concentration ϕ is constant, equal to 0.08 and the volume fractions
210 of each phase keep constant values, equal to $\phi_{rich} = 0.21$ and $\phi_{lean} = 0.79$,
211 respectively, as calculated by the lever rule.

212 Now, when considering the coupling between phase separation and sol-
213 vent evaporation, the global polymer concentration is expected to gradually
214 increase in the system in such a way that the system follows a composition
215 path that will ultimately reach the right of the phase diagram, following the
216 dotted line at constant $\chi = 0.7$ (Figure 2).

217 For the first set of simulations in the 2D XY plane, the nondimensional
218 mass transfer coefficient k was fixed at 0.1. In Figures 3 a-j, the patterns ob-
219 tained in a closed system (upper row, without evaporation) and in presence of
220 continuous solvent evaporation (lower row) were compared. Without solvent
221 evaporation (Figures 3 a-e), a spontaneous phase separation starts with the
222 formation of droplets of polymer-rich phase into a continuous polymer-lean
223 phase. The concentration of the polymer-rich phase tends to $\phi_{rich}^{eq} = 0.386$
224 while the concentration of polymer-lean phase tends to $\phi_{lean}^{eq} = 1.4 \cdot 10^{-4}$ but
225 these concentrations are not reached within the simulation timeframe, as
226 shown by Minkowski descriptors hereafter. Figures 3 f-j represent the simula-

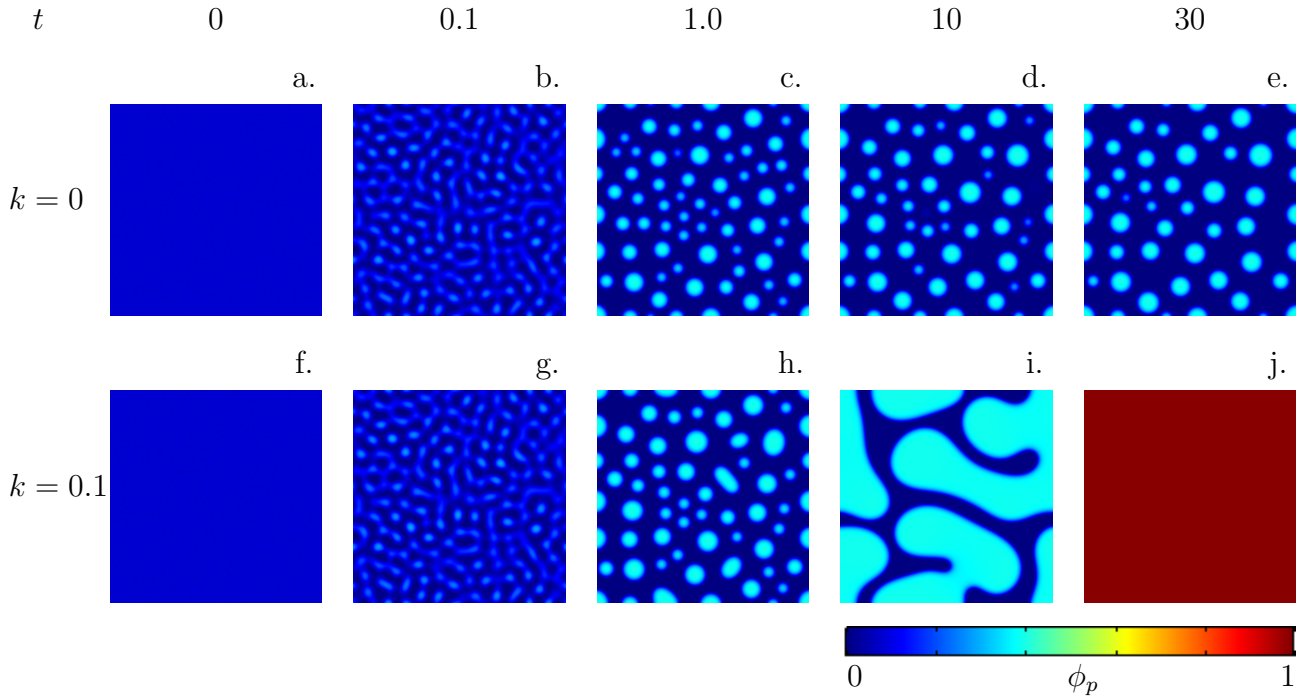


Figure 3: Time evolution of the patterns obtained in closed system (a-e) and with a coupling between phase separation and solvent evaporation (f-j). ϕ is the polymer concentration.

227 tion run corresponding to the coupling between phase separation and solvent
 228 evaporation. The same initial quenching point $\chi = 0.7$ and initial polymer
 229 concentration $\phi_{init} = 0.08$ were chosen for comparison.

230 Figures 3 f-j clearly exhibit how the solvent evaporation affects the phase
 231 separation dynamics. The solvent loss leads to a displacement along a com-
 232 position path to the right of the phase diagram, and leads to an increase
 233 in the volume fraction of the polymer-rich phase. The system undergoes a
 234 percolation inversion between Figure 3 i ($t = 10$) and 3 j ($t = 30$) and in
 235 the same time, the continuous increase of the global polymer volume frac-

236 tion promotes the coalescence of the rich phase droplets. Around $t = 10$
237 a bicontinuous polymer-rich phase is formed coexisting with a bicontinuous
238 polymer-lean phase although very dissymmetrical. The percolation inversion
239 leads to the formation of droplets of polymer-lean phase in a continuous
240 polymer-rich phase. Later, on the composition path leaves the diphasic re-
241 gion, leading to the formation of a continuous phase, highly concentrated in
242 polymer (Figure 3 j).

