Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Spontaneous particle desorption and "Gorgon" drop formation from particle-armored oil drops upon cooling

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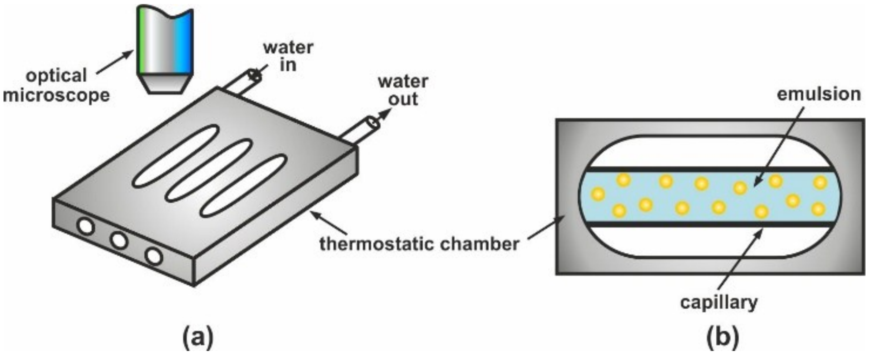


Figure S1. Experimental setup for optical observations of emulsion drops in a glass capillary upon cooling.

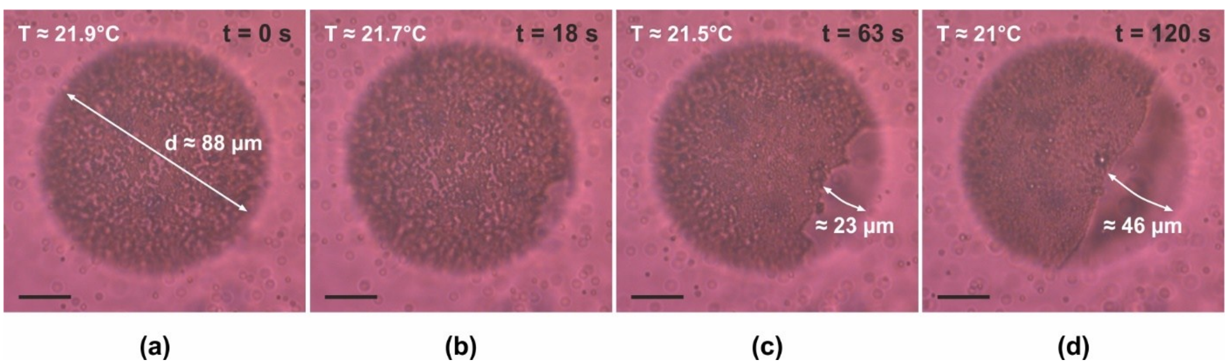


Figure S2. Sequence of microscopy images showing the particle ordering upon freezing of the surfactant adsorption layer. The velocity of the front of squeezed particles in this particular experiment is ≈ 0.37 µm/s. This experiment is performed with a non-purified hexadecane drop, decorated with 1 µm chloromethyl latex particles and immersed in aqueous solution containing 3 mM $C_{18}EO_{20}$ surfactant and 100 mM NaCl, cooling rate 0.5°C/min. Scale bars = 20 µm.

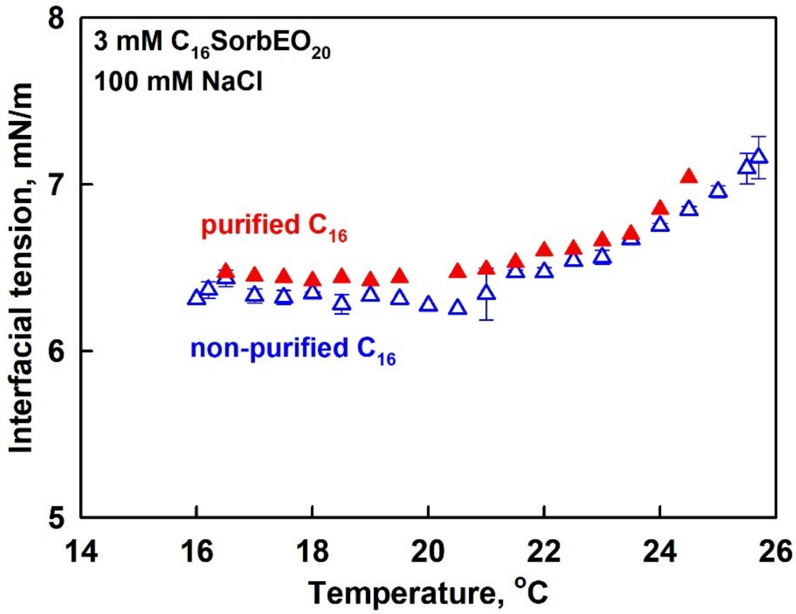


Figure S3. Interfacial tension as a function of temperature for purified (full red symbols) and non-purified (empty blue symbols) hexadecane drop immersed in aqueous solution containing 3 mM $C_{16}SorbEO_{20}$ and 100 mM NaCl. Note that these commercial surfactants are multicomponent mixtures and the changes in the interfacial tension include possible variations in the chemical composition of the surfactant adsorption layer.

