Assembling Ellipsoidal Particles at Fluid Interfaces using Switchable Dipolar Capillary Interactions

Citation for published version:
Davies, GB, Krueger, T, Coveney, PV, Harting, J & Bresme, F 2014, 'Assembling Ellipsoidal Particles at Fluid Interfaces using Switchable Dipolar Capillary Interactions' Advanced Materials, vol 26, pp. 6800. DOI: 10.1002/adma.201402419

Digital Object Identifier (DOI):
10.1002/adma.201402419

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
Advanced Materials
Assembling Ellipsoidal Particles at Fluid Interfaces using Switchable Dipolar Capillary Interactions

Gary B. Davies,* Timm Krüger, Peter V. Coveney, Jens Harting, and Fernando Bresme

The fabrication of novel soft materials is an important scientific and technological challenge. We investigate the response of ellipsoidal particles adsorbed at fluid-fluid interfaces to external magnetic fields. By exploiting previously discovered first-order orientation phase transitions,[1–3] we show how to switch on and off dipolar capillary interactions between particles, leading to the formation of distinctive self-assembled structures and allowing dynamical control of the bottom-up fabrication of novel-structured materials.

Particles adsorb strongly at fluid-fluid interfaces: detachment energies of spherical particles can be orders of magnitude greater than the thermal energy, $k_B T$. Once particles are adsorbed at an interface, competing hydrodynamic, electromagnetic and capillary interactions can lead to particles self-assembling into materials with specific mechanical, optical, or magnetic properties.[6,7]

Capillary interactions[8] have attracted interest for their role in assembling mosquito eggs adsorbed at air-water interfaces,[9] suppressing the coffee ring effect,[10] and aggregating Cheerios.[11,12] Capillary interactions occur because of the creation of menisci around particles, and these particle-induced interface deformations, called capillary charges, interact with one another analogously to electric charges.[13,14]

The height of the interface deformation, $h$, due to the presence of a particle obeys Young’s equation, $\nabla^2 h = 0$, which can be solved using a multipole expansion.[8,15,16] Heavy particles deform the interface symmetrically in a monopolar fashion leading to $\log r$ interaction potentials between particles, where $r$ is the inter-particle distance. [8,11,12] However, for micron-sized particles, gravitational forces are usually small compared to surface-tension forces.[8]

Non neutrally-wetting micron-sized ellipsoidal particles adsorbed at fluid-fluid interfaces contort the interface around them in a quadrupolar fashion purely because of their shape.[8,17] the interface is depressed more at the tips than it is elevated at the sides, leading to orientation-dependent interaction potentials between particles.[8,15–17] The resulting capillary interaction energies can be several orders of magnitude larger than the thermal energy, $E \approx 10^5 k_B T$, providing a strong driving force for self-assembly.[8,17] However, neither the monopolar nor the quadrupolar interactions are dynamically tunable.

Dipolar capillary charges are created by anisotropic particles influenced by torques. External torques can be caused by particles with uneven mass distributions interacting with gravity, complex surface chemistries (e.g., Janus particles) interacting with fluids,[18–20] or—the focus of this Communication—embedded dipoles interacting with external magnetic fields, opening up new routes for the manipulation of particle monolayers.

Materials science advances[6,21] have enabled the production of anisotropic particles with embedded ferromagnetic dipoles[22] or (super)-paramagnetic dipoles[23,24] so that particles can interact with external magnetic fields.

Bresme et al.[2] investigated the behaviour of magnetic ellipsoidal particles adsorbed at fluid-fluid interfaces under the action of a magnetic field, predicting that particles undergo a discontinuous, first-order phase transition from a tilted state to a vertical state if a critical dipole-field strength is reached.[3] Davies et al.[1] provided further evidence that the transition exists and also showed that particle-induced interface deformations significantly affect the transition.

When a magnetic prolate spheroidal particle with dipole moment, $\mu$, is adsorbed at a fluid-fluid interface and subjected to an external magnetic field, $\mathbf{H}$, directed normal to the interface, it experiences a torque, $\mathbf{T} = \mu \times \mathbf{H}$, which attempts to align the particle with the external field. Surface-tension forces oppose the magnetic torque, and so for a given dipole-field strength, $\mathbf{B} = |\mu| |\mathbf{H}|$, the particle is tilted with respect to the external field, rather than aligned with it. When the particle is...
titled with respect to the interface, the constant contact-angle condition stipulated by Young’s equation means that the particle deforms the interface; the interface is depressed on one side and elevated on the other, as shown in Figure 1.