243 In a previous paper [15], we analyzed the patterns using both Fourier
244 transform and Minkowski descriptors. The latter method was used in this
245 work to analyze more deeply the influence of the coupling between solvent
246 evaporation and phase inversion dynamics: the patterns were binarized using
247 a chosen threshold, and then the binarized images were analyzed with three
248 Minkowski descriptors: volume fraction, connectivity, Euler characteristics.

249 The use of Minkowski descriptors requires performing a prior binarization
250 of the patterns. The choice of the threshold is not trivial since it could
251 significantly affects the curves interpretation. In our previous paper, the
252 binarization threshold was chosen equal to the initial polymer concentration
253 in such a way that during the phase separation, the regions characterized
254 by higher polymer concentration than the initial polymer concentration were
255 represented in white color, while the regions with lower concentrations than
256 the initial polymer concentration were represented in black color. In this
257 way, it was easy to catch the formation of the polymer-lean and polymer-rich
258 phases as soon as the demixing process started [15]. Although the problem
259 is different in this work since the solvent evaporation induces a continuous
260 increase of the polymer concentration, the same thresholding procedure was

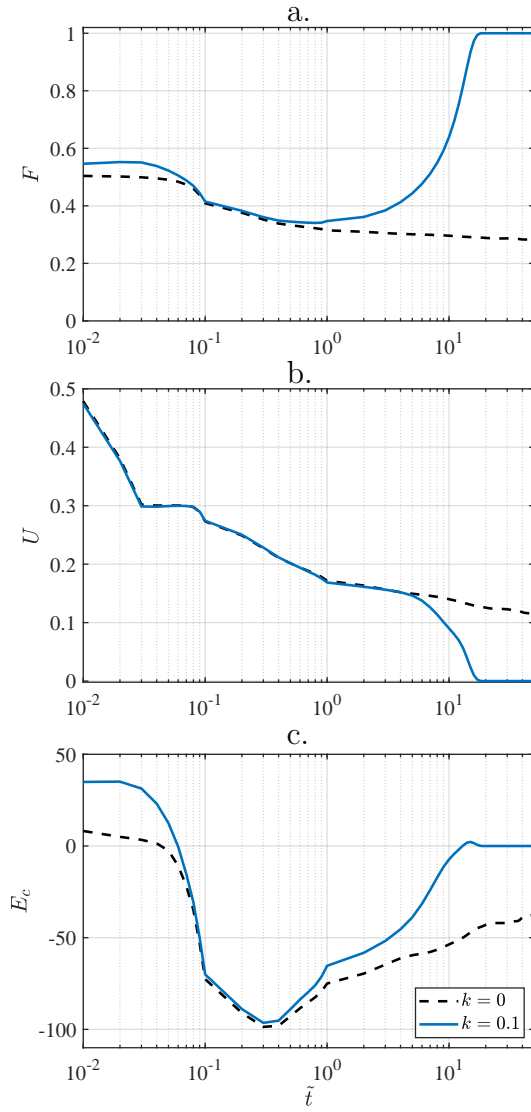


Figure 4: Time evolution of the Minkowski descriptors in closed system (dash line) and for the coupling between phase inversion and solvent evaporation (blue line) for $k = 0.1$. a. represents the variation of the covered area F occupied by the rich phase with time, b. the interface density U and c. the Euler characteristic E_c .

261 chosen¹.

262 The binarization threshold was thus fixed at a polymer concentration
263 of 0.08 for the Minkowski analysis presented in Figure 4. In this context,
264 the polymer-rich phase corresponds to regions where $\phi_p > 0.08$ and the
265 polymer-lean phase corresponds to regions where $\phi_p < 0.08$. Following this
266 procedure, it should be noted that a fraction of the interfaces was counted as
267 polymer-rich phase since the interface is characterized by a polymer concen-
268 tration gradient between the polymer-rich and polymer-lean concentrations
269 ($\phi_{rich}^{eq} = 0.386$ and , $\phi_{lean}^{eq} = 1.4 \cdot 10^{-4}$ respectively, when the concentrations
270 tend toward the equilibrium concentrations). The three Minkowski descrip-
271 tors were calculated and reported in Figure 4 versus time for the closed and
272 the open system with $k = 0.1$.

273 Figure 4.a represents the variation of the covered area occupied by the rich
274 phase with time. Without evaporation the volume fraction of each phase is
275 not expected to change during demixing process, so the Minkowski descriptor
276 F is shown to tend towards $F_\infty = 0.21$ with regards to the level rule. After
277 $t = 50$, at the end of the simulation, Figure 4.a exhibits that the system is
278 almost at equilibrium in terms of volume fraction of each phase (F is close to
279 0.21). On the contrary, when the evaporation is coupled to the phase separa-
280 tion, the system is continually in non-equilibrium state and the dynamics of

¹Actually, as shown by volume fraction temporal evolution, the average domains concentration is very quickly different from the initial value : this latter choice is then still suitable for defining separating domains. However, as the interface is rather steep between phases, the error is believed to be negligible since 0.08 is far from actual concentrations of evaporating phases

281 phase separation is different. Due to continuous solvent loss, the descriptor
282 F gradually increases until reaching unity, corresponding to pure polymer,
283 around $t = 20$. Note that no slope change was observed once the composition
284 path passes through the binodal curve, corresponding to a polymer concen-
285 tration close to 0.386. At this time (around $t = 20$), the system is composed
286 of a continuous phase characterized by a high concentration in polymer with
287 a covered area fraction of 1.

288 As reported in a previous paper [15], U is the interface density (boundary
289 length in 2D) and E_c is the Euler characteristic, useful for analyzing the
290 connectivity of domains. Without evaporation, Figure 4.b exhibits that the
291 boundary length U continuously decreases. The small droplets formed at
292 initial stage are expected to grow and they coalesce with other droplets or
293 disappear due to ripening effect, thus decreasing the total interface length.
294 In presence of solvent evaporation, the curve of the interface density U shows
295 the same trend as the curve without evaporation during the first time steps,
296 and then the interface density U is shown to decrease steeper until zero due
297 to the disappearance of solvent droplets.

