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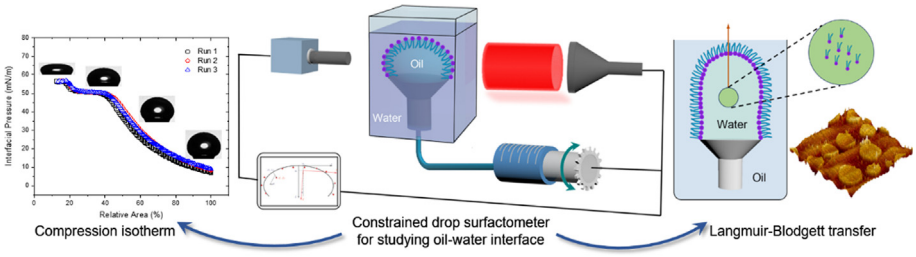
# Langmuir-Blodgett transfer from the oil-water interface

Guangle Li [a], Xiaojie Xu [a], Yi Y. Zuo [a,b,*]

[a] Department of Mechanical Engineering, University of Hawaii at Manoa, Honolulu, HI 96822, United States
[b] Department of Pediatrics, John A. Burns School of Medicine, University of Hawaii, Honolulu, HI 96826, United States

## GRAPHICAL ABSTRACT

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## ABSTRACT

*Hypothesis:* Almost all Langmuir-Blodgett (LB) films were prepared with the classical Langmuir film balance, developed more than a century ago. To date, the success of the classical Langmuir film balance and the LB transfer technique is primarily restricted to the study of self-assembled monolayers at the air-water surface. It is challenging to study self-assembled monolayers at the oil-water interface, since the Langmuir film balance requires stacked oil and water layers. We hypothesize that a newly developed experimental method, called constrained drop surfactometry (CDS), is capable of preparing and characterizing LB films from the oil-water interface.
*Experiments:* We have developed a novel droplet-based LB transfer technique capable of preparing LB films from the oil-water interface. In conjunction with atomic force microscopy, we have demonstrated the capacity of the CDS in studying a natural pulmonary surfactant film self-assembled at the perfluorocarbon-water interface, and have compared to the LB films prepared from the air-water surface using the classical Langmuir film balance.
*Findings:* Our findings have demonstrated a novel paradigm for studying self-assembled monolayers and for preparing LB films from the oil-water interface. The CDS holds great promise for expanding the applicability of the traditional LB transfer technique from the air-water surface to the oil-water interface.


## 1. Introduction

It has been a century since Irving Langmuir and Katharine Blodgett first developed the modern Langmuir film balance and the Langmuir-Blodgett (LB) transfer technique for studying self-assembled insoluble monolayers [1,2]. Owing to its precise control on the structure and thickness of the engineered films, and its capacity of incorporating with various characterization and analytical techniques, such as atomic force microscopy (AFM) and X-ray diffraction [3,4], the LB transfer technique has found extensive applications in physical chemistry, surface science, materials science, life science, and nanotechnology [5–8].

The success of the classical Langmuir film balance and the LB transfer technique, however, is primarily restricted to the study of self-assembled monolayers at the air-water surface. The design

* Corresponding author at: 2540 Dole St, Holmes Hall 302, Honolulu, HI 96822, United States.
*E-mail addresses:* guangle@hawaii.edu (G. Li), xiaojie@hawaii.edu (X. Xu), yzuo@hawaii.edu (Y.Y. Zuo).

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of the Langmuir film balance makes it extremely challenging to study self-assembled monolayers at the oil-water interface, which requires a stack of oil layer atop the water subphase in a Langmuir trough. The stacked design has intrinsic limitations that complicate interfacial tension measurements with a Wilhelmy plate, *e.g.*, difficulties in maintaining a zero contact angle [9], and LB transfer from the oil-water interface between stacked liquid layers [10–14].

Self-assembly of amphiphilic molecules and/or nanoparticles at the oil-water interface has gained increasing attention in recent years. There have been many emerging applications of self-assembly at the oil-water interface in emulsification, catalysis, complex fluids, environmental remediation, biophysics, and medical sciences [15–18]. For example, liquid ventilation is a mechanical ventilation technique in which the partial or total lung space is filled with oxygenated perfluorocarbon (PFC) liquids rather than air in conventional mechanical ventilation. It holds great promise in treating premature newborns and adults with acute lung injury and acute respiratory distress syndrome by mitigating ventilator-induced lung injury [19]. However, it is still unknown how the endogenous pulmonary surfactant self-assembles and functions at the oil-water interface of the PFC-filled lungs, in comparison to the conventional surfactant film adsorbed at the air-water surface of the air-filled lungs [20]. Lack of a reliable LB transfer technique from the oil-water interface has significantly limited the capacity of engineering and characterizing self-assembled thin-film materials at the oil-water interface.

