

## Electric Field Driven Hierarchical Self-assembly of Monolayers of Mixtures of Particles

N. Musunuri<sup>1</sup>, K. Shah<sup>1</sup>, M. Hossain<sup>2</sup>, S.K. Gurupatham<sup>1</sup>, E. Amah<sup>1</sup>, I. Fischer<sup>1</sup> and P. Singh<sup>1</sup>

<sup>1</sup>Department of Mechanical and Industrial Engineering  
New Jersey Institute of Technology, Newark, NJ 07102

<sup>2</sup>Department of Engineering Technology  
Queensborough Community College, CUNY, Bayside, New York

### ABSTRACT

We numerically study the self-assembly process of particle mixtures on fluid-liquid interfaces when they are subjected to an electric field in the direction normal to the interface. The electric and capillary forces that result cause particles to self-assemble into molecular-like hierarchical arrangements consisting of composite particles arranged in a pattern.

### INTRODUCTION

In recent years, many studies have been conducted to understand the behavior of particles trapped at fluid-liquid interfaces because of their importance in a range of physical applications and biological processes, e.g., formation of pollen and insect egg rafts, self-assembly of particles at fluid-fluid interfaces resulting in novel nano structured materials, stabilization of emulsions, and the formation anti-reflection coatings for high-efficiency solar cells, photonic crystals and biosensor arrays<sup>1-4</sup>.

Particles trapped in fluid-liquid interfaces interact with each other via lateral capillary forces that arise because of their weight, and when present also by other forces such as electrostatic forces, to form monolayer arrangements<sup>5-9</sup>. A common example of capillarity-driven self-assembly is the clustering of breakfast-cereal flakes floating on the surface of milk. The deformation of the interface by the flakes

gives rise to lateral capillary forces which cause them to cluster.

Capillarity-driven self-assembly produces monolayers which have defects and lack long-range order, and for monolayers containing two or more different types of particles, which is the focus of this paper, the technique does not allow for any control of the particle-scale structure as capillary forces simply cause particles to cluster.

It was recently shown that monolayers containing two or more types of particles with different dielectric properties can be self-assembled by applying an electric field in the direction normal to the interface<sup>9</sup>. The technique exploits the fact that the lateral dipole-dipole force between two particles can be repulsive or attractive depending on their polarizabilities and that the intensity of the force can be varied by selecting suitable upper and lower fluids. The force is repulsive when both particles are positively or negatively polarized, but attractive when one particle is positively polarized and the other is negatively polarized. The force also depends on the sizes of the particles and the electric field intensity.

The differences in the polarizabilities and sizes of the particles derive a hierarchical self-assembly process analogous to that which occurs at atomic scales. First, groups of particles combined to form composite particles (analogous to molecules) and then

these composite particles self-assembled in a pattern (like molecules arrange in a material). The force between similar particles was repulsive (because they have the same polarizabilities), and so they moved apart which allowed particles that attract to come together relatively unhindered to form composite particles. The net force among the particles forming a composite particle was attractive, and so after a composite particle was formed it remained intact while the electric field was kept on.

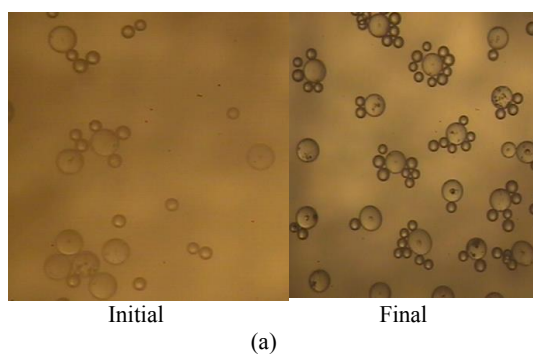
The energy needed for a particle to desorb from a fluid-liquid interface is several orders of magnitude larger than the thermal energy, and therefore, once nano-to-micron sized particles are adsorbed they remain adsorbed while moving laterally in the interface in response to lateral capillary and dipole-dipole forces. Furthermore, since particles trapped in a fluid-liquid interface are free to move laterally, they self-assemble even when the lateral forces driving the assembly are small. The only resistance to their lateral motion is hydrodynamic drag which can slow the motion but cannot stop it. This is obviously not the case for a monolayer assembled on a solid substrate since particles are not free to move laterally because of the presence of adhesion and friction forces. In fact, very-small particles do not self-assemble even on a fluid-liquid interface when lateral capillary forces become smaller than Brownian forces. For example, on an air-water interface, lateral capillary forces in the absence of an electric field become smaller than Brownian forces for particles smaller than about 10  $\mu\text{m}$ , and so particles smaller than this limiting size undergo Brownian motion on the interface and do not cluster<sup>10</sup>. However, when a sufficiently strong electric field is applied the electrically induced lateral forces remain stronger than Brownian forces making self-assembly of nano-particles possible.