298 Without solvent evaporation, the Euler characteristic E_c in Figure 4.c
299 was shown to sharply decrease at the beginning of the phase separation be-
300 cause of the creation of numerous dispersed droplets, and then E_c slightly
301 increases due to the reduction of the droplets number. The Euler character-
302 istics E_c was shown to keep negative values in a closed system, indicating
303 the absence of percolation inversion: the polymer-rich phase is always the
304 dispersed phase into a continuous polymer-lean phase. On the contrary, the
305 Figure 4.c exhibits that a percolation inversion is detected using this descrip-

306 tors. Now the Euler characteristics reaches positive values when the solvent
 307 evaporation takes place, which indicates that the percolation inversion oc-
 308 curred around $t = 12$. Then, droplets of polymer-rich phase disappeared
 309 and were rapidly replaced by droplets of polymer-lean phase in a polymer-
 310 rich continuous phase. The main interest of the analysis using Minkowski
 311 descriptors lies in the fact that the time of the percolation inversion can be
 312 detected with a good precision without the necessity to observe the patterns,
 313 which represents a significant time savings.

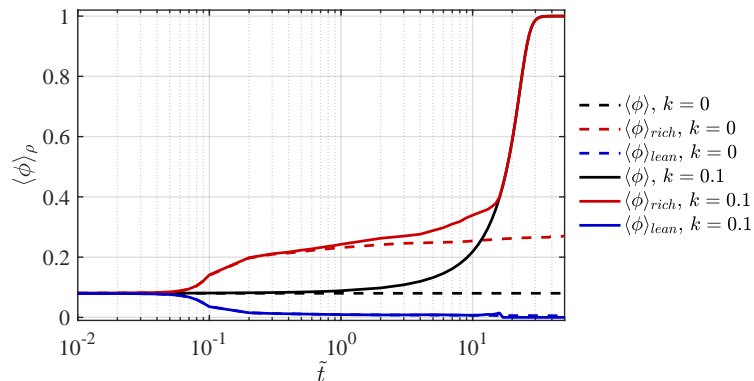


Figure 5: Variation of the global concentration (black curves), polymer concentration in the polymer-lean phase (blue curves) and polymer-rich phase (red curve). Dashed lines correspond to the closed system and solid lines correspond to the case with solvent evaporation.

314 To keep on analyzing how the solvent evaporation affects the phase sep-
 315 aration dynamics, we reported the composition of the polymer-lean and
 316 polymer-rich phases averaged on domains during the demixing process (Fig-
 317 ure 5). The binarization threshold was fixed at 0.08. The dashed lines cor-
 318 respond to the case without evaporation and the solid lines to the case with

319 solvent evaporation. The black, red and blue curves correspond to the global
320 polymer concentration in the whole domain, the polymer concentration in
321 the polymer-rich phase and the polymer concentration in the polymer-lean
322 phase, respectively. For instance, for the closed system (without evaporation)
323 the mean polymer concentration (black dotted line) is constant, equal to the
324 initial concentration ($\phi_{init} = 0.08$). The polymer concentrations in each sep-
325 arated phase tend toward the equilibrium concentration (0.386 for the rich
326 phase and $1.4 \cdot 10^{-4}$ for the lean phase). It is shown that the concentration in
327 the lean-phase is rather close from the equilibrium final concentration while
328 the concentration in the polymer-rich phase is still quite distant from the
329 final value since the separation was started at 0.08.

330 When coupling solvent evaporation and phase separation (solid curves),
331 the mean polymer concentration continuously increases, in agreement with
332 the displacement of the composition path in the phase diagram toward higher
333 polymer concentrations. For the lean phase, the curve is slightly above the
334 curve corresponding to the closed system until around $\tilde{t} = 12$, which sug-
335 gests that the relaxation dynamics due to the phase separation is too slow to
336 compensate the continuous solvent loss. In other words, the system is contin-
337 uously forced to be in non-equilibrium state because of solvent evaporation.

338 The same conclusion can be drawn considering the polymer-rich phase:
339 the solvent evaporation leads to a faster increase of the polymer-rich phase
340 concentration. In the polymer-rich phase too, the relaxation time scale of the
341 phase separation is clearly slow enough to evidence the solvent evaporation.

342 This first simulation run conducted in horizontal 2D plane exhibited how
343 the solvent evaporation affects the phase separation dynamics, leading to an

344 inversion percolation when starting at an initial polymer concentration of
345 $\phi_{init} = 0.08$ and then to the formation of a monophasic system when the
346 composition path goes through the binodal line of the phase diagram.

