Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

For

Understanding the Multiple Orientations of Isolated Superellipsoidal Hematite Particles at the Oil-Water Interface

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Experimental Details

Materials

Reagent grade iron(III) chloride hexahydrate, hexadecane, methanol, sodium hydroxide, phytagel, PDMS (200 fluid, 10cSt), and PVP-K30 (40,000 g mol^{-1}) were all used as received from Sigma Aldrich. Phytagel was obtained from Sigma Aldrich. Deionized water was produced by a Milli-Q purification unit with a conductivity of 18MΩ. Beer bottles and their swing tops were obtained from JBC glassware.

Preparation of Hematite Superellipsoids

Superellipsoidal hematite particles were prepared by the route originally described by Muramatsu.[1] Iron(III) chloride hexahydrate (2.0M, 100mL) was added to a 200mL beer bottle fitted with a ceramic swing top, and sealed with a Teflon-lined rubber seal. Sodium hydroxide solution (6.0M, 90mL) was slowly fed into the iron chloride solution under vigorous stirring over a period of 5 minutes before a small aliquot of deionized water (10mL) was added. The bottle was sealed and transferred to an oven at 100°C where it was left for 8 days.

The amber-colored supernatant was removed and the sediment re-dispersed in water before 3 rounds of centrifugation at 2000rpm, re-dispersing in water each time. PVP-K30 (10.0g) was added and the solution was allowed to stir for 48 hours to ensure complete absorption before they were cleaned by a further 3 rounds of centrifugation/dispersion in water, and drying in an oven under vacuum at 60°C for 48 hours.

Assembly and Immobilisation of Particle onto the Oil-Water Interface

A 2.0 wt% solution of phytagel was made up by dissolving in water at 80°C with vigorous stirring, and then left to cool to 50°C with light stirring, until no bubbles remained in the system. This solution was placed in a Petri dish and n-hexadecane at 50°C was layered on top. 100μl of a 1.0 wt% hematite particle suspension in isopropanol was injected at the oil-water interface by syringe, and the Petri dish was left to cool for 30 minutes at room temperature until the aqueous phase gelled. The oil layer was gently removed by pipette and replaced by a Sylgard 184 elastomer at a mass ratio of 9:1 PDMS:curing agent ratio, which had previously been degassed in a vacuum. The liquid PDMS was gently poured over the gel surface and left to cure for 2 days at room temperature. At this point the PDMS layer was peeled from the hydrogel surface and immersed in hot water for two minutes to remove any residual phytagel.

Imaging of Trapped Hematite Particles

Squares of PDMS (1cm x 1cm) were cut before cleaning in boiling deionized water for 2 minutes.

Atomic force microscopy (AFM) images were obtained using an Asylum Research MFP-3D (Santa Barbara, USA) in AC mode using AC240TS cantilevers (Olympus).

SEM sample were prepared by sputter-coating PDMS squares with platinum at a 45° angle. An operating voltage of 15kV was used, calculated to give a surface thickness of 5nm. Imaging was performed at a 14.1° angle with respect to the plane of the interface on a Zeiss Supra 55VP SEM, operated at 10kV. Particle sizes were averaged over 100 isolated particles. A simple trigonometric correction factor was applied when measuring particle height in order to account for the tilt of the stage.

MATLAB Simulations of Stable Particle Orientations

Simulations were performed in Matlab using a triangular tessellation method similar to that described by van Roij *et al.*[2] The particles are created from a series of points which all fit the unique expression for a superellipsoid (**Equation 1**).

$$\left(\frac{x}{r_x}^{2/n_2} + \frac{y}{r_y}^{2/n_2}\right)^{n_2/n_1} + \frac{z}{r_z}^{2/n_1} = 1 \qquad (1)$$

Where x, y, and z denote the coordinates of the point r_x, r_y, and r_z, which are the particles x, y, and z radii. n_1 and n_2 act as the "squareness" parameters in the z axis and the x-y plane respectively, with $0<n_1,n_2<\infty$. From the input parameters of r_x, r_y, r_z, n_1, n_2, and the number of points to be created, the particle shape is computed. The point coordinates are obtained by first generating an evenly distributed set of points around a sphere with $r_x = r_y = r_z = 1$ using the golden section spiral method. The x, y, and z coordinates from the sphere are converted into spherical coordinates and the x, y, and z values for the superellipsoid are calculated from the parametric equations (**Equation 2-4**)

$$x = r_x \cos^{n_1}\theta \cos^{n_2}\varphi \qquad (2)$$

$$y = r_y \cos^{n_1}\theta \sin^{n_2}\varphi \qquad (3)$$

$$z = r_z \sin^{n_1}\theta \qquad (4)$$

The surface of the particle is obtained from this set of data points by taking the convex hull of the data set, resulting in a series of triangles that connect the points.