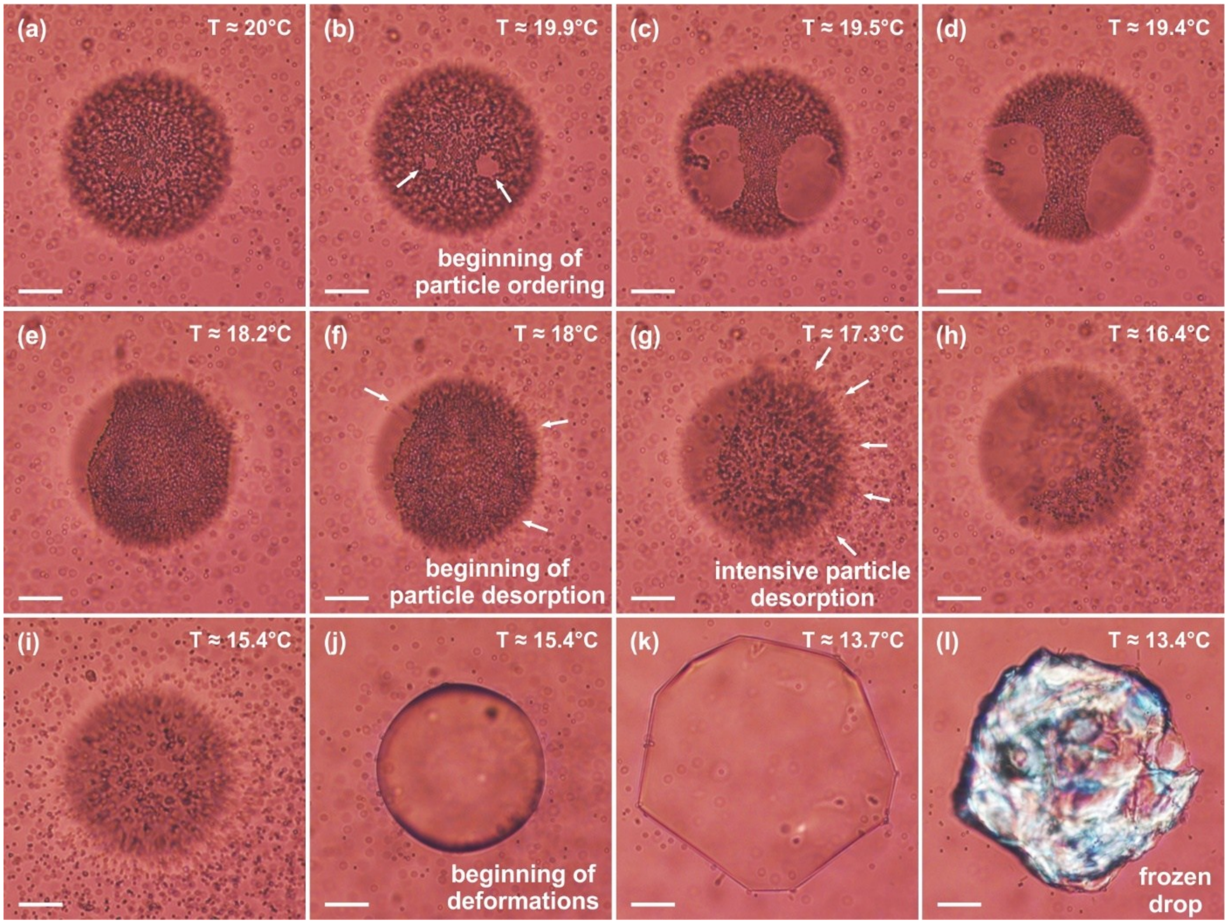


Figure S4. Evolution observed upon cooling with 0.1°C/min of purified hexadecane drop, decorated with 1 μm chloromethyl latex particles and dispersed in solution of 3 mM surfactant $C_{16}SorbEO_{20}$ and 100 mM NaCl. Scale bars = 20 μm.