Here we developed a novel droplet-based Langmuir film balance capable of preparing LB films from the oil-water interface. This miniaturized Langmuir film balance is designed based on an experimental method called constrained drop surfactometry (CDS) developed in our laboratory [21,22]. We have further developed the CDS to allow the study of self-assembled Langmuir monolayers at the oil-water interface, and the preparation of LB films from the oil-water interface. In conjunction with AFM, we have demonstrated the capacity of the CDS in studying a natural pulmonary surfactant, Infasurf, self-assembled at the PFC-water interface. To validate the method, we have compared the surface activity, topography and lateral structure of Infasurf at the PFC-water interface to those at the air-water surface obtained with a classical Langmuir film balance. Our findings have demonstrated a novel paradigm for studying self-assembled monolayers and for preparing LB films at the oil-water interface. The CDS holds great promise for expanding the applicability of the traditional LB transfer technique from the air-water surface to the oil-water interface.

## 2. Materials and methods

### 2.1. Materials

Infasurf was donated by ONY Biotech (Amherst, NY). Infasurf was prepared with centrifugation and organic extraction of bronchoalveolar lavage of newborn calves. It contains approximately 90 % phospholipids, 5–8 % cholesterol, and 2 % surfactant proteins, SP-B and SP-C [23]. Infasurf was stored at −20 °C with a total phospholipid concentration of 35 mg/mL. It was extracted with chloroform-methanol, dried under a nitrogen stream, and re-dissolved in chloroform to a final concentration of 1 mg/mL. Perfluorooctane ($C_8F_{18}$) was purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. Water used was Mill-Q ultrapure water (Millipore, Billerica, MA).

### 2.2. Langmuir-Blodgett trough

A Langmuir-Blodgett (LB) trough (KSV Nima, Coventry, UK) was used to study surfactant films at the air-water surface at room temperature (20 ± 1 °C). As shown in Fig. 1**A**, the LB trough is equipped with two Delrin barriers to reduce film leakage. The trough has a subphase volume of ∼160 mL and a surface area of ∼300 $cm^2$. Surface monolayers were prepared by depositing droplets of chloroform-extracted Infasurf throughout the air-water surface using a microsyringe. After spreading, the monolayer was given 10 min to allow equilibrium and solvent evaporation. The spread monolayer was compressed at a rate of 20 $cm^2$/min, *i.e.*, 0.1 % initial surface area per second. Infasurf films at the air-water surface were transferred to freshly cleaved mica surfaces by elevating previously submerged mica vertically through the air-water surface, at a rate of 1 mm/min under controlled surface pressures.

### 2.3. Constrained drop surfactometry

CDS is a droplet-based surface tensiometry technique developed in our laboratory for studying self-assembled monolayers at the air-water surface [21,22]. As shown in Fig. 1**B**, CDS uses a droplet pedestal (3–5 mm in diameter) with knife-sharp edges to maintain the droplet integrity even at low surface tensions. The droplet pedestal provides a leakage-proof environment so that the surfactant film is "constrained" at the air-water surface of the droplet without leaking over the pedestal. The spread film at the air-water surface of the droplet can be oscillated by regulating fluid flow with a motorized syringe. Closed-loop axisymmetric drop shape analysis (CL-ADSA) was used to determine the surface tension ($\gamma$) and surface area of the droplet [24]. The surface pressure ($\pi$) can be calculated with, $\pi = \gamma_0 - \gamma$, in which $\gamma_0$ is the surface tension of the air-water surface.

We have further developed the CDS technique to allow the study of compression isotherms and preparation of LB film at the oil-water interface. The oil-water interface can be constructed with either the oil-in-water configuration or the water-in-oil configuration. The resultant droplet shape depends on the relative densities of the oil and water [25]. Since perfluorooctane is heavier than water (see Table 1 for physical properties of perfluorooctane), the oil-in-water configuration assumes the shape of a sessile drop (Fig. 1**B**), while the water-in-oil configuration assumes the shape of a pendant bubble (Fig. 1**C**).

