ELECTRIC STRESS–INDUCED SLIP LINES IN JAMMED PARTICLE MONOLAYERS
LÍNEAS DE DESLIZAMIENTO INDUCIDAS POR STRESS ELÉCTRICO EN MONOCAPAS DE PARTÍCULAS EN ESTADO DE "JAMMING"

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Drops fully covered by particles, so called Pickering emulsion drops, are used to stabilize emulsions and are ideal templates for producing particles and advanced capsules. Recent studies show how electrohydrodynamic circulation flows in drops can structure free particles on their surfaces. In this article, we study the structure of Pickering drops subjected to DC E-fields. Due to its effects, we observe plastic (irreversible) deformation of the two-dimensional granuar solid covering the droplet, including particle reorganisation similar to the "grain layer gliding" and "block gliding" typical of jammed granular matter.

Las gotas cubiertas por partículas, llamadas gotas en emulsión de Pickering, se usan para estabilizar emulsiones, y son ideales para producir partículas y cápsulas avanzadas. Estudios recientes muestran que los flujos electro-hidrodinámicos circulantes en gotas pueden estructurar partículas libres sobre la superficie de las mismas. En este trabajo, estudiamos la estructura de gotas Pickering sometidas a un campo eléctrico de DC. Debido al mismo, observamos deformación plástica (irreversible) en el sólido granular bi-dimensional que cubre a la gota, incluyendo reorganizaciones de las partículas similares al "grain layer gliding" y el "block gliding" típico de la materia granular en estado de jamming.

Drops covered by capillary bound particles, known as armoured drops or Pickering emulsion drops, are ideal templates for producing particles and advanced capsules [1–3] and can be adsorbed efficiently at fluid–fluid interfaces to stabilise emulsions, thus preventing drops from coalescing [4]. Beyond their technological importance, Pickering drops are good model systems for understanding ordering and dynamics in two dimensions [5]. When the interfacial particle concentration exceeds the maximum packing fraction, jamming prevents relaxation to spherical geometry and allows for the existence of nonminimal surfaces [1, 6, 7]. The stability of Pickering drops and their properties in flow, rheology and adhesion are mainly affected by their mechanical properties such as their Young moduli, bending stiffness and Poisson ratios [8]. Pickering drops have been found to be mechanically robust and able to recover from large deformations without disintegration [9].

In response to external stress, armoured drops and bubbles have demonstrated both plastic and elastic behaviour [6–8], as well as crumpling instabilities (*i.e.*, out-of-plane deformation) [10, 11]. Similar to granular flow, grain-layer mechanisms [12], grain boundaries and scars in colloidal crystals [5], plastic capsule deformation occurs when the particle monolayer at a capsule's interface flows, giving particles space to move relative to one another. The particles rearrange to accommodate shear deformation as a new irreversible shape is formed [6].

Pickering drops respond to mechanical forces [6, 9, 13] and shear flows [14, 15]. This also includes the behaviour of clay laden Pickering drops in electric fields (E-fields)

[16–19] An understanding of the mechanical response of particle-covered drops in E-fields is important for controlling Pickering emulsions and microcapsules. In this work, we have applied uniaxial stress to Pickering drops through the use of DC E-fields and have investigated the plastic deformation of Pickering drops. In particular, we have studied particle rearrangements at the drop interface at the start of plastic deformation.

The Pickering drops studied in our experiments were made of 50 *cSt* silicone oil (Dow Corning 200/50 *cSt*, electric conductivity $\sigma_{in} \sim 0.3 \, pSm^{-1}$, relative permittivity $\varepsilon_{in} = 2.8$, and density $\rho_{in} = 0.961 \, gcm^{-3}$) and polyethylene (PE) particles (purchased from Cospheric LLC with electric conductivity $\sigma_{pe} < 10^{-20} \, Sm^{-1}$, relative permittivity $\varepsilon_{pe} \sim 2.1$, and density $\rho_{pe} = 1.0 \, gcm^{-3}$) with diameters ranging between 45 and 53 μm. The amounts of silicone oil and PE particles were measured by weight, stirred together, shaken and ultrasonicated to minimise particle aggregation.

Castor oil (Sigma-Aldrich 83912, specific density $\rho_{ex} = 0.961 \, gcm^{-3}$, electric conductivity $\sigma_{ex} \sim 56 \, pSm^{-1}$, relative permittivity $\varepsilon_{ex} = 4.7$, and viscosity $\mu_{ex} \sim 750 cSt$) was poured into a sample cell ($15 \times 15 \times 30 \, mm$) consisting of glass and two indium tin oxide (ITO) walls acting as electrodes.

