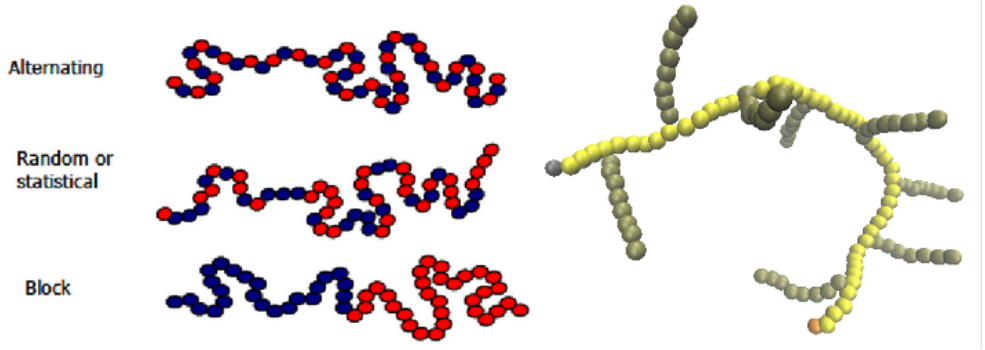
1 Introduction

Copolymers are polymers formed when two (or more) different types of monomers are linked in the same polymer chain, as opposed to homopolymers where only one monomer is used. They are obtained via a chemical process called copolymerization, where the different monomers are polymerized together and usually, when just two types of monomers are involved, they are called bipolymers (terpolymers and quaterpolymers for three and four types of monomers respectively).

Copolymers can also be classified based on how the monomers are arranged into the chain(s), but a first great distinction can be introduced between linear copolymers, which have a single main chain, and branched copolymers, consisting in a single main chain with one or more polymeric side chains.

In Figure 1 we show some examples of the various types of copolymers we can encounter:



(a) The three types of linear copolymers: alternating, random or statistical and block.

(b) An example of a branched copolymer: a graft polymer

While the previous figure covers all types of linear copolymers, more structures are available for branched copolymers, corresponding to various conformations in which side chains can be placed; an other example for that are star copolymers.

Copolymers are actually pretty useful in modern technologies and are currently utilized in industry; in the following figure (Figure 2) we show some examples of useful copolymers with some of their current application:

Monomer A	Monomer B	Copolymer	Uses
$H_2C=CHCl$	$H_2C=CCl_2$	Saran	films & fibers
$H_2C=CHC_6H_5$	$H_2C=C-CH=CH_2$	SBR styrene butadiene rubber	tires
$H_2C=CHCN$	$H_2C=C-CH=CH_2$	Nitrile Rubber	adhesives hoses
$H_2C=C(CH_3)_2$	$H_2C=C-CH=CH_2$	Butyl Rubber	inner tubes
$F_2C=CF(CF_3)$	$H_2C=CHF$	Viton	gaskets

Figure 2: Some examples of useful copolymers in industry.

To add an example also for terpolymers, ABS rubber (formed of acrylonitrile, butadiene and styrene) is used for high-impact containers, pipes and gaskets.

Anyway, the main interest of our study is the self-assembly behaviour they show in solutions: due to that they are able to form spontaneously different kind of structures that can be advantageous, for example, in nanotechnologies, such as photonics and biotechnological applications. Furthermore, under certain specific conditions, it was found that copolymers can form vesicles (onion shaped in [4]) which have a great potential application in biomedical sciences and industry, such as promoting cell recognition, the communication and adhesion process, microcapsules, microreactors, drug delivery and so on.

From that the purpose of our project to simulate the behaviour in water of different kind of copolymers using DPD simulations, in order to better understand which parameters really influence the structures that are formed. We will change for example the structure of the polymers (number of side chains, symmetry, length etc.), the repulsive strength between monomers of different kinds, their concentration in the box and others more. This could open doors to lots of applications, since, potentially, we will be able, setting different parameters, first in our simulations, then in experiments and real world situations, to obtain the structure that is needed to perform specific functions.

2 Method

To perform all of our simulations we used Dissipative Particle Dynamics (DPD). It is a stochastic simulation method that works on the mesoscopic scale and was first introduced by Hoogerbrugge and Koelman in 1992. It is also a coarse-graining technique; this means that the particles (beads) do not represent single atoms but rather molecules (or parts of them) and even fluid regions. The time evolution of the motion of a set of particles is obtained by solving Newton's equation:

$$\mathbf{F} = m\mathbf{a}, \tag{1}$$

where the force term is actually made of three parts: the conservative force $\mathbf{F}_{ij}^C$, that gives the particles an identity (e.g. hydrophobic), the dissipative force $\mathbf{F}_{ij}^D$, that destroys the relative momentum between pairs of interacting particles, and the random force $\mathbf{F}_{ij}^R$, which creates this relative momentum:

$$\mathbf{F}_i = \sum_{i \neq j} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R). \tag{2}$$

The index i represent the i-th particle on which the force is acting and the sum is over all other particles within a certain cut-off radius r_0, that sets the maximum interaction distance (we will set it off to 1).

The expression for the three types of forces are the following: for the soft repulsive conservative force between the beads i and j we have:

$$\mathbf{F}_{ij}^C = a_{ij}(1 - \frac{r_{ij}}{r_0})\hat{\mathbf{r}_{ij}}, \tag{3}$$

where a_{ij} is the repulsive interaction parameter between particles i and j, and the force is only defined for $r_{ij} < r_0$.