When a critical dipole-field strength, \( B_c \), is reached, however, the magnetic torque overcomes surface-tension forces and the particle undergoes a first-order phase transition and flips from a tilted orientation to a vertical orientation, with respect to the interface. In the vertical orientation, interface deformations are absent because of the rotational symmetry of the three-phase contact-line in this configuration.

The interface deformations that occur before the particle transitions to the vertical state are important because they are analogous to electrostatic charges, with a twist; depressions attract depressions, elevations attract elevations, and depressions repel elevations: opposites repel, rather than attract. Therefore, if more than one particle is adsorbed at a fluid-fluid interface and under the influence of an external magnetic field such that the dipole-field strength is less than the critical dipole-field strength, \( B < B_c \), we expect these capillary charges to interact with each other.

Due to the anti-symmetric, dipolar nature of the interface deformations, these interactions are orientation dependent and will give rise to torques orthogonal to the interface causing in-plane rotation and ordering. Further, since the magnitude of the interface deformations depend on the dipole-field strength, it is possible to tune the strength of these dipolar capillary interactions by changing the strength of the external field, particle dipole moment, or both.

We employed lattice-Boltzmann simulations\(^1,25–36\) to investigate magnetic prolate spheroidal particles with aspect-ratio \( \alpha = 2 \) adsorbed at a liquid-liquid interface under the influence of a magnetic field applied parallel to the interface normal, implemented in our LB3D code\(^37\) with the same model and parameters as described in Davies et al.\(^1\). In our simulations, the dipole-field strength, \( B \), is dominated by a strong external magnetic field and weak dipole moment so that magnetic dipole-dipole interactions are neglected. This means that the structures we observe are purely a result of dipolar capillary interactions between particles.

In Figure 2 we show the particles undergoing a first-order transition into the vertical orientation by exceeding the critical dipole-field strength for a single particle, \( B_c \), demonstrating the unique phenomenology of the dipolar capillary interaction mode. The particles begin randomly oriented on the interface (Figure 2a). An external field is applied such that the dipole-field strength is \( B = 0.5B_c \), creating capillary charges and causing the particles to interact with each other (Figure 2b). The particles assemble into “capillary caterpillars”, which we analyse further in Figure 3. Finally, the dipole-field strength is increased beyond the single particle critical dipole field, \( B > B_c \), where the particles transition into the vertical configuration (Figure 2c and 2d) and capillary interactions are spontaneously switched off.

After the particles have transitioned to the vertical orientation, they order according to a complex balance of other forces, such as magnetic dipole-dipole interactions, thermal fluctuations, and van der Waals forces, which depend strongly on different combinations of external field strength, dipole moment, particle size and shape, surface packing fraction and fluid properties, making final structures in the absence of capillary interactions difficult to predict. Figure 2d illustrates a situation in which thermal fluctuations are greater than magnetic dipole-dipole interactions, and the particles order randomly.

The above mentioned parameters can be varied to observe the transition experimentally. For a typical system with a super-paramagnetic particle of long-axis radius \( R_0 \approx 1 \mu m \), saturated

---

**Figure 1.** Anti-symmetric meniscus formation (solid red lines) for a single magnetic ellipsoidal particle with dipole moment, \( \mu \), under the influence of an applied magnetic field, \( H \), directed normal to the undeformed interface (blue dashed).

**Figure 2.** (a) The particles are distributed randomly in their equilibrium orientations with surface fraction \( \phi = 0.38 \). (b) Applying a magnetic field parallel to the interface normal, \( H \), causes them to self-assemble due to dipolar capillary interactions. (c) Once the critical field strength is reached, particles transition to the vertical state, halting dipolar capillary interactions. (d) Illustration: once capillary interactions have been turned off, the particles may order randomly if magnetic dipole-dipole and van der Waals interactions are weak compared to thermal fluctuations.
magnetic moment $\mu = 80 \text{ Am}^2\text{kg}^{-1}$ and surface-tension $\gamma = 0.05 \text{ Nm}^{-1}$, a magnetic field strength $H < 1 \text{T}$ should suffice to observe the first-order phase transition.\[^2\]

In Figure 3 we present a systematic investigation of the intermediate dipole-field strength regime before the particles have transitioned to the vertical configuration i.e. the particles are tilted with respect to the interface, for several surface-fractions, $\phi = N A_p / A$, where $N$ is the number of particles adsorbed at the interface, $A_p$ is the interface cross sectional area of a single particle, and $A$ is the area of the interface.