The experimental set-up is displayed in Figure 1. A silicone oil drop with PE particles is made and immersed in castor oil using a regular plastic pipette. We use particle sedimentation to bring particles to the drop interfaces where they adsorb to the oil-oil interface as a result of capillary binding forces [4]. With particles confined to the drop interface, the application of a DC E-field across the sample cell induce

electro-hydrodynamic (EHD) liquid flows [20] inside and outside the drop, which are used to structure the particles at the interface. Extensive details of the method can be found in previous work [16, 21].
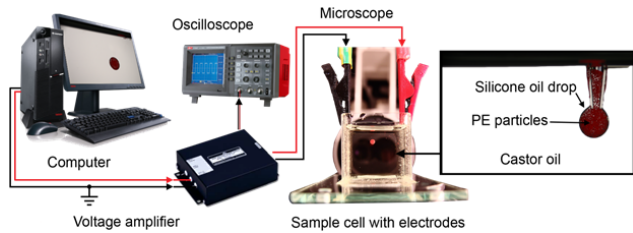

Figure 1. The experimental set-up consists of a sample cell placed on a mechanical stage, a microscope connected to a camera, a voltage amplifier, an oscilloscope to monitor signal amplitude, and a computer to control the applied voltage and record images. The sample cell is made of glass (15 × 15 × 30 mm), and two of the walls are coated with a conductive ITO layer. A drop containing colloidal particles is formed using a regular plastic pipette.

Videos and pictures were recorded using a digital camera mounted on a stereoscope, and the observation view was always in the perpendicular direction of the E-field, which was horizontal, as illustrated in all figures below.
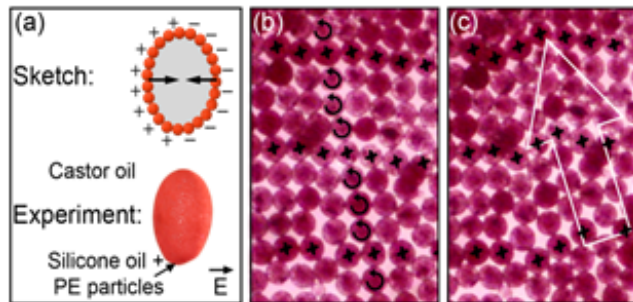

Figure 2. (**a**) A sketch and experimental images demonstrating the drop deformation process. (**b**) The Pickering drop surface in the beginning and (**c**) 3 seconds after plastic deformation. Some of the particles are marked with crosses and small arrows to illustrate how particles move and rotate relative to one another. The large white arrow illustrates how particles move collectively in a slip plane. The drop size is 1 mm, and the particle size is around 50 μm.

Figure 2**a** shows a sketch and experimental images of the silicone oil and PE Pickering drop suspended in castor oil. The application of a DC electric field was used to exert uniaxial electric stress along the Pickering drop's major axis. Since the Pickering drop and surrounding fluids have finite electric conductivities, charges accumulate at the Pickering drop interface, creating interfacial electrical shear stress [20]. The polarity of any induced surface charge depends on the conductivity of the given Pickering drop compared to the external fluid [20]. In our case, the surrounding castor oil conduct better than the Pickering drop, so the drop dipole is oriented antiparallel to the E-field direction and the electric stresses exert a compressive force on the Pickering drop. The induced electric stress is balanced by capillary stress (surface tension), which works to reduce the energy of the system and make the Pickering drop spherical. Particle jamming at the interface keep the Pickering drop non-spherical [1] and also

allows for crumpled shapes [10, 11]. The particle packing at the Pickering drop surface was hexagonal, though with many irregularities at least partly due to the polydispersity of our PE particles. The structure of the particle layer may be regarded as a two dimensional granular solid. Turning off the E-field does not bring back the initial Pickering drop shape, so the deformation is plastic (irreversible).