For the hydrodynamic drag force (dissipative force) we have:

$$\mathbf{F}_{ij}^D = \gamma_{ij}(1 - \frac{r_{ij}}{r_0})^2(\hat{\mathbf{r}_{ij}} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}_{ij}}, \tag{4}$$

where γ_{ij} is a friction parameter and $\mathbf{v}_{ij}$ is the vector of relative speeds between two beads. Again the force vanish for $r_{ij} > r_0$.

Lastly, for the random force we have:

$$\mathbf{F}_{ij}^R = \sqrt{2\gamma_{ij}k_BT}(1 - \frac{r_{ij}}{r_0})\zeta_{ij}\hat{\mathbf{r}_{ij}}, \tag{5}$$

where ζ_{ij} is a randomly fluctuating parameter, and the force is equal to 0 for $r_{ij} > r_0$.

In addition, we need to define two other quantities to set up our simulations: one is the extra harmonic spring force acting between adjacent particles of polymers:

$$\mathbf{F}_{i,i+1} = -k_2(|\mathbf{r}_{i,i+1}| - l_0)\hat{\mathbf{r}}_{i,i+1} \tag{6}$$

where k_2 is the Hookean spring constant and will be changed during our simulations, and $i, i+1$ are the index of two adjacent particles; the other is the potential that controls the stiffness of a polymer chain, in particular between adjacent bead triples:

$$U_{i-1,i,i+1} = k_3[1 - \cos(\phi - \phi_0)], \tag{7}$$

where k_3 is the bond angle potential strength, ϕ is the bond angle between two bond connecting the particle $i-1$, i and $i+1$ and ϕ_0 is the equilibrium bond angle (set to 0).

The code then uses a discrete version of the Verlet algorithm to computationally solve the equation:

$$\mathbf{x}(t+dt) = 2\mathbf{x}(t) - \mathbf{x}(t-dt) + \mathbf{a}(t)dt^2 + \mathcal{O}(dt^4), \tag{8}$$

$$\mathbf{v}(t) = \frac{\mathbf{x}(t+dt) - \mathbf{x}(t-dt)}{2dt} + \mathcal{O}(dt^2). \tag{9}$$

It is obtained using Taylor's expansion of the $\mathbf{x}(t+dt)$ and $\mathbf{x}(t-dt)$ terms and provides a 4-th order error, which is better then the second order of the error of Euler's algorithm, maintaining almost the same computational cost.

For the parameters and the constants that will not be changed during our simulations, we decided to follow the work of Groot and Warren in [2] (for example, l_0 is set to 0.5, γ_{ij} is 4.5, k_3 is equal to 15 and the product k_BT is kept at the value 1). Anyway, for further knowledge about this simulation technique and detailed explanations about setting the values of the parameters, we refer to [1] and [2].

It is to note that all the simulations will be run starting from a random state, as we want to analyze the self-assembling spontaneous behaviour of copolymers.

Regarding the box size and the time of the simulations, they were changed in different runs in order to find an optimal size and to understand the needed

time to observe some results. A box size suggested in [4] was 48x48x48, with 25000 as time period but, as we will show, we tried also different sizes and periods. Further discussion on the matter will follow in the result section.

3 Results

We decided to start with a pretty simple polymer as proposed in [4]:

```
Copolymer "( B (* (S S) ) B B (* (S S) ) B B (* (S S) ) B)"
```

In Figure 3 we show the actual architecture that correspond to the DPD command we just showed:

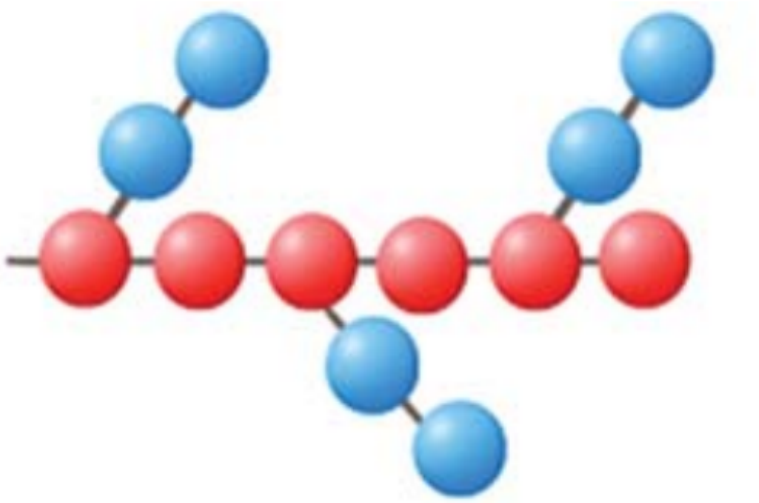


Figure 3: Copolymer used for the simulations: in red the main chain (beads of type B), in blue the side chains (beads of type S).

