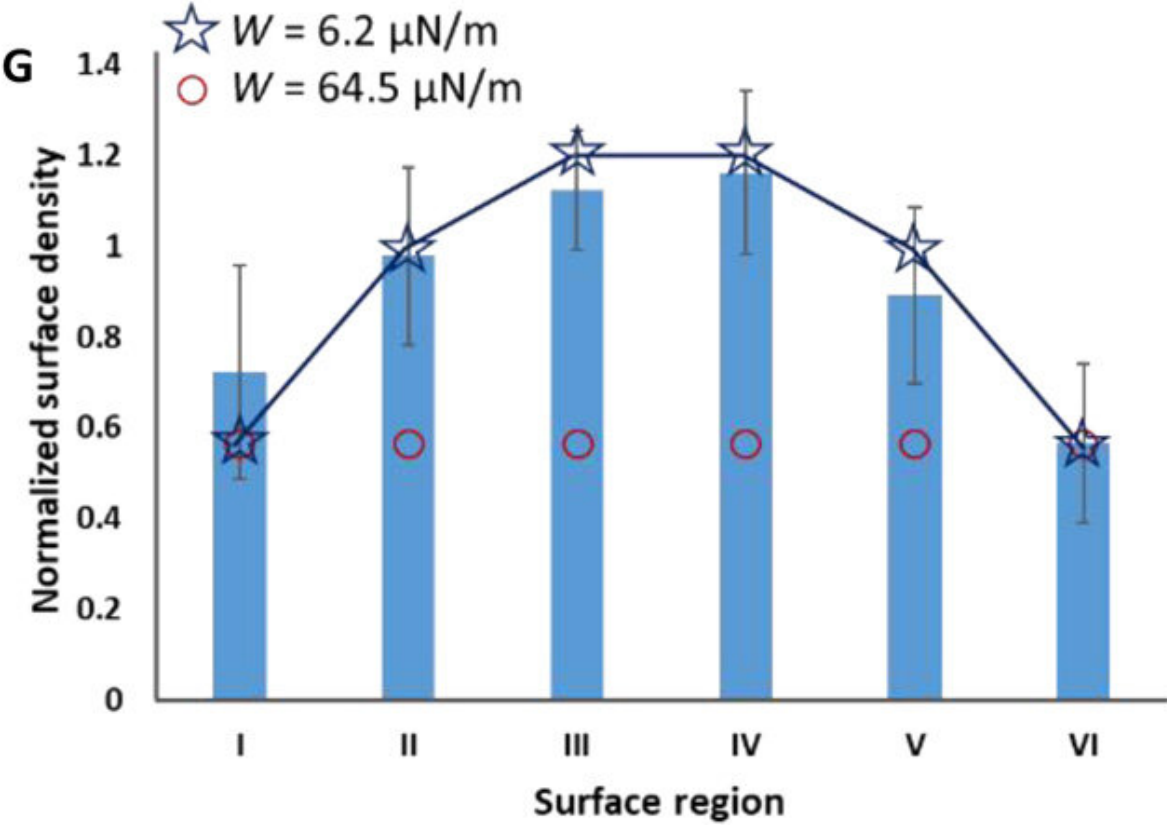
