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**Colloidal particles at liquid interfaces**

Guest Editor: Professor B. P. Binks

Please take a look at the full [table of contents](#) for this issue

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**Papers in this issue include:**

*Stepwise interfacial self-assembly of nanoparticles via specific DNA pairing*
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DOI: [10.1039/b709123k](http://10.1039/b709123k)
Fabrication of magnetically-functionalized lens- and donut-shaped microparticles by a surface-formation technique†

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We report a simple method for the preparation of magnetically-functionalized lens-like and donut-shaped polymeric microparticles, based on spreading a magnetite-doped paraffin–polymer solution at the air/water interface in the presence of an external magnetic field. We examine the parameters that affect the particle morphology and interfacial aggregation behaviour.

Anisotropic microparticles have been a subject of considerable interest over the past few years.1 Particle anisotropy may arise from their (non-spherical) shape and/or non-uniform surface properties. In both cases, their physical properties differ from those of isotropic particles, making them potentially useful for assembling photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and electrorheological fluids.1,2 Other applications of anisotropic colloids include the control of suspension rheology and optical properties,2,3 stabilization of emulsions4 and foams5 and engineering of biomaterials6 and complex colloidal composites.7 A range of techniques for the fabrication of anisotropic particles have been developed, including micro-contact printing,8 lithography-based micro-stamping,9 clusterization of microspheres10 or partial coating of particle monolayers,11 micro-fluidics,12 electrohydrodynamic jetting13 and controlled nucleation and precipitation.14 Formation of non-spherical particles from emulsion templates is opposed by the interfacial tension, which favours spherical shapes at all length scales. Recently, “in bulk” preparation of anisotropic polymeric particles from emulsions has been reported by deforming droplets in a stretched gel matrix during polymerization,15 by solvent attrition of polymer solution droplets in shear flow,16 and by using liquid crystal droplets in surfactant director fields.17 Other successful “in bulk” techniques focus on directed crystallization of supercooled emulsions in an electric field,18 swelling of seed polymer particles in monomer solutions19 or controlled phase separation in seeded polymerization,20 and evaporation of aqueous latex suspension droplets deposited onto the surface of fluorinated oil.21 Here, we present a simple methodology which allowed us to produce anisotropic microparticles of several different morphologies. Solid lens-like microparticles can be produced by spreading liquid monomer (or a polymer melt) on the surface of another immiscible liquid (e.g., water). At equilibrium, it will form either a film or particles with the lens morphology, depending on the relative magnitude of the three interfacial tensions, which can be tuned using surfactants. These lenses can subsequently be solidified or polymerized.

The experimental procedure, which enables attainment of different morphologies, is as follows. We formed 3–10% w/w solutions of a polymer melt of controlled melting temperature \( T_m \) (paraffin–ceresin, \( T_m = 55 \) °C, from Sigma) in a spreading solvent that is fully miscible with water (isopropanol 99%, from Fisher Chemicals, Ltd). The spreading solution was pre-heated to a temperature slightly exceeding the \( T_m \) and a few drops of it were deposited with a syringe onto the surface of a pre-heated aqueous surfactant solution in a vapour-saturated, thermostatized cell. The following surfactants were used: 3–10 mM sodium dodecylbenzosulfonate (SBDS), from Sigma, 1–2 mM hithenol BC-20, from Montello, Inc. USA, both being over the critical micelle concentration. Once the spreading solution is deposited, the solvent evaporates and diffuses into the subphase, leading to an increase of the melt (paraffin–ceresin) concentration in the spreading film. Under the conditions of our experiment, the film breaks up and forms a large number of microdrops. If, at this stage, the subphase temperature \( T \) is higher than \( T_m \), these microdrops attain the equilibrium lens shape and can subsequently be solidified by cooling the subphase, yielding particle morphologies that reflect the crystalline nature of the paraffin. If the temperature of the aqueous sub-phase is well below \( T_m \), the melt solidifies before attaining equilibrium and the final shape of the micro-particles is the result of “freezing in” kinetic effects during solvent attrition. Another important factor affecting the particle morphology is the paraffin–polymer concentration \( c \) in the spreading solution, which determines the kinetics of spreading and solvent attrition. We found that at low values of \( c \), the solution is further spread out before film break-up and/or solidification due to the occurrence of solvent attrition. At \( T \leq T_m \), \( c \) affects both particle size and morphology, while at \( T > T_m \) the value of \( c \) affects only the particle size.

