REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
13-09-2014	Final Report	21-May-2010 - 20-May-2014

4. TITLE AND SUBTITLE
Final Report: Novel Colloidal and Dynamic Interfacial Phenomena in Liquid Crystalline Systems

5a. CONTRACT NUMBER
W911NF-10-1-0181

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Nicholas L. Abbott

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Wisconsin - Madison
Suite 6401
21 N Park St
Madison, WI 53715 -1218

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
57490-CH.31

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Fundamental processes involving the assembly of molecular amphiphiles and nano/microparticles at the interfaces of isotropic liquids have been widely studied over the past century, and knowledge that emerged from these past studies has impacted a broad range of technologies of relevance to DoD (e.g., design of emulsions for decontamination, or design of interfaces for chemical and biological detection). The investigation supported by this grant moved beyond past studies of interfacial and colloidal phenomena involving isotropic liquids to explore and understand a range of new phenomena that take place at the interfaces of anisotropic liquids, namely liquid crystals

15. SUBJECT TERMS
liquid crystals, interfacial phenomena, colloids, amphiphiles, responsive interfaces, supramolecular chemistry

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			NICHOLAS ABBOTT
UU	UU	UU	UU		19b. TELEPHONE NUMBER 608-265-5278

Report Title

Final Report: Novel Colloidal and Dynamic Interfacial Phenomena in Liquid Crystalline Systems

ABSTRACT

Fundamental processes involving the assembly of molecular amphiphiles and nano/microparticles at the interfaces of isotropic liquids have been widely studied over the past century, and knowledge that emerged from these past studies has impacted a broad range of technologies of relevance to DoD (e.g., design of emulsions for decontamination, or design of interfaces for chemical and biological detection). The investigation supported by this grant moved beyond past studies of interfacial and colloidal phenomena involving isotropic liquids to explore and understand a range of new phenomena that take place at the interfaces of anisotropic liquids, namely liquid crystals. The program of research unmasked new behaviors of molecular amphiphiles and micro/nanoparticles at the interfaces of liquid crystals. The study revealed that the ordering of a liquid crystal can mediate new types of interactions between interfacial adsorbates (molecular and particulate), leading to new phase states and the ability to drive dynamic interfacial events with a level of control that is not possible with isotropic liquids. These results have the potential to impact, in the long term, strategies for materials synthesis, stabilization of emulsions, design of stimuli-responsive materials, creation of tunable plasmonic metamaterials, as well as the interfacial design of chemical and biological sensors.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
05/13/2013 15.00	Daniel S. Miller, Rebecca J. Carlton, Peter C. Mushenheim, Nicholas L. Abbott. Introduction to Optical Methods for Characterizing Liquid Crystals at Interfaces, Langmuir, (03 2013): 0. doi: 10.1021/la304679f
08/16/2012 13.00	Rebecca J. Carlton, Jugal K. Gupta, Nicholas L. Abbott, Candice L. Swift. Influence of Simple Electrolytes on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces, Langmuir, (01 2012): 0. doi: 10.1021/la203729t
08/16/2012 14.00	Daniel Abras, Gaurav Pranami, Nicholas L. Abbott. The mobilities of micro- and nano-particles at interfaces of nematic liquid crystals, Soft Matter, (01 2012): 0. doi: 10.1039/c1sm06794j
08/29/2013 16.00	Frédéric Mondiot, Xiaoguang Wang, Juan J. de Pablo, Nicholas L. Abbott. Liquid Crystal-Based Emulsions for Synthesis of Spherical and Non-Spherical Particles with Chemical Patches, Journal of the American Chemical Society, (07 2013): 9972. doi: 10.1021/ja4022182
08/29/2013 17.00	Jacob T. Hunter, Nicholas L. Abbott. Dynamics of the chemo-optical response of supported films of nematic liquid crystals, Sensors and Actuators B: Chemical, (07 2013): 71. doi: 10.1016/j.snb.2013.03.094
08/29/2013 19.00	Daniel S. Miller, Nicholas L. Abbott. Influence of droplet size, pH and ionic strength on endotoxin-triggered ordering transitions in liquid crystalline droplets, Soft Matter, (01 2013): 374. doi: 10.1039/c2sm26811f
08/29/2013 18.00	Rebecca J. Carlton, Fumito Araoka, Nicholas L. Abbott, Hideo Takezoe, Guksik Lee. Amplification of the Stereochemistry of Biomolecular Adsorbates by Deracemization of Chiral Domains in Bent-Core Liquid Crystals, Advanced Materials, (01 2013): 245. doi: 10.1002/adma.201203302
08/29/2013 20.00	Wilder Iglesias, Nicholas L. Abbott, Elizabeth K. Mann, Antal Jákli. Improving Liquid-Crystal-Based Biosensing in Aqueous Phases, ACS Applied Materials & Interfaces, (12 2012): 6883. doi: 10.1021/am301952f
08/29/2013 21.00	C. Derek Ma, Jugal K. Gupta, Nicholas L. Abbott, Rebecca J. Carlton. Influence of Specific Anions on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces, Langmuir, (11 2012): 12796. doi: 10.1021/la3024293
09/13/2014 25.00	Ankit Agarwal, Patricia R. Kierski, Maggie Herron, Diego F. Calderon, Leandro B. C. Teixeira, Michael J. Schurr, Christopher J. Murphy, Charles J. Czuprynski, Jonathan F. McAnulty, Nicholas L. Abbott. Reduction in Wound Bioburden using a Silver-Loaded Dissolvable Microfilm Construct, Advanced Healthcare Materials, (06 2014): 916. doi: 10.1002/adhm.201300537
09/13/2014 26.00	Rishabh Jain, Diego Calderon, Patricia R. Kierski, Michael J. Schurr, Charles J. Czuprynski, Christopher J. Murphy, Jonathan F. McAnulty, Nicholas L. Abbott. Raman Spectroscopy Enables Noninvasive Biochemical Characterization and Identification of the Stage of Healing of a Wound, Analytical Chemistry, (04 2014): 3764. doi: 10.1021/ac500513t
09/13/2014 27.00	Jacob T. Hunter, Nicholas L. Abbott. Adsorbate-Induced Anchoring Transitions of Liquid Crystals on Surfaces Presenting Metal Salts with Mixed Anions, ACS Applied Materials & Interfaces, (02 2014): 2360. doi: 10.1021/am404632r

09/13/2014 28.00 Emre Bukusoglu, Santanu Kumar Pal, Juan J. de Pablo, Nicholas L. Abbott. Colloid-in-liquid crystal gels formed via spinodal decomposition,
Soft Matter, (03 2014): 1602. doi: 10.1039/c3sm51877a

09/13/2014 29.00 Daniel S. Miller, Xiaoguang Wang, James Buchen, Oleg D. Lavrentovich, Nicholas L. Abbott. Analysis of the Internal Configurations of Droplets of Liquid Crystal Using Flow Cytometry,
Analytical Chemistry, (11 2013): 10296. doi: 10.1021/ac4021193

09/13/2014 30.00 Daniel S. Miller, Xiaoguang Wang, Nicholas L. Abbott. Design of Functional Materials Based on Liquid Crystalline Droplets,
Chemistry of Materials, (01 2014): 496. doi: 10.1021/cm4025028

10/15/2011 1.00 J. A. Moreno-Razo, E. J. Sambriski, G. M. Koenig, E. Díaz-Herrera, N. L. Abbott, J. J. de Pablo. Effects of anchoring strength on the diffusivity of nanoparticles in model liquid-crystalline fluids,
Soft Matter, (03 2011): 6828. doi: 10.1039/c0sm01506g

10/15/2011 2.00 D. S. Miller, I.-H. Lin, P. J. Bertics, C. J. Murphy, J. J. de Pablo, N. L. Abbott. Endotoxin-Induced Structural Transformations in Liquid Crystalline Droplets,
Science, (05 2011): 1297. doi: 10.1126/science.1195639

10/15/2011 3.00 Yiqun Bai, Nicholas L. Abbott. Recent Advances in Colloidal and Interfacial Phenomena Involving Liquid Crystals,
Langmuir, (05 2011): 5719. doi: 10.1021/la103301d

10/15/2011 4.00 Lie Na Tan, Paul J. Bertics, Nicholas L. Abbott. Ordering Transitions in Nematic Liquid Crystals Induced by Vesicles Captured through Ligand?Receptor Interactions,
Langmuir, (02 2011): 1419. doi: 10.1021/la103975s

10/15/2011 5.00 Santanu Kumar Pal, Claribel Acevedo-Ve?lez, Jacob T. Hunter, Nicholas L. Abbott. Effects of Divalent Ligand Interactions on Surface-Induced Ordering of Liquid Crystals,
Chemistry of Materials, (10 2010): 5474. doi: 10.1021/cm1011058

10/15/2011 6.00 Michael I. Kinsinger, Maren E. Buck, Nicholas L. Abbott, David M. Lynn. Immobilization of Polymer-Decorated Liquid Crystal Droplets on Chemically Tailored Surfaces,
Langmuir, (06 2010): 10234. doi: 10.1021/la100376u

10/15/2011 7.00 G. M. Koenig, I.-H. Lin, N. L. Abbott. Chemoresponsive assemblies of microparticles at liquid crystalline interfaces,
Proceedings of the National Academy of Sciences, (01 2010): 3998. doi: 10.1073/pnas.0910931107

TOTAL: 22

Number of Papers published in peer-reviewed journals: 6

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
08/16/2012	9.00	Yiqun Bai, Nicholas L. Abbott. Recent Advances in Colloidal and Interfacial Phenomena InvolvingLiquid Crystals, Langmuir, (11 2010): 5719. doi:
TOTAL:		**1**

Number of Papers published in non peer-reviewed journals: 7

(c) Presentations

Presentation #1
(a) Electrical double layer and specific ion effects at interfaces between thermotropic liquid crystals and aqueous phases
(b) Nicholas L Abbott, Rebecca Carlton.
(c) Ions play a central role in a wide range of interfacial phenomena, including colloidal stability, formation of emulsions, fusion events involving biological membranes and charging of electrochemical interfaces. At relatively low concentrations, the effects of ions often reflect the presence of electrical double layers, whereas at high concentrations of ions, phenomena connected to the hydration of ions can dominate and pronounced specific ion phenomena are observed. In this presentation, observations of orientational ordering transitions of thermotropic, water-immiscible liquid crystals (LCs) at aqueous interfaces (i.e., an oil-water interface) that are triggered by the interactions of simple ions will be described. Because the ordering of the molecules in the LC phase is long range, the interfacial ionic events are amplified into bulk ordering transitions within the LC phase that are readily quantified by optical methods. A particularly surprising finding is salt-induced patterned orientations of LCs, suggesting the lateral segregation of species at these oil-water interfaces. The results are significant in that they offer new fundamental insights into ionic phenomena at oil-water interfaces and provide guidance for the design of dynamic and responsive materials based on LCs.
(d) ACS Fall Meeting, Denver Colorado, and August 28, 2011.