347 *Evaporation simulations in a (YZ) 2D plane*

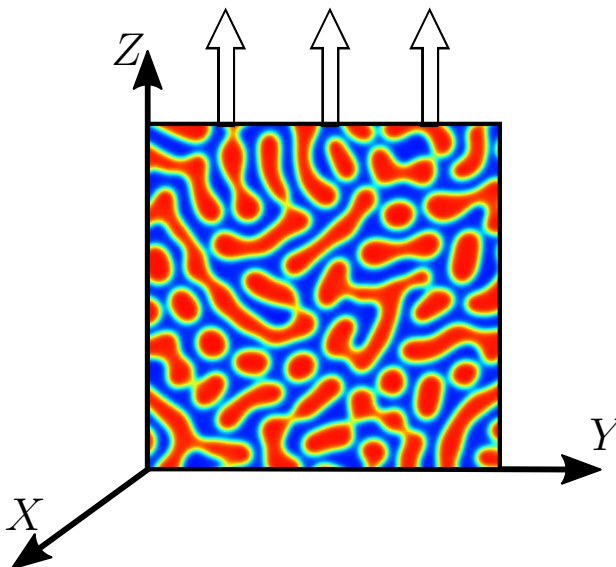


Figure 6: Schematic representation of the evaporation process in YZ plane

348 Another set of simulations were performed in a vertical YZ plane as repre-
349 sented in Figure 7. The 2D plane can now be assimilated to the cross-section
350 of the system of $1 [\mu m] \times 1 [\mu m]$. The bottom of the system at $Z = 0$ is
351 closed, hence assuming no mass exchange, whereas the upper-layer (coordi-
352 nate $Z = L$ at $t = 0$) is assumed to be in contact with the external environ-
353 ment in such a way that solvent evaporation can occur. Periodic boundary
354 conditions were imposed at the left and right boundaries of the system. The
355 global mass balance was calculated at each time step assuming density con-

356 servation and the thickness $l(t)$ of the YZ domain was expected to decrease
357 because of solvent loss assuming the following equation:

$$\frac{dl}{dt} = J_{evap} \quad (9)$$

358 J_{evap} is determined by the flux of solvent, expressed by the equation
359 (7). Simulations were performed assuming three different quenching points
360 at three initial polymer concentrations ($\phi_{init} = 0.08, 0.14$ and 0.20 , respec-
361 tively), and four nondimensional values of the mass transfer coefficient k that
362 correspond at the Biot number ($Bi = 0.01, Bi = 0.1$ and $Bi = 0.5$).

363 At early times, a surface directed phase separation is evidenced due to
364 breaking of symmetry caused by evaporation. This is evidenced as a surface
365 composition wave limited in extension to a few wavelengths (see top of figures
366 7 at $t=1$ where horizontal domains are evidenced) and whose wavelength
367 value is close to the bulk phase separation characteristic length.

368 These surface directed phase separation patterns have been evidenced
369 both experimentally due to preferential wetting constraints [42] or theoret-
370 ically because of thermal gradients on one side [43] or, more recently, because
371 of solvent replacement in a ternary solution [30]. The evaporating surface can
372 be viewed as a wetting constraint breaking isotropy, contrary to the neutral
373 sides and bottom surfaces where isotropy is maintained by periodic boundary
374 conditions and Dirichlet condition respectively.

375 At later times, when the surface directed phase separation wave has dis-
376 appeared, a dense layer is formed in the vicinity of the upper interface.

377 In Figure 8 are reported the patterns obtained for the three initial quench-
378 ing points, without evaporation and with solvent evaporation for the interme-

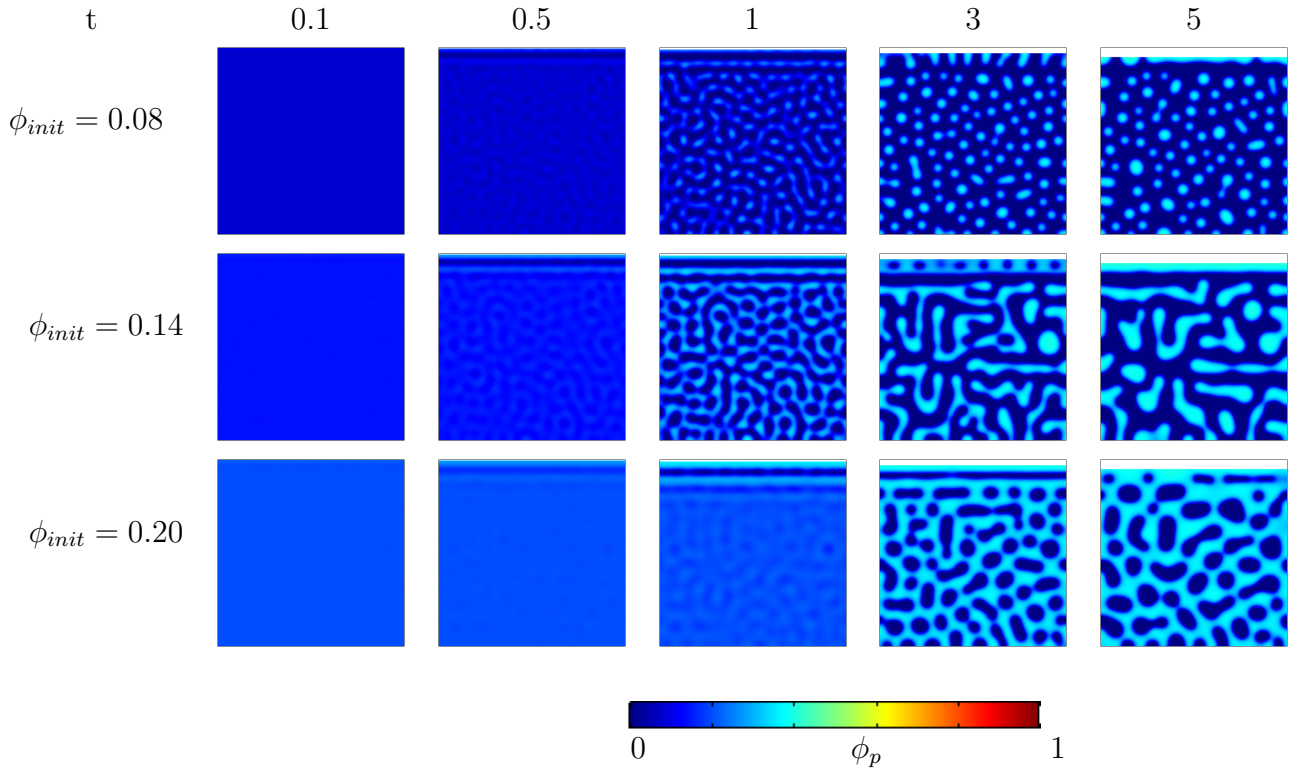


Figure 7: Early times phase separation patterns under evaporation of solvent by the top most surface for $Bi = 0.1$. A surface composition wave is established more rapidly than the bulk PS. This wave eventually transforms in the top skin layer which is characteristic of late times evolution.