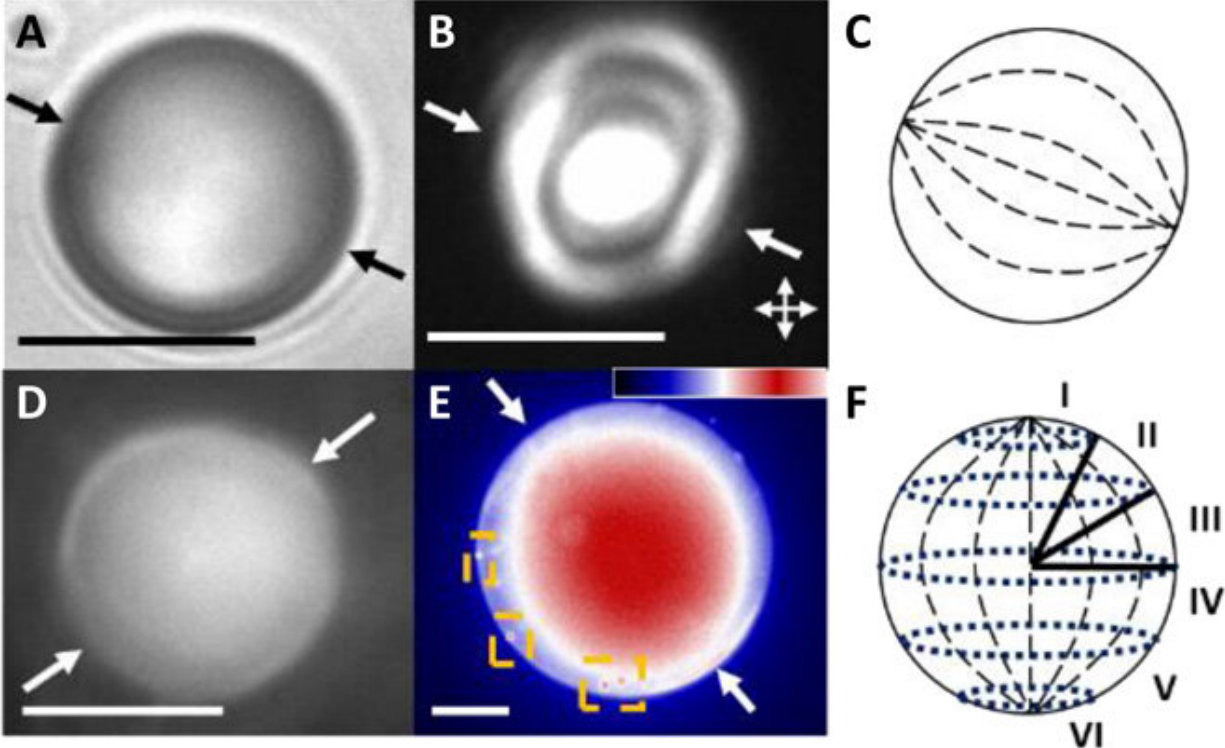