Compared to the planar surface of a Langmuir film balance, the curvature of a sessile drop varied between 1.3 and 4.0 $cm^{-1}$, while the curvature of a pendant bubble varied between 5.7 and 13 $cm^{-1}$, when gradually compressing the oil-water interface of an Infasurf monolayer-covered droplet (see Fig. S1 of the Supplementary Material). Macroscopic curvatures of the sessile drop and pendant bubble are approximately 6–7 orders of magnitude smaller than the intrinsic microscopic curvature of phospholipid monolayers [22]. Therefore, it is safe to ignore the curvature of the droplet and to assume a flat oil-water interface when studying phospholipid monolayers with CDS.

Specifically, a small amount of Infasurf samples was spread at the oil-water interface. After spreading, the droplet was slowly expanded to decrease the interfacial pressure to ∼5 mN/m. Subsequently, the film was compressed at a rate of 0.075 $cm^2$/min, corresponding to 0.3 % initial interfacial area per second. For LB transfer, a water-in-oil configuration was used to avoid contamination of the mica substrate submerged in the droplet *prior to* the transfer (Fig. 1**C**). The Infasurf monolayer was deposited onto the mica surface held by an anti-capillary tweezer, by elevating the mica vertically through the oil-water interface at a rate of 1 mm/min, under a constant interfacial pressure controlled by the CL-ADSA. All experiments were conducted at room temperature, in order to compare with results obtained with the classical LB trough.

