Bilayers of Janus and homogeneous particle mixtures trapped at an air/water interface†

Anna Kozina, [ID] *[a] Salvador Ramos,[b] Pedro Díaz-Leyva[c] and Rolando Castillo[b]

We study mixtures of amphiphilic Janus and homogeneous hydrophobic particles trapped at an air/water interface. In contrast to an expected monolayer formation, bilayers of colloidal particles are produced. Despite their strong interfacial adsorption, Janus particles form the upper layer. They are not placed on top of the other particles but rather shifted about one-third of the particle diameter. To understand the mechanism of bilayer formation, particle behaviour at the surface and in the bulk of the spreading solvent is considered. The vertical shift and the bilayer formation are assisted by the momentous formation of two interfaces during spreading.

Amphiphilic spherical Janus particles (JPs) have a broken symmetry due to their surface chemical anisotropy that results in orientation-dependent inter-particle interactions.[1] Similar to molecular amphiphiles, Janus particles adsorb strongly to liquid interfaces, forming colloidal monolayers.[2–5] Their behaviour at an air/water (a/w) interface has recently been reported in a wide range of area fractions and compared with that of homogeneous particles.[6–9] The structure of these monolayers is governed by an interplay between van der Waals attraction, electrostatic (dipole–dipole) repulsion and capillary interaction, which is much stronger in the case of amphiphilic Janus particles.[6] The strength and specificity of particle interactions ensure dynamically arrested monolayers. While the structure of monolayers made of spherical isotropic or amphiphilic Janus colloids has already been studied, interfacial colloidal bilayer formation has not been observed before. Unlike naturally found bilayer structures made of amphiphilic molecules (e.g. cell membranes mainly made of phospholipid mixtures), colloidal bilayers can be made from amphiphilic and hydrophobic particles forming each

leaflet of such a bilayer. Thus, we suggest that bilayers made of a mixture of homogeneous and amphiphilic Janus colloids trapped at an air/water interface are rather different from their molecular counterparts, which once again reveals the rich organization behaviour of amphiphilic colloids.

Taking into account the behaviour of each species, the structure of their mixture should be governed mainly by their capillary interactions,[10,11] while the vertical position of each species should be determined by its three-phase contact angle. In contrast to the expected monolayer picture, in this Communication we demonstrate that the formed structures are bilayers in which JPs form the upper layer. At first glance, this contradicts their high interfacial activity and the expected a/w contact angle. Nevertheless, the situation becomes clear considering the mechanism of such a bilayer formation starting from particle spreading. Therefore, our most important questions are related to the structure and ordering of the bilayer and the discussion of its physical origin.

We use hydrophobic homogeneous particles produced by chemical modification of silica microspheres (3.13 μm, PDI = 2.11%) with dichlorodimethylsilane (DCDMS). Janus particles of type 1 (JP1) are prepared by modification of one hemisphere of clean silica spheres with DCDMS. Janus particles of type 2 (JP2) are prepared by attaching 3-aminopropyltriethoxysilane (APTES) to the hydroxyl groups of JP1. Rhodamine B isothiocyanate (RBITC) is coupled to the attached amino groups to allow particle fluorescence imaging.[6,12] The particles are deposited on a carefully cleaned a/w interface in a Langmuir trough. The images are recorded with a CCD camera and 20×, 40× or 63× objectives attached to an optical microscope (Carl Zeiss, Germany). To prepare a mixture, equal amounts of each species are weighed, mixed and dispersed in chloroform.

