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Analyzing refractive index profiles of confined fluids by interferometry part II: Multilayer and asymmetric systems

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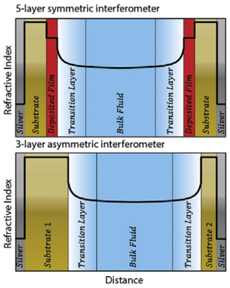
HIGHLIGHTS

- Non-contact thin film measurement technique is extended to complex interferometers.
- Methods for 3-layer asymmetric and 5-layer interferometers are considered in detail.
- Technique is verified using realistic simulations and an experimental system.
- Criteria for extension to more complicated systems is also developed.

GRAPHICAL ABSTRACT



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ABSTRACT

Methods for determining the substrate properties and the optical thickness of thin films or any variation in the refractive index of a fluid or film near a surface for unknown 5-layer symmetric and 3-layer asymmetric interferometers are presented. Both systems can be fully resolved without any known layer properties and without contact or confining the films. The method was tested using realistic simulated interferometer data, and was found to consistently yield accurate values for all desired properties. The method was experimentally validated through analysis of an asymmetric three layer interferometer system of linear polyethyleneimine (LPEI) adsorbed onto mica substrates of differing thickness and identical refractive index. The results were in excellent agreement with the dry polymer film properties measured using conventional SFA contact measurements. More complicated systems were also evaluated for feasibility, and any additional parameter specifications required for analysis were determined. The utility of this method is broad, as a single experiment in a laboratory setting can independently provide non-contact film properties and the effects of confinement on the film structure, which can be correlated to a simultaneously measured interaction force profile.

1. Introduction

The surface force apparatus (SFA), which has primarily been used to measure interaction force profiles, can also be used to measure refractive index profiles of fluids confined between surfaces [1–7]. While the measurements are limited to mean refractive index profiles, and are lower resolution than alternative techniques used for evaluating liquid properties near a solid surface such as X-ray and neutron scattering [8] and recently nanoultrasonics [9], the coupling of refractive index with force measurements and the ability to confine the fluid present advantages over other methods. With these abilities, any structurally induced interaction between

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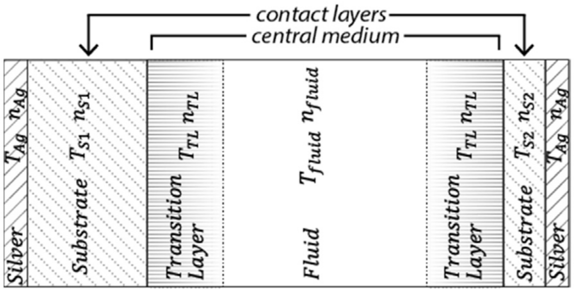
surfaces can be observed. Additionally, the method is convenient because it uses the visible spectrum and will work over a wide range of geometries and materials.

The SFA uses multiple beam interferometry (MBI) to measure the separation distance between two surfaces and the refractive index of the medium separating those surfaces (central medium). Measurements are taken in the SFA by directing collimated white light through an etalon, generating intensity peaks at discrete wavelengths called fringes of equal chromatic order (FECO) [10]. Spectrographic measurements allow the wavelength of the FECO to be determined via peak fitting. FECO simulated using the multilayer matrix method [11] are fit to the measured FECO to determine optical properties of the system such as layer thickness and refractive index [12].

Recently, we developed a method based on the SFA for determining the variation in the fluid refractive index near a surface without confining or contacting the surfaces [5]. The approach can be used to probe surface effects on a fluid's structure independent of the effect of confinement, which was previously not possible. This capability could be extremely valuable for deducing any changes in the structure of a fluid upon confinement. Such measurements have only seldom been performed using very specialized equipment [13–18] and were incapable of measuring interaction forces. Moreover, characterizing thin films without contact or confinement is advantageous for fragile deposited film, polymer brushes whose distributions change with confinement, or other systems with concentration and density gradients.

