Physicochemical Hydrodynamics of Langmuir-Blodgett Ultrathin Film Depositions

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Extended Abstract: Introduction

The transfer on to the surface of a solid substrate of successive monolayers of divalent soaps compressed on the surface of water in a Langmuir trough, was described by Blodgett (1935). A Langmuir trough is a container with moving barriers for manipulation of a film of an amphiphilic compound at the air-water interface. By moving a solid substrate up and down, out and into the water subphase, the films are deposited on the solid surface. The term Langmuir-Blodgett technique (LB) is currently used to denote the successive deposition of monolayers by transfer from the air-water interface onto a solid surface. We use the term Langmuir films (L-films), to name the monolayers floating on the air-water interface and as Langmuir-Blodgett films (LB-films), the single or multiple monolayers deposited on a solid surface.

LB-films show remarkable ordered structure. The precise thickness of mono-molecular assemblies and the degree of control over their molecular architecture have firmly established LB-films as an essential building block of micro- and nano-technologies, for the manufacture of bio-sensors, nonlinear optic devices, and photo-lithography patterns for MEMS and NEMS fabrication (Barraud et al., 1993, Bykov, 1996).

The Langmuir-Blodgett Deposition Technique

A schematic view of our experimental setup is shown in Figure 1. A 612D Nima Technology trough is the centerpiece of this experimental setup. The trough and some peripherals are enclosed inside a Sterilgard III Advance Class II Laminar Flow cabinet. The sub-phase and the monolayer are maintained at constant temperature by a Lauda Ecoline RE204 water circulator and heater. A few drops of a dilute solution of an amphiphilic compound showing a hydrophilic and a hydrophobic headgroup in an organic solvent such as chloroform or ethyl ether, are spread out on top of the pure water surface in the Langmuir trough. The solvent evaporates leaving a loose layer of the amphiphilic compound floating on the water surface due to the repulsive forces on their hydrophobic ends. The surface pressure at the interface is controlled by a Wilhelmy plate balance and computer-activated moving barriers are used to compress the molecular layer on the water surface. The solid substrata, (glass microscope slides, silicone wafers, etc), are moved up and down, out and into the water by a computer controlled device. By moving the substrate in and out of the water, the monolayer can be transferred to its surface.

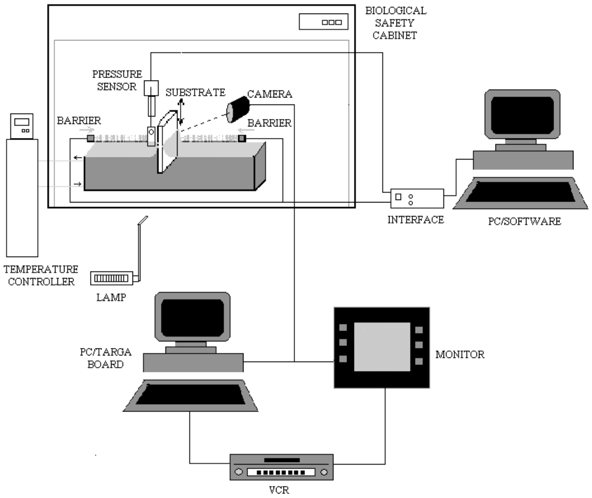

Figure 1: Sketch of experimental setup

Despite of many years of practice, LB depositions amount to a real challenge due to apparently unreliable behavior. However, most experimental data can be consistently explained on the basis of hydrodynamic models including molecular level-forces. The use of molecular-level forces in the description of thin film behavior is one of the areas of greater current research activity in physicochemical hydrodynamics.

Molecular forces at the three-phase contact line

Molecular, structural and electrical double layer forces have a strong effect on dynamic contact angles and moving contact lines. Solid and liquid are dense phases with large molecular concentrations while the gas phase, for the purpose of computing interaction potentials, is essentially a void. Contact angles and flow patterns are symptoms of the effect of highly asymmetric molecular and structural force fields in the vicinity of a contact line. In the wedge-like shape of the moving contact line the electrical double layers of the solid-liquid and film-liquid interface overlap. The sign and magnitude of the electrical forces created by the presence of the electrical double-layers has been recognized as the fundamental principle to determine wetting properties and static contact angles (Churaev, 1995).