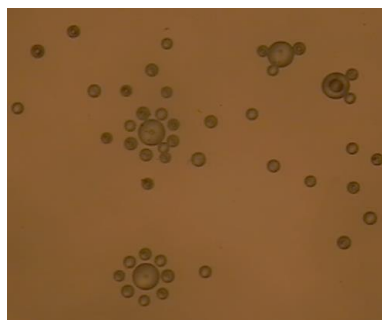
## SELF-ASSEMBLY OF MONOLAYERS OF MIXTURES OF PARTICLES

A monolayer of a mixture of particles on an air-liquid interface was formed by sprinkling the mixture onto the liquid surface, and then covering the chamber with a transparent upper electrode and applying an electric field to derive the self-assembly process.

Three distinct size dependent regimes were identified for the mixtures of glass and copolymer particles on corn, castor and silicone oils<sup>9</sup>. Glass particles were positively polarized and copolymer particles were negatively polarized which was ensured by selecting suitable lower and upper fluids.

When glass particles were about two times larger than copolymer particles, the former attracted the copolymer particles to form composite particles on a mixture of corn and castor oils (see Fig. 1a). These composite particle consisted of a glass particle at the center which was surrounded by a ring of copolymer particles. In this case, the spacing between the composite particles increased with increasing electric field intensity, but the spacing between the copolymer particles in the rings remained unchanged. However, when the monolayer was formed on the surface of silicone oil the particles on the rings did not touch as they were more intensely polarized than in the mixture of corn and castor oils.



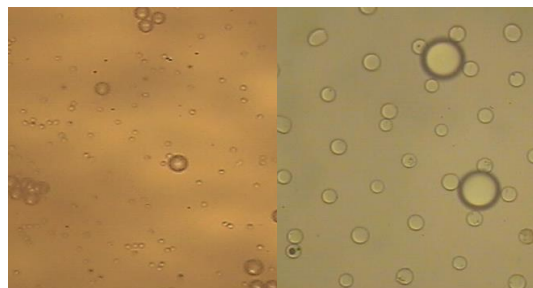


(b) Figure 1. Monolayers of mixtures of 71  $\mu\text{m}$  copolymer and 150  $\mu\text{m}$  glass particles. The magnification is 50X. (a) On the surface of a 30% castor oil and 70% corn oil mixture. The applied electric field was 5000 V. (b) On the surface of a silicone oil. The applied electric field was 5300 V.

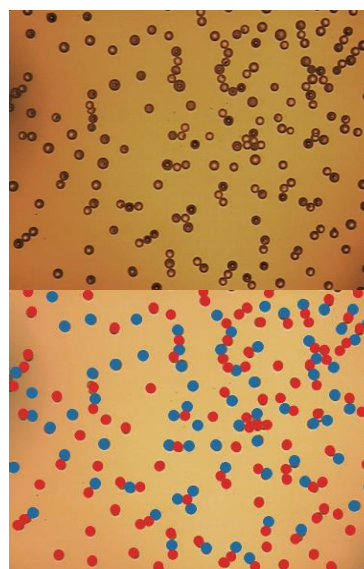
A second regime was obtained when the size of glass particles was about three times smaller (see Fig. 2). Although smaller in size, the glass particles formed a triangular lattice in which the copolymer particles were imbedded, as the former were more intensely polarized and repelled each other more strongly. The copolymer particles attracted nearby glass particles to form composite particles. In this regime the intra-composite particle forces were weaker than for the first regime. The particles forming the rings did not touch each other and interacted strongly with the lattice of glass particles. In fact, some of the glass particles escaped from the rings to occupy positions in the lattice when the field strength was increased above a critical value. The number of particles in the ring of copolymer particle decreased as the electric field intensity was increased.

A third regime was obtained when the sizes of glass and copolymer particles were comparable (see Fig. 2). Here instead of forming ring-like arrangements, particles arranged in chains in which the positively and negatively polarized particles alternated. In some instances, the chains contained sub-branches. This formation of chains is analogous to the formation of long chained

polymeric molecules, except that the former were formed by particles in two dimensions on the surface of a liquid.