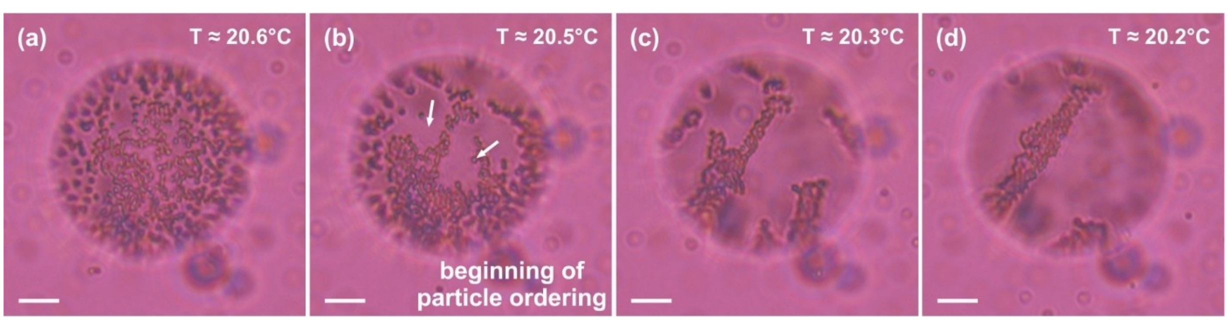


Figure S5. Evolution observed upon cooling with 0.1°C/min of non-purified hexadecane drop, decorated with 1 μm chloromethyl latex particles and immersed in solution of 3 mM surfactant $C_{16}SorbEO_{20}$ and 100 mM NaCl. Scale bars = 10 μm.