Programming van der Waals interactions with complex symmetries into microparticles using liquid crystallinity

July 1 2020, by Thamarasee Jeewandara



Bipolar LC microparticles, experiments, and theoretical predictions.

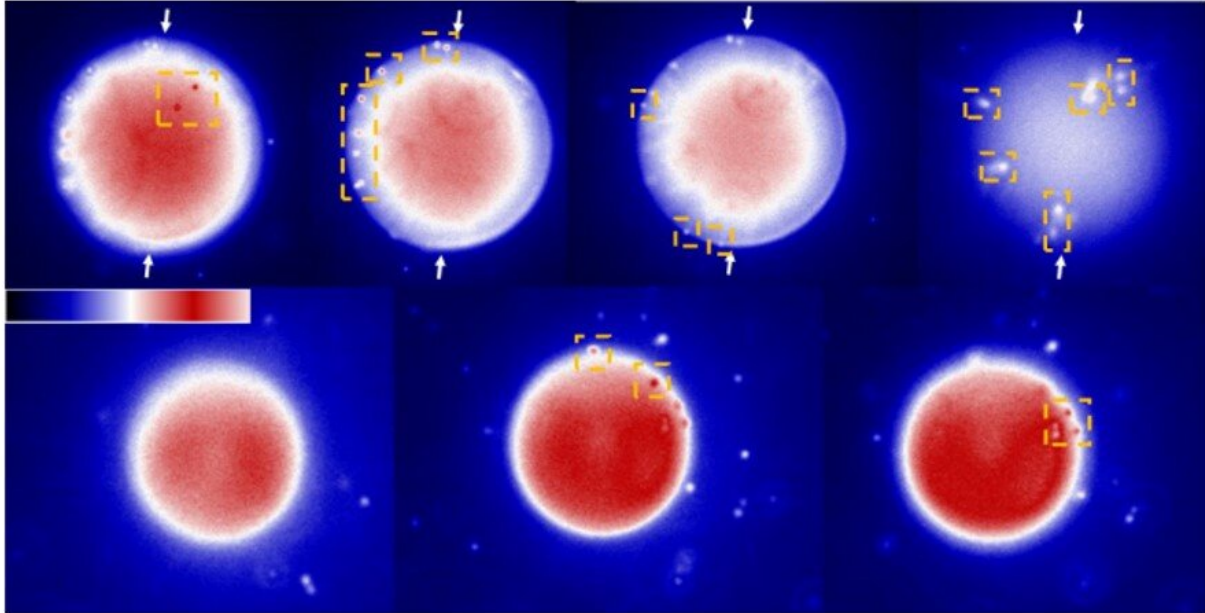
Representative (A) bright-field and (B) polarized light micrographs (double-headed arrows show orientations of polarizers) of a polymerized bipolar LC microparticle. (C) Illustration of the internal ordering of the microparticle in (A) and (B). (D) Fluorescence micrograph of a polymerized bipolar microparticle in the presence of probe PS colloids but no added NaCl and (E, colorized) in the presence of probe colloids and 10 mM aqueous NaCl. Orange boxes highlight the location of four in-focus adsorbed probe colloids. (E) Inset: Lookup table (LUT) for the colorized fluorescence micrograph (ImageJ, “UnionJack”). (F) Microparticle surface regions used to classify probe colloid locations on the surfaces of polymerized bipolar microparticles. (G) Blue bars: Normalized surface densities of probe colloids measured to adsorb onto the surfaces of polymerized bipolar microparticles. The bipolar microparticle data were calculated from 11 independent experiments, with 84 polymerized LC microparticles and 952 probe colloids adsorbed onto the surfaces of these microparticles. The error bars are 95% confidence intervals on the averages for the 84 microparticles. (stars and circles) Theoretical predictions of adsorbed colloid densities on the surfaces of bipolar microparticles, with indicated tangential anchoring strength. The white single-headed arrows on micrographs indicate the locations of the surface defects. Scale bars, 15 μm ($\lambda_{\text{ex}} = 505 \text{ nm}$, $\lambda_{\text{em}} = 515 \text{ nm}$). Credit: *Science Advances*, doi: 10.1126/sciadv.abb1327

Versatile approaches to engineer asymmetric van der Waals interactions can expand the palette of materials development through [bottom-up engineering](#) processes. In a new study, H.A. Fuster and a research team in chemical and biological engineering, and mathematics at the University of Wisconsin-Madison, Wisconsin, and Cornell University New York, U.S., demonstrated the polymerization of liquid crystals (LC) to program van der Waals interactions. They performed the experiments using a kinetically controlled probe colloid adsorption process and conducted complementary calculations to indicate that LC ordering could program van der Waals interactions across the surfaces of microparticles. They engineered the diverse LC configurations by confinement to provide fresh ideas in order to program van der Waals

interactions, to assemble soft matter. The results are now published on *Science Advances*.

The assembly of particles into clusters and networks underlies the formation of [different forms of soft matter](#) including foams, emulsions, and thin-film coatings. While most studies in the past had focused on materials formed through interparticle interactions, recent studies have moved on to design soft materials via a bottom-up assembly of particles that encode [anisotropic](#) interparticle interactions. Van der Waals interactions are ubiquitous [across all particulate systems](#) and represent another promising approach to [program the assembly](#) of [soft matter](#). In this report, Fuster et al explored an approach to control the symmetry of van der Waals interactions in particulate systems based on the synthesis of polymeric microparticles from liquid crystals (LCs). They described how the compositionally homogenous and spherical polymeric microparticles have well-defined patterns of orientational order to encode van der Waals interactions with complex symmetries.

Manipulating liquid crystals (LCs) confined in micro-scale domains.