The need to introduce molecular and structural forces to explain flow patterns near a moving contact line was recently recognized (Fuentes,et al. 2004) and flow patterns near moving contact lines have been used to explain the windows of operation of LB depositions (Cerro 2003). When a contact line moves, unbalanced molecular and structural forces produce a residual shear stress at the solid-liquid and fluid-fluid interface. In addition, the presence of surfactants or contaminants at the interface cause Marangoni-like effects due to changes in surface concentration. On clean interfaces an elasticity component is present, from stretching and compressing the interface (Edwards et al. 1991).

Regardless of the source of molecular forces, moving contact lines are inherently asymmetric. Electrical potentials of double layers in a solid-liquid interface can be different in magnitude and in sign to the potentials of the air-liquid interface on the same liquid pool. Thus, one may have attractive or repelling forces at the contact line, depending on the nature of the interfaces and on the pH of the liquid phase (Petrov et al, 1998). The nature and the effect of these forces on contact angles has been analyzed (Churaev 1995).

A framework was developed to analyze the hydrodynamics of LB depositions under the presence of electrical double layers on the solid-liquid interface and on the air-liquid interface (Diaz et al, 2004). Due to molecular compression, L-films at the air-water interface and LB-films deposited on the solid-water interface, behave essentially as two-dimensional solids. When a solid phase is in contact with a liquid, electrons or ions are attracted in different ways by the different phases and dipolar molecules are oriented selectively (Hunter, 1981). The solid phase may be charged due to ionization of the carboxylic acid group and to the difference between the affinities of solid and liquid phases for ions or ionizable species. To maintain electro-neutrality, the charged interface is surrounded by ions of opposite sign (counterions) within the liquid phase. This typical arrangement of an electrical double-layer is described by the Gouy-Chapman-Grahame-Overbeek theory of potential and charge distributions in electrical double-layers (Overbeek 1952). Although in LB depositions there is not strictly a contact line, there is a sub-micrometer region where the solid, liquid and air phases coincide and the double layers on the L-film and LB-film, overlap. The sign and magnitude of the electrical forces created by the presence of the electrical double-layers determine the dynamic contact angle and shape the flow patterns near the three-phase region. For an interface conformed by a thin film of an amphiphilic compound with the hydrophilic end of the molecule in contact with the water subphase, the equilibrium of charges is based on pH and subphase concentration. The effect of pH is associated to the definition of the pKa of the carboxylic acid, where the pKa is equal to the pH when half of the carboxylic acids are ionized. Values of pKa depend slightly on the length of the hydrocarbon chain attached to the carboxylic group and are

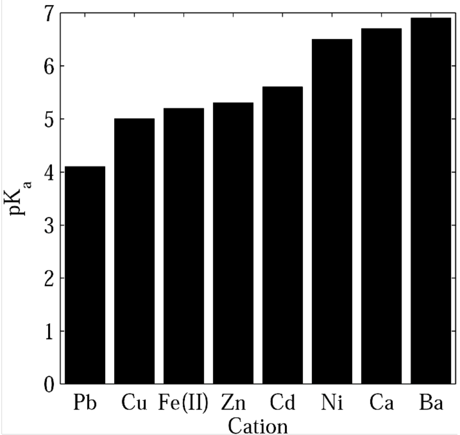

Figure 2: pK_A of arachidic acid with different divalent cation slats.

modified by the presence of a metal subphase counterion and its matching group. When an amphiphilic carboxylic acid and its subphase are at the pKa, the intermolecular distances between molecules at the air-water interface reaches a minimum (Kanicky et al. 2000) and macroscopic properties, such as foam height and stability as well as surface viscosity are at a maximum value. The *acidity* of a carboxylic acid in contact with a divalent salt is determined by the pK_A of the system. See Figure 2. A system is considered more acidic, the lower the value of its pK_A. Systems of high acidity, such as arachidic acid in the presence of Pb^{++}, do not deposit films during removal at any deposition velocities. Systems of intermediate acidity, such as arachidic acid with Zn^{++} and Cd^{++} salts, can be deposited during removal at high deposition velocities, but not at low velocities. Finally, systems of low acidity, such as arachidic acid in the presence of Ca^{++} and Ba^{++} salts, deposit during removal at all deposition speeds. See Figure 3.