Fig. 1 shows the monolayers formed by mixtures of hydrophobic and Janus particles JP1. As can be seen from the images of Fig. 1(a) and (b), there are particles that look brighter and darker. This is due to the difference in their vertical z-positions. Bright particles are slightly shifted up as compared to the dark particles. Bright particles form hexagonally arranged islands similar to those formed by Janus particles alone.[6] Dark particles

[a] Instituto de Química, Universidad Nacional Autónoma de México, P. O. Box 70-213, 04510, Mexico City, Mexico. E-mail: akozina@unam.mx

[b] Instituto de Física, Universidad Nacional Autónoma de México, P. O. Box 20-364, 01000, Mexico City, Mexico

[c] Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, San Rafael Atlixco 186, 09340, Mexico City, Mexico

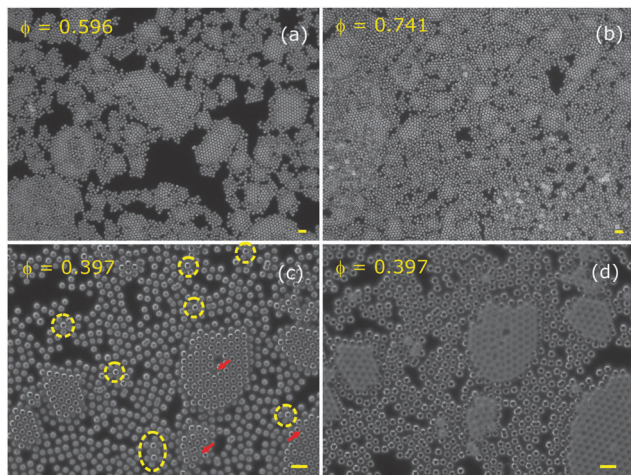† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7sm02418e

Fig. 1 Dark-field optical microscopy images of JP1/hydrophobic particle mixtures: (a) ϕ = 0.596, (b) ϕ = 0.741, (c) ϕ = 0.397, the upper layer is in focus and (d) ϕ = 0.397, the lower layer is in focus. The circles mark the "flowers" and the red arrows mark the "pillars" discussed in the text; scale bars = 10 μm.

are more disordered and are situated mainly around the islands, although one can often find a few dark particles encrusted in the bright domains. The higher magnification in Fig. 1(c) and (d) shows the two species more prominently by focusing each layer. The images confirm a vertical shift of the hexagonally ordered particles up relatively to the disordered ones. Taking into account the structures formed by Janus or homogeneous spheres alone,[6] this implies that Janus particles do not acquire their equilibrium position at the a/w interface according to their contact angle but rather move up. This sounds counter-intuitive: homogeneous hydrophobic particles have more contact with water than amphiphilic Janus spheres. Thus, there are at least two questions that arise: (1) how large is the z-shift in the bilayer? and (2) are Janus spheres really the ones shifted up?

To answer the first question a more precise z-stack experiment is performed. Fig. 2 shows the images of the monolayer taken by changing the focus from above and going deeper with a step of 1 μm. Movie S1 in the ESI,† shows the images taken with smaller z-steps. The dark particles in Fig. 2 are equivalent to the bright particles in Fig. 1. As one can see in Fig. 2(a), the dark particles are almost in focus, while the bright particles are completely out of focus. This image is the upper part of the bilayer. Focusing 1 μm deeper, Fig. 2(b), one observes the dark

particles well in focus, while the bright ones are slightly out of focus. As we go deeper, Fig. 2(c), the bright particles come into focus, while the dark ones go slightly out of focus. Finally, both species go out of focus in Fig. 2(d) but the dark particles are out of focus more strongly. Taking into account the particle diameter of 3 μm, the conclusion is that the dark particles are shifted up relatively to the bright ones and their displacement is about one-third of the particle diameter.