Initial Final  
Figure 2. Monolayers of mixtures of 20  $\mu\text{m}$  glass and 71  $\mu\text{m}$  copolymer particles formed on the surface of a 30% castor oil and 70% corn oil mixture. The magnification for the first photograph is 50X and for the second 200X. The electric field was 5300 V.



● 63  $\mu\text{m}$  glass particles  
● 71  $\mu\text{m}$  copolymer particles

Figure 3. Monolayer of a mixture of 63  $\mu\text{m}$  glass and 71  $\mu\text{m}$  copolymer particles on the surface of silicone oil. The magnification is 50X. The graphical representation (lower image) of the monolayer showing glass and copolymer particles in different colors is also included.

## NUMERICAL SIMULATIONS OF SELF-ASSEMBLY

We numerically simulated the above regimes by solving the governing time dependent equations for the motion of particles. In these simulations, the particles and fluids properties were held fixed and only the sizes of the particles were changed.

Let us assume that there are  $n$  particles in a monolayer. To numerically simulate the self-assembly process, we compute the total lateral force on particle  $i$  due to the dipole-dipole interactions and the lateral capillary forces with the other particles by a pair-wise addition of the interaction forces. The total lateral force on particle  $i$  (in spherical polar coordinates) is given by

$$\mathbf{F}_i = \sum_{j=1, j \neq i}^n \left( -\frac{w_i w_j \mathbf{e}_{ij}}{2\pi\gamma r_{ij}} + \frac{3p_i p_j \mathbf{e}_{ij}}{4\pi\epsilon_o \epsilon_L r_{ij}^4} \right) \quad (1)$$

Here  $\mathbf{e}_{ij}$  is the unit vector from the center of particle  $i$  to the center of particle  $j$ , and  $r_{ij}$  is the distance between the centers of particle  $i$  and particle  $j$ . Here  $w_i$  and  $w_j$  are the vertical forces acting on the  $i^{\text{th}}$  and  $j^{\text{th}}$  particles,  $p_i$  and  $p_j$  is the induced dipole moment of  $i^{\text{th}}$  and  $j^{\text{th}}$  particles,  $\epsilon_o$  is the permittivity of free space,  $\epsilon_L$  is the permittivity of the lower liquid, and  $\gamma$  is the interfacial tension.

The particle also experiences a drag force when it moves in a fluid-liquid interface under the action of the above inter-particle forces. Since the particle velocity during the self-assembly process remains small, we can use the Stokes equation to estimate the drag

$$\mathbf{F}_{di} = -6\pi\mu\xi a_i \mathbf{u}_i, \quad (2)$$

where  $\mu$  is the viscosity of the lower fluid,  $\mathbf{u}_i$  is the velocity, and  $\xi$  is a parameter which accounts for the fact that the particle is immersed in both upper and lower fluids [4]. The drag force becomes zero after the particles of the monolayer reach their equilibrium positions and stop moving.

The momentum equation of particle  $i$  can be obtained by setting the force equal to the sum of Eq. 1 and Eq. 2

$$m_i \frac{d\mathbf{u}_i}{dt} = \sum_{j=1, j \neq i}^n \left( -\frac{w_i w_j \mathbf{e}_{ij}}{2\pi\gamma r_{ij}} + \frac{3p_i p_j \mathbf{e}_{ij}}{4\pi\epsilon_o \epsilon_L r_{ij}^4} \right) - 6\pi\mu\xi a_i \mathbf{u}_i, \quad (3)$$

where  $m_i$  is the effective mass of the  $i^{\text{th}}$  particle which includes the added mass contribution. The above system of equations for  $n$  particles was discretized using a second order scheme in time. A hard sphere potential was used to avoid overlapping of the particles.

The self-assembly process was simulated by placing  $n$  particles on a regular grid, and then these positions were moved randomly such that the particles did not overlap. The equations were integrated in time until a stable monolayer arrangement was obtained.