Regarding the other parameters of the simulations, we decided to start with a box of 15x15x15 and a polymer concentration of 0.036. The small size of the box is picked in order to fasten the simulations and allow us to perform a lot of them with different parameters set-ups, while the low concentration is chosen because it is known that a large concentration always

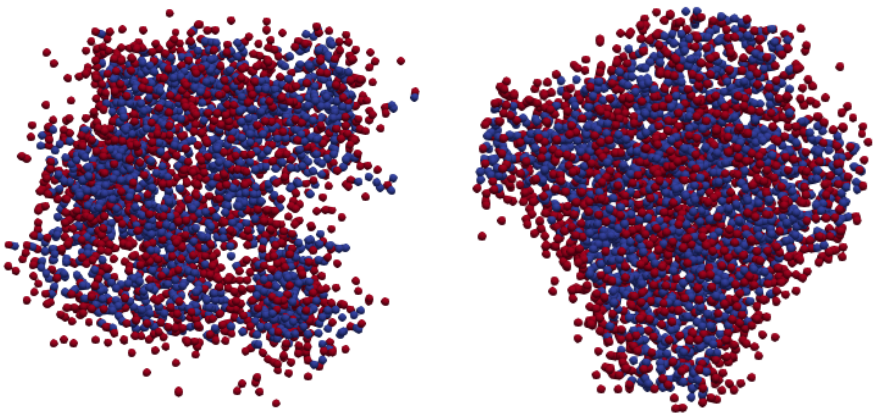
lead to connected structures, making it harder to visualize the results and to obtain a certain shape. A low concentration, on the other hand, should lead to micelles, that are easier to observe and, as we said, more useful in real life applications ([5]). Also to keep the simulations fast we started with a sample period of 10000. The interaction parameters that will remain constant during the simulations were set following [4] as we will show in the section below.

3.1 Changes in the repulsive interaction parameter a_{BS}

Using the conditions described above, we run multiple simulations changing the interaction parameter between the beads of type B and S; here we show a schematic representation of the matrix containing this parameters:

```
Bead  W
      25
Bead  B
      100   25
Bead  S
      27    30    25
```

As we can note the initial value we chose for a_{BS} is 30 (similar to the self-interaction parameter), so it is probable we won't to obtain significant results from this low values.



(a) Random initial state: in red the S beads, in blue the B beads.

(b) Final state of the simulation (time 10000).

We observe that no particular structure is formed under this specific conditions, apart from a slight tendency of the blue particles to hide from the water, since, of course, they are more hydrophobic, having an interaction parameter a_{WB} of 100.

However, before changing a_{BS}, we decided to run the simulation for more time, to see if it was needed to form something; in Figure 4 we show the same simulation at time 30000:

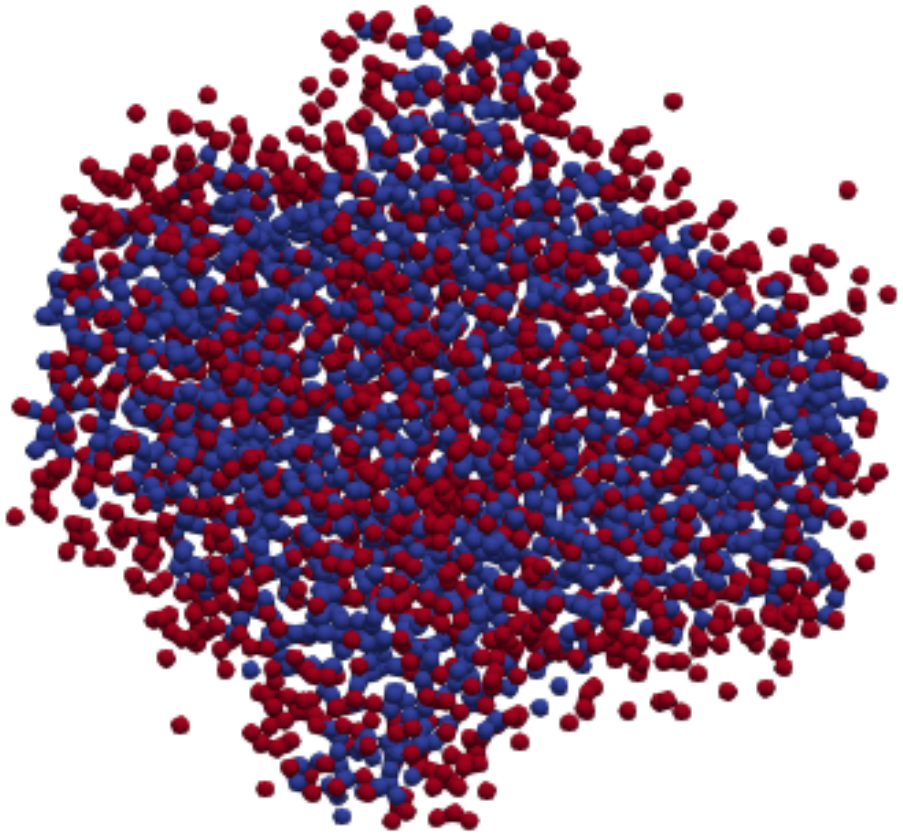
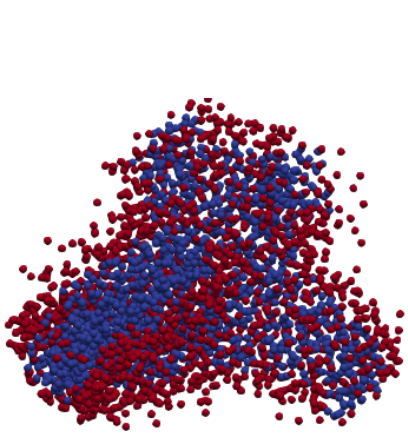
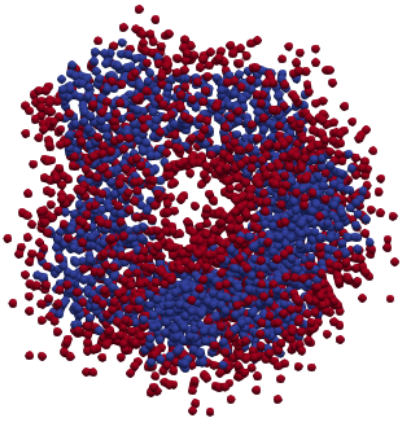


Figure 5: State of the simulation at time 30000.