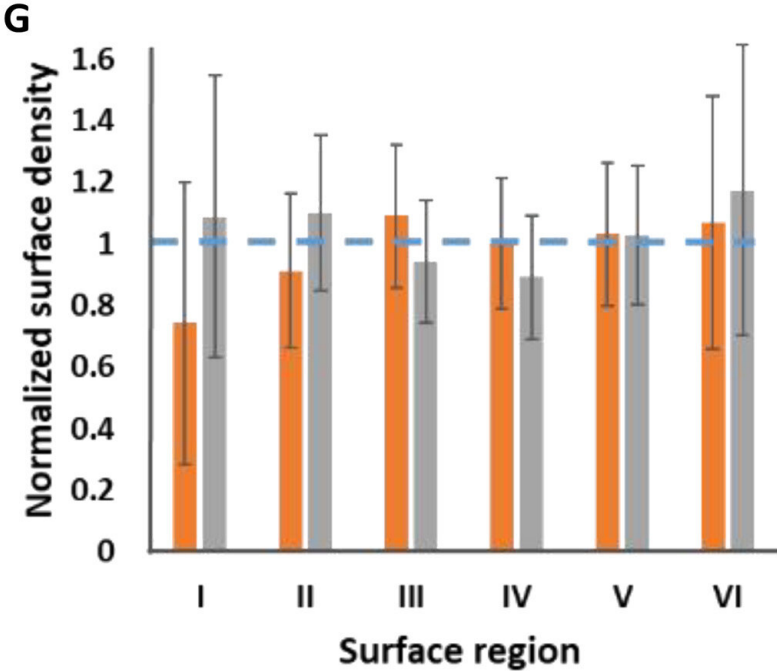
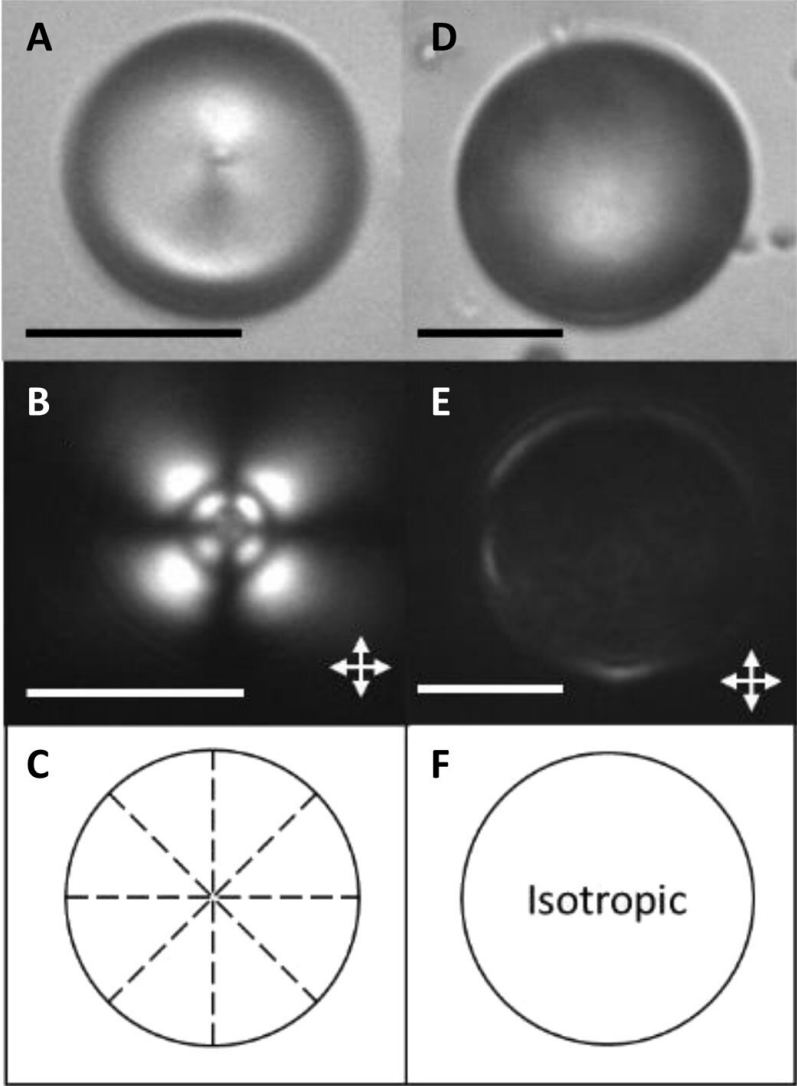
Fluorescence microscopy characterization of microparticles. Colorized fluorescence micrographs of bipolar (top row) and radial (bottom row) microparticles with adsorbed probe colloids. The rows of images were obtained by moving the focal plane of the microscope in the z direction. White arrows indicate the location of the surface defects on the bipolar microparticle. Orange boxes indicate the location of probe colloids as they come into focus in the image plane. The bipolar microparticle is $38\ \mu\text{m}$ in diameter and the radial microparticle is $28\ \mu\text{m}$ in diameter. (Inset) LUT for the color shift (ImageJ, ‘UnionJack’). Credit: Science Advances, doi: 10.1126/sciadv.abb1327