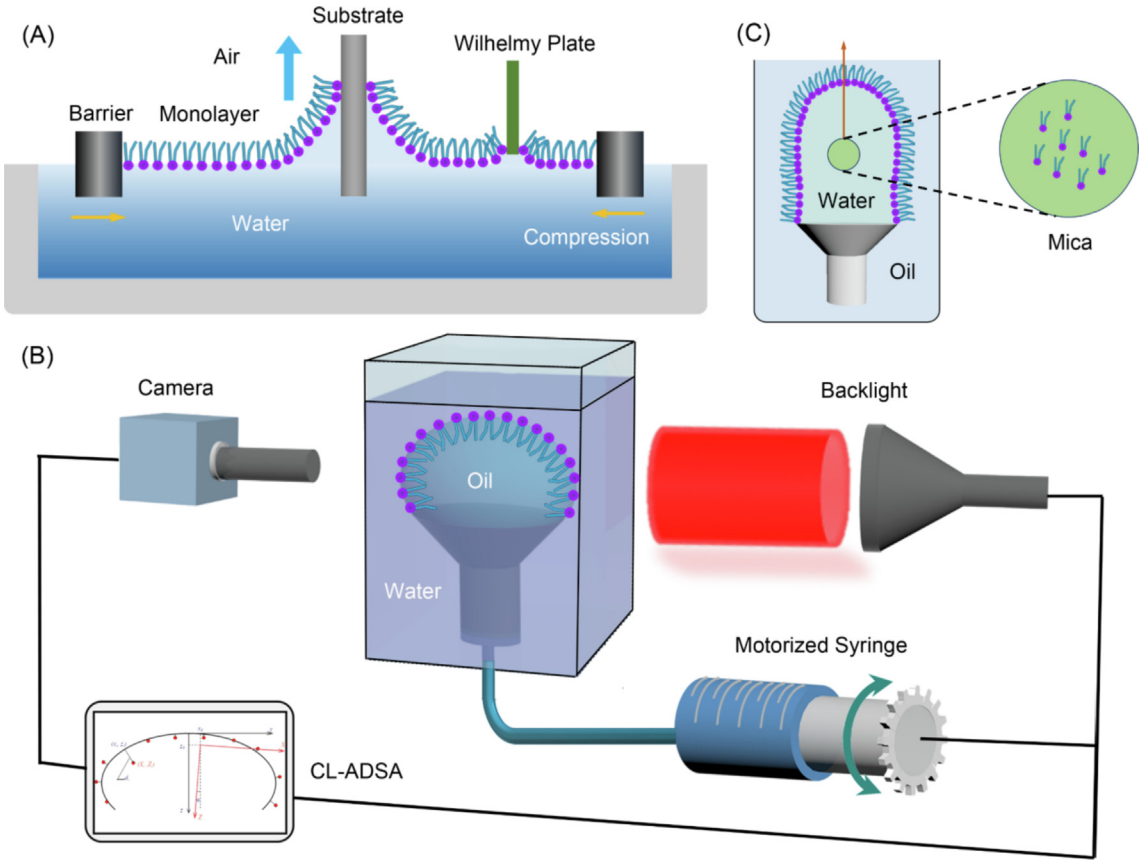


**Fig. 1.** Schematics of the experimental methodologies for studying self-assembled monolayers at the air-water surface and the oil-water interface. (A) Classical Langmuir-Blodgett (LB) film balance for engineering LB film from the air-water surface. Surface pressure ($\pi$) of the monolayer is determined with a Wilhelmy plate in contact with the air-water surface. (B) Constrained drop surfactometry (CDS) for studying self-assembled monolayers at the oil-water interface of a perfluorooctane droplet submerged in water. Since perfluorooctane is heavier than water, the oil droplet appears as a sessile drop. Interfacial tension ($\gamma$) of the monolayer-covered droplet is determined in real-time, photographically from the shape of the droplet using closed-loop axisymmetric drop shape analysis (CL-ADSA). (C) LB transfer from the oil-water interface of a water droplet submerged in perfluorooctane. Since perfluorooctane is heavier than water, the water droplet appears as a pendant bubble. The LB film is prepared by lifting a freshly peeled mica surface across the oil-water interface under controlled interfacial pressure using CL-ADSA.

**Table 1**
Physicochemical parameters used in controlling Langmuir-Blodgett (LB) transfer from the oil-water interface with constrained drop surfactometer (CDS).

| Oil phase properties | Perfluorooctane ($C_8F_{18}$) |
|---|---|
| - Density | 1.766 g/mL |
| - Viscosity | 1.26 mPa·s at 25 °C |
| - Solubility in water | 10 mg/L |
| - Boiling temperature | 103 °C |
| - Surface tension | 14 mN/m |
| - Oil-water interfacial tension | 59 mN/m |
| Droplet properties | Pendant bubble |
| - Droplet configuration | Water-in-oil |
| - Initial volume of the droplet | 40 μL |
| - Initial area of the droplet | 0.5 $cm^2$ |
| LB transfer properties | Freshly peeled mica |
| - LB transfer rate | 1 mm/min |
| - LB deposition ratio | 1.1–1.4 |
| - Film compression rate during LB transfer | 0.017 $cm^2$/min |
| - Interfacial pressure variation during LB transfer | ±1 mN/m |

### 2.4. Atomic force microscopy

AFM images of the LB transferred Infasurf film were obtained in air using an Innova AFM (Bruker, Santa Barbara, CA). Tapping mode was used with a silicon cantilever (spring constant 42 N/m and resonance frequency 300 kHz). Topography and lateral structures of the surfactant films were analyzed using Nanoscope Analysis.

## 3. Results and discussion

### 3.1. Comparison of compression isotherms at the air-water surface and the oil-water interface

Fig. 2 shows the comparison of compression isotherms of Infasurf at the air-water surface obtained with the Langmuir trough, and at the air-water surface and oil-water interface obtained with the CDS. For the compression isotherms at the oil-water interface, both the oil-in-water (sessile drop) and water-in-oil (pendant bubble) configurations were studied. A video clip (Movie S1) that shows the compression process of the Infasurf film at the oil-water interface of the CDS can be found in the supplementary material. Each isotherm was repeated at least three times to demonstrate reproducibility. The increase of surface/interfacial pressure upon film compression is evidenced by the shape change of the sessile drop and pendant bubble, as shown in insets of Fig. 2-**B-D** and Movie S1.

The compression isotherms of Infasurf at the air-water surface obtained with the classical Langmuir film balance (Fig. 2**A**) and the CDS (Fig. 2**B**) have demonstrated an excellent agreement. These compression isotherms show a well-studied characteristic shape [20,23,26,27]. (Fig. S2 shows a negative control in which the surface area of the PFC-water interface, without the spread Infasurf film, was gradually reduced. No variations of interfacial tension have been found in the negative control.) The surface pressure first increases with film com-