Fig. 1 shows optical micrographs of a range of typical microparticle morphologies, obtained by spreading polymer solutions of different concentrations onto aqueous subphases at different temperatures, at fixed surfactant concentration (SBDS, 10 mM). The 3 rows of images in Fig. 1 correspond...
to 3 different values of the subphase temperature: $T = 53 \, ^\circ\text{C}$, $T = 55 \, ^\circ\text{C}$ ($= T_m$) and $T = 57 \, ^\circ\text{C}$, respectively. For both concentrations of the paraffin melt, the shape of the obtained microparticles varies from irregular flat micro-lenses at $T = 53 \, ^\circ\text{C}$ to donut-like shapes at $T = 55 \, ^\circ\text{C}$ to hexagons at $T = 57 \, ^\circ\text{C}$, and the average particle size decreases with increasing $T$. At $c = 10\%$, we observe the formation of larger micro-lenses and hexagons compared to these at low paraffin concentration ($c = 3\%$). At $T = T_m$ and low paraffin concentration we obtain neat donuts, while at higher paraffin concentration ($c = 10\%$), particles of intermediate shapes between circular and hexagonal donuts were produced. How the lens shape responds to changing the surfactant concentration is difficult to evaluate from these initial experiments, since both the surfactant concentration and the temperature affect the three-phase contact angle of the micro-lenses in dynamic conditions (during the solvent attrition and evaporation).

Images of paraffin micro-donuts with triangular symmetries that were obtained at $T = T_m$ and polymer concentrations $c = 3\%$ are shown in Fig. 2. In these experiments, a mixture of 5 mM SDBS and 2 mM hithenol BC-20 was used as the aqueous subphase. We stained the paraffin solution with 10% w/w perylene (from Sigma) to explore the 3D structure of the obtained microparticles. The fluorescence microscopy images (the 2nd row in Fig. 2) show that the perylene has concentrated in the inner part of the microparticle, indicating that it has dried last during the evaporation of the spreading solvent. The size distribution of these microparticles was measured using laser diffraction method (average diameter is $\sim 20 \, \mu\text{m}$) and this was compared with that estimated from optical microscopy (average diameter $\sim 18 \, \mu\text{m}$) and was found to be consistent with each other. The microparticles are polydisperse with different morphologies (see the ESI for more images†).

The anisotropic particles obtained in this way can be easily functionalized by embedding various nanocolloids (e.g., magnetic particles or semiconductor nanocrystals) into the paraffin–polymer melt. We demonstrated this by using magnetite nanoparticles to produce anisotropic magnetic microlenses and micro-donuts, which are susceptible to magnetically-driven manipulation and/or self-organization. Magnetite nanoparticles were prepared as follows: 8.11 g FeCl$_2$·4H$_2$O, 19.88 g FeCl$_3$, 5 mL 5 M HCl and 40 mL milliQ water were mixed in a 100 mL flask followed by heating to 40 °C until complete dissolution of the salts followed by precipitation with 30% ammonia solution. The magnetite residue was filtered.

**Fig. 1** Optical microscope images of typical microparticles of various morphologies produced by spreading an isopropanol solution of paraffin–ceresin at different temperatures of the aqueous sub-phase (10 mM SBDS). Column (A) corresponds to 3% w/w paraffin–ceresin; column (B) to 10%. All scale bars are 20 μm.

**Fig. 2** Optical microscope images of donut-shaped microparticles produced by spreading an isopropanol solution of paraffin–ceresin doped with perylene onto an aqueous solution of (A) 5 mM SDBS and (B) 2 mM hithenol BC-20 at $T = T_m = 55 \, ^\circ\text{C}$. The second row shows the corresponding fluorescence images with filter set for perylene. Scale bars are 20 μm.
and washed with milliQ water followed by hydrophobization with 5% oleic acid in acetone (both from Sigma) at 50 °C for 30 min. These hydrophobized magnetite particles were washed with isopropanol, then added to the spreading solution, at a concentration of 10% w/w with respect to the paraffin content; the resulting suspension was used to form microparticles on the surface of the aqueous phase as described earlier. Since each of the magnetite nanoparticles carries a permanent dipolar magnetic moment, the magnetic properties of the resulting microparticles depend on the state of alignment of the magnetite nanoparticles within the paraffin matrix.