Presentation #2
(a) Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
(b) Nicholas Abbott
(c) Processes leading to the self-organization of molecules and colloids within and at the interfaces of isotropic liquids have been widely studied in the past. This talk will focus beyond those past studies by addressing interfacial and colloidal phenomena in systems in which the isotropic solvent is replaced by a nematic liquid crystal (LC). Observations derived from two experimental systems will be described. The first system involves LC-in-water emulsion droplets, and the influence of droplet size and interfacial chemistry on the structure of the droplets. Recent experimental observations in our laboratory have unmasked size-dependent ordering of the LC droplets that is not predicted by classical theories of LCs. Ordering transitions that are exquisitely sensitive to certain classes of biological lipids (e.g., endotoxin) have also been discovered. The second experimental system to be discussed involves the interfacial organization of solid microparticles at aqueous-LC interfaces. Our observations have revealed that the nematic order of a LC can give rise to new classes of inter-particle interactions at these interfaces. Significantly, the symmetries of the interactions differ from those encountered in isotropic solvent systems, thus giving rise to interfacial organizations of particles not previously reported. This presentation will highlight fundamental and unresolved issues related to the behaviors of these LC-colloidal systems.
(d) Texas A&M University, Department of Chemical Engineering, September 13, 2011.

Presentation #3
a) Optical Transduction of Endotoxin-Induced Structural Transformations in Liquid Crystalline Droplets
b) I-Hsin Lin, Daniel S. Miller, Nicholas L. Abbott
c) We report that picogram per milliliter concentrations of endotoxin in water cause the director structure of micrometer-sized liquid crystalline (LC) droplets to change from bipolar to radial configurations. The ordering transitions, which occur at surface concentrations of endotoxin that are less than 10-5 Langmuir (1 Langmuir = 1 monolayer), are not due to adsorbate-induced changes in the interfacial energy of the LC but rather involve the interaction of endotoxin with localized regions of the LC droplets. The sensitivity of the LC to endotoxin was measured to change by six orders of magnitude with the geometry of the LC (droplet versus slab), supporting the hypothesis that topological defects in the LC mediate the response of the droplets. The LC ordering transitions depend strongly on glycophospholipid structure and provide new designs for responsive soft matter.
d) Optics in Liquid Crystals Conference, Yerevan, Armenia, September 27, 2011

Presentation #4
a) Diffusion of Colloids at Liquid Crystalline Interfaces
b) Nicholas L. Abbott
c) This presentation will focus on the use of single-particle tracking to measure the diffusion coefficients of chemically functionalized micro- and nano-particles at interfaces between aqueous phases and a nematic liquid crystal (LC). For hydrophobic particles with diameters of 2.3 ± 0.2 μm that homeotropically anchoring the LC, we have measured anisotropic diffusion, qualitatively consistent with the influence of nematic ordering of the LC at the interface on the local rheological environment. Analysis of the magnitudes of the diffusion coefficients reveal that the ordering of the LC about the microparticles is perturbed in the interfacial environment relative to the bulk, leading to low drag on the microparticles at the aqueous-nematic interface. In contrast, for hydrophobic nanoparticles (diameters of 141 ± 11 nm) at the LC-aqueous interface, almost indistinguishable diffusion coefficients were measured at the interface and in bulk LC when the displacements of the nanoparticles in the two environments were in the same directions relative to the far-field director of the LC. These results and others to be described in this presentation reveal fundamental differences to exist between the interfacial mobilities of micro and nanoparticles at LC-aqueous interfaces, and that a relative insensitivity to interfacial environment appears to be a property of the smaller particles studied in our experiments. These findings will be discussed in light of past experimental and theoretical studies of the diffusion of particles at either isotropic liquid interfaces or in bulk LCs.
d) Planer-Smoluchowski Soft Matter Workshop on Liquid Crystal Colloids, Lviv, Ukraine, October 6, 2011.

Presentation #5
a) Recent Advances in Colloidal and Interfacial Phenomena Involving Liquid Crystals
b) Nicholas L. Abbott

c) This presentation will address recent advances in several areas of research involving the interfacial ordering of liquid crystals (LCs). The first advance revolves around the ordering of LCs at bio/chemically functionalized surfaces. Whereas the majority of past studies of surface-induced ordering of LCs have involved surfaces of solids that present a limited diversity of chemical functional groups (surfaces at which van der Waals forces dominate surface-induced ordering), recent studies have moved to investigate the ordering of LCs on chemically complex surfaces. For example, surfaces decorated with biomolecules (e.g. oligopeptides and proteins) and transition metal ions have been investigated, leading to an understanding of the roles that metal-ligand coordination interactions, electrical double-layers, acid-base interactions, and hydrogen bonding can have on the interfacial ordering of LCs. The opportunity to create chemically-responsive LCs capable of undergoing ordering transitions in the presence of targeted molecular events (e.g., ligand exchange around a metal center) has emerged from these fundamental studies. The second area of research to be addressed in this presentation is focused on investigations of the ordering of LCs at interfaces with immiscible isotropic fluids, particularly water. In contrast to prior studies of surface-induced ordering of LCs on solid surfaces, LC-aqueous interfaces are deformable and molecules at these interfaces exhibit high levels of mobility and thus can reorganize in response to changes in interfacial environment. A range of fundamental investigations involving these LC-aqueous interfaces have revealed that (i) the spatial and temporal characteristics of assemblies formed from biomolecular interactions can be reported by surface-driven ordering transitions in the LCs, (ii) the interfacial phase behaviour of molecules and colloids can be coupled to (and manipulated via) the ordering (and nematic elasticity) of LCs, and (iii) confinement of LCs leads to unanticipated size-dependent ordering (particularly in the context of LC emulsion droplets). The third advance to be discussed involves interactions between colloids mediated by LCs. Recent experiments involving microparticles deposited at the LC-aqueous interface have revealed that LC-mediated interactions can drive interfacial assemblies of particles through reversible ordering transitions (e.g., from one-dimensional chains to two-dimensional arrays with local hexagonal symmetry). In addition, single nanoparticle measurements suggest that the ordering of LCs about nanoparticles differs substantially from micrometer-sized particles and that the interactions between nanoparticles mediated by the LCs are far weaker than predicted by theory (sufficiently weak that the interactions are reversible and thus enable self-assembly). Finally, LC-mediated interactions between colloidal particles have also been shown to lead to the formation of colloid-in-LC gels that possess mechanical properties relevant to the design of materials to interface with living biological systems. Overall, the three areas of research summarized above will be used to illustrate the broad opportunities that exist to do fundamental interfacial science and discovery-oriented research involving LCs.
d) Annual Meeting of AIChE, Plenary Lecture in Area 1C (Colloid and Interfacial Phenomena), Minneapolis, MN, October 2011.

Presentation #6
a) Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
b) Nicholas L. Abbott
c) Processes leading to the self-organization of molecules and colloids within and at the interfaces of isotropic liquids have been widely studied in the past. This talk will focus beyond those past studies by addressing interfacial and colloidal phenomena in systems in which the isotropic solvent is replaced by a nematic liquid crystal (LC). Observations derived from two experimental systems will be described. The first system involves LC-in-water emulsion droplets, and the influence of droplet size and interfacial chemistry on the structure of the droplets. Recent experimental observations in our laboratory have unmasked size-dependent ordering of the LC droplets that is not predicted by classical theories of LCs. Ordering transitions that are exquisitely sensitive to certain classes of biological lipids (e.g., endotoxin) have also been discovered. The second experimental system to be discussed involves the interfacial organization of solid microparticles at aqueous-LC interfaces. Our observations have revealed that the nematic order of a LC can give rise to new classes of inter-particle interactions at these interfaces. Significantly, the symmetries of the interactions differ from those encountered in isotropic solvent systems, thus giving rise to interfacial organizations of particles not previously reported. This presentation will highlight fundamental and unresolved issues related to the behaviors of these LC-colloidal systems.
d) University of Delaware, Wohl Memorial Lecture, Department of Chemical Engineering, November 2011 (named lectureship).

Presentation #7
a) Recent Advances in the Interfacial Engineering of Biological and Synthetic Materials
b) Nicholas L. Abbott
c) The past decade has witnessed important advances in methodologies that permit engineering of the interfaces of soft materials with precisely controlled properties relevant to a broad range of technological contexts. This presentation will present an overview of these advances and then illustrate their application through two focused examples. The first example will address the creation of functional interfaces of liquid crystalline materials. Whereas interfacial engineering of liquid crystals underlies the realization of liquid crystal display technology, it is now possible to control the bio/chemical functionality of LC interfaces in ways that were not previously possible. These advances are opening new potential applications of liquid crystals related to chemical and biological sensing. The second example to be discussed in this presentation will address the use of soft polymeric films to modify the interfacial properties of biological tissues. Specifically, recent efforts to use ultrathin polymeric films to engineer the interfacial properties of wound beds so as to promote wound healing will be described.
d) University of Alabama, College of Engineering Lecture, Huntsville, AL, January 2012(College-wide lecture)

Presentation #8
a) Bio-inspired Design of Soft Materials on the Nanoscale
b) Nicholas L. Abbott
c) The convergence of research involving the life sciences and nanoscience is presenting new opportunities to address unresolved fundamental issues regarding the origins of intermolecular forces that direct the assembly of soft materials on the nanoscale, as well as technological opportunities to create new functional devices that recapitulate designs found in biology. This presentation will illustrate how bio-inspired designs of materials on the nanoscale are enabling new science and new technology. The first example will address the design

of organic nanostructures using oligomers of non-natural amino acids and the use of these unique nanostructures to elucidate how patterns of chemical functional groups encode intermolecular interactions that direct self-assembly on the nanoscale. A particular focus will be directed to understanding hydrophobic interactions. The second example will highlight the technological opportunity that is emerging from the engineering of mechanical stresses and nanoscopic defects in soft organic materials. Specifically, the engineering of defects in liquid crystalline materials will be demonstrated to permit detection of specific bacterial lipids with high sensitivity and selectivity. These advances are opening new potential applications of liquid crystals related to chemical and biological sensing.
d) International Conference on Nanoscience and Nanotechnology, Perth, Western Australia, February, 2012 (Plenary Lecture)

Presentation #9
a) Directed Assembly on the Nano-Scale using Liquid Crystals.
b) Nicholas L. Abbott
c) The self-assembly of colloidal and macromolecular species in isotropic organic and aqueous solvents has been widely explored in the past. This presentation moves to consider the assembly of nanoscopic particles and molecular assemblies under the influence of forces that are mediated by liquid crystalline solvents. To illustrate the fundamental challenges and technological opportunities in this area, two examples will be addressed. First, the interactions between inorganic colloidal particles in liquid crystalline solvents will be discussed. In this example, the anisotropic elastic properties of the liquid crystalline phase, as well as topological defects induced in the liquid crystal by the particles, are observed to lead to inter-particle interactions that have symmetries that are different from those typically encountered in isotropic solvent systems. The second example will focus on emulsions formed by dispersions of thermotropic liquid crystals in water. We have recently found evidence that the self-assembly of lipids in nano-scale defects formed within the liquid crystalline droplets can lead to ordering transitions in the droplets. The potential use of this phenomenon for selective detection of bacterial lipids will be discussed.
d) Technion-Israel, Winter School on Complex Fluids and Nanoscience, Israel, March 1, 2012.