379 diate evaporation rate ($Bi = 0.1$) at late times ($t \geq 6$). With evaporation,
 380 the formation of a dense layer and the decrease of the total height were clearly
 381 observed, whatever the initial polymer concentration ϕ_{init} .

382 When the initial polymer concentration (ϕ_{init}) is lower than 0.14, droplets
 383 of polymer-rich phase are dispersed into a continuous polymer-lean phase.
 384 Besides, symmetrical interconnected phases are observed when $\phi_{init} \approx 0.14$
 385 and droplets of polymer-lean phase are dispersed into a continuous polymer-

386 rich phase when $\phi_{init} \approx 0.20$. In all cases the dense phase (or skin) on top
387 is clearly inhomogeneous along z and forms a quasi-planar interface with the
388 phase-separating region below for $\phi_{init} = 0.08$ whereas the skin is continu-
389 ously linked with the phase-separating region in the other cases.

390 A qualitative visual observation of the snapshots suggests that the forma-
391 tion of the upper dense polymer layer weakly affects the dynamics of phase
392 separation beneath the dense layer: the patterns are very similar with and
393 without the solvent evaporation. The simulations launched with $\phi_{init} = 0.14$
394 that show interconnected structures, exhibit slight differences near the dense
395 layer region. At $\phi_{init} = 0.08$ and $\phi_{init} = 0.20$ the differences are even weaker
396 with and without solvent evaporation (see below Figure 12 for a quantitative
397 analysis).

398 To refine the previous observations, we reported in Figure 9 the patterns
399 obtained at $t = 1$ of the twelve simulations (3 concentrations, 4 evaporation
400 rates). The first, second and third lines correspond to quenching point at
401 initial concentrations ($\phi_{init} = 0.08$), $\phi_{init} = 0.14$ and $\phi_{init} = 0.20$, respec-
402 tively. The evaporation rate taken into account for those simulations were
403 $Bi = 0.01$, $Bi = 0.1$ and $Bi = 0.5$ a, for columns 1, 2 and 3 respectively.

404 Not surprisingly, increasing the mass transfer coefficient leads to faster
405 evaporation, to a faster decrease of domain height. A dense layer is formed
406 which seems thicker when increasing not only the initial polymer concentra-
407 tion, but also the mass transfer coefficient Bi .

408 The dense layer is fairly easy to define when the continuous phase is
409 the polymer-lean phase (case for $\phi_{init} = 0.08$) since an interface is clearly
410 formed. For the other cases ($\phi_{init} = 0.08$ and $\phi_{init} = 0.20$), the dense layer