The parameters for our simulations have been selected to match the values in our experiments. For particle mixtures adsorbed on the corn oil surface, the fluid and particle properties appearing in the equations were:  $\epsilon_a = 1.0$ ,  $\epsilon_L = 2.87$ ; the dielectric constants of glass and copolymer particles were 6.5 and 2.5, respectively; and the density of glass and copolymer particles were 2.5 and 1.05, respectively. The corn oil viscosity was assumed to be 65 cP. Based on these values, the theoretical estimates of the Clausius-Mossotti (CM) factors of the particles were  $\beta_1 = 0.297$  and  $\beta_2 = -0.045$ . Here the subscripts "1" and "2" refer to glass and copolymer particles respectively. The values of the remaining parameters were estimated to be  $fv_1 = 0.1$ ,  $fv_2 = 0.1$ ,  $fb_1 = 1.5$ ,  $fb_2 = 0.05$  and  $\xi = 0.5$  (see [4]). The particle sizes were assumed to be equal to the values in our experiments and the electric field strength  $E_0$  was obtained in terms of the applied voltage ( $V$ ) and the gap between the electrodes ( $L$ ). Using these parameter

values, the values of  $p_1$ ,  $p_2$ ,  $w_1$  and  $w_2$  were obtained.

The number of particles in our simulations was held fixed at 144, but the ratio of the number of positively to negatively polarized particles was varied. For the results presented in Figs. 4-6, all of the parameter values were held fixed and *only* the particle sizes were varied. The lengths have been nondimensionalized such that the size of larger particles is 0.1. The diameter of circles used to represent particles is proportional to the size of the particles.

The three distinct size dependent regimes identified in our experiments for the mixtures of glass and copolymer particles on corn oil were also found in our numerical simulations. In Fig. 4, the larger sized particles were positively polarized (the same properties as of the glass particles in our experiments) and the smaller particles were negatively polarized (the same properties as of the copolymer particles in our experiments). The larger sized particles attracted the smaller ones to form composite particles similar to those seen in the experiments (see Fig. 1). Also, as in our experiments, the spacing between the composite particles increased with increasing electric field intensity, while the spacing between the copolymer particles in the rings remained unchanged. This agreement is good considering the fact that approximations were made in modelling the forces and a pair-wise addition was used to obtain the total particle-particle force.

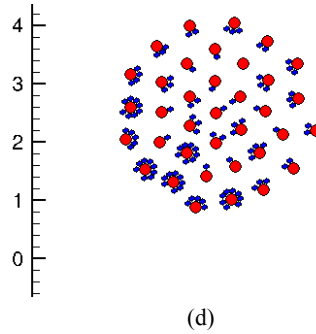
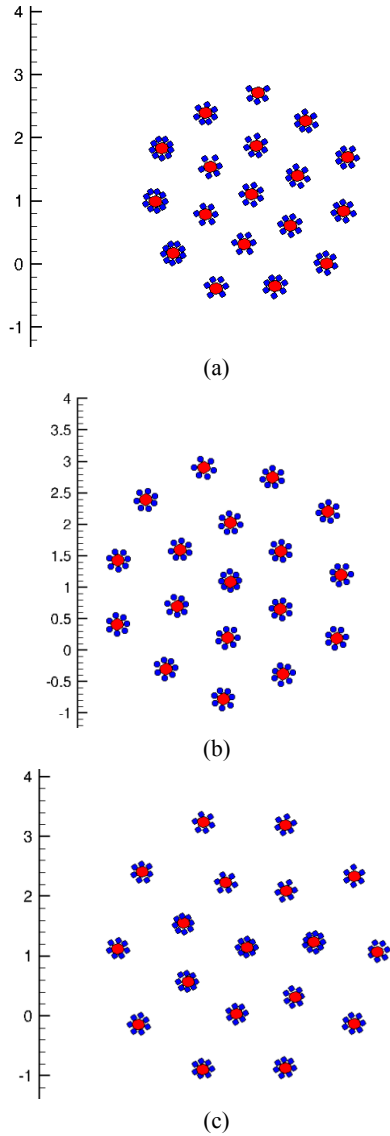
In Fig. 4d, we consider the case where the ratio of the number of small to larger particles is 3:1 and so there were not enough smaller particles to form complete rings around all of the larger particles. Also, we placed a higher concentration of smaller particles near the left and bottom sides. Notice that the composite particles in this case contain fewer particles and the number of particles in the rings of composite

particles farther away from the left and bottom sides is smaller. This shows that to obtain composite particles with uniform composition that the mixture should be uniformly mixed.