Presentation #10
a) Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
b) Nicholas L. Abbott
c) Processes leading to the self-organization of molecules and colloids within and at the interfaces of isotropic liquids have been widely studied in the past. This talk will focus beyond those past studies by addressing interfacial and colloidal phenomena in systems in which the isotropic solvent is replaced by a nematic liquid crystal (LC). Observations derived from two experimental systems will be described. The first system involves LC-in-water emulsion droplets, and the influence of droplet size and interfacial chemistry on the structure of the droplets. Recent experimental observations in our laboratory have unmasked size-dependent ordering of the LC droplets that is not predicted by classical theories of LCs. Ordering transitions that are exquisitely sensitive to certain classes of biological lipids (e.g., endotoxin) have also been discovered. The second experimental system to be discussed involves the interfacial organization of solid microparticles at aqueous-LC interfaces. Our observations have revealed that the nematic order of a LC can give rise to new classes of inter-particle interactions at these interfaces. Significantly, the symmetries of the interactions differ from those encountered in isotropic solvent systems, thus giving rise to interfacial organizations of particles not previously reported. This presentation will highlight fundamental and unresolved issues related to the behaviors of these LC-colloidal systems.
d) Tufts University, Jeanne and Martin Sussman Lectureship, Department of Chemical and Biological Engineering, April 23, 2012 (Named lecture)

Presentation #11
a) Understanding Hydrophobic Interactions on the Nano-Scale
b) Nicholas L. Abbott
c) Water-mediated interactions involving hydrophobic domains are known to play a central role in a broad range of colloidal and interfacial phenomena, including molecular self-assembly and macromolecular (e.g., protein) folding processes. In the majority of these systems, although polar and charged groups are present in close proximity to hydrophobic domains, how these proximal groups modulate hydrophobic interactions is not understood. Theories and simulations have predicted these proximity effects to be significant, but the lack of suitable experimental systems has prevented such ideas from being tested. This presentation will describe an experimental investigation of the forces experienced by conformationally well-defined, single oligomers of ß-amino acids ("ß-peptides") that are designed to display a nanoscopic hydrophobic domain proximal to three lysine groups. Measurements of the interactions of single ß-peptides with a hydrophobic surface reveal that changes in the charge status of the lysine groups lead to pronounced changes in adhesive interactions through two effects: (i) when protonated, the cationic lysine groups generate an adhesive interaction with the hydrophobic surface via screened, electrostatic interactions, due to an accumulation of negative surface charge on the hydrophobic surface (verified by zeta potential measurements); (ii) as revealed by addition of methanol, the charge status of the lysine impacts the strength of the hydrophobic interaction of the hydrophobic nanodomain of the ß-peptide with the hydrophobic surface. Specifically, these results reveal that charged (ammonium) groups proximal to a hydrophobic domain strengthen hydrophobic interactions involving that domain. Overall, the experiments to be reported in this presentation identify two influences of proximal cationic groups on hydrophobic interactions, and validate an experimental system that has the potential to substantially advance our understanding of intermolecular forces associated with hydrophobic domains at the nanoscopic length scale.
d) 7th Meeting of the Eastern Mediterranean Chemical Engineering Conference (EMCC-7), Corfu, Greece. April 28, 2012.

Presentation #12
a) Design of Chemo- and Bio-Responsive Materials based on Liquid Crystals
b) Nicholas L. Abbott

c) This presentation will describe principles for the design of liquid crystalline materials that respond to the presence of targeted chemical and biological species. The presentation will be organized into three parts. First, an overview of fundamental properties of liquid crystals that enable their use as stimuli-responsive materials will be presented. Concepts related to the formation of topological defects, curvature strain in liquid crystals and surface-induced ordering will be introduced. The second part of the talk will move to a discussion of chemo-responsive liquid crystalline systems, with a focus on interfacial design principles that enable the presence of parts-per-billion concentrations of targeted vapor phase agents (e.g., organophosphonates) to trigger macroscopic ordering transitions in liquid crystals. Ongoing efforts to translate these principles to composite liquid crystalline materials (such as liquid crystalline gels) that are readily processed (e.g., molded) and sufficiently robust to be placed into a range of environments will be described. The third part of the talk will address the design of liquid crystals to report the presence of biological species. Here the discussion will revolve around interfaces between thermotropic liquid crystals and aqueous phases, and the use of confinement of liquid crystals to tune their response to biological interactions. Examples will be presented to demonstrate that ordering transitions can be triggered in liquid crystalline systems through structure-selective interactions with targeted biological molecules and their assemblies. In addition, the use liquid crystalline materials to direct the organization of biological molecules at interfaces will be discussed. Overall, the ability to report and direct the organization of biomolecules at interfaces hints at new principles by which liquid crystalline materials might be used to trigger a response for biological defense.
d) Targeting and Triggering Basic Research Workshop, Cambridge University, UK, May 15, 2012.

Presentation #13
(a) Emulsions formed from Structured Oils
(b) Nicholas L. Abbott
(c) This presentation will discuss oil-in-water emulsions that are formed using a thermotropic liquid crystal as the oil. Several issues will be addressed. First, the influence of confinement within the emulsion droplets on the ordering of the liquid crystal will be addressed. The competing influences of topological defects, elastic energies associated with strained states of the liquid crystal, as well as surface anchoring of the liquid crystal, will be discussed. Examples of adsorbate-induced ordering transitions that are strongly dependent on the structure of the adsorbate will be presented. The second focus of the presentation will move to electrical double layers formed at the aqueous-oil interface of the emulsion droplets. Evidence of the formation of double layers on the oil-side of the interface will be presented, based on ordering transitions observed in the liquid crystalline oil within the droplets. The third focus will address proteins adsorbed at aqueous-oil interfaces, and demonstrate the use of the liquid crystals to probe changes in the states of proteins adsorbed to the interfaces of oil droplets. Overall, the topics addressed in this talk will highlight the opportunity presented by liquid crystal-in-water emulsions to provide fundamental insights into interfacial phenomena occurring in oil-in-water emulsion systems. It will also hint at the opportunity that exists to create new technologies based on these systems.
(d) ACS Colloids and Interfaces Symposium, Baltimore, June 12, 2012.

Presentation #14
a) Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
b) Nicholas L. Abbott
c) Processes leading to the self-organization of molecules and colloids within and at the interfaces of isotropic liquids have been widely studied in the past. This talk will focus beyond those past studies by addressing interfacial and colloidal phenomena in systems in which the isotropic solvent is replaced by a nematic liquid crystal (LC). Observations derived from two experimental systems will be described. The first system involves LC-in-water emulsion droplets, and the influence of droplet size and interfacial chemistry on the structure of the droplets. Recent experimental observations in our laboratory have unmasked size-dependent ordering of the LC droplets that is not predicted by classical theories of LCs. Ordering transitions that are exquisitely sensitive to certain classes of biological lipids (e.g., endotoxin) have also been discovered. The second experimental system to be discussed involves the interfacial organization of solid microparticles at aqueous-LC interfaces. Our observations have revealed that the nematic order of a LC can give rise to new classes of inter-particle interactions at these interfaces. Significantly, the symmetries of the interactions differ from those encountered in isotropic solvent systems, thus giving rise to interfacial organizations of particles not previously reported. This presentation will highlight fundamental and unresolved issues related to the behaviors of these LC-colloidal systems.
d) Zheijiang University, May 17, 2012.

Presentation #15
a) Enantiomeric Anchoring of Liquid Crystals at Surfaces Presenting Spontaneously Formed Monolayers of Chiral Adsorbates
b) Nicholas L. Abbott
c) This presentation will describe an experimental investigation of the orientational ordering of nematic liquid crystals (LCs) supported on organized monolayers of chiral dipeptides. By characterizing the orientations of nematic LCs on monolayers of either L-cysteine-L-tyrosine, L-cysteine-L-phenylalanine or L-cysteine-L-phosphotyrosine formed on crystallographically textured films of gold, we reveal that patterns of hydrogen bonds presented by the organized monolayers of dipeptides are transduced via macroscopic orientational ordering of the LCs. This conclusion is supported by the observation that the ordering exhibited by the achiral LCs is specific to the enantiomers used to form the dipeptide-based monolayers. The dominate role of the –OH group of tyrosine in dictating the patterns of hydrogen bonds that orient the LCs was also evidenced by the effects of phosphorylation of the tyrosine on the ordering of the LCs. Overall, these results reveal that crystallographic texturing of gold films can direct the formation of monolayers of dipeptides with long-range order, thus unmasking the influence of hydrogen bonding, chirality and phosphorylation on the macroscopic orientational ordering of LCs supported on these surfaces. These results suggest new principles for the design of surfaces that orient LCs in electrooptical devices. They also address the design of chemooptic devices that use LCs to report the chemical functionality and stereochemistry of synthetic and biological peptide-based

molecules displayed at surfaces.
d) SPIE Meeting in San Diego, August 14, 2012.

Presentation #16
a) Design of biotic-abiotic interfaces using liquid crystals
b) Nicholas L. Abbott
c) Many biological molecules form liquid crystalline materials. The unique combination of long-range molecular ordering and mobility found in these materials has been exploited by nature to create functional interfaces. Inspired in part by natural systems, we have recently initiated studies that seek to engineer synthetic liquid crystalline materials to create tailored interfaces between biotic and abiotic systems. In one approach, we exploit the long-range ordering of liquid crystalline materials near interfaces to amplify nanoscopic biomolecular interactions into the optical scale. In a second approach, we seek to use the mechanical properties of liquid crystals to design materials than can be used to regulate the organization and function of biological systems. This talk will sketch examples that illustrate each of the above approaches. Fundamental challenges and technological opportunities will be discussed.
d) ACS 2012 Fall National Meeting in Philadephia, August 22, 2012.

Presentation #17
Title: Stimuli-Responsive Liquid Crystalline Materials
Authors: Nicholas Abbott
Abstract: None
Location: Workshop on “Liquid Crystals Beyond Displays”, Liquid Crystal Institute, Kent State University, September 26, 2012.