Changes in deposition behavior with deposition speed are associated to molecular rearrangements when films are immersed in the water subphase. Molecular rearrangement causes the formation of fatty acid soaps with a centro-symmetric structure, exposing the hydrophobic hydrocarbon chains (Diaz et al, 2004). As a result of molecular rearrangement, the solid surface becomes partially hydrophobic and deposition during removal cannot take place.

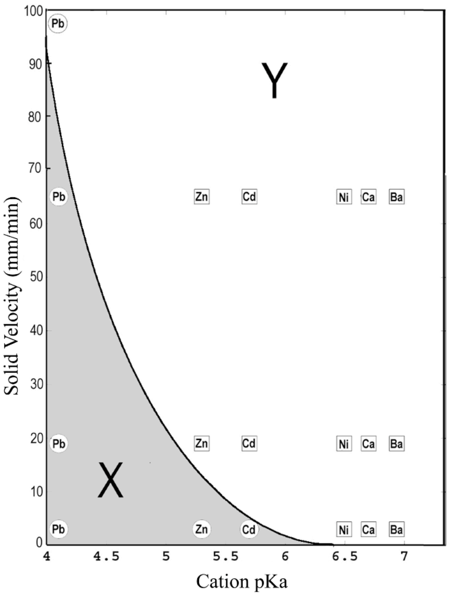

Figure 3: Deposition removal speeds versus pK_A

Theoretical tools for modeling and interpreting double layer properties and electrokinetic behavior has been known for a long time but it was only recently that ζ-potentials and electrokinetic properties could be measured accurately (Gu, 2000; Usui, 2002). Carboxylic acid heads of L-films and LB-films, submerged in a water subphase and in the presence of a salt of a divalent cation develop double layers, with similar sign and magnitude of charge. To accurately describe electrical double layers and ionization equilibrium properties of fatty acid-divalent salt systems, all ionic species must be included through the equilibrium constants describing dissociation of the fatty acid molecule, RCOOH, formation of the positively charged intermediate compound, $RCOOMe^+$, and formation of the electrically neutral divalent soap $(RCOO)_2Me$.

Augmented film evolution equation

An augmented version of the film evolution equation (AFE) was developed, introducing the contribution of the disjoining pressure due to molecular forces as well as the shear stress contribution at the interface due to the elasticity of the L-film. When the interface is stretched due to fluid motion, a Marangoni-like effect creates a large force that pulls the interface up to the speed of the liquid interface and controls the deposition of the LB film. The AFE is a version of the film evolution equation where molecular contributions to disjoining pressure are included [Teletzke, 1983] and has been extended later by other authors [Hocking, 1993] to introduce the variation of disjoining pressure with film inclination. The AFE is an integro-differential equation where the details of the two-dimensional flow field are traded for an integrated solution that satisfies the momentum balance on the average. To complete this description one must introduce a generic velocity profile that allows, by integration, elimination of components of velocity and stresses. To create a generic velocity profile one uses the boundary conditions that the velocity must satisfy at the solid substrate and at the air-liquid interface.

A main departure with previous developments based on the AFE is the introduction of the gradient of a scalar potential function reflecting the effect of unbalanced molecular, structural and electrical forces on the jump momentum balance. Although the normal component of these forces has been included before in the AFE, molecular forces define, in addition, a shear stress component that is used to determine the dynamic contact angle and flow patterns near the moving contact line. A surface tension gradient is also computed introducing the derivative of surface tension with concentration. The derivative of surface tension with respect to concentration of surfactant components at the interface can be obtained from the slope of the interfacial pressure isotherm that is customarily measured as part of the operating variables during LB-film depositions and it is a very significant physical property of the interfacial system.