The team polymerized LC (liquid crystal) microdroplets prepared as oil-in-water emulsions to demonstrate how the internal orientational order could tune the spatial variation of van der Waals interactions across the surfaces of microparticles. They probed these interactions with a micron-sized polystyrene (PS) colloid. Van der Waals interactions collectively include dipole-dipole (Keesom), dipole-induced dipole (Keesom), dipole-induced dipole (Debye) and instantaneous dipole-induced dipole (London) interactions. The interactions can be calculated using the

[Lifshitz theory](#) through low-frequency and high-frequency components of the dielectric response function relative to the constituting materials. Fuster et al used LCs to synthesize microparticles with desired internal orientational order and used that internal configuration to program complex yet predictable spatial patterns of van der Waals interactions. The results and calculations showed how LCs provided the basis to a versatile approach to program van der Waals interactions, similar to the conventional bottom-up assembly processes in materials science.

Previous studies had reported a [remarkably diverse array](#) of organization of LCs in microdroplets, which include [chiral](#) and achiral LCs formed from organic and aqueous phases. The team first examined achiral LCs formed via several different chemical mixtures in this work, where the compounds had anisotropic dielectric response functions. The team then dispersed the LC mixture into glycerol and formed micron-sized LC droplets with a bipolar configuration. The polymeric microparticles preserved the bipolar configuration of LC droplets from which they were formed after photopolymerization as confirmed with bright-field and polarized light micrographs. The scientists then mapped the spatial variation of the van der Waals interactions across surfaces of polymerized bipolar microparticles by reversibly adsorbing polystyrene probe colloids (1 μm diameter) on such microparticle surfaces.

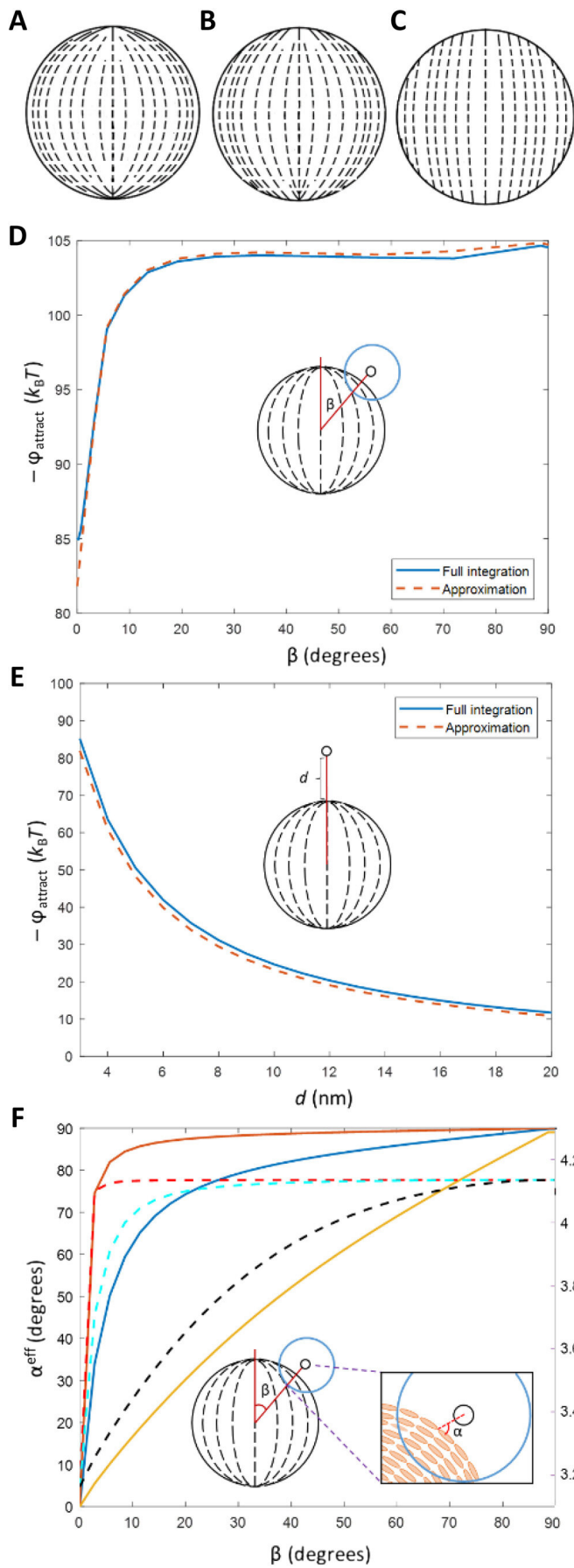
Investigating van der Waals interactions between the probe colloids and microparticles.