Presentation #18
Title: Design of Amphiphile-Nucleic Acid Complexes
Authors: Nicholas Abbott
Abstract: Numerous past studies have characterized the nanostructure and physical properties of complexes formed by cationic amphiphiles and long-chain DNA (>1000 base pairs), largely motivated by the goal of developing methods to separate, purify and concentrate DNA, as well as deliver genomic DNA (plasmids) to cells. This presentation will address recent investigations performed in our laboratory that move beyond these past studies in two respects. First, the design of functional cationic amphiphiles that undergo reversible association with long-chain DNA will be described. Specifically, effects of changes in the oxidation state of ferrocene within ferrocenyl amphiphiles will be discussed. Principles leading to spatial and temporal control of amphiphile-nucleic acid complexes, and thus control over functional properties, will be presented. Second, the results of an investigation of the interactions of single- and double-stranded oligonucleotides and cationic surfactants will be presented. These studies unmask pronounced effects of nucleotide composition on the nanostructure of complexes formed by single--stranded oligonucleotides. They also reveal changes in nanostructure to accompany hybridization to double-stranded oligonucleotides. Overall, these results provide insights into the intermolecular interactions that occur between cationic amphiphiles and oligonucleotides and provide guidance for the design of amphiphile-nucleotide complexes with new functional properties.
Location: World Congress on Oleo Science, Sasebo, Japan, October 1, 2012.

Presentation #19
Title: Biotic-Abiotic Interfaces based on Liquid Crystals
Authors: Nicholas Abbott
Abstract: None
Location: Lion Corporation, Tokyo, October 5, 2012.

Presentation #20
Title: Colloid-in-Liquid Crystal Gels
Authors: Nicholas Abbott
Abstract: This presentation will describe investigations of the collective properties of colloidal particles that are dispersed in liquid crystalline solvents. A focus will be directed to recent observations of the gelation of particles dispersed in thermotropic liquid crystals. While a series of studies over the past decade have revealed two distinct mechanisms leading to gelation of particles in liquid crystalline solvents, our recent observations are inconsistent with both and hint at a third mechanism of gelation. These observations will be described along with examples of how the unique mechanical and optical properties of colloid-in-liquid crystal gels enable the design of biotic-abiotic interfaces.
Location: New Horizons in Colloid Science, Montpellier, France, October 18, 2012.

Presentation #21
Title: Characterization of the Nanostructure of Complexes Formed by Single- or Double-Stranded Oligonucleotides with Cationic Surfactants
Authors: Nicholas Abbott
Abstract: This presentation will describe the use of dynamic light scattering (DLS), small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS) measurements to compare and contrast the nanostructure of complexes formed by single- or double-strand oligonucleotides with the single-tailed cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), in aqueous solutions. Whereas SAXS and SANS spectra show that single-stand oligonucleotides and CTAB form multilamellar vesicles, double strand oligonucleotides and CTAB form a hexagonal nanostructure. In addition, our results reveal that the nucleotide composition of the single-strand

oligonucleotides has a pronounced impact on the number, size and nanostructure of the complexes formed with CTAB. In contrast, for double-strand oligonucleotides, no evidence of a composition dependence on nanostructrure was measured. These results support the proposition that hydrophobic interactions, as well as electrostatics, play a central role in the formation of complexes between cationic amphiphiles and single-strand oligonucleotides and thus giving rise to interactions that depend on nucleotide composition. Overall, these results provide insights into the intermolecular interactions that occur between cationic amphiphiles and oligonucleotides, and thereby also provide guidance for the design of such complexes.
Location: ACS Meeting in New Orleans, April 11, 2013

Presentation #22
Title: Understanding Hydrophobic Interactions on the Nano-Scale using ß-Peptide Oligomers
Authors: Nicholas Abbott
Abstract: Helical oligomers of ß-peptides represent a particularly promising type of organic nanostructure for investigations of intermolecular forces because (i) the helical secondary structure can be designed to be very stable and because (ii) control of the ¿-amino acid sequence can lead to precise patterning of chemical functional groups over the surfaces of the helices. This presentation will describe the use of force spectroscopy to quantify the interactions of single ß-peptide oligomers, each of which display stable and well-defined three-dimensional chemical nanopatterns, with hydrophobic surfaces. Whereas many prior reports of single molecule force measurements of oligo-¿-peptides and macromolecules exist – the secondary and/or tertiary structures of these species are not preserved during their interactions at interfaces, and thus the three-dimensional chemical patterns that underlie previously reported force measurements are generally not known. By using ß-peptide oligomers that display the same chemical functional groups in stable and distinct spatial nano-patterns, we have demonstrated that it is possible to relate changes in measured forces to changes in three-dimensional chemical nano-patterns. Overall, the results to be described in this presentation will show how ß-peptide oligomers can be used to study intermolecular interactions that arise from precisely defined chemical nano-patterns. A particular focus of the talk will be directed to understanding hydrophobic interactions, thus providing insights into the mechanisms through which changes in chemical patterns presented by organic nanoscopic objects can dramatically affect their self-assembly behavior in aqueous environments.
Location: AIChE National Meeting, Pittsburgh, PA, October 30, 2012.

Presentation #23
Title: Design of Biotic-Abiotic Interfaces using Liquid Crystals
Authors: Nicholas Abbott
Abstract: Many biological molecules form liquid crystalline materials. The unique combination of long-range molecular ordering and mobility found in these materials has been exploited by nature to create functional interfaces. Inspired in part by natural systems, we have recently initiated studies that seek to engineer synthetic liquid crystalline materials to create tailored interfaces between biotic and abiotic systems. In one approach, we exploit the long-range ordering of liquid crystalline materials near interfaces to amplify nanoscopic biomolecular interactions into the optical scale. In a second approach, we seek to use the mechanical properties of liquid crystals to design materials, including liquid crystal-based gels, that can be used to regulate the organization and function of biological systems. This talk will sketch examples that illustrate each of the above approaches. Fundamental challenges and technological opportunities will be discussed.
Location: Society of Polymer Science of Japan, 9th International Conference, Kobe, Japan, December 13, 2012

Presentation #24
Title: Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
Authors: Nicholas Abbott
Abstract: Processes leading to the self-organization of molecules and colloids within and at the interfaces of isotropic liquids have been widely studied in the past. This talk will focus beyond those past studies by addressing interfacial and colloidal phenomena in systems in which the isotropic solvent is replaced by a nematic liquid crystal (LC). Observations derived from two experimental systems will be described. The first system involves LC-in-water emulsion droplets, and the influence of droplet size and interfacial chemistry on the structure of the droplets. Recent experimental observations in our laboratory have unmasked size-dependent ordering of the LC droplets that is not predicted by classical theories of LCs. Ordering transitions that are exquisitely sensitive to certain classes of biological lipids (e. g., endotoxin) have also been discovered. The second experimental system to be discussed involves the interfacial organization of solid microparticles at aqueous-LC interfaces. Our observations have revealed that the nematic order of a LC can give rise to new classes of inter-particle interactions at these interfaces. Significantly, the symmetries of the interactions differ from those encountered in isotropic solvent systems, thus giving rise to interfacial organizations of particles not previously reported. This presentation will highlight fundamental and unresolved issues related to the behaviors of these LC-colloidal systems.
Location: University of Minnesota, Department of Chemical Engineering and Materials Science, January 24, 2013.

Presentation #25
Title: Colloid-in-liquid crystal gels.
Authors: Nicholas Abbott
Abstract: This presentation will describe investigations of the collective properties of colloidal particles that are dispersed in liquid crystalline solvents. A focus will be directed to recent observations of the gelation of particles dispersed in thermotropic liquid crystals. While a series of studies over the past decade have revealed two distinct mechanisms leading to gelation of particles in liquid crystalline solvents, our recent observations are inconsistent with both and hint at a third mechanism of gelation. These observations will be described along with examples of how the unique mechanical and optical properties of colloid-in-liquid crystal gels enable the design of biotic-abiotic interfaces.

Location: APS Meeting, Baltimore, March 22, 2013.

Presentation #26
Title Design of Chemo- and Bio-Responsive Materials based on Liquid Crystals.
Authors: Nicholas Abbott
Abstract: This presentation will describe principles for the design of liquid crystalline materials that respond to the presence of targeted chemical and biological species. The presentation will be organized into three parts. First, an overview of fundamental properties of liquid crystals that enable their use as stimuli-responsive materials will be presented. Concepts related to the formation of topological defects, curvature strain in liquid crystals and surface-induced ordering will be introduced. The second part of the talk will move to a discussion of chemo-responsive liquid crystalline systems, with a focus on interfacial design principles that enable the presence of parts-per-billion concentrations of targeted vapor phase agents (e.g., organophosphonates) to trigger macroscopic ordering transitions in liquid crystals. Ongoing efforts to translate these principles to composite liquid crystalline materials (such as liquid crystalline gels) that are readily processed (e.g., molded) and sufficiently robust to be placed into a range of environments will be described. The third part of the talk will address the design of liquid crystals to report the presence of biological species. Here the discussion will revolve around interfaces between thermotropic liquid crystals and aqueous phases, and the use of confinement of liquid crystals to tune their response to biological interactions. Examples will be presented to demonstrate that ordering transitions can be triggered in liquid crystalline systems through structure-selective interactions with targeted biological molecules and their assemblies. In addition, the use liquid crystalline materials to direct the organization of biological molecules at interfaces will be discussed. Overall, the ability to report and direct the organization of biomolecules at interfaces hints at new principles by which liquid crystalline materials might be used to trigger a response for biological defense.
Location: Army Research Laboratory, Natick MA, March 26, 2013.

Presentation #27
(a) Liquid Crystal-Based Emulsions for Synthesis of Spherical and Non-Spherical Particles with Chemical Patches
(b) Frederic Mondiot, Xiaoguang Wang, and Nicholas Abbott
(c) Abstract
(d) European Conference in Colloids and Interface Science, Sofia, Bulgaria, September 4, 2013.

Presentation #28
(a) Defect-Mediated Interactions of Biological Analytes and Liquid Crystals
(b) Nicholas Abbott
(c) Abstract(s)
(d) Exploratory Workshop on Defect-Assembled Soft Matter for Nanoscience and Nanotechnology, Rogaska Slatina, Slovenia, September 14, 2013

Presentation #29
(a) Bioanalytics based on Liquid Crystalline Droplets
(b) Nicholas Abbott
(c) Abstract(s)
(d) 15th Topical Meeting on Optics of Liquid Crystals, Honolulu, Hawaii, September 30, 2013

Presentation #30
(a) Targeting and Triggering using Liquid Crystals
(b) Nicholas L. Abbott
(c) Abstract(s)
(d) Targeting and Triggering Workshop, University of Massachusetts, Amherst, October 15, 2013

Presentation #31
(a) Colloid and Interfacial Phenomena involving Liquid Crystals
(b) Nicholas Abbott
(c) Abstract(s)
(d) Department of Chemical Engineering, University of Puerto Rico, Mayaguez, October 23, 2013

Presentation #32
(a) Ordering Transitions Triggered by Specific Binding of Vesicles to Protein-Decorated Interfaces of Thermotropic Liquid Crystals
(b) Nicholas Abbott
(c) Abstract(s)
(d) Joint US-Japan Session on Colloid Science, AIChE Meeting, San Francisco, November 5, 2013.