Conclusions

The AFE allows introduction of molecular level forces that are crucial to describing experimental behavior of clean films as well as films contaminated or in the presence of an L-film at the air-water interface. Figure 4 shows a sample of results obtained from computations of the augmented film evolution equation. The solid straight line shows the results of Park (1991) where Marangoni

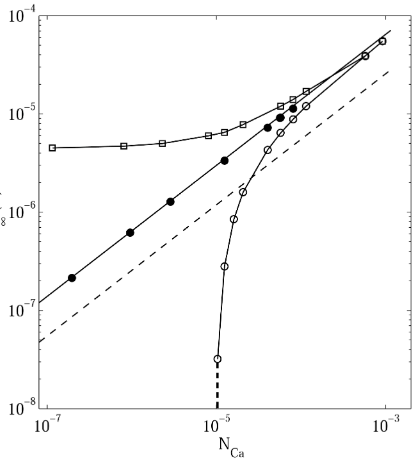

Figure 4: Film thickness versus Capillary number

effects are introduced by the presence of contaminants. The dotted line represents the results from the classical Landau-Levich solution. Open circles result from computations of the AFE for a non-wetting film, i.e. a fluid that has a non-zero contact angle and the open squares are results for a perfectly wetting fluid when the contact angle is equal to zero. For perfectly wetting films there is always an equilibrium film of small thickness, even when the solid substrate moves at very small velocities (Teletzke, 1983). For films with a finite contact angle, there is a limit Capillary number for the film to be stable.

The complexities of the LB deposition technique cannot be mastered without a comprehensive theoretical tool that takes into account changes in behavior due to changes in deposition speed, pH, divalent salt concentration, substrate properties and cation acidity. We have introduced such a tool and checked its accuracy against experimental data.

References:

Barraud, A., et al., *Study of immunoglobulin G thin layers obtained by the LB method: application to immunosensors*, Biosensors and Bioelectronics. 1993. p. 39-48.

Blodgett, K.B., *Films built by depositing successive monomolecular layers on a solid surface.* J. of the American Chemical Society, 1935. 57: p. 1007-1022.

Bykov, V.A., *Langmuir-Blodgett films and nanotechnology*. Biosensors and Bioelectronics, 1996. 11: p. 923-932.

Cerro, R.L., *Moving Contact Lines and Langmuir-Blodgett Film Deposition*. J. Colloid and Interface Science, 2003. 257: p. 276-283.

Diaz Martin, M.E., F.J. Montes, and R.L. Cerro, *Surface Potentials and Ionization Equilibrium in Y-type Deposition of Multiple Langmuir-Blodgett Films: II. Theoretical Model*, Submitted to J. Colloid and Interface Science. 2004.

Edwards, D.A., H. Brenner, and D.T. Wasan, **Interfacial Transport Processes and Rheology**. Butterworth-Heinemann Series in Chemical Engineering, ed. H. Brenner. 1991, Boston: Butterworth-Heinemann.

Fuentes, J., M. Savage, and R.L. Cerro, *The Role of Molecular and Electrical Double-Layer Forces on the Dynamics of Three-Phase Contact Lines*. To be submitted, J. Fluid Mechanics, 2004.

Gu, Y. and Y. Li, D., *The Zeta-Potential of Glass Surface in Contact with Aqueous Solutions*, J. Colloid and Interface Science. 2000. 226: 328-339.

Hocking, L. M., *The influence of intermolecular forces on thin fluid layers,* Physics of Fluids A, **5**, 793-798

Hunter, R.J. **Zeta Potential in Colloid Science**. 1981, Academic Press.

Kanicky, J. R., Poniatowski, A. F., Mehta, N. R. and Shah, D. O. *Cooperativity among Molecules at Interfaces in Relation to Various Technological Processes: Effect of Chain Length on the pKa of Fatty Acid Salt Solutions*, Langmuir. 2000, 16. 172-177.

Overbeek, J.T.G., Electrochemistry of the Double Layer, **Colloid Science**, H.R. Kruyt, Editor. 1952, Elsevier Publishing Corp. p. 115-193.

Park, C.-W., *Effects of insoluble surfactants on dip-coating*, Journal of Colloid and Interface Science. 1991. 146: 382-394

Petrov, J.G. and P.G. Petrov, *Molecular hydrodynamic description of Langmuir-Blodgett deposition,* Langmuir. 1998. 14: 2490-2496.

Teletzke, G.F., *Thin Liquid Films: Molecular Theory and Hydrodynamic Applications*, in PhD Thesis. 1983, University of Minnesota: Minneapolis.

Usui, S. and T.W. Healy, *Zeta potential of stearic acid monolayer at the air-acqueous solution interface*, J. Colloid and Interface Science. 2002. 250: 371-378.