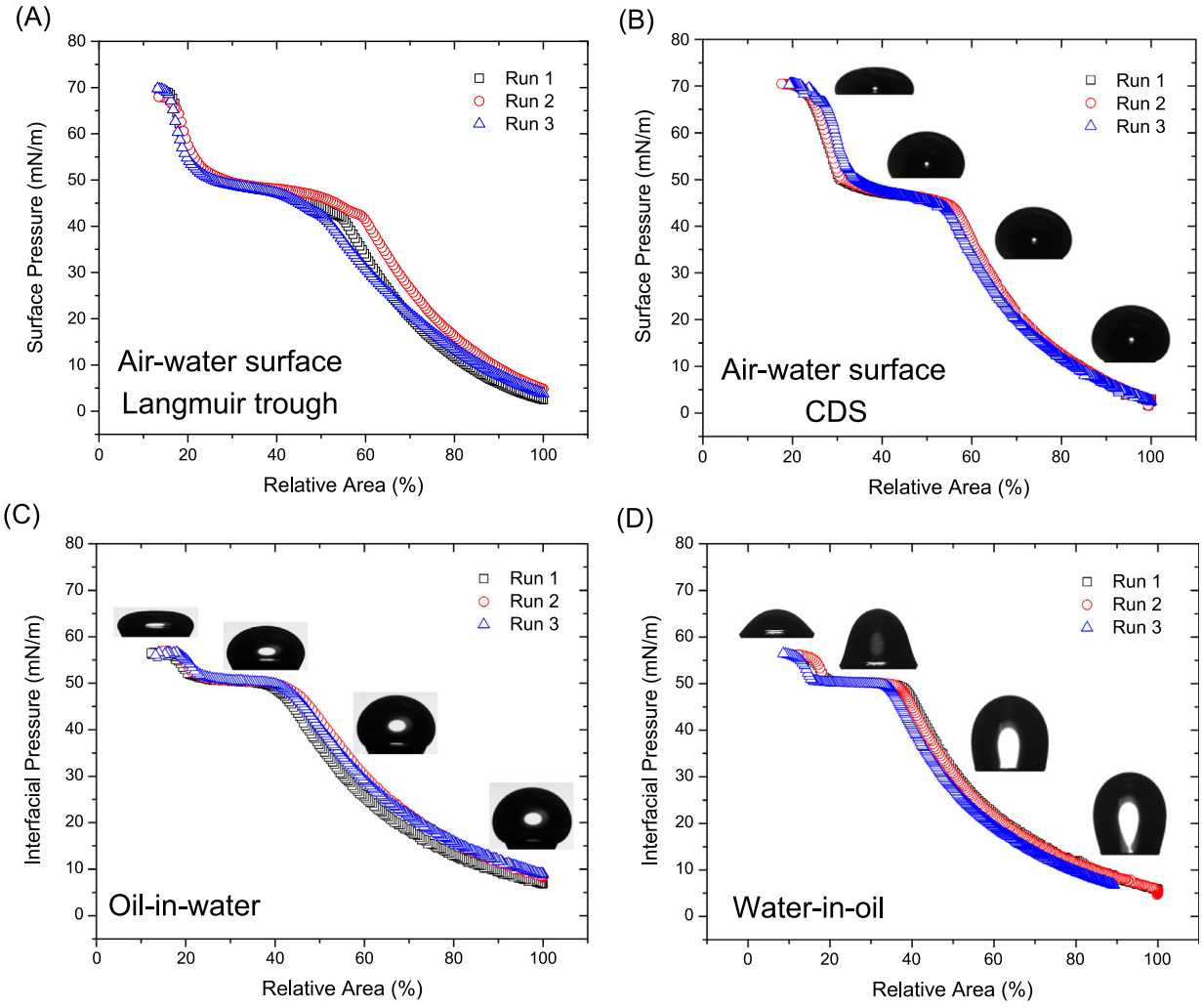


**Fig. 2.** Comparison of compression isotherms of Infasurf at the air-water surface and the oil-water interface. Compression isotherms of Infasurf at the air-water surface obtained with a classical Langmuir film balance (A) and the CDS (B). Compression isotherms of Infasurf at the oil-water interface obtained with the CDS in an oil-in-water (sessile drop) configuration (C) and a water-in-oil (pendant bubble) configuration (D). Insets shown in (B-D) demonstrate the correlation between the surface/interfacial pressure and the drop shape. For comparison, all compression isotherms were determined at room temperature. Under each condition, the compression isotherms were repeated for three times to demonstrate reproducibility.

pression, and then reaches a plateau region at the surface pressure between 40 and 50 mN/m, followed by a steep increase of the surface pressure after passing the plateau and a final film collapse at the surface pressure of 70 mN/m, corresponding to a near-zero surface tension. Previous studies of surfactant films at the air-water surface have convincingly demonstrated that this plateau region indicates a monolayer-to-multilayer transition in which the fluid phospholipids of pulmonary surfactant are selectively squeezed-out to form a solid-like monolayer highly enriched in disaturated phospholipids, mostly dipalmitoyl phosphatidylcholine (DPPC), with the squeezed out fluid phospholipids closely and functionally attached to the interfacial monolayer [23,27,28].