Presentation #33
(a) Colloid and Interfacial Phenomena in Liquid Crystalline Systems
(b) Nicholas Abbott
(c) Abstract(s)

(d) Department of Chemical Engineering, Pirkey Lectureship, University of Texas at Austin, November 12, 2013.

Presentation #34
(a) Novel Colloidal and Interfacial Phenomena in Liquid Crystalline Systems
(b) Nicholas Abbott
(c) Abstract(s)
(d) Winter Meeting on Statistical Physics, Taxco, Mexico, January 8, 2014

Presentation #35
(a) Directed Assembly at Liquid Crystalline Interfaces
(b) Nicholas Abbott
(c) Abstract(s)
(d) Soft Matter at Interfaces, Stuttgart Max Planck Institute, April 30, 2014

Presentation #36
(a) Bioanalytics based on Liquid Crystalline Microdroplets
(b) Nicholas Abbott
(c) Abstract(s)
(d) International Forum on Biomedical Engineering, South East University, Nanjing, June 1, 2014.

Presentation #37
(a) Tuning the Strength of Hydrophobic Interactions using Immobilized Ions
(b) Nicholas Abbott
(c) Abstract(s)
(d) US-Poland Workshop on Thermodynamics of Complex Fluids and Interfaces, Warsaw, June 13, 2014.

Presentation #38
(a) Templated Assembly of Colloids using Liquid Crystalline Droplets
(b) D. Miller, X. Wang, J. Whitmer, J. de Pablo, and N. Abbott
(c) Abstract(s)
(d) ACS Colloids and Surface Science Symposium, Keynote Lecture, University of Pennsylvania, June 24, 2014.

Presentation #39
(a) Behaviors of Motile Bacteria at Interfaces of Lyotropic Liquid Crystals
(b) Nicholas Abbott
(c) Abstract(s)
(d) International Liquid Crystal Conference, Dublin, Ireland, July 1, 2014.

Number of Presentations: 39.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper
08/16/2012 8.00	Authors: Guksik Lee, Rebecca J. Carlton, Fumito Araoka, Nicholas L. Abbott, Hideo Takezoe. Amplification of the Stereochemistry of Biomolecular Adsorbates by Deracemization of Chiral Domains in Bent-Core Liquid Crystals, Advanced Materials (08 2012)
08/16/2012 12.00	Carlton, R.J., Ma, C.D., , Gupta, J.K., , Abbott, N.L.,. Influence of Specific Anions on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces", Langmuir (06 2012)
08/16/2012 11.00	Ye Liu, Daming Cheng, I-Hsin Lin, Nicholas L. Abbott , Hongrui Jiang. Microfluidic sensing devices employing in situ-formed liquid crystal thin film for detection of biochemical interactions, Lab-on-a-Chip (06 2012)
08/16/2012 10.00	Daniel S. Miller, Nicholas L. Abbott,. Influence of droplet size, pH and ionic strength on endotoxin-triggered ordering transitions in liquid crystalline droplets, Soft Matter (08 2012)
08/29/2013 22.00	Daniel S. Miller, Xiaoguang Wang, Nicholas L. Abbott. Design of Functional Materials based on Liquid Crystalline Droplets, Chemistry of Materials (06 2013)
08/29/2013 23.00	Daniel S. Miller, Xiaoguang Wang, James Buchen, Oleg D. Lavrentovich , Nicholas L. Abbott. Rapid Analysis of the Internal Configurations of Droplets of Liquid Crystal using Flow Cytometry, Analytical Chemistry (06 2013)
08/29/2013 24.00	Santanu Kumar Pal, Juan J. de Pablo, Nicholas L. Abbott, Emre Bukusoglu. Colloid-in-Liquid Crystal Gels Formed via Spinodal Decomposition, Soft Matter (06 2013)
TOTAL:	**7**

Number of Manuscripts: 17

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

1. LIQUID CRYSTAL DEVICES WITH MIXED ANION METAL SALTS (US PATENT APPLICATION)

Patents Awarded

Awards

2014 Hilldale Professorship

2014 Member of National Academy of Engineering

2013 Pirkey Centennial Lectureship, University of Texas, Austin

2013 Keynote Lecture, New Horizons in Colloid Science, Sete, France

2013 Amundson Lectureship, University of Minnesota

2013 Key Lecture, IV International Conference on Colloid Chemistry and Physicochemical Mechanics, Moscow, June

2012 Alpha Chi Sigma Award of AIChE for chemical engineering research

2012 Jeanne and Martin Sussman Lectureship, Tufts University

2012 Plenary Lecture, International Conference on Nanoscience and Nanotechnology (Perth, Australia)

2011 Chair-Elect of Gordon Research Conference on Liquid Crystals

2011 Appointed as Co-editor-in-Chief of Current Opinion of Colloid and Interface Science.

2011 Kurt Wohl Memorial Lecture, University of Delaware

2011 Plenary Lecture, 11th European Conference on Liquid Crystals (Slovenia)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Jacob Hunter	1.00	
Dan Miller	0.25	
Rishabh Jain	0.25	
FTE Equivalent:	**1.50**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Abhijit Dan	0.25
FTE Equivalent:	**0.25**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Nicholas Abbott	0.50	Yes
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Kristopher Richardson	0.00	
Tessa Chia	0.00	
Jose Alberto Gomez	0.00	
Chaval Punyatanasakchai	0.00	
Fernando Borges	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**5**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	4.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	4.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:	2.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	3.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Jacob Hunter	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Nicholas Abbott is a co-founder and consultant of Platypus Technologies LLC, a company that has commercialized liquid crystal-based sensors of toxic gases. The designs of the commercialized sensors are based on DoD-sponsored research at University of Wisconsin-Madison. They were transferred to Platypus Technologies via licensing of patents filed by the UW-Madison technology transfer office (WARF). Over the past year, Nicholas Abbott has made several presentations to Platypus Technologies on new designs of biological sensors based on liquid crystals that have arisen out of this ARO-sponsored research in the PI's laboratories.

In addition to Platypus Technologies LLC, Nicholas Abbott is a co-founder of Imbed Biosciences Corp, a company created to translate discoveries in the PI's laboratory related to designs of advanced wound dressings. Nicholas Abbott has served as a consultant to Imbed Biosciences Corp, and is actively engaged in developing new designs of dressings that permit better management of the bioburden of wounds, including wounds of warriors.

The research supported by this ARO grant over the past 3 years moved beyond past studies of interfacial and colloidal phenomena involving isotropic liquids to explore and understand a range of new phenomena involving amphiphiles and colloids at the interfaces of anisotropic liquids, namely liquid crystals (LCs). As described below, key accomplishments of the research include (i) unmasking of a fundamentally new mechanism of interaction of lipids and LC-in-water emulsion droplets, (ii) advancing our understanding of how LC ordering impacts the interfacial phase behavior of amphililes, (iii) the discovery of previously unknown effects of salts on the interfacial ordering of LCs, and (iv) advancing our understanding of the equilibrium and dynamic behaviors of colloids at interfaces of LCs. Overall, the knowledge that emerged from this fundamental program of colloid and interfacial science has the potential to impact, in the long term, strategies for materials synthesis, stabilization of emulsions, design of stimuli-responsive materials, creation of tunable plasmonic metamaterials, as well as the interfacial design of chemical and biological sensors. Many other potential applications of these fundamental principles can be envisaged. Below we detail our research accomplishments.

1.Coupling of LC Order and Organization of Bacterial Lipids

A particularly exciting discovery relates to the interfacial behavior of lipid A from bacterial endotoxin. Past studies have established that the interfacial energetics, and thus the presence of adsorbates that change interfacial energies, can play a central role in the orientational ordering of liquid crystals (LCs). We made the unexpected observation that ordering transitions in micrometer-sized LC droplets dispersed in water can be triggered by pg/ml concentrations of a specific bacterial glycophospholipid (endotoxin, as well as lipid A, the lipid component of endotoxin that possesses six tails) in the water. These ordering transitions, which occur at concentrations of lipid A on the surfaces of the LC droplets that are less than 10^{-5} Langmuir (1 Langmuir = 1 monolayer), are not due to adsorbate-induced changes in interfacial energetics but rather are driven by the interaction of lipid A with defects (so-called boojums) of the LC droplets. The central role of the topological defects in the ordering transitions is demonstrated by an extreme dependence on geometry of the LC; the response of LC to lipid A changes by 6 orders of magnitude with geometry. Scaling arguments were also been developed to confirm the role of the energetics of defects in driving the ordering transitions in the LC droplets. Overall, our research established a fundamentally new mechanism by which very low concentrations of adsorbates can trigger ordering transitions in LC systems.

The defect-driven ordering transitions described above was also been found to be strongly dependent on lipid structure. Specifically, double-tailed phospholipids and synthetic surfactants were shown to trigger ordering transitions in LC droplets only at concentrations that are at least 6 orders of magnitude higher than endotoxin and lipid A. This result is significant because endotoxin is an indicator of bacterial contamination. Detection of endotoxin in purified water (in the 1-100pg/ml range) is widely performed during manufacturing processes for pharmaceutical products (including validation of water used in such processes) and biomedical devices, and for biological research. The sensitivity and structure-based selectivity of the ordering transition in LC droplets suggests new principles for the design of responsive LC systems, particularly for the design of sensors that respond to targeted biological analytes such as endotoxin.

In additional studies of the interactions of lipid A with LCs, we revealed that the ordering transitions induced by endotoxin – from a bipolar state of the droplets to a radial state – are strongly dependent on the size of the LC droplets. Specifically, as the diameters of the LC droplets increased from 2 μm to above 10 μm (in phosphate buffered saline with an ionic strength of 90 mM and a pH of 7.2), we measured the percentage of droplets exhibiting a radial configuration in the presence of 100 pg/mL endotoxin to decrease from 98 ± 1 % to 3 ± 2 %. In addition, we measured a decrease in either the ionic strength or pH of the aqueous phase to reduce the percentage of droplets exhibiting a radial configuration in the presence of endotoxin. These results, when interpreted within the context of a simple thermodynamic model that incorporated the contributions of elasticity and surface anchoring to the free energies of the LC droplets, lead us to conclude that (i) the elastic constant K_{24} plays a central role in determining the size-dependent response of the LC droplets to endotoxin, and (ii) endotoxin-triggered ordering transitions occur only under solution conditions (pH, ionic strength) where the combined contributions of elasticity and surface anchoring to the free energies of the bipolar and radial configurations of the LC droplets are similar in magnitude. Our analysis also revealed that the presence of endotoxin perturbs the free energies of the LC droplets by $\sim 10^{-17}$ J/droplet, which is comparable to the standard free energy of self-association of $\sim 10^{3}$ endotoxin molecules. These results, when combined with prior reports of localization of endotoxin at the center of LC droplets, supported our hypothesis that self-assembly of endotoxin within micrometer-sized LC droplets provides the driving force for the ordering transitions. Overall, these results advanced our understanding of ordering transitions triggered by the interactions of lipids with LC droplets and, more broadly, provided guidance to the design of LC droplet systems as the basis of stimuli-responsive soft materials.