Radial LC and isotropic microparticles and their characterization. Representative (A and D) bright-field and (B and E) polarized light micrographs (double-headed arrows show orientations of polarizers) of a polymerized radial LC (A and B) and isotropic (D and E) microparticle. (C and F) Illustrations of the internal orderings of the microparticles in (A) and (B) and (D) and (E), respectively. (G) Bars: Normalized surface density of PS probe colloids adsorbed onto the surfaces of polymerized radial LC (orange) and isotropic (gray) microparticles. The radial microparticle data were calculated from 12 independent experiments, with 132 polymerized LC microparticles and 503 adsorbed probe colloids. The isotropic microparticle data were calculated from 20 independent experiments with 179 polymerized microparticles and 521 adsorbed probe colloids. The error bars are 95% confidence intervals on the averages for the 132 radial LC and 179 isotropic microparticles. The horizontal dashed line corresponds to a uniform adsorption density across all surface regions. Scale bars, 15 μm . Credit: Science Advances, doi: 10.1126/sciadv.abb1327

They interpreted the experimental observations relative to van der Waals interactions between the probe colloids and LC microparticles. For instance, the team quantified the distribution of probe colloids adsorbed on surfaces of bipolar microparticles in the presence of salt water, where the number increased with time in a kinetically controlled aggregation process. For control experiments, they repeated the methods using LC (liquid crystal) microparticles polymerized in the radial configuration. Based on the results, Fuster et al hypothesized that the patterning of probe colloids on bipolar microparticles arose from the van der Waals interactions encoded through orientational ordering of molecules within the bipolar microparticles. They supported the hypothesis with calculations to indicate that the orientations of LCs within microparticles could be used to encode sufficiently large variations in van der Waals interactions, allowing for direct bottom-up assembly of soft-matter

systems.