We find that the self-assembled structures depend strongly on the dipole-field strength. For weak fields, $B = 0.2B_c$, particles show some ordering, orienting in the side-by-side and tip-to-tip configuration (Figure 3b, 3g, and 3l). As the dipole-field strength is increased to $B = 0.5B_c$, the particles begin to form long, curved ordered chains, or “capillary caterpillars”, in which particles are oriented side-by-side and separate caterpillars prefer to face each other tip-to-tip (c), (h), (m). As the field strength is increased to $0.8B_c$, the caterpillars begin to prefer sharper, 90° corners instead of curved chains (d), (i), (n). We see a further increase in corner sharpness for field strengths of $B = 1.2B_c$, and we observed small numbers of flipped particles in the vertical state for $\phi = 0.38$ (e). As the surface fraction is increased to $\phi = 0.51$ (j) and $\phi = 0.60$ (o), fewer flipped particles are observed.

Compared with the self-assembled structures observed due to quadrupolar capillary interactions,\[^8,9,17,38,39\] we find that the
dipolar capillary interactions also favor side-side orientations. Only once individual capillary caterpillars have formed do the particles in each caterpillar arrange tip-tip with particles in other caterpillars. Fully understanding dipolar capillary-induced chain formation is a priority for future study. For quadrupolar capillary interactions, tip-tip configurations occur when electrostatic repulsion between particles exists, and capillary arrows can form when the particles are of unequal size. The effect of particle size, aspect-ratio, contact-angle, charge and magnetic moment remain unexplored for the dipolar capillary interactions we report here.

By using magnetic anisotropic particles interacting with external magnetic fields, we have shown how to dynamically tune dipolar capillary interactions between particles by varying the dipole-field strength, and how to switch these dipolar capillary interactions on and off by making the particles undergo a first-order orientation transition. Our simulations reveal novel self-assembled structures that depend on the surface coverage of particles and the dipole-field strength. We observed the formation of “capillary caterpillars”, in which particles align in side-side configurations, and “capillary couples” where particles in individual caterpillars align in tip-tip chains with particles in other caterpillars, due to the anti-symmetric meniscus formation. In addition to providing motivation for new experiments on the bottom-up fabrication of new materials, the novel assembly behaviour reported here should also be observable in colloidal-liquid crystal mixtures and has implications for liquid crystals in general. Further, the discontinuous transition of the prolate spheroidal particles and the on-off tunability of capillary interactions could find applications in photonic systems that require dynamic control of optical properties, such as e-readers. Finally, the sensitivity of the first order orientation transition, and hence the assembly process, to the particle size and shape, external field strength and interface surface tensions has potential applications in colloidal metrology for sensors that respond to small changes in interface properties.

Acknowledgements
GBD & PVC are grateful to EPRSC and Fujitsu Laboratories Europe for funding GBD’s PhD studentship. JH acknowledges financial support from NWO/STW (VIDI grant 10787 of J. Harting). FB thanks EPSRC for awarding a Leadership Fellowship and TK acknowledges the University of Edinburgh for awarding a Chancellor’s Fellowship. We ran our simulations on HECToR and ARCHER, the UK’s HPC service, via CPU time awarded by grants EPSRC “Large Scale Lattice Boltzmann for Biocolloidal Systems” (EP/I034602/1), “2020 Science” (EP/I017909/1), “UK Consortium on Mesoscale Engineering Sciences” (EP/L00030X/1) and EU-FP7 CRESTA grant (Grant No. 287703).