The surface created by the above equation is bound by a sphere of minimum radius (R) centered at the origin which can be rotated about the x (θ_2) and y (θ_1) axes, and translated in the z axis to give any position and orientation of the particle with respect to the interface. The particle movement in the z axis is defined by the vertical coordinate ž (**Equation 5**).

$$\check{z} = z/R \tag{5}$$

Where z is the distance from the center of the sphere bounding the particle to the interface, and R is the radius of the bounding sphere (where ž=1 the particle is in the oil phase and where ž=-1 is in the water phase). The particle is scanned through various positions by translating and rotating the points, and at each position the associated energy is calculated. The energy is calculated by summing the area of triangles above and below the interface and multiplying by the interfacial tension. Triangles which intersect the interface are subdivided further and the new triangles are designated into the appropriate phase in a method analogous to that of van Roij *et al.* The area of the interface that is 'removed' upon adsorption of the particle is determined by connecting the points where lines from the triangular tessellation intersect the liquid-liquid interface and then the areas of the described polygon is calculated. This can be summarized mathematically (**Equation 6**).

$$E = S_{P1}A_{P1} + S_{P2}A_{P2} - S_{12}A_{12} \tag{6}$$

Where E is the energy S is the surface tension and A is the area. The subscripts *P1*, *P2* and *12* denote the particle-oil interface, particle-water interface and oil-water interface respectively.

Particle trajectories and transitions between states were calculated by taking the negative gradient at each point in the 3-dimensional free energy landscape (**Equation 7**) calculated in the above section.

$$-\nabla E\,(\theta_1, \theta_2, z) = -\left(\frac{d\theta_1}{dE} + \frac{d\theta_2}{dE} + \frac{dz}{dE}\right) \tag{7}$$

Trajectories that follow the path of the steepest descent in terms of energy from an initial point $P^0(\theta_1^{\,0},\ \theta_2^{\,0},\ z^0)$ are calculated by interpolating between the values of the recorded gradient and using the constituent $d\theta_1$, $d\theta_2$, and dz values to determine direction of the particle motion. A zero temperature string method was used to find pathways with an energy barrier, which allows one to calculate the minimum energy pathway between two energy minima.[3]

Particle Size Distribution Measurements with Mie Scattering

A Malvern Mastersizer Hydro 2000S was used to measure the particle size and particle size distribution (**Figure 1**). The number average particle size was 1.159μm and the polydispersity was 0.225.

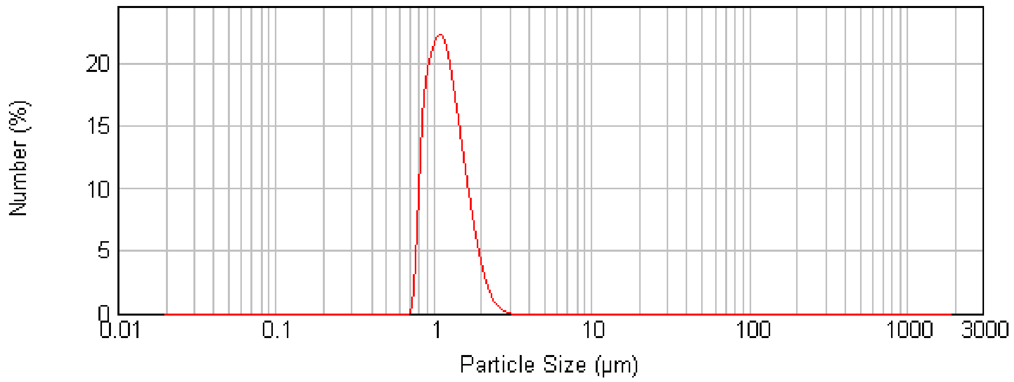

Figure 1. Dynamic Light Scattering Measurement shows a monomodal size distribution of the hematite particles.

SEM Image Analysis of Particles

Hematite superellipsoids were analyzed by SEM to determine the characteristic length and polydispersity (**Figure 2**). Over 100 particles the characteristic length was 1.361μm ± 0.124. Deviations from the mean were within 9%.