The shape of the compression isotherms obtained at the oil-water interface is almost identical for both the oil-in-water (Fig. 2**C**) and water-in-oil (Fig. 2**D**) configurations. The interfacial pressure first increases with film compression, and then reaches a plateau region at the interfacial pressure of 50 mN/m, followed by a steep increase of the interfacial pressure after passing the plateau and a final film collapse at the interfacial pressure of 56 mN/m. Since the PFC-water interfacial tension is 59 mN/m (Fig. S3 and Table 1), the collapse pressure of Infasurf at the PFC-water interface corresponds to a very low interfacial tension of ~3 mN/m, thus indicating that phospholipid molecules of Infasurf are capable of closely packing at the oil-water interface.

Given the similarity in the shape of these compression isotherms, it is hypothesized that a similar monolayer-to-multilayer transition must occur at the oil-water interface. This hypothesis is also supported by the similar width of the plateau region, *i.e.*, spanning ~20 % area reduction, between isotherms at the air-water surface and the oil-water interface, indicating that the same amount of unsaturated lipids needs to be squeezed out from the Infasurf monolayer. The specific location and shape of the plateau region, however, are different. While the plateau region at the air-water surface covers a surface pressure range from 40 to 50 mN/m, the plateau region at the oil-water interface is nearly flat at a constant interfacial pressure of 50 mN/m, thus indicating more steric and/or hydrophobic restriction for conformational changes of lipid molecules at the oil-water interface than those at the air-water surface [18].

### *3.2. Comparison of film topography and lateral structure at the air-water surface and the oil-water interface*

To characterize the topography and lateral structure of the Infasurf film at the PFC-water interface using AFM, we first LB transfer

the Infasurf film onto mica substrates under controlled interfacial pressures. For LB transfer from the oil-water interface, the water-in-oil configuration (Fig. 1**C**) was used to avoid contamination of the mica substrate submerged in the droplet *prior to* the transfer. The entire LB transfer process is shown in Movie S2. All physicochemical parameters pertinent to the LB transfer process are summarized in Table 1. Among these parameters, the deposition ratio can be used to evaluate the quality of the LB transfer. It is defined as the ratio between the decrease in the area of the Langmuir film during the transfer process in order to maintain a constant surface/interfacial pressure, and the surface area of the solid substrate used for the LB transfer. A deposition ratio much larger than one indicates film collapse and leakage during the transfer process, while a deposition ratio much smaller than one indicates incomplete transfer due to insufficient affinity between the amphiphilic molecules and the solid substrate [29]. The deposition ratio of the LB transfer is estimated to be between 1.1 and 1.4 (Table 1), thus indicating a high-fidelity deposition from the oil-water interface to the solid substrate.

Fig. 3 shows the comparison of the topography and lateral structure of the Infasurf film LB transferred from the air-water surface and from the oil-water interface. For each of these surface/interface, two characteristic surface/interfacial pressures, one below and one beyond the critical surface pressure for the monolayer-to-multilayer transition, were studied. Fig. S4 shows the detailed height analysis of these AFM images.

For the air-water surface, at a surface pressure (30 mN/m) lower than the plateau region, Infasurf at the air-water surface assumes a monolayer conformation (Fig. 3**A**). Phase separations are evident by the formation of tilted-condensed (TC) domains between 1 and 6 μm in diameter and approximately 1 nm higher than the surrounding liquid-expended (LE) phase. At a surface pressure (60 mN/m) higher than the plateau region, the Infasurf film is transformed into a multilayered conformation with uniformly distributed protrusions 4–12 nm in height, corresponding to 1 to 3 stacks of fully-hydrated lipid bilayers (Fig. 3**B**).