2. Coupling of Order of LCs and Interfacial Phase Behavior of Phosophlipids

The results described above included observations related to the effects of lipid molecular structure on the coupling of LC order and amphiphile order. To further strengthen our understanding of this coupling, we performed a systematic investigation of the influence of spontaneous curvature on the phase behavior of amphiphiles at the aqueous-LC interface. Spontaneous curvature is and intrinsic property of lipids which impacts the way they assemble at interfaces and form ordered structures. In order to investigate the influence of spontaneous curvature on the phase behavior of lipids at aqueous-LC interfaces we performed Langmuir-Schaefer (LS) transfers of monolayers of lipids with different spontaneous curvatures from an aqueous-air interface to the aqueous-5CB interface at a constant molecular area and characterized the optical appearance of the LC. The three lipids tested were 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC, **Figure 1A**), 1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine (DOPE, **Figure 1B**) and 1-(9Z-octadecenoyl)-*sn*-glycero-3-phosphoethanolamine (Lyso-18-PE, **Figure 1C**). The spontaneous curvature values reported for these lipids are -1/28.5 nm^{-1} for DOPE, -1/87.3 nm^{-1} for DOPC and a small positive value for Lyso-18-PE.

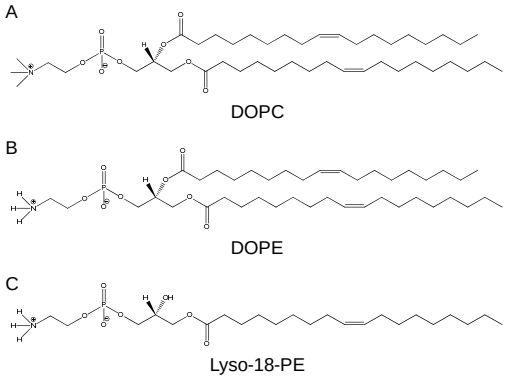

Figure 1. Molecular structures of (A) 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC), (B) 1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine (DOPE) and (C) 1-(9Z-octadecenoyl)-*sn*-glycero-3-phosphoethanolamine (Lyso-18-PE).

Before performing the LS transfers, we characterized the phase behavior of the lipids at the aqueous-air interface at 25°C using a NIMA Langmuir trough. The resulting Langmuir isotherms are displayed in **Figure 2**. All three lipids remained in a liquid-expanded state throughout the compression of the lipid film until eventual monolayer collapse. However, the onset of surface pressure and monolayer collapse occurred at different molecular areas for each lipid. The onset of surface pressure was observed at 145 Å^2 for DOPC, 121 Å^2 for DOPE, and 69 Å^2 for Lyso-18-PE. Monolayer collapse was observed at 64 Å^2 for DOPC, 51 Å^2 for DOPE, and 19 Å^2 for Lyso-18-PE.

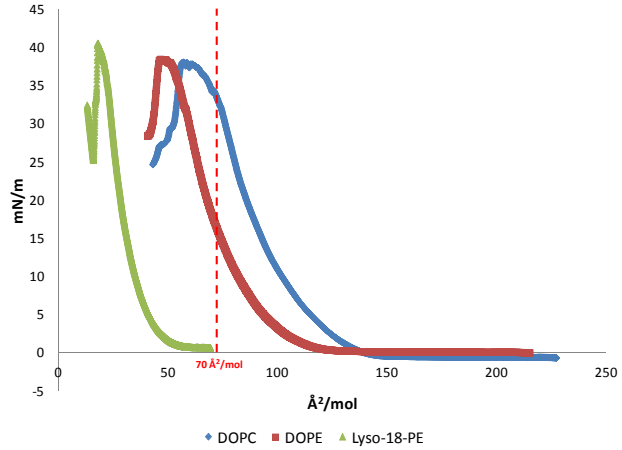

Figure 2. Langmuir isotherms for DOPC (♦), DOPE (■), and Lyso-18-PE (▲) at 25°C. The dash line indicates the areal density under which Langmuir-Schaefer transfer was performed.

Based on the isotherms, we performed LS transfers of each lipid at a molecular area of 70 Å^2 to avoid collapse of DOPC. The results of the LS transfers are displayed in **Figure 3**. Before transfer, the optical appearance of the LC was bright (**Figure 3A**) indicating a near-planar orientation (parallel) of the 5CB molecules at the aqueous-LC interface. After transfer of DOPC, the optical appearance of the LC was uniformly dark (**Figure 3B**), indicating homeotropic (perpendicular) alignment of the 5CB molecules at the aqueous-LC interface. In contrast, transfer of DOPE resulted in a mixture of bright and dark domains (**Figure 3C**) corresponding to a mixture of homeotropic and tilted orientations. Finally, transfer of 18-Lyso-PE resulted in a

uniform bright appearance (**Figure 3D**) corresponding to a tilted orientation. Overall, these results strongly support our hypothesis that spontaneous curvature of a lipid impacts the interaction between 5CB and lipid molecules at an aqueous-LC interface. All three lipids tested had a different spontaneous curvature and elicited a different ordering of 5CB at the interface.

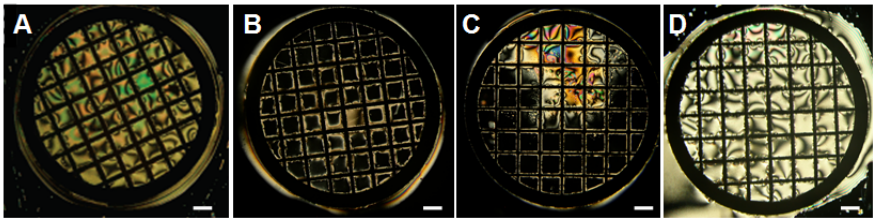

Figure 3. Polarized light micrographs of an aqueous-LC interface: (A) prior to LS transfer of a lipid film, (B) after LS transfer of DOPC, (C) after LS transfer of DOPE, after LS transfer of Lyse-18-PE. All transfers were performed at an areal density of 70 $Å^2$. Scale bars are 283 μm.

We also advanced our understanding of the interfacial phase behavior of phospholipids at aqueous interfaces of LCs. Specifically, previously, we had reported that dilauroyl phosphatidylcholine (DLPC) vesicles spontaneously transferred to and assembled within a monolayer at the nematic 5CB-aqueous interface. The phase behavior exhibited by DLPC gives rise to an easily observable change in the optical appearance of the film of liquid crystal (LC), from bright to dark, when viewed between crossed polars. To determine if other lipids exhibited a similar phase behavior at the interfaces of nematic films of 5CB, we investigated the transfer and assembly of dipalmitoyl phosphatidylcholine (DPPC) at the 5CB-aqueous interface. Unlike DLPC (T_m = -1°C) vesicles which exist in a fluid liquid-crystalline state at room temperature, DPPC (T_m = 41°C) vesicles are in the gel phase at room temperature. Additionally, whereas DLPC monolayers exist in a liquid expanded (L_α) phase at all lipid areal densities, DPPC monolayers display both liquid expanded (L_α) and liquid condensed (L_β) phases as lipid area density increases with a region of coexistence (L_α-L_β) at intermediate densities.
Our observations revealed that DPPC vesicles, when incubated against a nematic 5CB film, give rise to a complex interfacial phase behavior of the lipid that is strikingly different from DLPC. After the initial appearance and growth of homeotropic regions in the film (**Figure 5B**), small planar domains nucleated within them (**Figure 5C**). These planar domains grew and coalesced over time, eventually nearly covering the entire LC film (**Figure 5D-F**). Quantification of the fraction of the LC interfacial area corresponding to homeotropic anchoring over time (**Figure 5G**) further illustrates these trends. The shift towards planar anchoring at long times, following the maximal homeotropic anchoring, was initially surprising, as in the DLPC system, planar domains correspond to lipid-lean regions. However, since DPPC monomers are essentially insoluble in water, it seemed implausible that lipid would desorb from the LC-aqueous interface once there. We hypothesized instead that the planar domains which nucleate and grow are regions of densely packed, L_β phase DPPC. Although this has not been observed before at the LC-aqueous interface, previous studies in which Langmuir-Blodgett monolayers of phosphatidylcholine lipids were contacted with LC films found that L_β phase lipid monolayers gave rise to planar or tilted LC orientations.

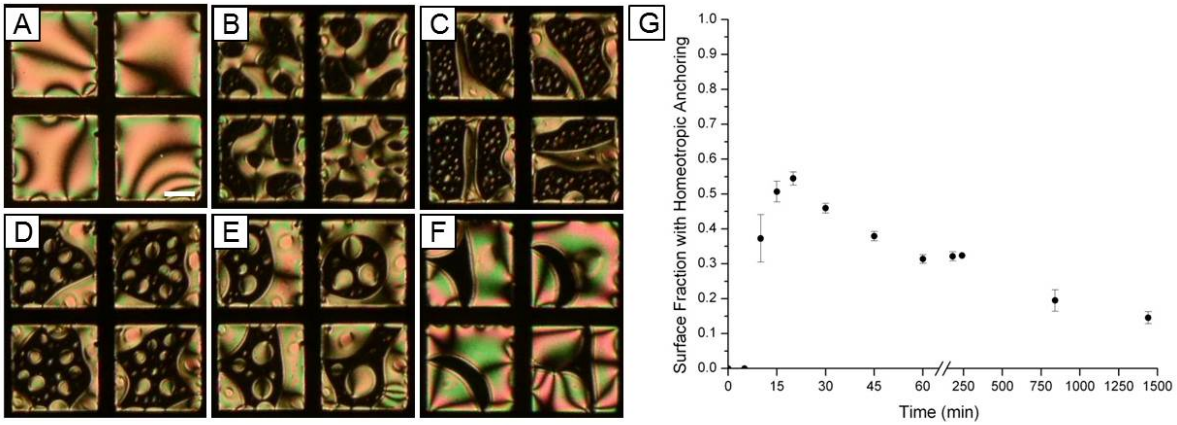

Figure 5. (A-F) Optical images (crossed polars) of a 5CB film in a PBS solution taken following (A) 0 min, (B) 10 min, (C) 15 min, (D) 30 min, (E) 60 min and (F) 24 h of contact with 0.1 mM DPPC vesicles. Scale bar = 100 μm. (G) Plot of the area fraction of the 5CB-aqueous interface exhibiting a homeotropic orientation as a function of the time. Data points are the average value for the four grid squares depicted in A-F.