Shortly before and during the Pickering drop collapse, we observed particle rearrangements at the Pickering drop surface (Figure 2(**b**,**c**) and Figure 3). In response to compressive electric stress, the surface particles started to move relative to one another. At low particle concentrations or when subjected to strong shear flow, particle monolayers are observed to flow with strings of particles slipping past one another, while at higher concentrations or at weak shear flow, particle domains stretch and rotate. During the plastic deformation of Pickering drops, we do not observe rotation of particles' domains or flow [22], but we do observe particle reorganisation similar to the 'grain-layer gliding' and 'block gliding' mechanisms of slow granular flow as described by Drake [12]. As particle domains widen and compress to accommodate global shear deformation, particles within domains roll onto their nearest neighbours as particle rows slide on top of one another (Figure 3). Subramaniam *et. al.* observed similar dynamics of colloidal particle monolayers rearranging in shear bands (localised sliding) in mechanically and plastically deformed bubbles covered by colloidal particles [7]. For a short moment, the particle layer displays fluid-like behaviour as the particles rearrange, and several slip lines appear at the interface.
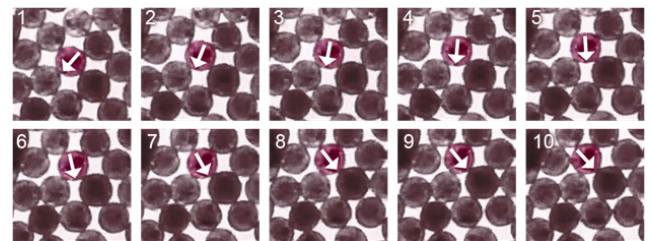

Figure 3. (1-10) A close up of particle rearrangements at the drop interface during plastic deformation. The time between each image is 2/25 seconds and the particle size is around 50 μm. The white arrows illustrate the rotation of one of the particles in the gliding plane.

These results may provide new insights regarding the mechanical strength of Pickering drops and their response to inhomogeneous stress, in particular regarding the role of slip line dynamics in jammed particle monolayers.

REFERENCES

[1] Z. Rozynek, A. Mikkelsen, P. Dommersnes and J. O. Fossum, Nature Communications 5 (2014).

[2] A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz, Science 298, 1006 (2002).

[3] A. B. Subramaniam, M. Abkarian and H. A. Stone, Nat. Mater. 4, 553 (2005).

[4] R. Aveyard, B. P. Binks, and J. H. Clint, Advances in Colloid and Interface Science 100, 503 (2003).

[5] C. Negri, A. L. Sellerio, S. Zapperi and M. C. Miguel, Proceedings of the National Academy of Sciences 112, 14545 (2015).

[6] A. B. Subramaniam, M. Abkarian, L. Mahadevan and H. A. Stone, Nature 438, 930 (2005).

[7] A. B. Subramaniam, M. Abkarian, L. Mahadevan and H. A. Stone, Langmuir 22, 10204 (2006).

[8] A. Fery and R. Weinkamer, Polymer 48, 7221 (2007).

[9] S.-Y. Tan, R. F. Tabor, L. Ong, G. W. Stevens and R. R. Dagastine, Soft Matter 8, 3112 (2012).

[10] H. Xu, S. Melle, K. Golemanov and G. Fuller, Langmuir 21, 10016 (2005).

[11] C. Monteux, J. Kirkwood, H. Xu, E. Jung, and G. G. Fuller, Physical Chemistry Chemical Physics 9, 6344 (2007).

[12] T. G. Drake, Journal of Geophysical Research: Solid Earth (1978–2012) 95, 8681 (1990).

[13] J. K. Ferri, P. Carl, N. Gorevski, T. P. Russell, Q. Wang, A. Boker and A. Fery, Soft Matter 4, 2259 (2008).

[14] I. Buttinoni, Z. A. Zell, T. M. Squires and L. Isa, Soft matter 11, 8313 (2015).

[15] S. Frijters, F. Gunther and J. Harting, Soft Matter 8, 6542 (2012).

[16] Z. Rozynek, P. Dommersnes, A. Mikkelsen, L. Michels and J. O. Fossum, Eur. Phys. J. Special Topics 223, 1859 (2014).

[17] R. B. Karyappa, S. D. Deshmukh and R. M. Thaokar, Physics of Fluids (1994-present) 26, 122108 (2014).

[18] M. Ouriemi and P. M. Vlahovska, Langmuir 31, 6298 (2015).

[19] J. W. Ha and S. M. Yang, Phys Fluids 12, 1671 (2000).

[20] G. Taylor, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 291, 159 (1966).

[21] P. Dommersnes, Z. Rozynek, A. Mikkelsen, R. Castberg, K. Kjerstad, K. Hersvik and J. O. Fossum, Nature Communications 4, 2066 (2013).

[22] E. J. Stancik, G. T. Gavranovic, M. J. Widenbrant, A. T. Laschitsch, J. Vermant and G. G. Fuller, Faraday discussions 123, 145 (2003).