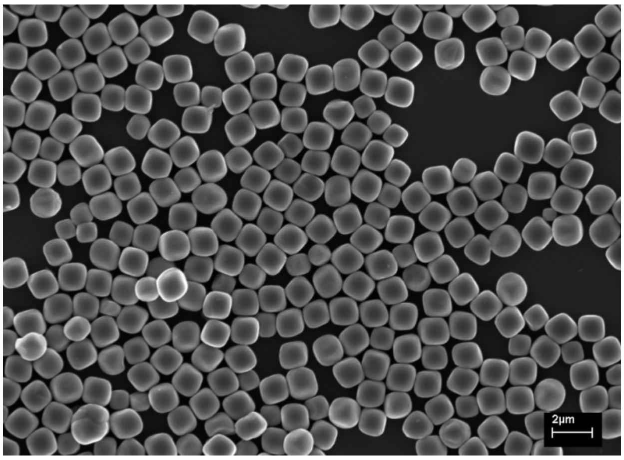

Figure 2. SEM image showing monodisperse hematite particles. Scale bar is 2μm.

All SEM images analyzed can be found in the corresponding .ZIP file accompanying this supporting information. Some images were used to analyze more than one particle.

The results of SEM image analysis of all 100 particles can be found below. Note that the perceived height was obtained by measuring the distance from the highest point on the particle to the plane of the PDMS interface using the software ImageJ. Height corrections were made through simple trigonometric calculations to account for differences in the apparent height and actual height due to the viewing angle of the detector, which was 14.1°

Particle Number	***File Name***	***Orientation***	***Perceived Height (nm)***	***Corrected Height (nm)***
1	*Hematite 001*	*Tilted*	*837*	*863*
2	*Hematite 002*	*Tilted*	*756*	*780*
3	*Hematite 003*	*Tilted*	*867*	*894*
4	*Hematite 004*	*Tilted*	*811*	*836*

5	*Hematite 005*	*Flat*	*1000*	*1031*
6	*Hematite 006*	*Flat*	*1061*	*1094*
7	*Hematite 007*	*Tilted*	*914*	*942*
8	*Hematite 008*	*Tilted and Sunk*	*514*	*530*
9	*Hematite 009*	*Flat*	*1062*	*1095*
10	*Hematite 010*	*Flat*	*1057*	*1090*
11	*Hematite 011*	*Flat*	*979*	*1009*
12	*Hematite 012*	*Flat*	*952*	*982*
13	*Hematite 013*	*Tilted*	*865*	*892*
14	*Hematite 014*	*Flat*	*1033*	*1065*
15	*Hematite 015*	*Tilted*	*850*	*876*
16	*Hematite 016*	*Flat*	*1035*	*1067*
17	*Hematite*	*Flat*	*726*	*749*

	017			
18	*Hematite 018*	*Tilted and Sunk*	*495*	*510*
19	*Hematite 019*	*Flat*	*1079*	*1113*
20	*Hematite 020*	*Tilted*	*759*	*783*
21	*Hematite 021*	*Flat*	*1049*	*1082*
22	*Hematite 022*	*Flat*	*1082*	*1116*
23	*Hematite 023*	*Flat*	*1068*	*1101*
24	*Hematite 024*	*Flat*	*1032*	*1064*
25	*Hematite 025*	*Tilted*	*932*	*961*
26	*Hematite 026*	*Tilted*	*900*	*928*
27	*Hematite 027*	*Tilted*	*838*	*864*
28	*Hematite 028*	*Flat*	*1022*	*1054*
29	*Hematite 029*	*Flat*	*995*	*1026*

30	*Hematite 030*	*Flat*	*1023*	*1055*
31	*Hematite 031*	*Flat*	*1042*	*1074*
32	*Hematite 032*	*Flat*	*952*	*982*
33	*Hematite 033*	*Flat*	*851*	*878*
34	*Hematite 034*	*Flat*	*1002*	*1033*
35	*Hematite 035*	*Tilted*	*917*	*946*
36	*Hematite 036*	*Flat*	*1103*	*1137*
37	*Hematite 037*	*Flat*	*1044*	*1077*
38	*Hematite 038*	*Tilted*	*910*	*938*
39	*Hematite 039*	*Tilted*	*778*	*802*
40	*Hematite 040*	*Tilted*	*710*	*732*
41	*Hematite 041*	*Flat*	*1064*	*1097*
42	*Hematite*	*Tilted*	*785*	*809*

