Final report

Project Title:	**In situ studies of nucleation and assembly at soft-hard interfaces** *(title has changed several times; above title is from last renewal)*
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The overall goal of this project was the exploration of new ways to make organic and hybrid (organic-inorganic) materials for energy-related applications. Towards this end, our research has focused on the structure and behavior of molecular monolayers at interfaces (including floating monolayers, transferred Langmuir-Blodgett monolayers, and self-assembled monolayers), as well as the biomimetic nucleation of inorganic crystals at soft-hard interfaces.

We list here some particularly notable achievements resulting from this project (citations refer to the complete list of project-supported publications at the end of this document):

(a) The first observation of ordered structure in a condensed phase of floating (Langmuir) monolayers [70]
(b) Determination of the structures and phase transitions in the complex phase diagram of floating fatty acid monolayers [55]
(c) Discovery of chiral structures in floating monolayers and development of a Landau theory to explain the observations [35]
(d) The first in situ observation, using synchrotron X-ray scattering, of the evolution of structure during Langmuir-Blodgett deposition [34]
(e) The first direct measurements of the small-amplitude complex shear response of floating monolayers [33]
(f) A review article in Revs. Mod. Phys [28] that is still the primary reference in this field
(g) The first in situ X-ray reflectivity study of molecular self-assembly from solution [24]
(h) The first observation of epitaxy during oriented nucleation of inorganic crystals templated by ordered organic surfaces [21]
(i) The discovery that biominerals such as calcite [8] and calcium oxalate [3] can be grown in the laboratory as oriented crystals templated by biomimetic surfaces
(j) Direct experimental resolution of the debate regarding the mechanism (charge/stereochemistry/epitaxy) responsible for the templated nucleation of calcite expressing the biologically relevant 001 face [1].

In addition, we have performed extensive studies of the Langmuir-Blodgett deposition process; of molecular self-assembly processes; and of ionic lattices forming at charged surfaces in contact with solutions. All these studies were published in major peer-reviewed journals, and full details can be found in the papers listed below.

Publications supported by this grant

1 B. Stripe, A. Uysal, B. Lin, M. Meron, and P. Dutta, "Charge, stereochemistry, or epitaxy? Toward controlled biomimetic nucleation at mixed monolayer templates", Langmuir 28, 572 (2012).

2 B. Stripe, A. Uysal, and P. Dutta, "Orientation and morphology of calcite nucleated under floating monolayers: A magnesium-ion-enhanced nucleation study", Journal of Crystal Growth 319, 64 (2011).

3 A. Uysal, B. Stripe, K. Kim, and P. Dutta, "Epitaxy driven interactions at the organic-inorganic interface during biomimetic growth of calcium oxalate", Crystengcomm 12, 2025 (2010).

4 R. Kaminker, L. Motiei, A. Gulino, I. Fragala, L. J. W. Shimon, G. Evmenenko, P. Dutta, M. A. Iron, and M. E. van der Boom, "Stepwise assembly of coordination-based metal-organic networks", Journal of the American Chemical Society 132, 14554 (2010).

5 K. Kim, A. Uysal, S. Kewalramani, B. Stripe, and P. Dutta, "Effects of chitosan on the alignment, morphology and shape of calcite crystals nucleating under Langmuir monolayers", Crystengcomm 11, 130 (2009).

6 M. Altman, O. V. Zenkina, T. Ichiki, M. A. Iron, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Positive constructs: Charges localized on surface-confined organometallic oligomers", Chemistry of Materials 21, 4676 (2009).

7 L. Motiei, M. Altman, T. Gupta, F. Lupo, A. Gulino, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Self-propagating assembly of a molecular-based multilayer", Journal of the American Chemical Society 130, 8913 (2008).

8 S. Kewalramani, K. Kim, B. Stripe, G. Evmenenko, G. H. B. Dommett, and P. Dutta, "Observation of an organic-inorganic lattice match during biomimetic growth of (001)-oriented calcite crystals under floating sulfate monolayers", Langmuir 24, 10579 (2008).

9 A. Gulino, T. Gupta, M. Altman, S. Lo Schiavo, P. G. Mineo, I. L. Fragala, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Selective monitoring of parts per million levels of co by covalently immobilized metal complexes on glass", Chemical Communications, 2900 (2008).