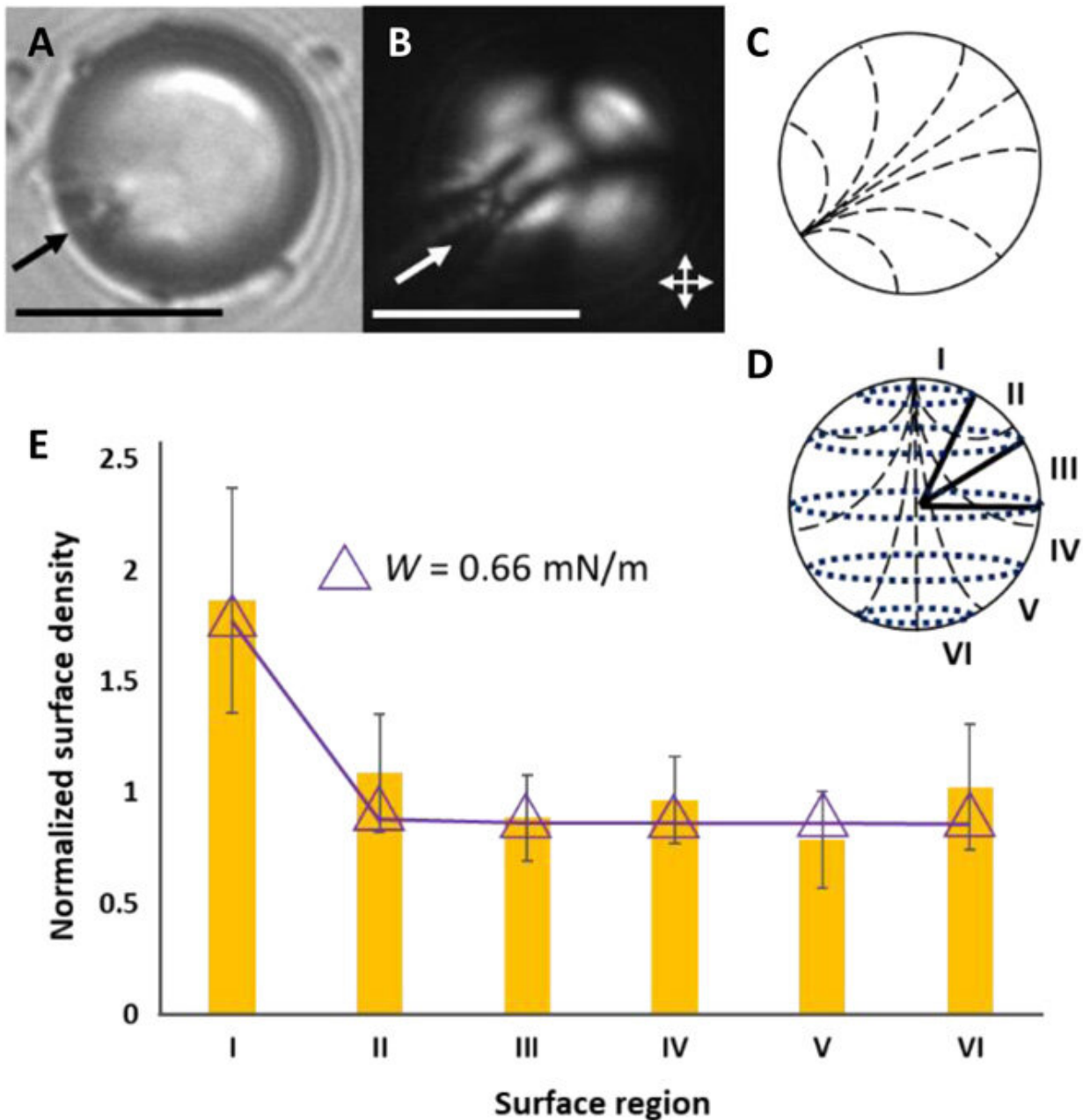


Theoretical predictions of bipolar LC microparticle internal ordering and attractive interaction energies. (A to C) Director profiles in the x-z plane of a bipolar LC microparticle calculated numerically for tangential surface anchoring energies of 64.5 $\mu\text{N/m}$ (A), 6.2 $\mu\text{N/m}$ (B), and 0.6 $\mu\text{N/m}$ (C). (D and E) Attractive interaction energy calculated using Eq. 1 derived in the study either by (solid lines) integrating overall volume elements of a bipolar microparticle with intermediate ($W = 6.2 \mu\text{N/m}$) tangential anchoring or by (dashed lines) approximating LC ordering at the surface nearest the probe colloid as representative of the entire volume, at various angles of incidence (β) at a surface-to-surface separation, d , of 3 nm (D) and at various surface-to-surface separations above the pole ($\beta = 0^\circ$) (E). (D) Inset: Illustration showing the angle of incidence, β . (E) Inset: Illustration showing location of probe colloid as surface-to-surface separation is varied. (F) Calculated average director angle, α_{eff} , sampled by a probe colloid as a function of β and a separation of 10 nm from the surface of the bipolar microparticle. (Solid lines) Results are shown for surface anchoring energies of 64.5 $\mu\text{N/m}$ (orange), 6.2 $\mu\text{N/m}$ (blue), and 0.6 $\mu\text{N/m}$ (gold). The corresponding effective Hamaker constant for interaction energies calculated according to Eq. 1 (dashed lines) for surface anchoring energies of 64.5 $\mu\text{N/m}$ (red), 6.2 $\mu\text{N/m}$ (cyan), and 0.6 $\mu\text{N/m}$ (black) is also shown. (F) Inset: Illustration of LC ordering near a probe colloid and the angle, α , between a probe colloid and the local LC director. Credit: Science Advances, doi: 10.1126/sciadv.abb1327