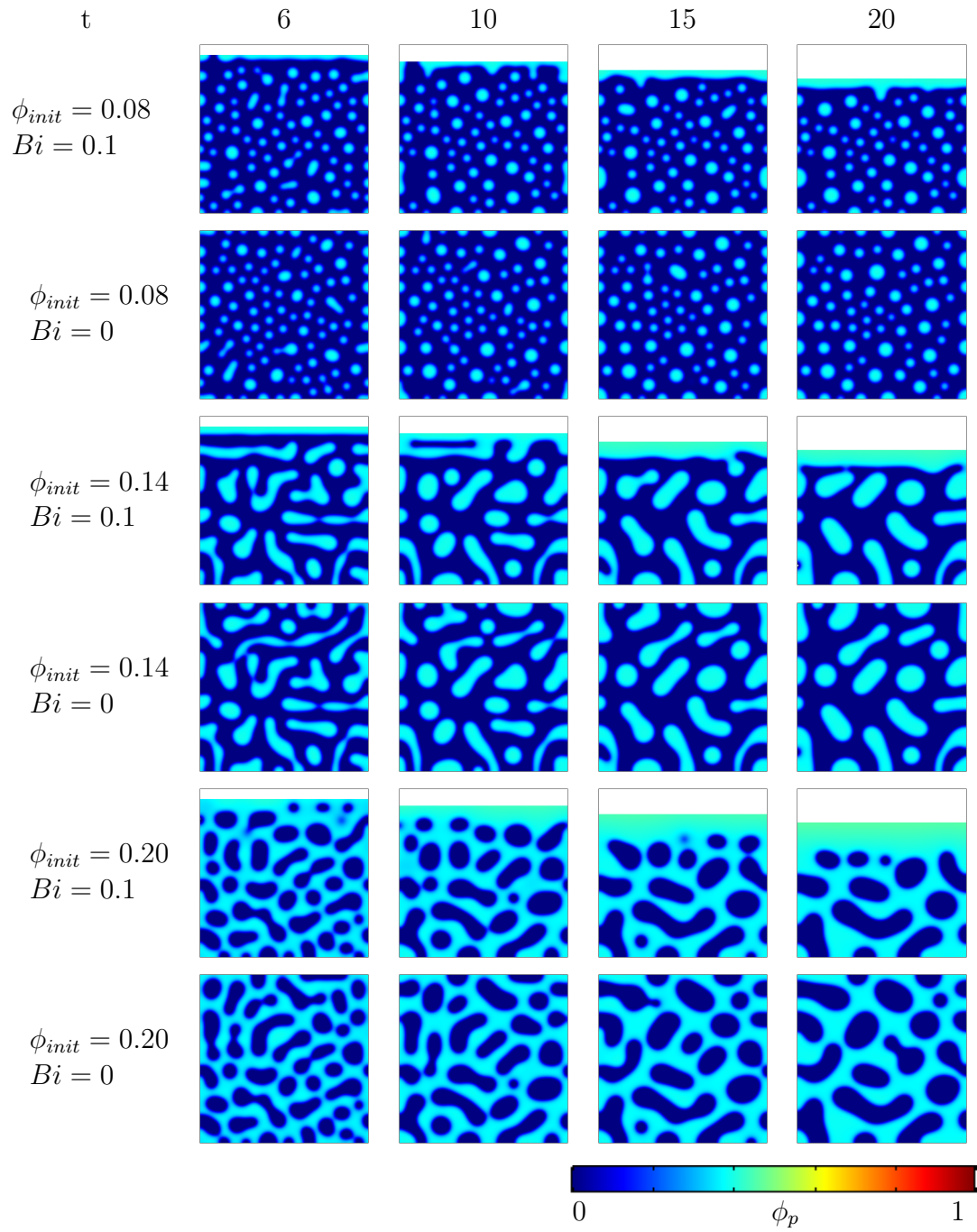


Figure 8: Patterns obtained at increasing time steps for different values of ϕ_{init} with $Bi = 0.1$.

411 thickness should be carefully evaluated (Figure 9). We decided to define the
412 lower boundary of the dense layer as the Z-coordinate where the polymer
413 concentration reaches the equilibrium concentration (0.386): actually a con-
414 centration larger than 0.386 is very quickly reached as soon as the thick layer
415 is detectable. The dense layer thickness was reported in Figure 10.b for the
416 aforementioned initial conditions of simulation ($\phi_{init} = 0.08, 0.14$ and 0.20
417 and $Bi = 0.1$ at $t=2$).

418 As visible in Figure 9, the thickness of the dense layer increases more
419 rapidly at higher initial polymer concentration ($\phi_{init} = 0.20$). This is due
420 to the fact that at higher initial polymer concentration, the binodal of the
421 dense phase is reached earlier compared to lower initial polymer concentration
422 when solvent evaporation occurs. Since the lower interface of the dense layer
423 was not perfectly flat in the simulated patterns due to the phase separation
424 and the presence of droplets or interconnected structures, its thickness was
425 estimated using an average along the Z-axis. The difficulty of identifying the
426 dense layer is exemplified by the wavy curve shape in Figure 10.b, especially
427 when droplets of polymer-lean phase are dispersed in a continuous phase of
428 polymer-rich phase ($\phi_{init} = 0.20$).

429 Below the dense (skin) layer, a visual observation of the polymer-rich and
430 polymer-lean phases indicates that no gradient exist in polymer concentration
431 in both phases. In other words, the patterns presented above suggest that the
432 relaxation dynamics below the skin layer are sufficiently fast to maintain the
433 polymer-rich and polymer-lean phases close to the equilibrium values despite
434 the solvent evaporation at the upper interface.

435 In order to better evidence this absence of gradients, we report in Figure

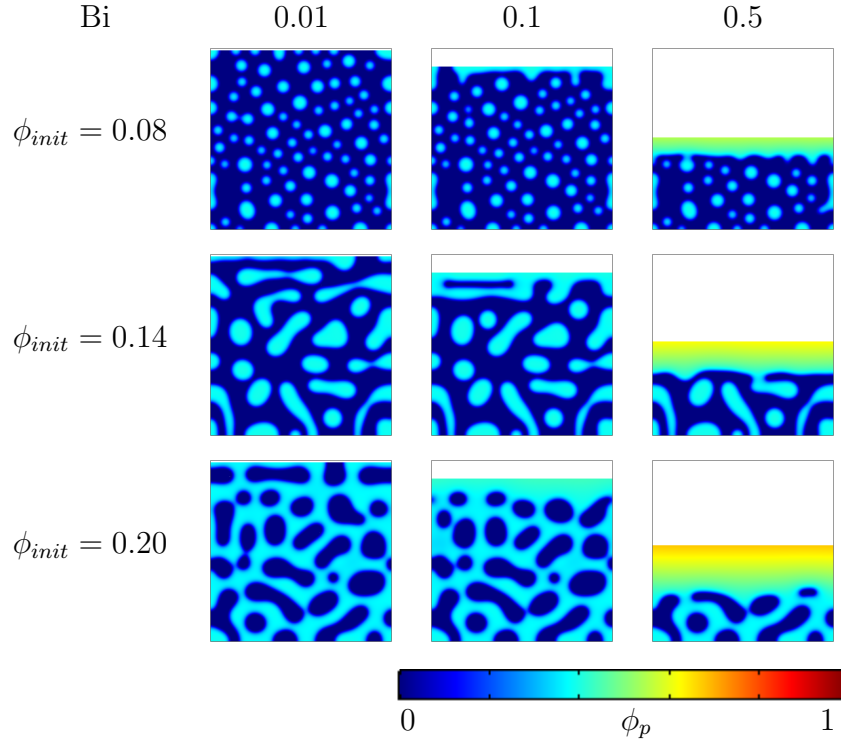


Figure 9: Patterns obtained at different initial polymer concentrations ϕ_{init} and different values of the mass transfer coefficients Bi for $t = 1$.