In order to support the above-described proposal, we performed an experiment to investigate the temperature dependence in the ordering of DPPC-laden LC films. This was done since it has been shown for monolayers of DPPC at various isotropic oil-water interfaces that the degree of condensation (i.e. the area fraction of the monolayer comprised of L_β domains) increases with decreasing temperature. If instead the planar domains were the result of lipid-lean domains, the area fraction would not be expected to change greatly with temperature within the nematic range of 5CB. We allowed DPPC to transfer to the LC-aqueous interface for fifteen minutes at 41°C before exchanging this solution with pure buffer. Then, the temperature of the system was incrementally decreased every 30 minutes and the ordering of the 5CB observed. As shown in **Figure 6**, planar domains only appeared upon cooling the system to 27.5°C. These observations are consistent with coexisting L_α (homeotropic) and L_β (planar) domains at the LC-aqueous interface. Overall, this advance indicates that condensed DPPC lipid phases can give rise to planar anchoring at the LC-aqueous interface.

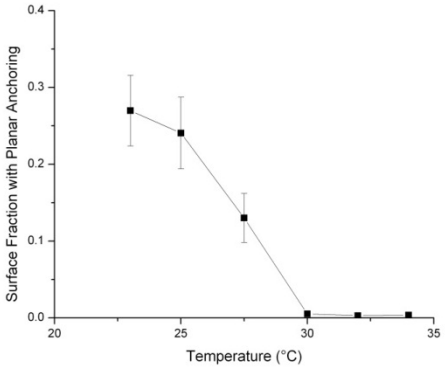

Figure 6. Plot of the area fraction of a DPPC-laden 5CB-aqueous interface exhibiting a planar orientation as a function of temperature. The 5CB film was contacted with an aqueous

dispersion of DPPC vesicles (0.1 mM) for 15 min. at 41°C and held at each temperature for 30 min. prior to analysis.

Finally, we note that we observed what appeared to be three distinct lipid phases coexisting at the LC-aqueous interface, as reported by the ordering of the LC film. **Figure 7** depicts an example of these coexisting domains on a LC-aqueous interface laden with lipids which were transferred from two-component DOPC/DOPG (0.75/0.25) vesicles. In addition to homeotropic domains, isolated circular planar domains are apparent within the large continuous planar domains. Similar coexistence of three phases has been observed following lipid transfer from several other lipid systems, as well. Interestingly, we have seen this behavior in lipid systems such as DOPC/DOPG in which the lipids do not form condensed monolayer phases, as well as in the DPPC system.

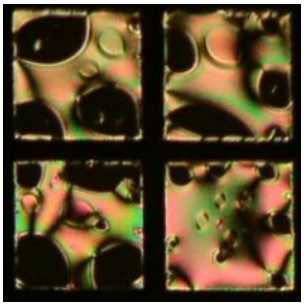

Figure 7. Optical appearance (crossed polars) of a 5CB film following contact with an aqueous dispersion of DOPC/DOPG (0.75/0.25) vesicles (0.1 mM total lipid concentration).

Finally, we comment that another key accomplishment is related to the influence of the chirality of lipids on the supramolecular organization of achiral liquid crystals (LCs). In brief, past studies have demonstrated that LC phases of bent-core mesogens spontaneously form racemic mixtures of chiral domains comprised of helical nanofilaments (the so-called B4 phase). In experiments performed through collaboration with Professor Takezoe of Tokyo Institute of Technology, we revealed that spontaneous adsorption of chiral (*D*- and *L*-) phospholipids from aqueous solution onto the interface of the B4 phase leads to the generation of an enantiomeric excess of chiral domains or rather a unichiral domain within the LC. This result suggests that bent-core LCs offer the basis of a class of materials that can be used to amplify the chirality of molecules into macroscopic phenomena. More broadly, the results of this study advance our understanding of how molecular chirality is expressed in supramolecular organization, which is one of the key challenges underlying the development of rational design principles for soft materials.

3. **Influence of Salts on the Ordering of Liquid Crystals at Aqueous Interfaces**

Whereas the studies described above addressed the coupling that occurs between amphiphiles and LCs, as a key dicovery to emerge from our research was the realization that simple salts can also perturb the ordering of LCs. We discovered that orientational ordering transitions at aqueous interfaces of a water-immiscible, thermotropic liquid crystal (LC) can be induced by either changes in pH of the aqueous solution or the addition of simple electrolytes (NaCl) to the

aqueous phase. Through a series of experimental studies, and development of a model based on the Poisson-Boltzmann equation, we established that the ordering transitions in the LC are driven by an electrical double layer extending into *the LC-side of the interface.* Overall, these results provide new fundamental insights into ionic phenomena at LC-aqueous interfaces, and expand the range of solutes known to cause orientational ordering transitions at LC-aqueous interfaces beyond previously examined amphiphilic adsorbates. Identification of the role of the electrical double layer in ordering LCs at aqueous interfaces, as discovered in our study, also provides new guidance to the design of stimuli-responsive LC interfaces

In addition to demonstrating that simple salts can impact LCs through the effects of electrical double layers, we discovered that specific anions (of sodium salts) added to aqueous phases at molar concentrations can also trigger rapid, orientational ordering transitions in water-immiscible, thermotropic liquid crystals (LCs; e.g., nematic phase of 4'-pentyl-4-cyanobiphenyl, 5CB) contacting the aqueous phases. Anions classified as chaotropic, specifically iodide, perchlorate and thiocyanate, caused 5CB to undergo continuous, concentration-dependent transitions from planar to homeotropic (perpendicular) orientations at LC-aqueous interfaces within 20 s of addition of the anions. In contrast, anions classified as relatively more kosmotropic in nature (fluoride, sulfate, phosphate, acetate, chloride, nitrate, bromide, and chlorate) do not perturb the LC orientation from that observed without added salts (i.e., planar orientation). Surface pressure-area isotherms of Langmuir films of 5CB supported on aqueous salt solutions revealed ion-specific effects ranking in a manner similar to the LC ordering transitions. Specifically, chaotropic salts stabilized monolayers of 5CB to higher surface pressures and areal densities (12.6 mN/m at 27 $Å^2$/molec. for $NaClO_4$) and thus smaller molecular tilt angles (30° from the surface normal for $NaClO_4$) than kosmotropic salts (5.0 mN/m at 38 $Å^2$/molec. with a corresponding tilt angle of 53° for NaCl). These results and others obtained over the past year suggest that anion-specific interactions with 5CB monolayers lead to bulk LC ordering transitions. Support for the proposition that these ion-specific interactions involve the nitrile group was obtained by using a second LC with nitrile groups (E7; ion-specific effects similar to 5CB were observed) and a third LC with fluorine-substituted aromatic groups (TL205; weak dipole and no ion-specific effects were measured). Finally, we have also established that anion-induced orientational transitions in micrometer-thick LC films involves a change in the easy axis of the LC.

Overall, these results provide new insights into ionic phenomena occurring at LC-aqueous interfaces, and reveal that the long-range ordering of LC oils can amplify ion-specific interactions at these interfaces into macroscopic ordering transitions.

4. Ordering and Dynamics of Colloids at Aqueous Interfaces

A large number of past studies have explored the adsorption and assembly of both micro- and nano-particles at interfaces of isotropic fluids. Key accomplishments in our research addressed the broad question of how *LC ordering* at an interface impacts the organization and dynamics of colloids. To address questions related to dynamics, we used single-particle tracking to measure the diffusion coefficients of chemically functionalized micro- and nano-particles at interfaces between aqueous phases and a nematic liquid crystal (LC). For hydrophobic particles with diameters of 2.3 ± 0.2 μm that homeotropically anchoring the LC, we measured anisotropic

diffusion, qualitatively consistent with the influence of nematic ordering of the LC at the interface on the local rheological environment. Analysis of the magnitudes of the diffusion coefficients revealed that the ordering of the LC about the microparticles is perturbed in the interfacial environment relative to the bulk, leading to low drag on the microparticles at the aqueous-nematic interface. In contrast, for hydrophobic nanoparticles (diameters of 141 ± 11 nm) at the LC-aqueous interface, almost indistinguishable diffusion coefficients were measured at the interface and in bulk LC when the displacements of the nanoparticles in the two environments were in the same directions relative to the far-field director of the LC. These results reveal fundamental differences to exist between the interfacial mobilities of micro- and nanoparticles at LC-aqueous interfaces, and that a relative insensitivity to interfacial environment appears to be a property of the smaller particles studied in our experiments. A surprising result was measurement of relatively slow diffusion of particles in the isotropic phase of 5CB, a result that we return to below.

We also investigated the equilibrium organization of nanoparticles at LC and surfactant-laden LCs interfaces. Previous studies with silica microparticle (functionalized with DMOAP) decorated 5CB-water interfaces had shown that the addition of a surfactant, sodium dodecyl sulfate (SDS), to the aqueous phase causes a change in the organization of particles from a chain-like conformation to a hexagonal conformation. This process can be explained by a change in orientation of the particle dipoles from planar to the surface to perpendicular to the surface. In contrast to microparticles, we measured gold nanoparticles (141 ± 11 nm) functionalized with a mixed monolayer of decanethiol and hexadecanethiol (4:1) to not form organized structures when adsorbed to a 5CB-aqueous interface (**Figure 8A**) suggesting that the interparticle interactions of nanoparticles at the 5CB-aqueous interface are much weaker than those of micrometer-sized particles. Upon the addition of SDS to the aqueous phase, to make the final concentration 2mM, we observed the growth of surfactant-rich domains on the 5CB-aqueous interface and exclusion of gold nanoparticles from them (**Figure 8B**). At long times, we observe equilibrium between surfactant-rich, particle-poor domains and surfactant-poor, particle-rich domains. This result highlights a fundamental difference in the behavior of microparticles and nanoparticles at surfactant-laden interfaces.

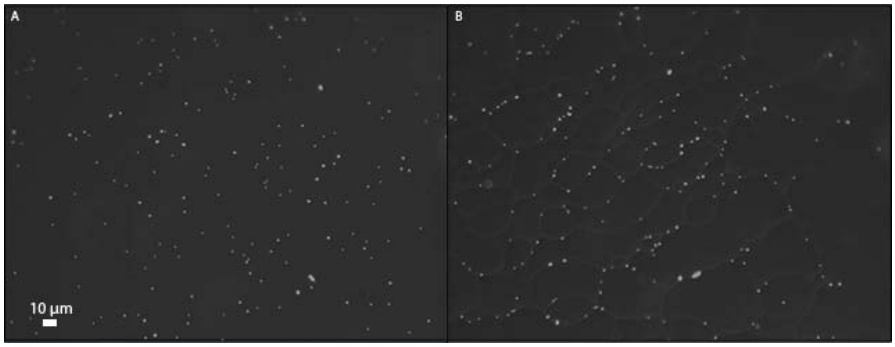

Figure 8: (A) Darkfield micrograph of 141 ± 11 nm gold particles at a 5CB-aqueous interface. (B) After the addition of SDS to the aqueous phase to achieve a final concentration of 2mM.