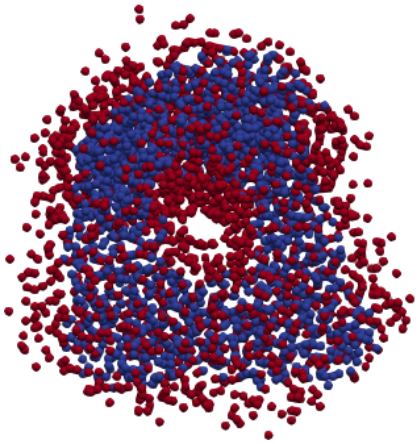
Again no significant behaviour is observed so we continued to increase a_{BS}, as shown in the following figure:



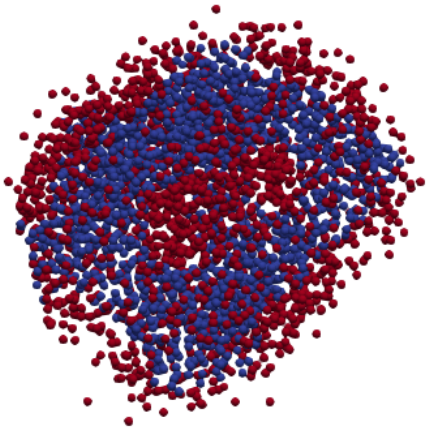
(a) $a_{BS} = 50$, Time=30000.



(b) $a_{BS} = 70$, Time=30000.



(c) $a_{BS} = 100$, Time=25000.



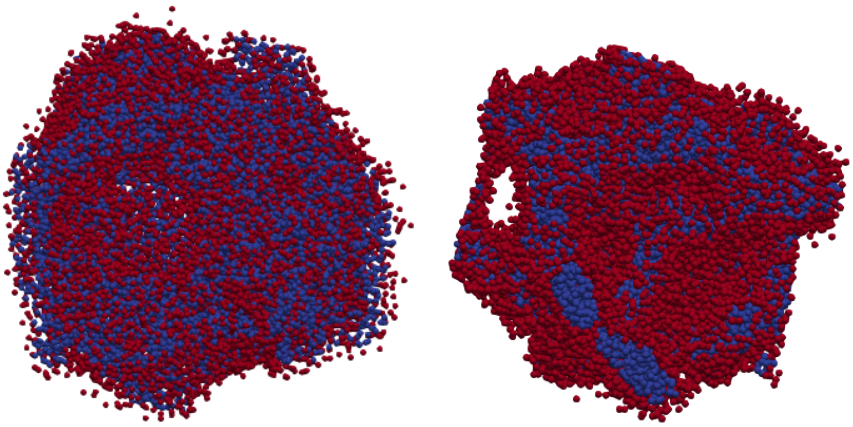
(d) $a_{BS} = 120$, Time=15000.

We can see that when a_{BS} is high enough, an onion shape appears after a certain time (again the simulations were run for more the 10000 to see some results), in accordance with the results of [4]. Also, the higher is the interaction between main and side chains, the lower is the time required to observe this sort of donut forming; in fact for the highest value we tried (120), the shape was appearing around 15000, while it was almost requiring all the simulation to appear at the value of 70.

However, we have to verify that another source of error is not modifying the result: the box size. In fact, in general, the resulting morphology pattern obtained using DPD simulations are dependent of the finite size of the sim-

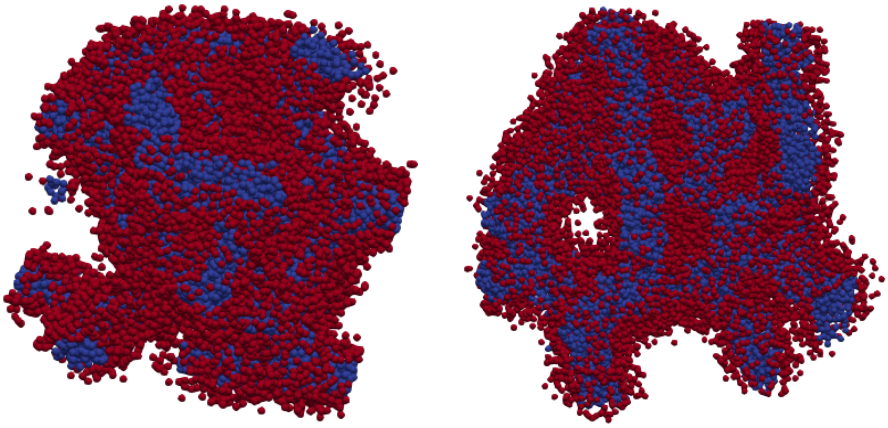
ulation box, even if periodic boundary conditions are imposed (it has been reported in other theoretical studies like [6]). So, we decided to increase the box size first to 30x30x30 and then to 48x48x48, to see if the results remained similar.

In the following figure we show the results for the box 30x30x30 with increasing values of a_{BS}:



(a) $a_{BS} = 30$, Time=30000. Box size: 30x30x30.