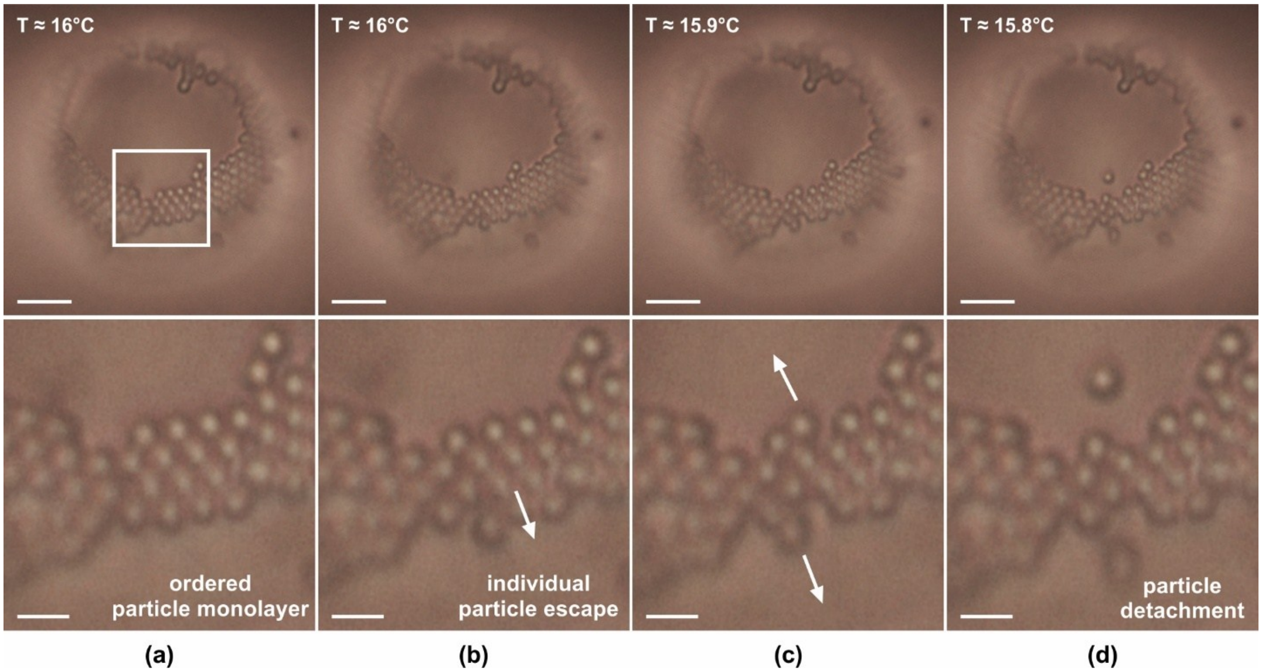


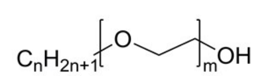
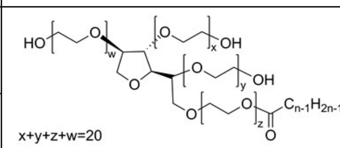
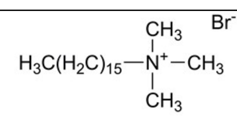
Figure S6. Sequence of microscopy images in reflected light which show the detachment of single particles from an ordered domain of particles. The images in the upper row (scale bars 10 μm) show the whole drop, while the images in the lower row (scale bars 3 μm) are zoomed images of the region bounded within the white square in (a). (a) Initially, the latex particles form an ordered domain. (b) One of the particles situated at the domain periphery has moved away from its neighbours in the ordered domain. (c) Second particle escapes from the ordered domain. (d) The particle separated in image (b) has certainly detached from the drop surface, as it is no longer at the same focal plane with the other particles, while the particle detached in image (c) is still in the same focal plane. The experiment is performed with a non-purified hexadecane oil drop, decorated with 1.6 μm chloromethyl latex particles and immersed in aqueous solution containing 1 mM $C_{18}EO_{20}$ surfactant and 100 mM NaCl, cooling rate 0.5°C/min.

Table S1. Properties of the alkanes studied.

Alkane	Number of C - atoms	Melting point, T_m, °C	Mass density, ρ, kg/m^3	Specific heat capacity, C_P, J/mol K	Thermal conductivity, κ, W/m K	Thermal diffusivity, χ, m^2/s
Tetradecane	14	5.5	762	439.2	0.136	8.2×10^{-8}
Pentadecane	15	8-10	769	471.82	0.143	8.3×10^{-8}
Hexadecane	16	18	770	502.49	0.146	8.7×10^{-8}

* All alkanes are purchased from Sigma-Aldrich and have analytical purity ≥ 99%.

Table S2. Properties of the surfactants studied.

Nonionic surfactant	**Nonionic surfactant (trade name)**	**Number of C atoms, n**	**Number of EO groups, m**	**HLB**	**Structural formula**
Polyoxyethylene alkyl ethers C_nEO_m	Brij 52	16	2	5	
	Brij 58	16	20	15.7	
	Brij S20	18	20	15.3	
Polyoxyethylene Sorbitan monoalkylate $C_nSorbEO_{20}$	Tween 40	16	20	15.5	
	Tween 60	18	20	14.9	
Ionic surfactant	**Abbreviation**	**Number of C atoms, n**	**Hydrophilic head group**	**Purity**	**Structural formula**
Cetyltrimethyl-ammonium bromide	CTAB	16	N^+ $(CH_3)_3(Br^-)$	> 99%	

Supplementary Movies

Supplementary Movie S1. Detachment of chloromethyl latex particles, observed upon cooling of C_{16} drop (non-purified oil) dispersed in 3 mM $C_{18}EO_{20}$ solution with 100 mM NaCl, cooling rate 0.5°C/min.

Supplementary Movie S2. Chloromethyl latex particles ordering and detachment, observed upon cooling of C_{16} drop (non-purified oil) dispersed in 3 mM $C_{18}EO_{20}$ solution with 500 mM NaCl, cooling rate 0.4°C/min.

Supplementary Movie S3. "Ejection" of jammed carboxylated particles adsorbed on the surface of pentadecane drop (non-purified oil) dispersed in 1 mM $C_{18}EO_{20}$ solution with 7.8 mM $CaCl_2$, cooling rate 0.3°C/min.

Supplementary Movie S4. Particle ordering followed by "ejection" of jammed particles observed during the drop shape deformation process. The system is: chloromethyl latex particles adsorbed on the surface of hexadecane drop (non-purified oil) dispersed in 1 mM $C_{18}EO_{20}$ solution with 500 mM NaCl, cooling rate 0.4°C/min.

Supplementary Movie S5. Formation of Gorgon drop particle observed upon cooling of hexadecane drop (non-purified) decorated with carboxylated latex particles. The aqueous solution contains 1 mM $C_{18}EO_{20}$ surfactant and 0.5 mM $CaCl_2$, cooling rate 2.5°C/min.

Supplementary Movie S6. Desorption of chloromethyl latex particles, followed by drop shape deformation into shape extruding thin fiber with attached particles on it. The system is: hexadecane drop (non-purified) dispersed in 3 mM $C_{18}EO_{20}$ solution with 500 mM NaCl, cooling rate 0.4°C/min.

Supplementary Movie S7. Desorption of chloromethyl latex particles, followed by drop shape deformation and extrusion of thin fiber with attached particles on it. The system is: hexadecane drop (non-purified) dispersed in 1 mM $C_{18}EO_{20}$ solution with 100 mM NaCl, cooling rate 0.2°C/min.