To identify Janus particles, fluorescent JP2 are used. Fig. 3 shows the images of the same a/w interface region observed in bright field and fluorescence modes as well as their overlap. In Fig. 3(a) and (d) we observe dark hexagonally packed domains surrounded by disordered bright particles, which indicates z-direction mismatch. Fig. 3(b) and (e) show fluorescent particles identified as labelled JP2 and black spots that correspond to non-fluorescent homogeneous spheres. The fluorescence intensity is different from one Janus particle to another, which indicates the difference in particle orientation. The preferable orientation is not clear taking into account possible internal refraction effects. Apparently, many orientations are present, indicating that a good fraction of particles are tilted from their equilibrium orientation, which is also observed for Janus particles alone (ESI†). Overlap of the two images indicates that the dark species seen in the bright-field is the fluorescent one and, therefore, these are Janus particles. As we saw before, the dark particles are the ones that are up-shifted in the layer; therefore, one concludes that Janus particles are shifted up relatively to the hydrophobic ones as we suspected in the beginning.

There is another question that arises, below Janus particles is there another layer of particles, or they are just shifted? Fig. 2 shows that the shift is smaller than a particle diameter, so one could assume that no particles are present below Janus spheres, although it is an indirect conclusion. To answer this question, the same interface region is observed from above (dark field) and from below (bright field) aligning two optical microscopes. Fig. 4 shows a selected region as seen under the two microscopes (another region is shown in the ESI†). As one can see in Fig. 4(a), there is a z-direction mismatch looking from above. Both bright and dark species can be focused. The brighter particles are the ones that are up-shifted, while the dark particles are shifted down relatively to the bright ones. The dark particles in Fig. 4(a) are also clearly focused by observing them from below in Fig. 4(b). The up-shifted particles looking from below, Fig. 4(b), are now darker and out of focus. The optical effects make it hard
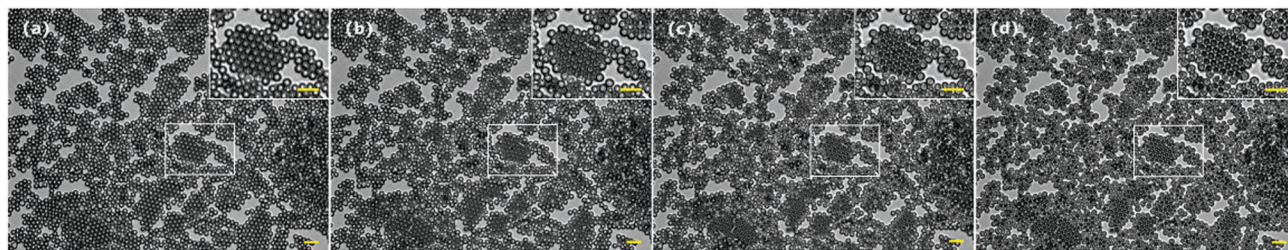

Fig. 2 Bright-field optical microscopy images of JP1/hydrophobic particle mixtures: (a) to (d) correspond to the change of the focal plane from up to down with a step of 1 μm. The insets show enlarged images of the selected area marked by the white rectangle. Scale bars = 10 μm.
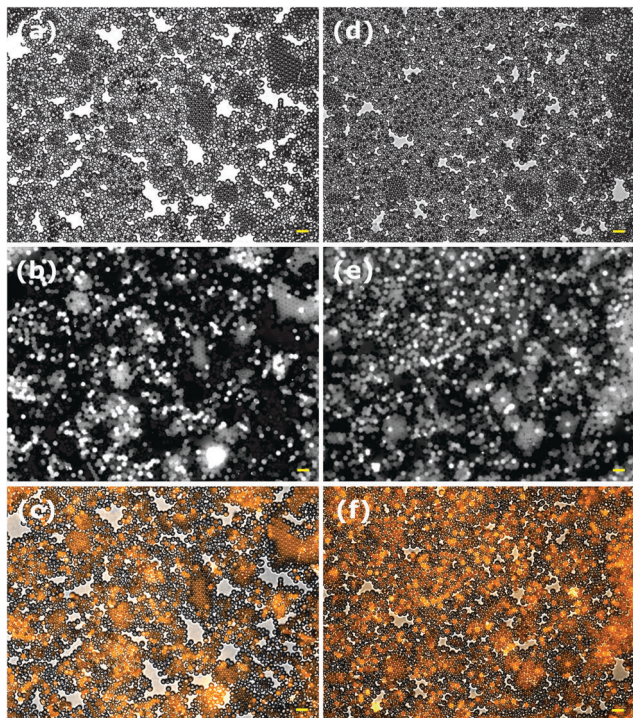
Fig. 3 Optical microscopy images of JP2/hydrophobic particle mixtures. Each column corresponds to a certain a/w interface region. (a) and (d) are bright-field images, (b) and (e) are fluorescence images, and (c) and (f) are overlaps of the bright-field and fluorescence adding an artificial colour to fluorescence. Scale bars = 10 μm.
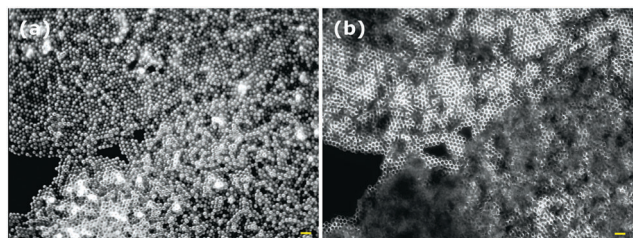