More specifically, the analysis developed in this work is capable of determining the change in optical thickness ($\Delta\Omega$)[1] from the bulk of a fluid or film with variable refractive index near the surface, as well as the specific substrate properties of the system. As described previously [5], the method was originally developed for analyzing symmetric, 3-layer interferometers which are the most optically simple system studied using the SFA. The technique requires a spectrum taken in the absence of the central medium (see Fig. 1) when the surfaces are in contact (referred to as the FECO contact spectrum), along with a sequence of spectra with the central medium present taken at different inter-surface separation distances that must include values ranging from 100 nm to 300 nm (referred to as the FECO profile spectra). Simply put, the analysis corrects systematic error in the refractive index profile by determining the substrate properties and the optical thickness of a ‘transition layer’ (see Fig. 1) at the substrate surface (incorporated to compensate for the variations in the refractive index of the “central medium” near (or at) the surface). This is a powerful tool because the optical properties of an entirely unspecified 3-layer symmetric interferometer can be fully determined without contact or confinement. Furthermore, the change in the optical thickness is analogous to the total increase or decrease in mass density, and the data from the transition layer analysis can be used to determine the refractive index profile or corresponding mass density profile over a long range of separation distances.

(a) 3-layer asymmetric interferometer



(b) 5-layer symmetric interferometer

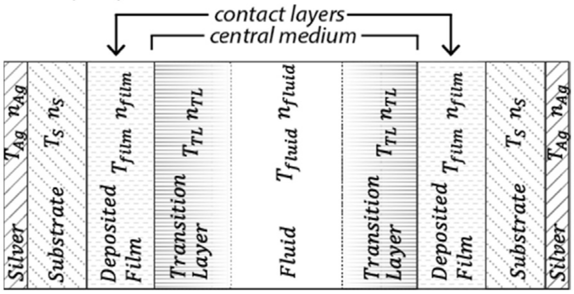


Fig. 1. Illustration of the interferometers that the extended RIPC method can analyze. T refers to the thickness and n refers to the refractive index of each layer. The Transition layer refers to a region of variable refractive index from the bulk medium.

The technique henceforth referred to as the refractive index profile correction (RIPC) method, is currently limited to simple 3-layer symmetric systems. As more complex systems are frequently of interest, the method is extended here to enable analysis of symmetric 5-layer and asymmetric 3-layer interferometers. For example, surfaces are often functionalized with materials to tailor properties. If the properties of the material can be determined in situ by independently measuring the substrate and deposited film properties without reorienting the sample or optics, extension of the 3-layer RIPC method only requires the inclusion of an additional known layer in the analysis. In many cases, however, the layers cannot be removed or deposited in situ without moving the sample. For example, hydrophobic surfaces are difficult to repeatably deposit directly onto mica with high stability, so more optically complicated systems are sometimes implemented such as the addition of layers to link the hydrophobic molecules to mica [19] or the use of alternative substrates. Some other commonly studied examples are silica layers deposited on mica [20,21], or thick and inert polymer films such as PDMS. When the additional layers cannot be reliably removed, the current RIPC method cannot be used.

It is also occasionally necessary to use substrates with non-uniform thickness, which results in opposing substrates with differing thicknesses within the etalon. For example, mica substrates are sometimes re-cleaved just before being mounted in the SFA box to remove any contamination that may have occurred during preparation [22]. This re-cleaving will result in substrates with different thicknesses. Another example that we are currently working on is the use of silica substrates that are made from blown quartz bubbles [23–25] which can have considerable variation in the thickness. These systems yield asymmetric 3-layer interferometers and cannot be analyzed using the current RIPC method. Indeed, many systems where information on the confined fluid structure would be valuable are difficult to study due to the current limitations in the RIPC method.

In this work, we have developed algorithms for extending the RIPC method to 3-layer asymmetric interferometers with substrates of the same refractive index (here on referred to as 3-layer asymmetric) and 5-layer symmetric interferometers, as depicted in Fig. 1a and b respectively. Using the methods developed here,

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[1] Optical thickness refers to the thickness times the refractive index. The change in optical thickness is defined as $\Delta\Omega = \int_0^\infty (n_{local}(z) - n_{bulk})dz$ where n_{local}, n_{bulk} and z are the local and bulk refractive indices and the normal distance away from an interface, respectively [5].