For the oil-water interface, at an interfacial pressure (30 mN/m) lower than the plateau region, Infasurf at the oil-water interface also assumes a monolayer conformation with a relatively uniform domain size distribution of 2.0 ± 0.5 μm (Fig. 3**C**). The TC domain size at the oil-water interface is in general smaller than those at the air-water surface (with a majority of domains larger than 3 μm) but much more uniform in size. These differences may be explained by the smaller diffusion coefficients of phospholipids at the oil-water interface than those at the air-water surface. Adalsteinsson and Yu found that at low surface pressures, the diffusion of phospholipids at the oil-water interface is controlled by the viscosity of the oil phase, thus being much slower than the lipid diffusion at the air-water surface [30].

At an interfacial pressure (53 mN/m) higher than the plateau region, the Infasurf monolayer is transformed into a multilayered conformation with uniformly distributed protrusions 4–8 nm in height, corresponding to 1 to 2 stacks of fully-hydrated lipid bilayers (Fig. 3**D**). It appears that the multilayered protrusions formed at the oil-water interface are in general lower than their counterparts at the air-water surface, thus indicating a steric and/or hydropho-

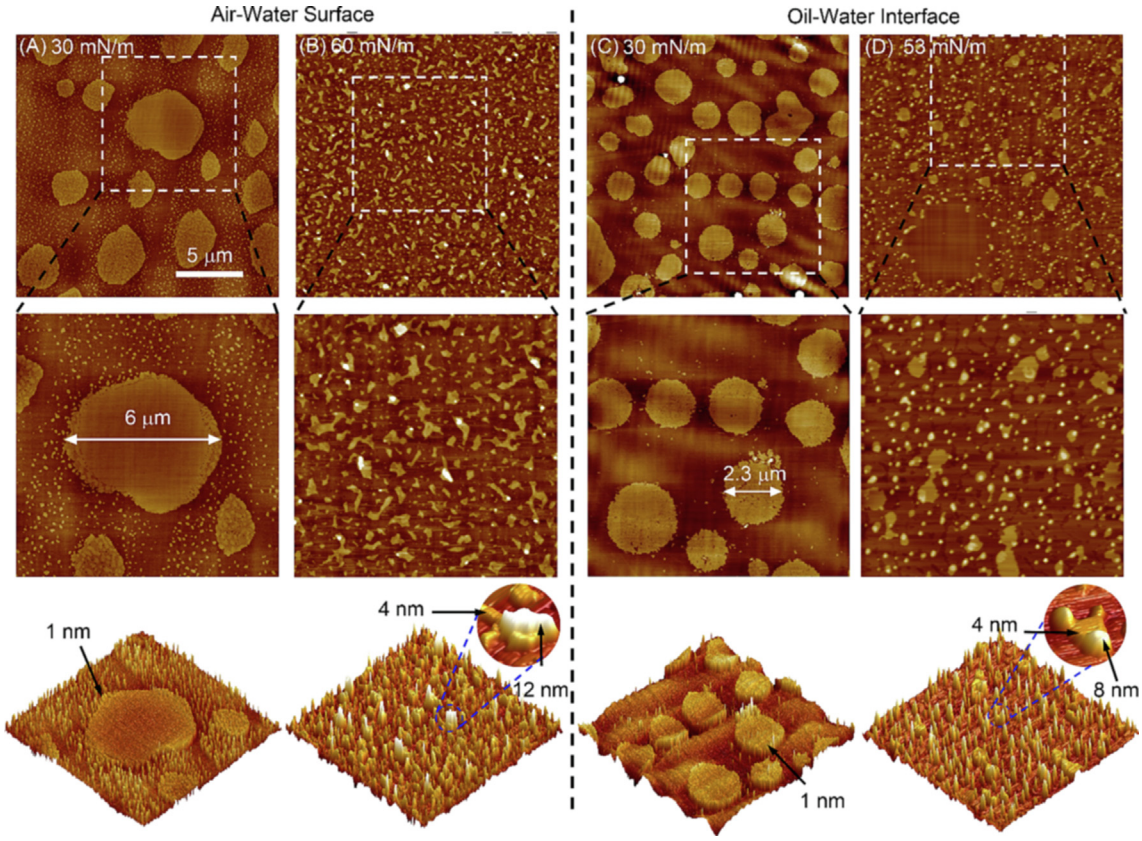


**Fig. 3.** Comparison of AFM topographic images of Infasurf films LB transferred from the air-water surface and from the oil-water interface at two characteristic surface/interfacial pressures, *i.e.*, one below and one beyond the plateau region in the corresponding compression isotherms. (A, B) Infasurf films LB transferred from the air-water surface, using the classical Langmuir film balance, at 30 and 60 mN/m, respectively. (C, D) Infasurf films LB transferred from the oil-water interface, using CDS, at 30 and 53 mN/m, respectively. All AFM images in the top row have the same scanning area of 20 × 20 μm. *z* range is 5 nm for monolayers and 20 nm for multilayers. AFM images in the middle row show zoom-in images indicated by the white boxes. AFM images in the bottom row show the 3D rendering of the zoom-in images. Detailed multilayer structures are shown in circles. White arrows indicate the lateral dimension of the domains, while black arrows indicate the height of the structures.