10 M. Altman, O. Zenkina, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Molecular assembly of a 3d-ordered multilayer", Journal of the American Chemical Society 130, 5040 (2008).

11 S. Kewalramani, J. Kmetko, G. Dommett, K. Kim, G. Evmenenko, H. Mo, and P. Dutta, "Pathways for oriented assembly of inorganic crystals at organic surfaces", Thin Solid Films 515, 5627 (2007).

12 S. Kewalramani, K. Kim, G. Evmenenko, P. Zschack, E. Karapetrova, J. Bai, and P. Dutta, "Mechanisms for species-selective oriented crystal growth at organic templates", Journal of Materials Research 22, 2785 (2007).

13 Q. Huang, J. Li, T. J. Marks, G. A. Evmenenko, and P. Dutta, "Triarylamine siloxane anode functionalization/hole injection layers in high efficiency/high luminance small-molecule green- and blue-emitting organic light-emitting diodes", Journal of Applied Physics 101 (2007).

14 T. Gupta, R. Cohen, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Reversible redox-based optical sensing of parts per million levels of nitrosyl cation in organic solvents by osmium chromophore-based monolayers", Journal of Physical Chemistry C 111, 4655 (2007).

15 S. Kewalramani, G. Dommett, K. Kim, G. Evmenenko, H. Mo, B. Stripe, and P. Dutta, "Aggregation-governed oriented growth of inorganic crystals at an organic template", Journal of Chemical Physics 125 (2006).

16 M. Altman, A. D. Shukla, T. Zubkov, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Controlling structure from the bottom-up: Structural and optical properties of layer-by-layer assembled palladium coordination-based multilayers", Journal of the American Chemical Society 128, 7374 (2006).

17 T. Zubkov, A. C. B. Lucassen, D. Freeman, Y. Feldman, S. R. Cohen, G. Evmenenko, P. Dutta, and M. E. van der Boom, "Photoinduced deprotection and zno patterning of hydroxyl-terminated siloxane-based monolayers", Journal of Physical Chemistry B 109, 14144 (2005).

18 S. Kewalramani, G. Evmenenko, C. J. Yu, K. Kim, J. Kmetko, and P. Dutta, "Evidence of surface reconstruction during 'bioinspired' inorganic nucleation at an organic template", Surface Science 591, L286 (2005).

19 J. Kmetko, C. Yu, G. Evmenenko, S. Kewalramani, and P. Dutta, "Organic-template-directed nucleation of strontium fluoride and barium fluoride: Epitaxy and strain", Physical Review B 68 (2003).

20 M. I. Boyanov, J. Kmetko, T. Shibata, A. Datta, P. Dutta, and B. A. Bunker, "Mechanism of pb adsorption to fatty acid Langmuir monolayers studied by x-ray absorption fine structure spectroscopy", Journal of Physical Chemistry B 107, 9780 (2003).

21 A. G. Richter, C. J. Yu, A. Datta, J. Kmetko, and P. Dutta, "Using x-rays to characterize the process of self-assembly in real time", Colloids and Surfaces a-Physicochemical and Engineering Aspects 198, 3 (2002).

21 J. Kmetko, C. J. Yu, G. Evmenenko, S. Kewalramani, and P. Dutta, "Evidence of registry at the interface during inorganic nucleation at an organic template", Physical Review Letters 89 (2002).

22 J. Kmetko, A. Datta, G. Evmenenko, and P. Dutta, "The effects of divalent ions on Langmuir monolayer and subphase structure: A grazing-incidence diffraction and bragg rod study", Journal of Physical Chemistry B 105, 10818 (2001).

23 J. Kmetko, A. Datta, G. Evmenenko, M. K. Durbin, A. G. Richter, and P. Dutta, "Ordering in the subphase of a Langmuir monolayer: X-ray diffraction and anomalous scattering studies", Langmuir 17, 4697 (2001).

24 A. G. Richter, C. J. Yu, A. Datta, J. Kmetko, and P. Dutta, "In situ and interrupted-growth studies of the self-assembly of octadecyltrichlorosilane monolayers", Physical Review E 61, 607 (2000).