Fig. 5 shows a case in which the smaller sized particles were more intensely polarized. This case corresponds to Fig. 2 where glass particles were about three times smaller than less intensely polarized copolymer particles. As in the experiments, the smaller particles formed a triangular lattice in which the larger particles were imbedded. The larger particles attracted nearby smaller particles in the lattice and together they formed composite particles. The number of smaller particles in the composite particles varied between 3 and 5 depending on the electric field intensity, which also agrees with the experimental results. We also varied the electric field intensity to investigate the strength of intra-particle forces. When the electric field strength was increased to 700 kV/m a smaller sized particle escaped from the rings reducing the number of particles to 4. The escaped particles were absorbed in the lattice which expanded to accommodate them. In this regime the intra-composite particle forces were weaker than in the first regime and the particles forming the rings did not touch each other.

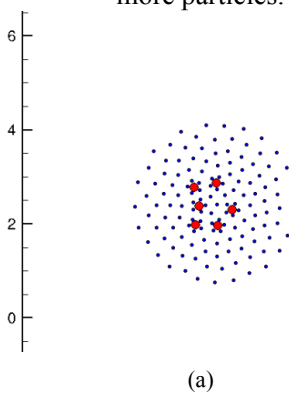
Fig. 6 shows a third regime for which the sizes of positively and negatively polarized particles were comparable. In this case, instead of forming ring-like arrangements, the particles arranged in chains in which the positively and negatively polarized particles alternated. Initially, the particles formed doublets of positively and negatively particle, and then these doublets merged to form longer chains. These simulation results are similar to those shown in Fig. 3 for a mixture of glass and polymer particles. Notice that particles came together with time to the equilibrium spacing. The exact distribution

depended on the initial distribution of particles. This shows that when the positively and negatively polarized particles are of the comparable sizes they self-assemble to form particle chains.



(d)

Figure 4. Numerical simulation of self-assembly of mixtures of particles on liquid surfaces. The parameters were selected to match 71  $\mu\text{m}$  copolymer and 150  $\mu\text{m}$  glass particles on corn oil. The applied electric field was 560 kV/m in (a), 700 kV/m in (b), 840 kV/m in (c), and 500 kV/m in (d). The ratio of the number of small to larger particles was 7:1 in (a)-(c) and 3:1 in (d). The scale is for reference to show how the monolayer expands or shrinks with the electric field intensity. Notice that the distance between the composite particles increased with increasing electric field intensity, but the number of particles in the rings of the composite particles remained constant. In (d) a larger fraction of particles were initially near the left and bottom sides. Notice that since there were not enough small particles and that their concentration was initially larger near the left and bottom sides, the particle rings in this region contain more particles.



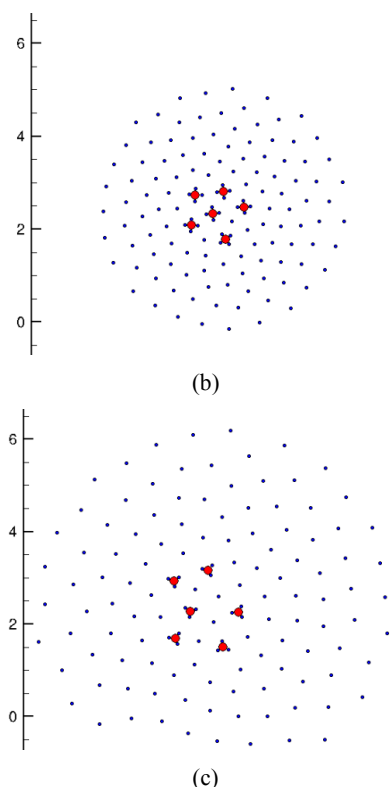


Figure 5. Numerical simulation of self-assembly of mixtures of particles on liquid surfaces. The parameters have been selected to match 71  $\mu\text{m}$  copolymer and 20  $\mu\text{m}$  glass particles on corn oil. The applied electric field was 530 kV/m in (a), 700 kV/m in (b), and 900 kV/m in (c). The ratio of the number of small to larger particles is 15:1. The scale is for reference to show how the monolayer expands or shrinks with the electric field intensity. Notice that the number of particles in the rings of composite particles decreased from 5 to 3 with increasing electric field intensity. The inter-particle spacing for the smaller particles increased with increasing electric field intensity, but the composition of composite particles changed only when the electric field intensity was increased above the threshold values. These results are in agreement with the experimental results shown in Fig. 2.