Fig. 4 Optical microscopy images of JP1/hydrophobic particle mixtures: (a) the dark-field image as seen from above; and (b) the corresponding bright-field image as seen from below. Scale bars = 10 μm.

to obtain a clearly focused image of them. This suggests that there are no additional particles below the up-shifted ones; otherwise, we would observe all the particles in focus looking from below. Therefore, Janus particles are not mounted on top of the other particles but rather only shifted up relatively to the hydrophobic ones.

Taking into account the previous observations, the main question to answer is, why Janus particles are shifted upwards as compared to the hydrophobic ones? We suggest the following. When particles are deposited on the water surface, they are spread in chloroform. Therefore, we should consider what occurs at the first moments of particle spreading. There are two interfaces that are formed: air/oil (a/o, oil = chloroform) and oil/water (o/w). The particles can be situated either at these two interfaces or in the bulk oil or water phases. The energy of interface desorption for Janus spheres is up to three times larger
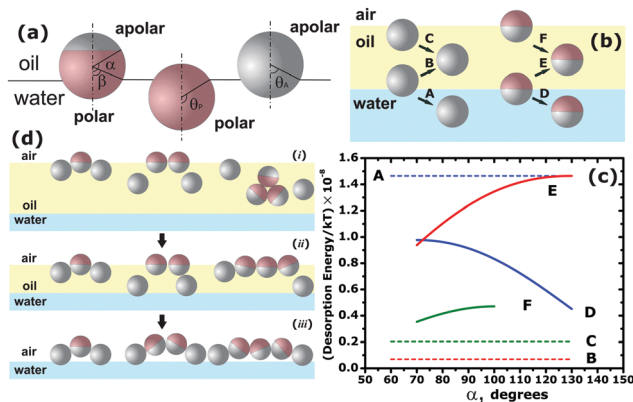

Fig. 5 (a) The positions of Janus, polar and apolar particles at an oil/water interface. Angle α defines the polar and apolar parts of the Janus sphere; β, θ_P and θ_A are the Janus, polar and apolar particle contact angles, respectively. (b) Schematic representation of the directions of desorption from the two interfaces towards the bulk phases for homogeneous hydrophobic (apolar) and amphiphilic Janus particles. (c) Desorption energy as a function of Janus geometry given by α. (d) Schematic representation of the particle behaviour on oil evaporation. (i) In the beginning, JPs are either at the a/o interface or in the bulk oil forming clusters, and hydrophobic particles are both at the a/o interface and in the bulk oil. (ii) JPs stay at the a/o interface or are trapped to it from the bulk clusters, and hydrophobic particles reach the o/w interface first. (iii) Janus and hydrophobic particles preserve their earlier configuration by freezing the structure at the a/w interface after complete oil evaporation.