25 P. Dutta, "What x-rays tell us about the ordering of molecular backbones in Langmuir monolayers", Colloids and Surfaces a-Physicochemical and Engineering Aspects 171, 59 (2000).

26 A. Dutta, J. Kmetko, C. J. Yu, A. G. Richter, K. S. Chung, J. M. Bai, and P. Dutta, "Ph-dependent appearance of chiral structure in a Langmuir monolayer", Journal of Physical Chemistry B 104, 5797 (2000).

27 A. Datta, J. Kmetko, A. G. Richter, C. J. Yu, P. Dutta, K. S. Chung, and J. M. Bai, "Effect of headgroup dissociation on the structure of Langmuir monolayers", Langmuir 16, 1239 (2000).

28 V. M. Kaganer, H. Mohwald, and P. Dutta, "Structure and phase transitions in Langmuir monolayers", Reviews of Modern Physics 71, 779 (1999).

29 M. K. Durbin, A. G. Richter, C. J. Yu, J. Kmetko, J. M. Bai, and P. Dutta, "Backbone orientational order in fatty acid monolayers at the air-water interface", Physical Review E 58, 7686 (1998).

30 M. K. Durbin, A. Malik, A. G. Richter, C. J. Yu, R. Eisenhower, and P. Dutta, "Ordered phases in Langmuir monolayers of an azobenzene derivative", Langmuir 14, 899 (1998).

31 A. Malik, W. Lin, M. K. Durbin, T. J. Marks, and P. Dutta, "Specular x-ray reflectivity studies of microstructure and ordering in self-assembled multilayers", Journal of Chemical Physics 107, 645 (1997).

32 R. S. Ghaskadvi, J. B. Ketterson, R. C. MacDonald, and P. Dutta, "Apparatus to measure the shear modulus of Langmuir monolayers as functions of strain amplitude and frequency", Review of Scientific Instruments 68, 1792 (1997).

33 R. S. Ghaskadvi, J. B. Ketterson, and P. Dutta, "Nonlinear shear response and anomalous pressure dependence of viscosity in a Langmuir monolayer", Langmuir 13, 5137 (1997).

34 M. K. Durbin, A. Malik, A. G. Richter, K. G. Huang, and P. Dutta, "In-situ x-ray diffraction study of Langmuir-Blodgett deposition", Langmuir 13, 6547 (1997).

35 M. K. Durbin, A. Malik, A. G. Richter, R. Ghaskadvi, T. Gog, and P. Dutta, "Transitions to a new chiral phase in a Langmuir monolayer", Journal of Chemical Physics 106, 8216 (1997).

36 A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang, and P. Dutta, "Order in Langmuir-Blodgett films of lead and cadmium stearate: An x-ray diffraction study", Thin Solid Films 284, 144 (1996).

37 R. S. Ghaskadvi, T. M. Bohanon, P. Dutta, and J. B. Ketterson, "Shear response of Langmuir monolayers of heneicosanoic (c-21) acid studied using a torsion pendulum", Physical Review E 54, 1770 (1996).

38 A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang, and P. Dutta, "Structures of headgroup and tail-group monolayers in a Langmuir-Blodgett-film", Physical Review B 52, 11654 (1995).

39 W. B. Lin, S. Yitzchaik, W. P. Lin, A. Malik, M. K. Durbin, A. G. Richter, G. K. Wong, P. Dutta, and T. J. Marks, "New nonlinear-optical materials - expedient topotactic self-assembly of acentric chromophoric superlattices", Angewandte Chemie-International Edition in English 34, 1497 (1995).

40 V. M. Kaganer, I. R. Peterson, R. M. Kenn, M. C. Shih, M. Durbin, and P. Dutta, "Tilted phases of fatty-acid monolayers", Journal of Chemical Physics 102, 9412 (1995).

41 M. K. Durbin, M. C. Shih, A. Malik, P. Zschack, and P. Dutta, "Isotherm and x-ray-diffraction studies of mixed monolayers", Colloids and Surfaces a-Physicochemical and Engineering Aspects 102, 173 (1995).