Received: May 30, 2014
Revised: July 11, 2014
Published online:

[1] G. B. Davies, T. Krüger, P. V. Coveney, J. Harting, F. Bresme, Soft Matter 2014, DOI: 10.1039/C4SM01124D.
[2] F. Bresme, J. Faraldo, J. Phys. Condens. Matter 2007, 19, 375110.
[3] F. Bresme, Eur. Phys. J. B 2008, 64, 487.
[4] B. P. Binks, Cur. Opin. Colloid Int. Sci. 2002, 7, 21.
[5] F. Bresme, M. Oettel, J. Phys. Condens. Matter 2007, 19, 413101.
[6] B. Madivala, S. Vandebril, J. Fransaer, J. Vermant, Soft Matter 2009, 5, 1717.
[7] G. A. Ozin, A. C. Arsenault, L. Cademartiri, Nanotechnology: a chemical approach to nanomaterials, Royal Society of Chemistry, 2009.
[8] L. Botto, E. P. Lewandowski, M. Caballero, K. J. Stebe, Soft Matter 2012, 8, 9957.
[9] J. C. Loundet, B. Pouliquen, Eur. Phys. J. E 2011, 34, 1.
[10] P. J. Yunker, T. Still, M. A. Lohr, A. G. Yodh, Nature 2011, 476, 308.
[11] I. Larmour, G. Saunders, S. Bell, Angew. Chem. Int. Edit. 2008, 47, 5043.
[12] D. Vella, L. Mahadevan, Am. J. Phys. 2005, 73, 817.
[13] P. A. Kračkevs'kyj, K. Nagayama, Langmuir 1994, 10, 23.
[14] P. A. Kračkevs'kyj, K. Nagayama, Adv. Colloid Interface Sci. 2000, 85, 145.
[15] H. Lehie, E. Noruzifar, M. Oettel, Eur. Phys. J. E 2008, 26, 151.
[16] M. Oettel, S. Dietrich, Langmuir 2008, 24, 1425.
[17] J. C. Loundet, A. M. Alsayed, J. Zhang, A. G. Yodh, Phys. Rev. Lett. 2005, 94, 018301.
[18] Z.-Q. Li, L. Zhang, Y. Song, X.-T. Chen, J. L. Musfeldt, Z.-L. Xue, Adv. Mater. 2013, 25, 2830.
[19] M. L. Brongersma, A. Polman, Adv. Mater. 2001, 13, 1511–1514.
[20] G. Zabow, S. J. Dodd, A. P. Koretsky, Small 2014, 10, 1902.
[21] T. Hyeon, Chem. Commun. 2003, 8, 927.
[22] F. Li, D. P. Josephson, A. Stein, Angew. Chem. Int. Edit. 2011, 50, 360.
[23] S. Chen, G. D. Doolen, Annu. Rev. Fluid Mech. 1998, 30, 329.
[24] H. Chen, S. Chen, W. H. Matthaeus, Phys. Rev. A 1992, 45, R5339.
[25] S. Chen, H. Chen, Phys. Rev. E 1993, 47, 1815.
[26] X. Shan, H. Chen, Phys. Rev. E 1994, 94, 2941.
[27] A. J. C. Ladd, J. Fluid Mech. 1994, 271, 285.
[28] A. J. C. Ladd, J. Fluid Mech. 1994, 271, 311.
[29] A. J. C. Ladd, R. Verberg, J. Stat. Phys. 2001, 104, 1191.
[30] P. L. Bhattacharjee, E. P. Cross, M. Krook, Phys. Rev. 1954, 94, 511.
[33] E. Orlandini, M. R. Swift, J. M. Yeomans, EPL 1995, 32, 463.
[34] M. R. Swift, E. Orlandini, W. R. Osborn, J. M. Yeomans, Phys. Rev. E 1996, 54, 5041.
[35] F. Jansen, J. Harting, Phys. Rev. E 2011, 83, 046707.
[36] S. Frijters, F. Günther, J. Harting, Soft Matter 2012, 8, 6542.
[37] P. Love, M. Nekovee, P. Coveney, J. Chin, N. González-Segredo, J. Martin, Comp. Phys. Comm. 2003, 153, 340.
[38] J. C. Loudet, B. Pouliqny, EPL 2009, 85, 28003.
[39] L. Botto, L. Yao, R. L. Leheny, K. J. Stebe, Soft Matter 2012, 8, 4971.
[40] S. P. Meeker, W. C. K. Poon, J. Crain, E. M. Terentjev, Phys. Rev. E 2000, 61, R6083.
[41] J. Cleaver, W. C. K. Poon, J. Phys. Condens. Matter 2004, 16, S1901.
[42] S.-H. Kim, S. Y. Lee, S.-M. Yang, G.-R. Yi, NPG Asia Mater. 2011, 3, 25.