436 10 the patterns at the time step ($t = 2$) after having performed a specific
 437 thresholding (note that it is not a usual binary thresholding i.e. black and
 438 white):

- 439 • to focus on the polymer-rich continuous phase (images a), b) and c)
 440 in Figure 10), a threshold was fixed at $\phi_{s1} = \phi_b - 0.05 = 0.33$ where
 441 all concentrations lower than ϕ_{s1} are assigned to a white color (inverse
 442 thresholding) whereas the color code is respected for $\phi > 0.33$. As a
 443 result, a concentration gradient is visible in the dense layer but not
 444 beneath it, i.e. in the diphasic region

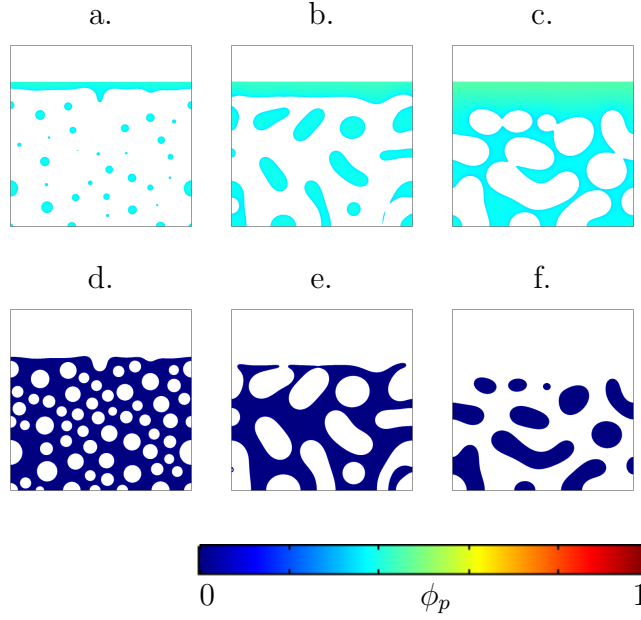


Figure 10: Bulk polymer concentration following the color code in the concentrated phase (a), b), c)) and the lean phase (d), e), f)) respectively for different quenching concentrations: left $\phi_{init} = 0.08$, middle $\phi_{init} = 0.14$ and right $\phi_{init} = 0.20$ at $t=2s$. Thresholds are chosen to render the lean (resp. the concentrated phase) white to reveal the other one (see text)

445 • to focus on the polymer-lean continuous phase (images d), e) and f) in
 446 Figure 10), a threshold was fixed at $\phi_{s2} = \phi_a + 0.05 \approx 0.05$ in such a
 447 way that when the concentration exceeded 0.05, its value was fixed to
 448 a white color. On the contrary, for concentrations between 0 and 0.05,
 449 the color scale is respected and exhibits the absence of color gradient,
 450 i.e. of concentration gradient in the z-direction in the polymer-lean
 451 phase.

452 The Z-average concentrations over the continuous phase were calculated
 453 along a vertical Z line at each Y-coordinate (Figure 11). the plots confirms
 454 that below the dense layer and at $t = 2$, the concentration in the polymer-

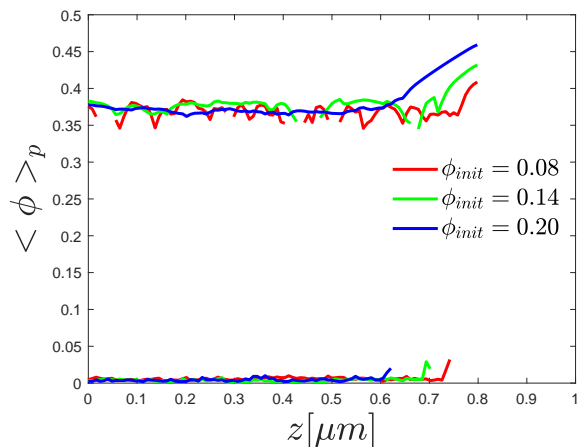


Figure 11: Z-average concentrations over the continuous phase for the three different concentrations after the thresholding procedure of Figure 10.

455 lean phase for $\phi_{init} = 0$ is very close to 1.10^{-4} and the concentration in the
 456 polymer-rich phase for $\phi_{init} = 0.37$ is also very close to 0.386. No concen-
 457 tration gradient was observed from the bottom to the dense layer interface,
 458 whatever the case.

459 To complete the quantitative image analysis, 2D Fourier transform (FFT)
 460 were calculated for the images to check to what extent the evaporation did
 461 affect the phase separation dynamics. For the three pictures at the latest
 462 times of separation and the three different initial concentrations, the struc-
 463 ture factors were calculated in two rectangular windows. Each window is
 464 rectangular of width 446 pixels and height 152 pixels and one is located close
 465 to the interface and the other down close to the lower border (see Figure
 466 12 for details). Structure factors are shown to be similar close and far to
 467 the interface, proving homogeneity. In particular, for each pair of curves at
 468 equal time and concentration, a peak at small wavevectors is evidenced de-

469 spite the large typical distance between domains which pushes the peak to
470 the y-axis. This peak is however distinguishable and representative of the
471 distance between domains, which is similar at the top and bottom.

472 To summarize the previous simulation results obtained in the YZ plane,
473 we exhibited that the continuous solvent loss at the top surface due to evap-
474 oration induces the formation of a skin layer (note here that no change of
475 dynamics such as gelation or glass transition was assumed to take place in
476 this layer [36]), which suggests that mass transfer localized at the upper in-
477 terface is faster than the potential inflow of solvent from deeper layers by
478 molecular diffusion. The system relaxes to minimize its free energy in such a
479 way that an equilibrium is reached between the lower part of the dense layer
480 and the adjacent bottom separating layer composed of polymer-lean phase
481 or polymer-rich phase. The thickness of the gradient zone was shown to in-
482 crease during time whatever the Biot number, i.e. the relative evaporation
483 rate driven by the air flow conditions. In this way, beneath this dense layer,
484 the phase separation in the bulk solution was shown not to be affected by
485 the mass transfer occurring at the upper system interface.