42 M. C. Shih, M. K. Durbin, A. Malik, P. Zschack, and P. Dutta, "Lattice structures and molecular tilts in Langmuir monolayers of saturated fatty-acid alcohol mixtures", Journal of Chemical Physics 101, 9132 (1994).

43 M. K. Durbin, A. Malik, R. Ghaskadvi, M. C. Shih, P. Zschack, and P. Dutta, "X-ray-diffraction study of a recently identified phase-transition in fatty-acid Langmuir monolayers", Journal of Physical Chemistry 98, 1753 (1994).

44 M. C. Shih, J. B. Peng, K. G. Huang, and P. Dutta, "Structures of fatty-acid monolayers transferred to glass substrates from various Langmuir monolayer phases", Langmuir 9, 776 (1993).

45 M. C. Shih, M. K. Durbin, A. Malik, T. M. Bohanon, P. Dutta, and P. Zschack, "X-ray-diffraction studies of pure and mixed Langmuir monolayers", Abstracts of Papers of the American Chemical Society 205, 176 (1993).

46 J. M. Mikrut, J. B. Ketterson, P. Dutta, and R. C. Macdonald, "Atomic force and fluorescence microscopies of deposited monolayers of l-alpha-dimyristoyl-phosphatidic acid", Biophysical Journal 64, A68 (1993).

47 J. M. Mikrut, P. Dutta, J. B. Ketterson, and R. C. Macdonald, "Atomic-force and fluorescence microscopy of Langmuir-Blodgett monolayers of l-alpha-dimyristoylphosphatidic acid", Physical Review B 48, 14479 (1993).

48 X. L. Yang, P. Dutta, G. K. Wong, and J. B. Ketterson, "Surface-plasmon resonance as a probe of the complexing process of valinomycin Langmuir-Blodgett-films by potassium-ions", Thin Solid Films 219, 210 (1992).

49 M. C. Shih, T. M. Bohanon, J. M. Mikrut, P. Zschack, and P. Dutta, "X-ray-diffraction study of the superliquid region of the phase-diagram of a Langmuir monolayer", Physical Review A 45, 5734 (1992).

50 M. C. Shih, T. M. Bohanon, J. M. Mikrut, P. Zschack, and P. Dutta, "X-ray-diffraction study of heneicosanol monolayers on the surface of water", Journal of Chemical Physics 97, 4485 (1992).

51 T. M. Bohanon, J. M. Mikrut, B. M. Abraham, J. B. Ketterson, S. Jacobson, L. S. Flosenzier, J. M. Torkelson, and P. Dutta, "Apparatus with an elastic barrier for radial compression of liquid supported monolayers", Review of Scientific Instruments 63, 1822 (1992).

52 T. M. Bohanon, A. M. Lee, J. B. Ketterson, and P. Dutta, "Surface-tension anisotropy and relaxation in uniaxially compressed Langmuir monolayers", Langmuir 8, 2497 (1992).

53 J. B. Peng, S. He, P. Dutta, and J. B. Ketterson, "Measurement of contact-angle relaxation during the deposition of Langmuir-Blodgett-films of cadmium stearate and valinomycin", Thin Solid Films 202, 351 (1991).

54 T. M. Bohanon, J. M. Mikrut, B. M. Abraham, J. B. Ketterson, and P. Dutta, "Fiberoptic detection system for capillary waves - an apparatus for studying liquid surfaces and spread monolayers", Review of Scientific Instruments 62, 2959 (1991).

55 B. Lin, M. C. Shih, T. M. Bohanon, G. E. Ice, and P. Dutta, "Phase-diagram of a lipid monolayer on the surface of water", Physical Review Letters 65, 191 (1990).

56 B. Lin, T. M. Bohanon, M. C. Shih, and P. Dutta, "X-ray-diffraction studies of the effects of ca2+ and cu2+ on Langmuir monolayers of heneicosanoic acid", Langmuir 6, 1665 (1990).

57 T. M. Bohanon, B. Lin, M. C. Shih, G. E. Ice, and P. Dutta, "Determination of lattice structure and calculation of molecular tilt in lipid monolayers on water using x-ray-diffraction", Physical Review B 41, 4846 (1990).