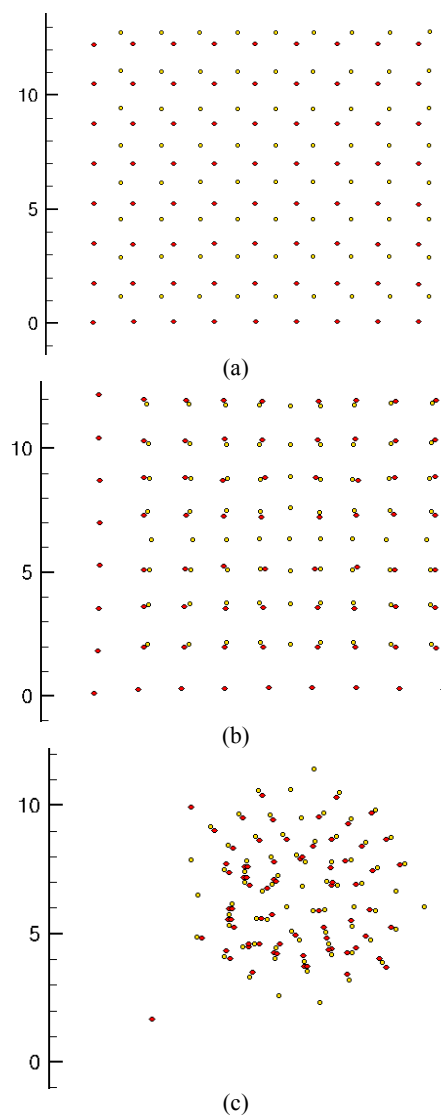


Figure 6. Numerical simulation of self-assembly of mixtures of particles on liquid surfaces. The parameters have been selected to match 71  $\mu\text{m}$  copolymer (red) and 63  $\mu\text{m}$  glass (yellow) particles on corn oil. The applied electric field was 500 kV/m. The ratio of the number of small to larger particles is 1:1. (a) Initial distribution, (b) intermediate distribution, and (c) final distribution. The two types of particles were placed on a periodic lattice. They rearranged to form doublets and then these doublets merged to form longer chains. These results

are in agreement with our experimental results shown in Fig. 3.

#### CONCLUSION

In conclusion, our numerical simulations show that the theoretical model given by Eq. 3 correctly captures the underlying physics of the self-assembly process. As for the experiments, the particle and fluid properties for the numerically simulated monolayers were the same and only the particle sizes and the electric field intensities were varied to obtain the three hierarchical monolayer arrangements.

#### ACKNOWLEDGMENTS

The work was supported by the National Science Foundation grants (Award # CBET-1067004 and CBET-1236035).

#### REFERENCES

1. Binks, B.P. (2002), "Particles as surfactants -similarities and differences", *Current opinion in Colloid and Interface Science*, **7**, 21-41.
2. Blanco, A., et al. (2000), "Large-scale synthesis of a silicon photonic crystal with a complete three-dimensional bandgap near 1.5 micrometres", *Nature*, **405**, 437-440.
3. Janjua, M., Nudurupati, S., Singh, P. & Aubry, N. (2011), "Electric field induced self-assembly of micro- and nanoparticles of various shapes at two-fluid interfaces. Electrophoresis", **32**, 518-526.
4. Cox, P. A. (1989), "Hydrophilous pollination", *Annu. Rev. Ecol, Syst.*, **19**, 261-280.
5. Kralchevsky, P.A. Paunov, V.N. Ivanov, I.B. & Nagayama, K., (1992), "Capillary Meniscus Interactions between Colloidal Particles Attached to a Liquid - Fluid Interface", *J. Colloid Interface Sci.*, **151**, 79-94.
6. Nikolaidis, M.G. et al. (2002), "Electric field induced capillary attraction between like-charged particles at liquid interfaces", *Nature*, **420**, 299-301.
7. Singh, P. & Joseph, D.D. (2005), "Fluid dynamics of Floating particles", *J. Fluid Mech.*, **530**, 31-80.
8. Singh, P., Joseph, D.D. & Aubry, N. (2010), "Dispersion and attraction of particles floating on fluid-liquid surfaces. *Soft Matter*", **6**, 4310-4325.
9. Singh, P., et al. (2014), "Molecular-like hierarchical self-assembly of monolayers of mixtures of particles", *Scientific Reports*, **4**, 7427.
10. Lucassen, J. (1992), "Capillary forces between solid particles in fluid interfaces", *Coll. Surf.* **65**, 131.