(b) $a_{BS} = 70$, Time=30000. Box size: 30x30x30.



(c) $a_{BS} = 100$, Time=30000. Box size: 30x30x30.

(d) $a_{BS} = 120$, Time=30000. Box size: 30x30x30.

Again for smaller values of the interaction parameters no significant struc-

ture is observed but for higher values we don't see a donut anymore, rather a sort of network with holes, which could be consistent with what shown in [3] (see Figure 8):

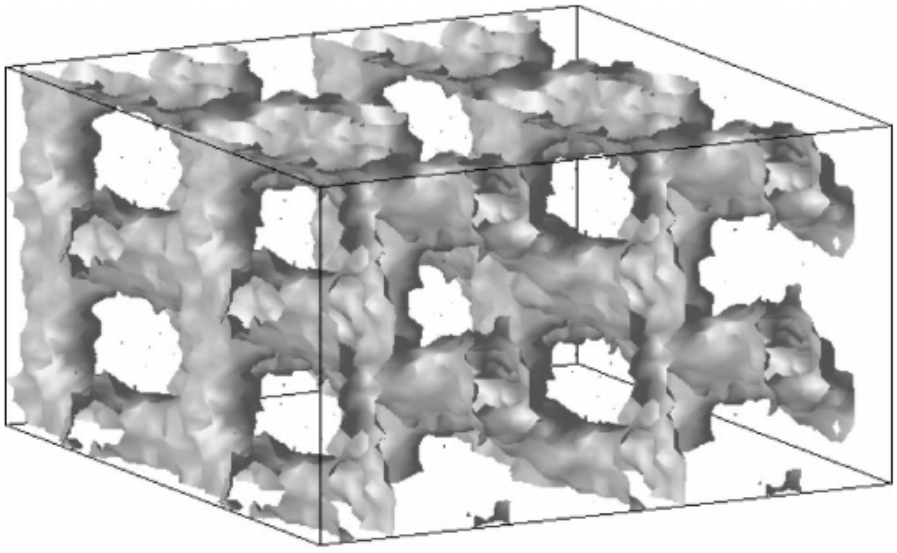
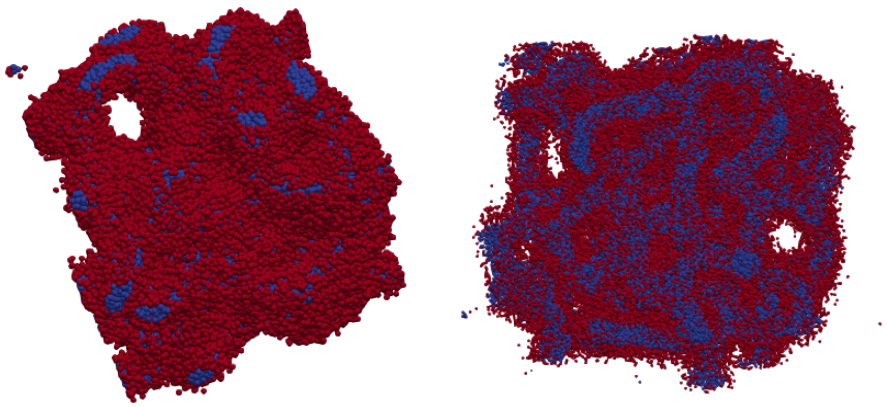


Figure 8: density snapshot obtained in [3] for diblock copolymer.

Anyway, unfortunately, the results were sort of different from the smaller box size, even if some similarities in the structures can be found, like the tendency to create holes in the box and the similar behaviour of the red and blue beads (the red ones try to surround the blue ones and hide them from the water).

To see if the box size was good enough we repeated the simulations for the largest box (48x48x48), as show in the following figure:



(a) $a_{BS} = 70$, Time=30000. Box size: 48x48x48.

(b) $a_{BS} = 120$, Time=30000.Box size: 48x48x48.

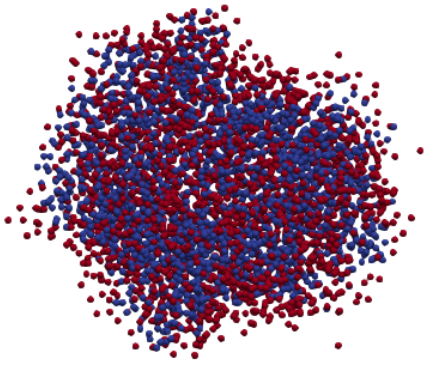
We observe that the architecture is pretty similar to the one showed in the 30x30x30 box, so, we could agree that it is a convenient box size. In the (b) picture the size for representing the molecules in Paraview was decreased in order to allow the reader to see the holes in the structure (they are, of course, more visible when rotating the box rather then in a snapshot).

Another interesting thing to note is the process by which the structure is formed. In fact, luckily, some polymers remained separated in the top left corner of the figure (a) and allowed to study their movements during the simulation time: we can note that this small micelles are first formed then, usually, when two or more come close to each other they tend to fuse, minimizing their entropy and reaching a more stable conformation. That is the reason why we observe this connected network.