	042			
43	*Hematite 043*	*Flat*	*1082*	*1116*
44	*Hematite 044*	*Tilted*	*902*	*930*
45	*Hematite 045*	*Flat*	*1013*	*1045*
46	*Hematite 046*	*Flat*	*1001*	*1032*
47	*Hematite 047*	*Flat*	*1006*	*1037*
48	*Hematite 048*	*Tilted*	*896*	*924*
49	*Hematite 049*	*Tilted*	*881*	*908*
50	*Hematite 050*	*Tilted*	*847*	*873*
51	*Hematite 051*	*Tilted*	*939*	*968*
52	*Hematite 052*	*Flat*	*1010*	*1041*
53	*Hematite 053*	*Flat*	*1080*	*1114*
54	*Hematite 054*	*Tilted*	*972*	*1002*

55	*Hematite 055*	*Flat*	*1032*	*1064*
56	*Hematite 056*	*Tilted and Sunk*	*639*	*659*
57	*Hematite 057*	*Flat*	*1044*	*1077*
58	*Hematite 058*	*Flat*	*1110*	*1145*
59	*Hematite 059*	*Tilted*	*872*	*899*
60	*Hematite 060*	*Flat*	*1052*	*1085*
61	*Hematite 061*	*Flat*	*1089*	*1123*
62	*Hematite 062*	*Flat*	*1055*	*1088*
63	*Hematite 063*	*Flat*	*881*	*908*
64	*Hematite 064*	*Flat*	*1010*	*1041*
65	*Hematite 065*	*Tilted*	*895*	*923*
66	*Hematite 066*	*Flat*	*1060*	*1093*
67	*Hematite*	*Tilted*	*804*	*829*

	066			
68	*Hematite 066*	*Tilted and Sunk*	*523*	*539*
69	*Hematite 067*	*Flat*	*1080*	*1114*
70	*Hematite 068*	*Flat*	*900*	*928*
71	*Hematite 069*	*Tilted and Sunk*	*578*	*596*
72	*Hematite 070*	*Tilted*	*782*	*806*
73	*Hematite 071*	*Flat*	*948*	*978*
74	*Hematite 072*	*Flat*	*1003*	*1034*
75	*Hematite 073*	*Flat*	*1084*	*1118*
76	*Hematite 073*	*Flat*	*1100*	*1134*
77	*Hematite 073*	*Flat*	*1066*	*1099*
78	*Hematite 074*	*Tilted*	*792*	*817*
79	*Hematite 075*	*Tilted*	*877*	*904*

80	*Hematite 076*	*Flat*	*1035*	*1067*
81	*Hematite 076*	*Flat*	*1027*	*1059*
82	*Hematite 076*	*Flat*	*1055*	*1088*
83	*Hematite 077*	*Flat*	*1015*	*1047*
84	*Hematite 078*	*Flat*	*1023*	*1055*
85	*Hematite 079*	*Flat*	*1057*	*1090*
86	*Hematite 080*	*Flat*	*1044*	*1077*
87	*Hematite 081*	*Flat*	*1105*	*1139*
88	*Hematite 082*	*Tilted*	*867*	*894*
89	*Hematite 083*	*Tilted*	*710*	*732*
90	*Hematite 084*	*Tilted*	*832*	*858*
91	*Hematite 085*	*Flat*	*873*	*900*
92	*Hematite*	*Tilted*	*784*	*808*

	086			
93	*Hematite 087*	*Tilted*	*743*	*766*
94	*Hematite 088*	*Flat*	*793*	*818*
95	*Hematite 089*	*Tilted and Sunk*	*403*	*416*
96	*Hematite 090*	*Tilted*	*615*	*634*
97	*Hematite 091*	*Flat*	*867*	*894*
98	*Hematite 092*	*Tilted*	*801*	*826*
99	*Hematite 093*	*Flat*	*1017*	*1049*
100	*Hematite 094*	*Flat*	*1081*	*1115*

Table 1. Tabulated SEM image analysis of particles trapped in PDMS after being assembled at a hexadecane-water interface.

The individual SEM files can be obtained from the authors upon request by email, or via http://www.bonlab.info

References

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_[2] J. de Graaf, M. Dijkstra, R. van Roij, *Phys. Rev. E.* **2009**, 80, 1.

_[3] E. Weinan, R. Weiqing, E. Vanden-Eijneden, *J. Chem. Phys*, **2007**, 126, 164103.