bic restriction for the growth of multilayers at the oil-water interface, which is consistent with the flat plateau region found in the compression isotherms (Fig. 2**C and D**). It has long been hypothesized that phospholipid monolayer at the oil-water interface upon extreme compression would undergo a 2D-3D monolayer-to-multilayer transformation [31]. The present study therefore provides direct experimental evidence for such a conformational transition at the oil-water interface.

### *3.3. Selection of the oil phase for studying LB transfer from the oil-water interface*

For the study of self-assembled amphiphilic molecules in general or phospholipid polymorphism in specific at the oil-water interface, it is essential to identify an oil phase that is inert enough not to disturb the self-assembled monolayer at the oil-water interface. Thoma and Möhwald have studied the effect of various hydrocarbons on studying phospholipid polymorphism at the oil-water interface [11,12]. They found that the selection of an inert oil phase depends on both headgroup and alkyl chains of the studied phospholipids. For phospholipids with relatively small headgroups, such as phosphatidylethanolamine (PE), it was found that alkane can partition into condensed lipid domains when there is a close match of the chain length between the lipid and the alkane [11]. For example, hexadecane ($C_{16}$ alkane) can easily penetrate into the condensed phase of 16:0, 16:0 PE, thus modifying its compression isotherms and domain morphologies. For phospholipids with relatively large headgroups, such as phosphatidylcholine (PC), it was found that alkane can partition into condensed lipid domains even if there is a considerable mismatch of the chain length between the lipid and the alkane [12].

Pulmonary surfactant is a mixture of various species of phospholipids and proteins, with DPPC (16:0, 16:0 PC) being the most abundant individual component in the mixture [23]. Hence, it would not be ideal to use hydrocarbons as the oil phase for studying self-assembled pulmonary surfactant film at the oil-water interface. Instead, perfluorocarbons, with most or all hydrogen atoms of hydrocarbons replaced with fluorine atoms, are much bulkier molecules than their hydrocarbon counterparts, thus preventing them from penetration into the phospholipid monolayer. The present study has demonstrated that perfluorooctane, with its ideal physicochemical properties (Table 1), appears to be an ideal oil phase for studying LB film at the oil-water interface.

## 4. Conclusions

Fundamental design of the classical Langmuir-Blodgett (LB) transfer technique has very little change since it was first developed nearly a century ago. In spite of its extensive success in studying insoluble monolayers self-assembled at the air-water surface, the LB transfer technique has very limited application at the oil-water interface [8]. We have developed a novel droplet-based LB transfer technique, called constrained drop surfactometry (CDS), capable of preparing LB films from the oil-water interface. This new technique utilizes the oil-water interface of a single droplet for accommodating the self-assembled monolayers, which is fundamentally different from the stacked oil and water layers used in the classical Langmuir film balance for constructing the oil-water interface [10–12]. In conjunction with atomic force microscopy, we have demonstrated the capacity of this new LB transfer technique in studying a natural pulmonary surfactant film self-assembled at the perfluorocarbon-water interface. The deposition ratio of the LB transfer was estimated to be between 1.1 and 1.4, thus indicating a high-fidelity deposition from the oil-water interface to the solid substrate. For the first time, we have revealed the lateral structure and molecular organization of the natural pulmonary surfactant film at the oil-water interface, and compared them to the lipid polymorphism of the pulmonary surfactant film studied at the air-water surface [23]. Our findings have demonstrated a novel paradigm for studying self-assembled monolayers and for preparing LB films at the oil-water interface. The CDS developed in this work holds great promise for expanding the applicability of the traditional LB transfer technique from the air-water surface to the oil-water interface.

## CRediT authorship contribution statement

**Guangle Li:** Data curation, Investigation, Methodology, Validation, Writing – original draft. **Xiaojie Xu:** Methodology, Validation. **Yi Y. Zuo:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

## Data availability

Data will be made available on request.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2022.10.063.

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