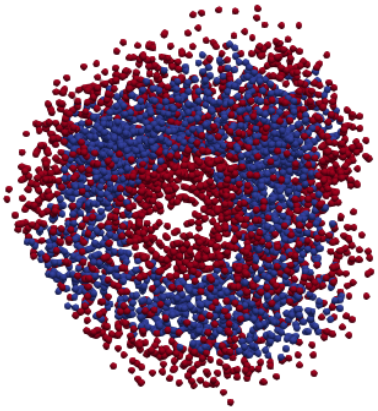
3.2 Changes in the polymer concentration

We decided to repeat the simulations of the previous section, using two higher concentration of copolymer: 0.05 and 0.1. Although for a lower concentration we found that a 15x15x15 box size was too small and influencing the results, we decided to retry it, to see if higher concentrations stabilize the structure even for smaller boxes.

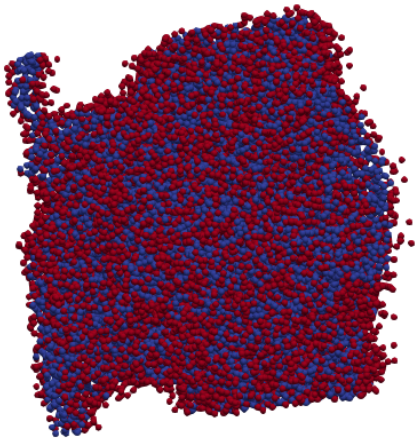
Here are some of the results for the 0.05 concentration, with the corresponding parameters settings:



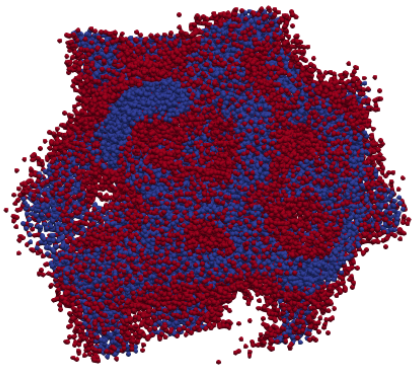
(a) a_{BS} = 30, conc=0.05, Time=30000. Box size: 15x15x15.



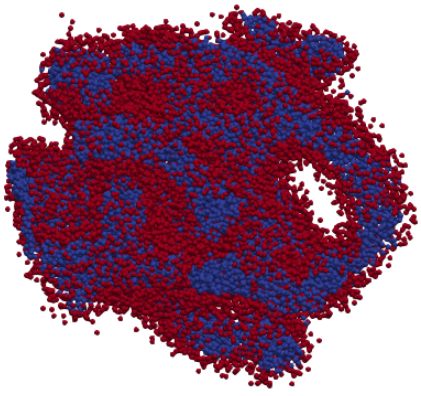
(b) a_{BS} = 120, conc=0.05, Time=30000. Box size: 15x15x15.



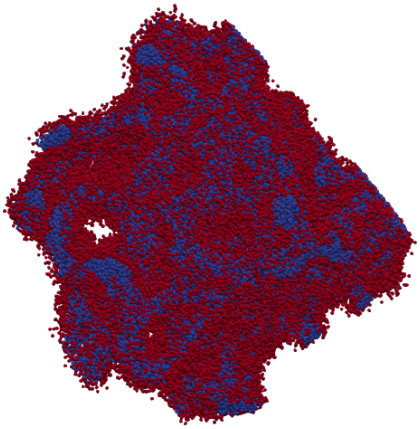
(c) a_{BS} = 30, conc=0.05, Time=30000. Box size: 30x30x30.



(d) a_{BS} = 70, conc=0.05, Time=30000. Box size: 30x30x30.



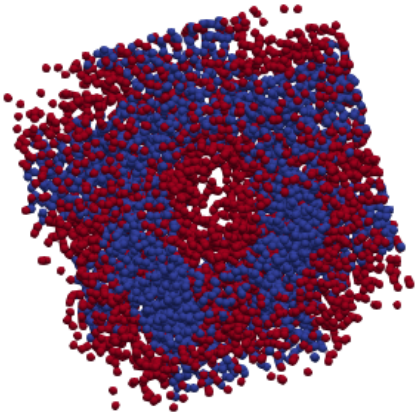
(e) a_{BS} = 120, conc=0.05, Time=30000. Box size: 30x30x30.



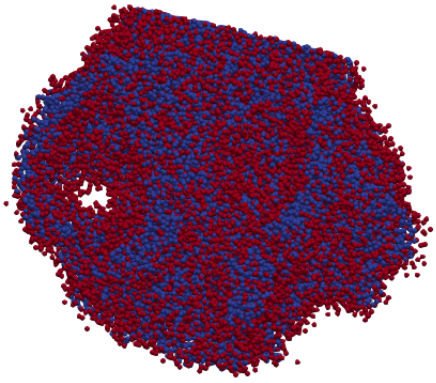
(f) a_{BS} = 70, conc=0.05, Time=30000. Box size: 48x48x48.

We note that no significant changes from the 0.036 concentration are observed: again a smaller box produced a donut for a higher repulsive force, while for a low one no particular structure seems to appear. Bigger boxes again produce this connected structures with holes that remain pretty stable even increasing the box size. This results were sort of expected since the concentration was not changed that much.