486 *Conclusion*

487 Herein, we developed a model that coupled the demixing process and
488 the solvent evaporation during the membrane formation by TIPS process.
489 Simulations have been performed in a 2D geometry in XY plane (membrane
490 surface) and YZ plane (cross-section). The simulations in the X-Y plane
491 clearly predicts the existence of an evaporation regime where an initially
492 minority phase rich in polymer will be turned into a majority phase (per-
493 colation inversion). This is confirmed in Y-Z simulations where a "polymer

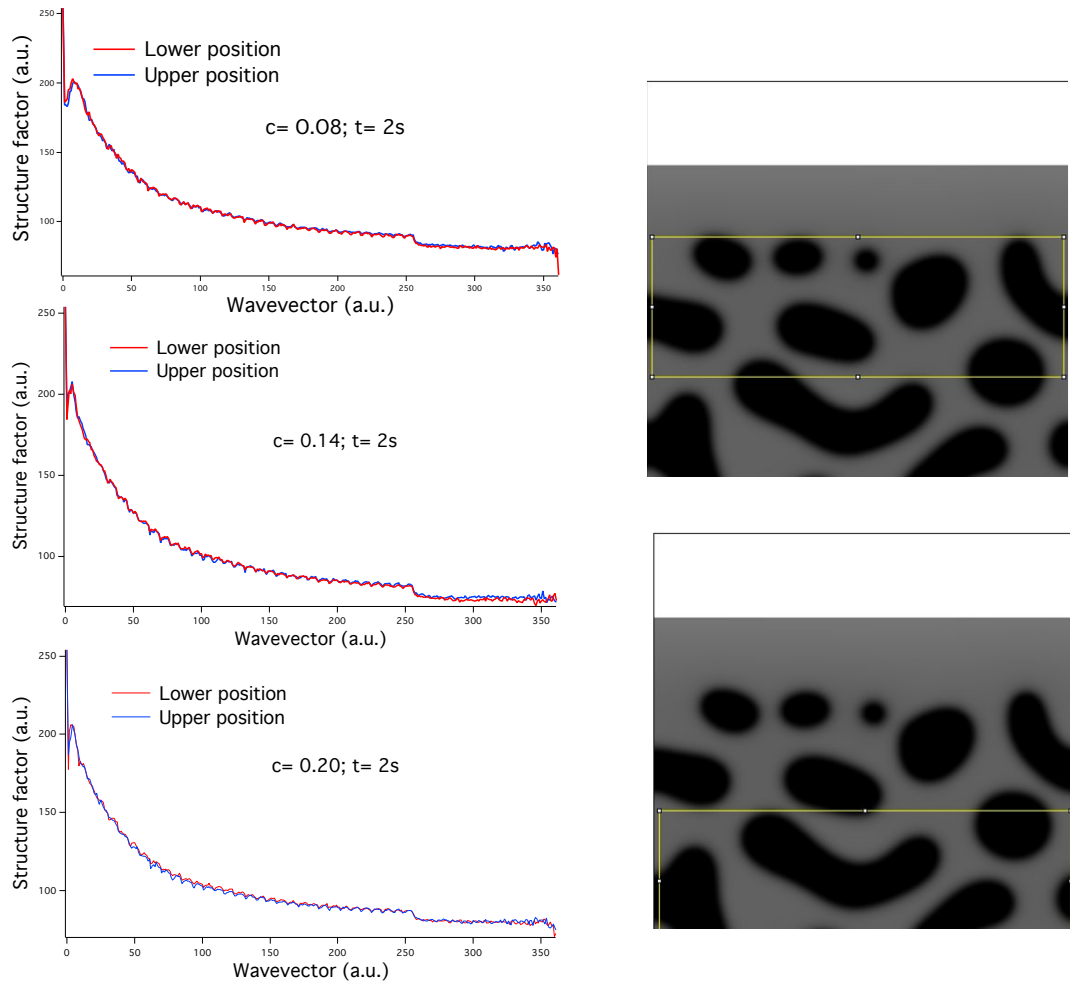


Figure 12: (left) Superposition of structure factors at two different distances from the dense evaporating layer and for the three concentrations at the latest time studied. Oscillations are non-physical and merely due to the pixellisation inhomogeneity whereas the dip at a wavevector of ca. 251 is due to the sudden drop in analyzed pixels number above the maximum inscribed circle radius. (right) Position of the chosen analysis rectangles.

494 skin layer” appears after some time on top of an initially dilute phase. Sur-
495 prisingly and interestingly enough, our results predict that the skin layer is a
496 gradient zone in concentration between a value that tends to one at the top
497 surface and the equilibrium value of the polymer-rich phase which is main-
498 tained throughout the evaporation process. This result demonstrates that
499 beneath the skin layer, the phase separation was not affected by the solvent
500 loss at the top surface and stays homogeneous through the entire bulk vol-
501 ume, which was not expected a priori. In this context, the simulation results
502 presented in this work allow a better understanding of the interplay between
503 the solvent evaporation and demixing process, especially for predicting the
504 skin layer thickness, which depend on the evaporation rate. The formation
505 of this skin layer (whose porosity is often facilitated by porogen additives
506 in industry) is of crucial importance for the membrane preparation since it
507 controls the membrane selectivity. The thickness of this layer also plays an
508 important role in the membrane permeability since the main resistance to
509 mass transfer is localized in it. Furthermore, the model provides an insight
510 on the interplay between the solvent evaporation and the demixing process
511 deeper in membrane. Indeed, this work demonstrated that the dynamics of
512 phase separation below the skin layer was not affected by the solvent evapo-
513 ration, meaning that the pore size within the membrane bulk is not affected
514 by the solvent evaporation. This suggests that the global membrane porosity
515 (the void ratio) would not be affected by the solvent evaporation. On the
516 theoretical side, our results are foreseen to be extended to a tridimensional
517 geometry for coupling X-Y and Y-Z processes.

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