The team then investigated the theoretical predictions of bipolar LC microparticle internal ordering and calculated their attractive interaction energies. They noted the van der Waals interactions between the probe colloids and the bipolar microparticles to be stronger at the equatorial region, and consistent with experimental observations. The change in dielectric response experienced by a probe colloid near a bipolar [microparticle](#) acted as a strong anchoring energy and van der Waals interactions were particularly sensitive to such surface anchoring

energies.

Fuster et al. then studied the net interaction energy between a probe colloid and the polymerized bipolar microparticles as the sum of attractive van der Waals and repulsive double-layer interactions. For additional support on their hypothesis that van der Waals interactions can be encoded by internal configurations of LC microparticles, the team prepared LC microparticles with dipolar symmetry. They noted the [zeta potential](#) measurements of these microparticles to yield values similar to the polymerized bipolar LC microparticles. Based on the experimental outcomes, Fuster et al. confirmed that manipulating the LC ordering within the microparticles provided a versatile approach to pattern van der Waals interactions across the surfaces of microparticles.



Pinned preradial LC microparticles, their characterization, and theoretical predictions. Representative (A) bright-field and (B) polarized light micrographs (double-headed arrows show orientations of polarizers) of a polymerized pinned preradial microparticle. (C) Illustration of the internal ordering of the microparticle in (A) and (B). (D) Coordinate system used to characterize the location of colloids adsorbed to the surfaces of the polymerized pinned preradial microparticles. (E) Bars: Normalized surface densities of PS probe colloids measured to adsorb onto the surfaces of polymerized pinned preradial

microparticles. The pinned preradial microparticle data were calculated from 46 independent experiments with 121 polymerized LC microparticles and 493 adsorbed probe colloids. The error bars are 95% confidence intervals on the averages for the 121 LC microparticles. Triangles: Calculated colloid density on pinned preradial microparticles, evaluated using a strong homeotropic anchoring strength. The single-headed arrows on micrographs indicate the locations of the surface defects. Scale bars, 15 μm . Credit: Science Advances, doi: 10.1126/sciadv.abb1327

In this way, H.A. Fuster and colleagues characterized anisotropic van der Waals interactions programmed into microparticles by controlling the internal LC ordering and quantifying kinetically controlled colloid adsorption across the surface of the LC microparticles. The experiments and supporting calculations showed the spatial variation of van der Waals interactions across the surfaces of LC microparticles to be as large as $20 K_B T$. This magnitude is large enough to engineer the [bottom-up assembly](#) of soft materials. The scientists interpreted the experimental observations relative to van der Waals interactions between LC (liquid crystal) microparticles and probe colloids. The results established the basis for a general and simple approach to program van der Waals interactions into colloidal soft matter systems, since the scientists could vary the ordering of LCs and manipulate them in [a range of experimental geometries](#). The principles of this study will be applicable to a range of soft matter phenomena including adhesion and wetting surfaces, including the [formation of colloidal assemblies](#) such as glasses, crystals, and gels.

More information: H. A. Fuster et al. Programming van der Waals interactions with complex symmetries into microparticles using liquid crystallinity, *Science Advances* (2020). [DOI: 10.1126/sciadv.abb1327](https://doi.org/10.1126/sciadv.abb1327)

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