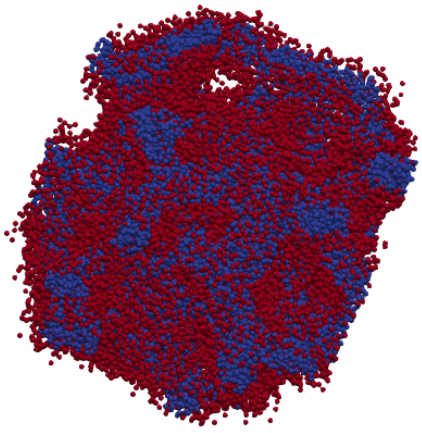
Here we try with the concentration of 0.1:



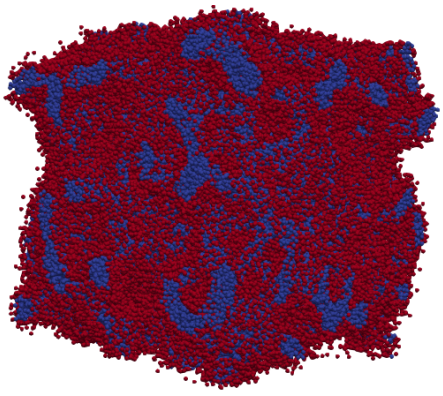
(a) $a_{BS} = 70$, conc=0.1, Time=30000. Box size: 15x15x15.



(b) $a_{BS} = 30$, conc=0.1, Time=30000. Box size: 30x30x30.



(c) $a_{BS} = 70$, conc=0.1, Time=30000. Box size: 30x30x30.



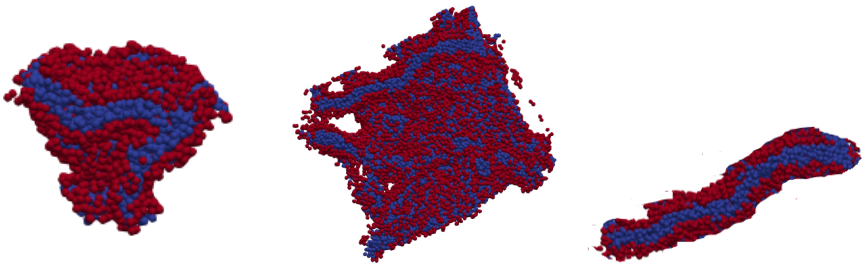
(d) $a_{BS} = 70$, conc=0.1, Time=30000. Box size: 48x48x48.

Again the result are kind of expected, as the small box produces the ring-like structure and the large ones produce connected structures.

One interesting thing to note is that with a higher concentration we observe that this conformations are appearing even with a small interaction parameter, as shown in picture (b), where some holes are already forming. This could potentially be useful in real life situations, since, in some cases, we could be forced to have low interactions between molecules and, maybe, a good way to obtain the wanted structure could be increasing the concentration.

3.3 Changes in the Hookean spring constant

Usually the Hookean spring constant is set to 128.0 during standard DPD simulations, however, in all the papers we have read it was suggested to use a way lower value (precisely 4), so we decided to investigate if it was really determining the structure of the polymers. In Figure 12 we show the results obtained for box sizes of 15x15x15 and 30x30x30, with $a_{BS} = 100$, a polymer concentration of 0.05 and the Hookean spring parameter equal to 128:



(a) Time=30000. Box: 15x15x15.

(b) Time=30000. Box: 30x30x30.

(c) Zoom of the top of the picture (b).

One thing to note is that no donut shape is appearing in the smaller box, so certainly the Hookean spring constant is affecting the structure. It is also possible to note some membrane-like pattern in both figures (a) and (b). In figure (c) we proposed a zoom of a zone (the top of picture (b)) that shows that behaviour.

3.4 Changes in the polymer structure

Finally, we decided to change the structure of the polymer, to se how it actually affects the structure formed.

The first polymer we tried is the following, in which we used longer side chains:

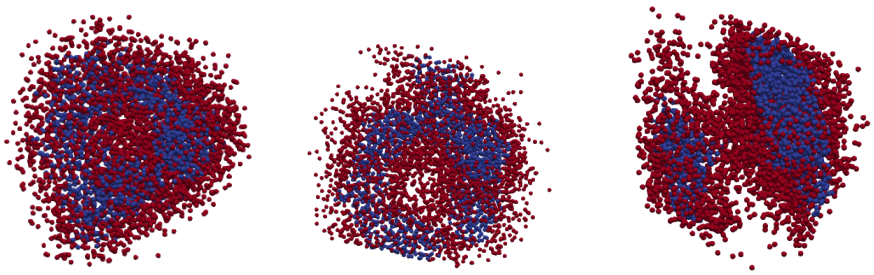
```
Copolymer ( B (* (S S S S) ) B B (* (S S S S) ) B B (* (S S S S) ) B)
```

And the second one is:

```
( B (* (S S S S S S) ) B B (* (S S) ) B B (* (S S S S S S) ) B)
```

in which we wanted to see the effect of asymmetrical side chains.

Here are the results for the first polymer with a box 15x15x15 and a polymer concentration of 0.036:



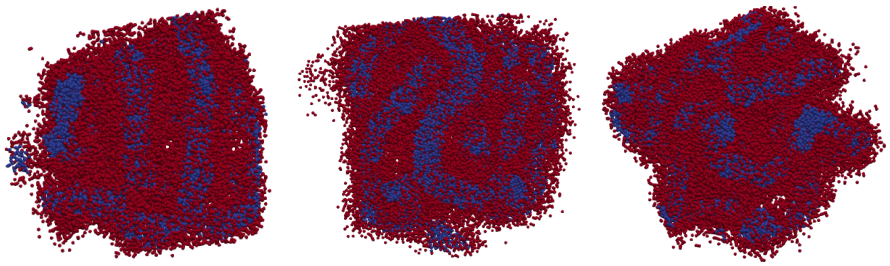
(a) a_{BS} = 30, Time=30000. (b) a_{BS} = 70, Time=30000. (c) a_{BS} = 120, Time=30000.