than that for homogeneous particles.[4] Therefore, it is more probable to find Janus particles trapped at an interface than in the bulk phases. Calculations of the interface desorption energies based on the suggested method[4,13] for the homogeneous particles and JP1 used in this work are shown in Fig. 5 for both o/w and a/o interfaces; details are in the ESI.† Apolar and polar particle contact angles at the two interfaces used in the calculations are $\theta_P^{o/w} = 130°$, $\theta_A^{o/w} = 70°$, $\theta_P^{a/o} = 60°$, $\theta_A^{a/o} = 90°$ according to our observations and previously reported data.[14–16] As one can see in Fig. 5(c), the desorption energy of hydrophobic particles ($\alpha = 0$) from the o/w interface into water is rather high (A), while that into oil is much smaller (B). At the same time, the desorption energy of JPs from the same interface is high into both oil and water for $\alpha = 90°$ (JP1 case) (D and E). This indicates the preference of JPs to stay adsorbed to the o/w interface at the vertical position determined by their contact angle $\beta = \alpha$ rather than desorb into the bulk phases. This excludes the possibility for Janus particles to be first adsorbed to the o/w interface and then shifted up. Now consider particle desorption from the a/o interface into the oil phase (C and F). While the hydrophobic particles are easily desorbed, the Janus spheres prefer the interface rather than the bulk oil. Therefore, the homogeneous apolar particles may be situated both at the a/o interface and in the bulk oil, while Janus particles prefer the a/o interface until they touch the o/w interface. The fact that a good fraction of particles can be found at the a/o interface is confirmed by our experiments at the air/toluene interface (ESI,† toluene is used as an oil instead of chloroform to avoid rapid evaporation, at 20 °C $\gamma^{tol} = 28.4$ mN m^{-1} and $\gamma^{chl} = 27.5$ mN m^{-1}). The particles have a vertical mismatch in the monolayer due to the difference in their three-phase contact

angle, with Janus spheres shifted up relatively to the hydrophobic ones, indicating their larger contact angle.

When the spreading solvent rapidly evaporates, the layer of the oil phase quickly decreases. The particles that are preferably situated in the bulk oil arrive at the water interface first, and those particles are the hydrophobic ones as discussed above. At the o/w interface, the capillary attraction freezes the formed structure, arresting the particle dynamics, as discussed previously.[6] Janus particles arrive at the water interface after the hydrophobic ones, so they arrange under the influence of the latter, preserving the initial upper shift observed at the a/o interface. The whole structure freezes resulting in what we observe after the solvent evaporation. A simplified schematic picture of the process occurring is shown in Fig. 5(d). There are several observations that should also be mentioned. First, it is curious to find a lot of "flower-like" structures made of a Janus sphere surrounded in the lower layer by five homogeneous particles, Fig. 1 and the ESI.† This is probably due to the fact that such a "flower-like" ensemble results in a net interface deformation in such a way that any other homogeneous particle would experience capillary repulsion.[10,11] Therefore, the six-fold symmetry is broken and a distorted five-fold symmetry is observed. This speaks in favour of the probable contact between water and Janus particles. Second, even large domains made of Janus spheres frequently have hydrophobic particles as "pillars" (Fig. 1 and the ESI†); these are probably the ones that got trapped among the remaining Janus particles starting from the a/o interface. Third, it is very rare to observe Janus spheres in the lower layer (ESI†), which indicates that the assembly is quite selective. Although Janus particles are preferentially situated at the a/o interface, obviously, there must be some of them in the bulk oil. We suggest that the selectivity is observed for the following reasons. First, the solvent evaporation is very fast, so that the a/o interface would decrease more rapidly than the particle diffusion. Therefore, the kinetics of the process favour particle trapping to the a/o interface and hinder their rearrangement. Janus particles that might still be situated in the bulk oil are expected to cluster, forming something similar to micelles with the hydrophilic groups pointing inside, similar to those observed before.[17–20] On the overall particle crowding due to solvent evaporation, the clustering slows down particle diffusion, hindering their further way to the o/w interface. Therefore, hydrophobic particles, again, are the faster ones to adsorb to the o/w and eventually to the a/w interface. Second, it has been shown that the spreading of the volatile solvent at the water surface produces a convective fluid circulation at the edge of the advancing front,[21] which may also favour particle flow towards the a/o interface. Interestingly, the use of toluene as a spreading solvent does not result in bilayer formation (ESI†), which speaks in favour of the critical role of the evaporation kinetics.