As reported above, we measured unexpectedly slow diffusion of particles at aqueous-isotropic 5CB interfaces, which hinted at the possible presence of an organized corona of 5CB about the particles in the isotropic phase. To provide additional insight into these observations, we

performed additional studies of the diffusion of nanoparticles in the isotropic phase of 5CB. We used single-particle tracking to measure the diffusion coefficients of gold nanoparticles (diameters of 146 ± 11 nm) dispersed in the isotropic phase of 5CB. Measurements were taken at temperatures ranging from 1°C to 9°C above the bulk clearing temperature of the LC (35°C). Particles were functionalized with either a single component monolayer of decanethiol or a mixed component monolayer of decanethiol and hexadecanethiol (4:1 ratio). Analysis of the diffusion coefficients at each temperature allowed us to calculate an average hydrodynamic radius which can be compared to the physical radius of the particle, as measured though SEM imaging. For particles functionalized with either the single component decanethiol monolayer and mixed component decanethiol/hexadecanethiol monolayer, we observed no significant difference between the hydrodynamic radius and physical radius of the particles when our sample is heated at least 7°C above the bulk clearing temperature **(Figure 9**). However, as the bulk clearing temperature is approached, we observed a significant increase in the hydrodynamic radius of the particles. At 36°C, 1°C above the bulk clearing temperature, we observed that particles with the mixed component thiol monolayer have a hydrodynamic radius that is 21 nm larger than their physical radius and particles with the single component thiol monolayer have a hydrodynamic radius 11 nm larger than their physical radius. We interpret the increase in hydrodynamic radius of the particles to be due to the formation of a surfaced induced nematic layer at the particle surface whose thickness depends on the chemical functionality of the particles. We note however, that the thickness of the nematic layer is much larger than the coherence length of 5CB at 36°C (approximately 3nm).

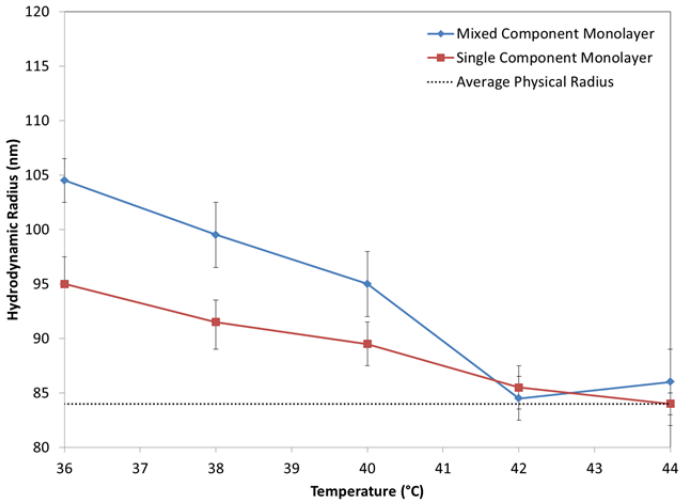

Figure 9: Hydrodynamic radius of 146 ± 11 nm gold particles functionalized with either a single component monolayer (red) of decanethiol or a mixed component monolayer (blue) of decanethiol and hexadecanethiol (4:1) in 5CB at various temperatures. A dotted line shows the physical radius of the gold particles measured by SEM

Motivated by the surprising thickness of the surface-induced LC layer reported above, we performed additional measurements to provide insight into its origin. Specifically, we measured the mobilities of gold nanoparticles (diameters of 85±7nm and 164±11nm) dispersed in an isotropic oil of 4-*n*-pentyl-4'-cyanobiphenyl to decrease upon illumination with white light. Single-particle optical tracking using band-pass filters revealed that hydrodynamic diameter of the nanoparticles in the oil to increase by 40nm when the wavelength of illumination resulted in

localized surface plasmon resonances (LSPR) in the gold nanoparticles, consistent with a solvent corona induced by interfacial fields associated with the LSPR. The mobility of the gold nanoparticles could thus be tuned by the choice of wavelength of the illuminating light. Because solvent structuring about nanoparticles also underlies particle-surface and particle-particle interactions, these results point to broadly applicable principles for optical manipulation of the dynamic and equilibrium properties of nanoparticulate systems in supramolecular solvents. Ongoing experiments seek to establish the magnitude of the interfacial electrical fields associated with the LSPR to provide additional insight into this unexpected and exciting finding.

A second broad area of research accomplishment related to colloids and LC interfaces is based on the use of nematic emulsions. Pickering emulsions have seen renewed interest over the last two decades since they provide new routes towards emulsion stabilization. In contrast to conventional emulsions stabilized by surfactants or polymers, Pickering emulsions are stabilized by solid particles, the adsorption energy of which at the oil/water interface can reach $10^6\ k_BT$. Because the interfacial particle organization underlies the stabilization of this class of emulsions, LC-mediated interfacial forces that can lead to particle organizations that are very different from those observed at isotropic oil-water interface were investigated. Our studies yielded some exciting results. Specifically, we discovered that defects that form in a predictable fashion in LC droplets can be used to "steer" particles adsorbed to the surfaces of the LC droplets to specific locations (the "poles" of the droplets). This provided the basis of a general and facile method to prepare "patchy" colloidal particles. We have reported the use of liquid crystal (LC)-in-water emulsions for the synthesis of either spherical or non-spherical particles with chemically-distinct domains located at the poles of the particles. The approach involved the localization of solid colloids at topological defects that form predictably at surfaces of water-dispersed LC droplets (see Figure 10). By polymerizing the LC droplets displaying the colloids at their surface defects, we demonstrated formation of both spherical and, upon extraction of the mesogen, anisotropic composite particles with colloids located at either one or both of the poles. Because the colloids protrude from the surfaces of the particles, they also define organized, chemical patches with functionality controlled by the colloid surface. While a rich range of phenomena and materials are enabled by non-spherical and/or surface-patterned particles, the synthesis of such particles remains challenging. Our approach to the synthesis of either spherical or non-spherical particles with organized surface-chemical patches is highly scalable. The method enables, in particular, the synthesis of either spherical or anisotropic (ellipsoid-like) composite particles with "poles" that are decorated by colloids possessing chemical compositions that are distinct from the remainder of the composite particle. Such composite particles are synthesized with dipolar or quadrupolar symmetry, and the chemical functionality presented at the poles is shown to be easily tuned by varying the material that constitutes the colloids. The composite particles are, moreover, prepared in bulk solution (in contrast to previously reported approaches that involve "shadow deposition" at macroscopic surfaces).

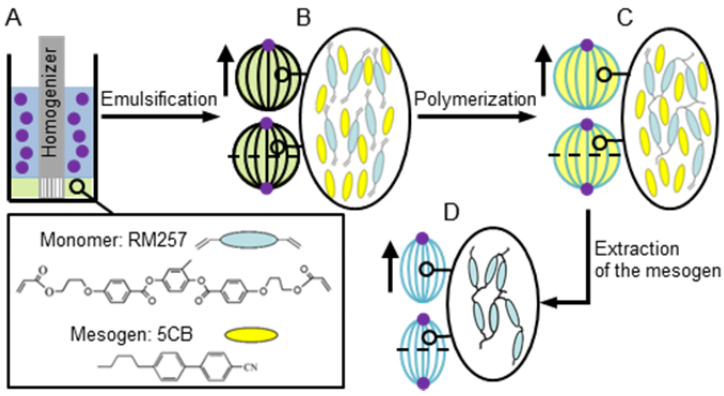

Figure 10. (A) Initial system before emulsification (blue color: aqueous phase; purple spots: colloids). (B) After emulsification, formation of bipolar nematic droplets with either 1 (dipolar symmetry) or 2 colloids (quadrupolar symmetry) located at the poles. (C) After polymerization of the monomer within the droplets, formation of spherical particles with dipolar or quadrupolar symmetry. (D) Upon extraction of the mesogen from the polymerized droplets, formation of anisotropic particles with dipolar or quadrupolar symmetry.

As noted above, the spontaneous positioning of colloids on the surfaces of micrometer-sized liquid crystalline droplets and their subsequent polymerization offers the basis of a general and facile method for the synthesis of patchy microparticles. The existence of multiple local energetic minima, however, can generate kinetic traps for colloids on the surfaces of the liquid crystal (LC) droplets and result in heterogeneous populations of patchy microparticles. To address this issue, we demonstrated that adsorbate-driven switching of the internal configurations of LC droplets can be used to sweep colloids to a single location on the LC droplet surfaces, thus resulting in the synthesis of homogeneous populations of patchy microparticles. The surface-driven switching of the LC was triggered by addition of surfactant or salts, and permitted the synthesis of dipolar microparticles as well as "Janus-like" microparticles. By using magnetic colloids, we demonstrated the utility of the approach by synthesizing magnetically-responsive patchy microdroplets of LC with either dipolar or quadrupolar symmetry that exhibit distinct optical responses upon application of an external magnetic field.

We have also reported on the formation of assemblies of 1 μm-in-diameter colloids (polystyrene (PS)) formed by multiple colloids at the poles of water-dispersed droplets (diameters 7 - 20 μm) of nematic liquid crystal (LC). For 4-cyano-4'-pentylbiphenyl droplets decorated with two to five PS colloids, we found 32 distinct arrangements of the colloids to form at the boojums of bipolar droplet configurations. Significantly, all but one of these configurations (a ring comprised of five PS colloids) could be mapped onto a local (non-close packed) hexagonal lattice. To provide insight into the origin of the hexagonal lattice, we investigated planar aqueous—LC interfaces, and found that organized assemblies of PS colloids did not form at these interfaces. Experiments involving the addition of salts revealed that a repulsive interaction of electrostatic origin prevented formation of assemblies at planar interfaces, and that regions of high splay near the poles of the LC droplets generated cohesive interactions between colloids that could overcome the repulsion. Support for this interpretation was obtained from a model that included (i) a long-range attraction between adsorbed colloids and the boojum due to the increasing rate of strain (splay) of LC near the boojum (splay attraction), (ii) an attractive inter-colloid interaction that reflects the quadrupolar symmetry of the strain in the LC around the

colloids, and (iii) electrostatic repulsion between colloids. The model predicts that electrostatic repulsion between colloids can lead to a ~1,000 k_BT energy barrier at planar interfaces of LC films, and that the repulsive interaction can be overcome by splay attraction of the colloids to the boojums of the LC droplets. Overall, the results reported above advance our understanding of the directed assembly of colloids at interfaces of LC droplets.