A significant thing to note is that the donut shape appears already with a_{BS} of 30 (figure (a)), suggesting that longer polymer side chains can promote the formation of interesting structures.

Also, if one follows the motion of the molecules during the simulations, it immediately appears that the donut shape is present way before in time, comparing it with the simulations with the other polymer, again suggesting that longer side chains could be pretty reactive.

With a_{BS} equal to 120 we observe a membrane-like structure that is a pretty unexpected shift from the ring shape.

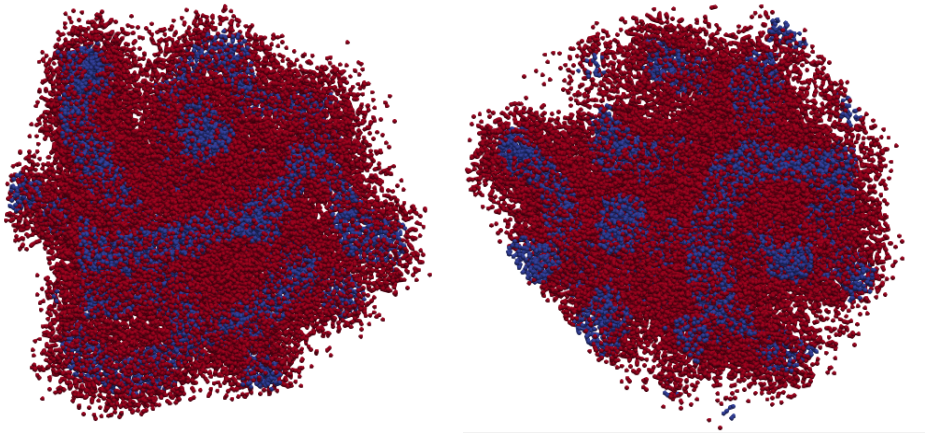
Below we show some of the results obtained with a box 30x30x30 and 0.036 polymer concentration for figure (a), 0.05 for (b) and (c):



(a) $a_{BS} = 70$, Time=30000. (b) $a_{BS} = 70$, Time=30000. (c) $a_{BS} = 120$, Time=30000.

Regarding this larger box size, interesting behaviour is shown already in figure (a), where something like repeated membranes appear. Moreover, the structure appears pretty soon in the simulation, pointing out the fact that longer side chains could lead to higher reactivity of the molecules so they interact faster. Images (b) and (c) follow the already highlighted behaviour.

For the second polymer we propose the results in a box 30x30x30 and with a concentration of 0.036:



(a) $a_{BS} = 70$, Time=30000. (b) $a_{BS} = 120$, Time=30000.

The behaviour shown in this simulations doesn't seem to vary that much from the usual network we obtained. One thing to note is that there are some visible circular shapes in the structure rather then only one big connected network. This could be due to the asymmetry of the side chains

that promotes the formations of curved structures and the bending of the polymers.

4 Conclusion

Given the results of our simulations, we can conclude that basically all the parameters we changed were somehow affecting the structure formed. The most significant one probably is the interaction parameter between main and side chains: a high value of it always brought to some patterns and structures at the end of the simulations. We saw also how the concentration of the polymers can affect the structure formed: a higher concentration led to interesting results even for lower values of a_{BS} and we already highlighted the potential relevance of this in real life situations. Regarding the Hookean spring constant, it was found that lower values are indeed needed to obtain complex architectures, while simulations with higher values suggest a shift to a membrane-like behaviour. Furthermore, concerning the length of side chains, it was interesting to note that they contributed in obtaining some structures sooner during the simulations and this could allow us to save some time but, also, could be useful in experiments, if a certain structure needs to be obtained quickly. Finally the asymmetry of side chains was not that significant, but it seemed to slightly improve the tendency of the polymers to bend and to form curved structures.

References

[1] Pep Español and Patrick B Warren. Perspective: Dissipative particle dynamics. *The Journal of Chemical Physics*, 146(15):150901, 2017.

[2] Robert D Groot and Patrick B Warren. Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *The Journal of chemical physics*, 107(11):4423–4435, 1997.

[3] Jaroslav M Ilnytskyi, Taras Patsahan, Myroslav Holovko, Peter E Krouskop, and Mike P Makowski. Morphological changes in block copolymer melts due to a variation of intramolecular branching. dissipative particles dynamics study. *Macromolecules*, 41(24):9904–9913, 2008.

[4] Ying-Tao Liu, Yan-Rong Li, and Xin Wang. Spontaneous onion shape vesicle formation and fusion of comb-like block copolymers studied by dissipative particle dynamics. *RSC Advances*, 7(9):5130–5135, 2017.

[5] Ying-Tao Liu, Ying Zhao, Hong Liu, Yu-Hua Liu, and Zhong-Yuan Lu. Spontaneous fusion between the vesicles formed by a 2 n (b 2) n type comb-like block copolymers with a semiflexible hydrophobic backbone. *The Journal of Physical Chemistry B*, 113(46):15256–15262, 2009.

[6] Uwe Micka and Kurt Binder. Unusual finite size effects in the monte carlo simulation of microphase formation of block copolymer melts. *Macromolecular theory and simulations*, 4(3):419–447, 1995.