58 J. B. Peng, S. X. He, P. Dutta, and J. B. Ketterson, "Flow of a surfactant across a thin liquid-film wetting a solid substrate", Physical Review A 40, 7421 (1989).

59 B. Lin, J. B. Peng, J. B. Ketterson, P. Dutta, B. N. Thomas, J. Buontempo, and S. A. Rice, "Kinetics of a structural phase-transition in Langmuir monolayers studied using x-ray-diffraction", Journal of Chemical Physics 90, 2393 (1989).

60 K. Halperin, J. B. Peng, M. Sailor, R. Gadwood, J. B. Ketterson, and P. Dutta, "Direct measurements of the mechanical-properties of polymerized and unpolymerized Langmuir-Blodgett films", Journal of Polymer Science Part B-Polymer Physics 27, 1289 (1989).

61 K. Halperin, J. B. Ketterson, and P. Dutta, "A study of the mechanical-behavior of surface monolayers using orthogonal wilhelmy plates", Langmuir 5, 161 (1989).

62 J. B. Peng, J. B. Ketterson, and P. Dutta, "A study of the transition from y-type to x-type transfer during deposition of lead stearate and cadmium stearate Langmuir-Blodgett films", Langmuir 4, 1198 (1988).

63 J. B. Peng, P. Dutta, and J. B. Ketterson, "Using the transfer of a Langmuir monolayer as a probe of wetting", Thin Solid Films 159, 215 (1988).

64 B. Lin, J. B. Peng, J. B. Ketterson, and P. Dutta, "Synchrotron diffraction studies of lead octadecanoate, tetracosanoic acid and 1-eicosanol monolayers on water", Thin Solid Films 159, 111 (1988).

65 B. Lin, J. B. Peng, P. Dutta, J. B. Ketterson, and G. Wong, "Apparatus for making a/b superlattice Langmuir-Blodgett films", Review of Scientific Instruments 59, 2623 (1988).

66 S. W. Barton, B. N. Thomas, E. B. Flom, S. A. Rice, B. Lin, J. B. Peng, J. B. Ketterson, and P. Dutta, "X-ray-diffraction study of a Langmuir monolayer of c21h43oh", Journal of Chemical Physics 89, 2257 (1988).

67 M. Prakash, J. B. Peng, J. B. Ketterson, and P. Dutta, "Deposition of Langmuir-Blodgett-films of ferric stearate", Thin Solid Films 146, L15 (1987).

68 J. B. Peng, M. Prakash, R. Macdonald, P. Dutta, and J. B. Ketterson, "Formation of multilayers of dipalmitoylphosphatidylcholine using the Langmuir-Blodgett technique", Langmuir 3, 1096 (1987).

69 J. B. Peng, B. M. Abraham, P. Dutta, J. B. Ketterson, and H. F. Gibbard, "Langmuir-Blodgett deposition of a ring-shaped molecule (valinomycin)", Langmuir 3, 104 (1987).

70 P. Dutta, J. B. Peng, B. Lin, J. B. Ketterson, M. Prakash, P. Georgopoulos, and S. Ehrlich, "X-ray-diffraction studies of organic monolayers on the surface of water", Physical Review Letters 58, 2228 (1987).

71 T. Armen, K. Halperin, P. Dutta, and J. B. Ketterson, "Apparatus for making superlattice Langmuir-Blodgett-films with atmosphere and temperature control", Review of Scientific Instruments 58, 822 (1987).

72 M. Prakash, J. B. Peng, J. B. Ketterson, and P. Dutta, "Verification of epitaxial-growth and determination of chain positions in Langmuir-Blodgett-films of lead stearate on mica", Chemical Physics Letters 128, 354 (1986).

73 M. Prakash, J. B. Ketterson, and P. Dutta, "Study of inplane structure in lead fatty-acid LB films using x-ray-diffraction", Thin Solid Films 134, 1 (1985).

74 J. B. Peng, B. M. Abraham, P. Dutta, and J. B. Ketterson, "Contact-angle of lead stearate-covered water on mica during the deposition of Langmuir-Blodgett assemblies", Thin Solid Films 134, 187 (1985)