We report the formation of a mixed bilayer made of homogeneous and Janus particles, with the latter forming the upper level. The mechanism of the bilayer formation is explained in terms of preferential adsorption of Janus particles to the a/o interface and the competition between the spreading solvent evaporation and particle diffusion. The resulting structure is frozen due to the strong inter-particle capillary attraction.

The study opens up the possibility of creation of novel colloidal membranes at larger length-scales using an appropriate system.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 A. Walther and A. H. E. Müller, *Chem. Rev.*, 2013, **113**, 5194.
2 C. Casagrande, P. Fabre, E. Raphaël and M. Veyssié, *Europhys. Lett.*, 1989, **9**, 251.
3 T. Ondaruhu, P. Fabre, E. Raphaël and M. Veyssié, *J. Phys.*, 1990, **51**, 1527.
4 B. P. Binks and P. D. I. Fletcher, *Langmuir*, 2001, **17**, 4708.
5 N. Glaser, D. J. Adams, A. Böker and G. Krausch, *Langmuir*, 2006, **22**, 5227.
6 A. Kozina, S. Ramos, P. Díaz-Leyva and R. Castillo, *J. Phys. Chem. C*, 2016, **120**, 16879.
7 B. J. Park, T. Brugarolas and D. Lee, *Soft Matter*, 2011, **7**, 6413–6417.
8 J. Lenis, S. Razavi, K. D. Cao, B. Lin, K. Y. C. Lee, R. S. Tu and I. Kretzschmar, *J. Am. Chem. Soc.*, 2015, **137**, 15370–15373.
9 L. C. Bradley, W.-H. Chen, K. J. Stebe and D. Lee, *Curr. Opin. Colloid Interface Sci.*, 2017, **30**, 25.
10 D. Stamou, C. Duschl and D. Johannsmann, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **62**, 5263–5272.
11 H. Rezvantalab and S. Shojaei-Zadeh, *Soft Matter*, 2013, **9**, 3640–3650.
12 L. C. Mugica, B. Rodríguez-Molina, S. Ramos and A. Kozina, *Colloids Surf., A*, 2016, **500**, 79.
13 S. Jiang and S. Granick, *J. Chem. Phys.*, 2007, **127**, 161102.
14 B. P. Binks and J. H. Clint, *Langmuir*, 2002, **18**, 1270.
15 A. Maestro, L. J. Bonales, H. Ritacco, R. G. Rubio and F. Ortega, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14115.
16 C. Chen, N. Zhang, W. Li and Y. Song, *Environ. Sci. Technol.*, 2015, **49**, 14680.
17 F. Sciortino, A. Giacometti and G. Pastore, *Phys. Rev. Lett.*, 2009, **103**, 237801.
18 G. Rosenthal, K. E. Gubbins and S. H. L. Klapp, *J. Chem. Phys.*, 2012, **136**, 174901.
19 L. Hong, A. Cacciuto, E. Luijten and S. Granick, *Langmuir*, 2008, **24**, 621–625.
20 A. Kirillova, G. Stoychev, L. Ionov and A. Synytska, *Langmuir*, 2014, **30**, 12765.
21 A. D. Dussaud and S. M. Troian, *Phys. Fluids*, 1998, **10**, 23.