We demonstrate that the extent and the direction of this alignment depend on the conditions during particle formation. To explore this, microparticles were formed from the magnetite suspension in isopropanol–paraffin solution under the following conditions: (1) exactly as described before, i.e., in the absence of an external magnetic field $B_{\text{ext}}$, and (2) subjecting the interface to a magnetic field $B_{\text{ext}}$ during spreading and solidification of the paraffin particles, by placing the thermostated spreading cell between the poles of two permanent magnets. The experiment was conducted in two different ways: (a) with the direction of the external magnetic field $B_{\text{ext}}$ perpendicular to the air/water interface, and (b) with $B_{\text{ext}}$ parallel to the air/water interface. We studied the aggregation behaviour of the anisotropic magnetic microparticles at the air/water interface as a function of the direction of $B_{\text{ext}}$ during their formation. For the latter, after formation, the particles were left at the surface to equilibrate in the absence of an external magnetic field at room temperature for 20 minutes. For the microlenses formed as in (1), in the absence of an external magnetic field during particle solidification, we expect the individual magnetite particles to be more-or-less randomly orientated (i.e., the relative orientations of the individual nano-dipoles to be only weakly correlated), leading to a negligible net dipolar magnetic moment of the composite microlenses once they are formed at the air/water interface. In our experiments, we observed no difference in their interfacial aggregation behaviour compared to that of non-magnetic microparticles. On the other hand, for composite microlenses formed as in (2) we expect the individual nano-dipoles to align (to some extent) with the external magnetic field $B_{\text{ext}}$ while the suspension droplets are still liquid and then to be “frozen” in this aligned configuration during solidification. This should lead to a net magnetic dipole moment $m$ of the microparticle pointing in the same direction as $B_{\text{ext}}$, if $m$ is large enough for the magnetic dipole–magnetic dipole interaction energies between the composite microlenses at the interface to become comparable to or greater than the lateral capillary interaction\(^{22}\) and the occasional convective drag, one would expect a noticeable effect on their interfacial aggregation behaviour.

Fig. 3A shows a typical configuration of particles formed with $B_{\text{ext}}$ perpendicular to the air–water surface with a relatively uniform distribution of equi-spaced particles. This is consistent with the net magnetic dipoles of the composite microlens particles being forced into a parallel configuration, thus repelling each other: although the particles are free to rotate around their vertical axis, the capillary force holds them flat at the air/water interface, thus maintaining the parallel orientation of their magnetic dipoles. The composite microlenses in Fig. 3B were formed with $B_{\text{ext}}$ parallel to the air/water surface and exhibit very different behaviour: they aggregate into clusters of low fractal dimension, separated by large voids. The linear structure of the aggregates corresponds to the most-favourable lateral orientation of their permanent magnetic dipoles which results in attraction and orientation of the particles at the air/water interface. Note that in this case again, the particles are only free to rotate around their vertical axis, but this time the dipole axis lies in the interfacial plane and can therefore be rotated until alignment with the surrounding dipoles is achieved. Both results together strongly suggest that the particles formed as in (2) indeed carry a permanent magnetic dipole moment in the direction of $B_{\text{ext}}$.

We have also recorded a few videos showing how these microparticles respond to the external magnetic field (by rotating a permanent magnet in the vicinity of the sample), indicating that they definitely contain a magnetic core, which can be clearly seen by rotating or moving the microparticles. Hence, most of the microparticles contain a magnetic core, which can be viewed under the optical microscope only from a certain direction (sideways).

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**Fig. 3** Optical microscope images of magnetite-doped (10% w/w) microlenses of various morphologies produced by spreading an isopropanol solution of paraffin–ceresin at $T = 55$ °C in the presence of external magnetic field which is (A) perpendicular to the air/water interface and (B) parallel to the air/water interface. The aqueous sub-phase is 10 mM SBDS.
In summary, we developed a simple method for fabricating anisotropic non-spherical polymeric microparticles of various morphologies, including microlenses, doughnuts and hexagons. It is based on spreading a paraffin–polymer solution on an air/water surface followed by solidification of the paraffin–polymer melt due to cooling and solvent attrition. The particle size and shape can be changed by adjusting the paraffin–polymer concentration in the spreading solution and the temperature of the aqueous sub-phase. By embedding colloidal magnetite in the polymer melt, we produced magnetic microparticles with a permanent magnetic dipole moment of controllable strength and direction, as deduced from their interfacial aggregation behaviour. Similar anisotropic magnetically-functionalized microparticles can also be produced by using photopolymerizable materials and one-sided surface chemistry modification (Janus particles), which can show even richer 3D aggregation behaviour. Such a study is under way and will be reported as a follow-up paper.

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