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Film thickness characterization in dual-axis spin coating of a sphere

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Abstract The versatility of spin coating technology makes it a preferred method for producing the thin film layers used to manufacture products from solar panels and smartphones to sunglasses and CDs. However, the process requires a flat, rigid substrate to produce uniform films, which limits its use to planar devices. A novel multi-axis manipulator has been developed to extend the application of spin coating, enabling controlled thin film deposition onto curved surfaces. Various rotational schemes were studied to link the flow of a liquid film over a curved surface to forces induced by complex rotational dynamics. When the angular velocity exceeds a threshold, centrifugal force dominates the flow, pushing the fluid away from the instantaneous axis of rotation. This produces axisymmetric coating profiles when using consistent single or dual-axis rotation. Areas of near uniformity present around the spin axis poles for single-axis rotation and around the substrate's equator for dual-axis schemes. Sensitivities between the spherical substrate dynamics and the evolving fluid flow were investigated, exploring the parameters that promoted the production of uniform curved film layers for microfabrication processes. This enabled the evolution of the spin coating technique to effectively form curved polymer coatings with improved thickness control. The presented research outlines the capabilities of a multi-axis spin coating machine when used to coat spherical substrates. Therefore, enabling the use of fluid mechanics models to identify the optimal motion kinematics required to create uniform curved films.

1 Introduction

Spin coating plays a critical role in the production of many common devices, from cell phones to solar cells, where thin film coatings are a key element of the manufacturing process. The conventional single-axis method involves the deposition of a liquid—often a solvent-based polymer resin—onto a flat substrate which is spun, dispersing the fluid through centrifugal forces. A balance occurs in the thin liquid layer, due to the viscous shear forces, which creates a uniform coating. The solvent is evaporated, which solidifies the coating into a thin film with a micrometre or even nanometre scale thickness [1].

These films are widely used across a range of industries where they are a fundamental component used in microdevice fabrication. Spin coating was first developed in the mid-twentieth century, where it played a critical role in the development of common technologies such as integrated circuit boards and data storage disks [2]. Today it is still a favoured manufacturing method for many thin film applications, ranging from optic displays to microfluidic chips. This is because it provides a low-cost but effective method of precisely controlling the deposition process. However, a key limitation of the technique is the requirement for a planar coating surface with a normal spin axis. Substrate curvature breaks the force balance within the fluid layer, leading to uneven coating distributions as depicted in Fig. 1. Instead, alternative deposition methods are required to accurately coat curved objects, increasing the cost and complexity of device production.

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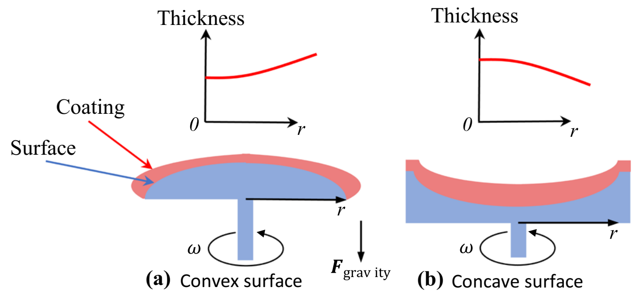

Fig. 1 Coating thickness distribution as a function of distance from the axis of rotation over convex **a** and concave **b** curved surfaces when using classical single-axis spin coating

The research presented here explores the effect of rotation about multiple axes on the uniformity of a thin liquid coating. Understanding the dynamics of a fluid layer on the surface of a rotating body was the first step in developing a multi-axis spin coating system. This led to the development of a prototype rotational manipulator capable of controlling the coating evolution through the induced rotational motion of a spherical substrate. Additionally, an optical analysis instrument was developed to measure the thin film layers produced on curved surfaces. Experimental trials investigated the potential to improve coating performance as optimizing the thin film deposition process is critical for the fabrication of devices with curved geometries. This is because there is a rising demand for conformal coatings with uniform thicknesses in modern manufacturing processes and technologies.

Rotating a rigid body causes apparent forces to act on any mass connected to the body, including a fluid layer on a spinning substrate. These 'fictitious' forces, called centrifugal, Coriolis, and Euler forces are products of the angular velocity $\boldsymbol{\Omega}$, position $\boldsymbol{R}$, and relative flow velocity $\boldsymbol{U}$, which are vectors defined in a rotating, body-fixed (or non-inertial) reference frame [3]. Gravity is fixed to the global (or inertial) reference frame with unit vector $\widehat{\boldsymbol{g}}$ and therefore is observed to rotate relative to the substrate and connected fluid layer. The total volumetric body force acting on the fluid is the combination of these respective forces, as shown in Eqs. (1–4) [4], where $\boldsymbol{T}_{\mathbf{r}}$ denotes the time-dependent rotational transformation matrix between the two reference frames [5]. Aligning the axis of rotation $\widehat{\boldsymbol{\omega}}$ with gravity $\widehat{\boldsymbol{g}}$ conserves the orientation of these vectors in both reference frames. This creates a constant gravitational force in the rotating reference frame, as observed in conventional single-axis spin coating.

$$\boldsymbol{F}_{\text{centrifugal}} = -\rho\boldsymbol{\Omega} \times (\boldsymbol{\Omega} \times \boldsymbol{R}) \tag{1}$$

$$\boldsymbol{F}_{\text{Coriolis}} = -2\rho(\boldsymbol{\Omega} \times \boldsymbol{U}) \tag{2}$$

$$\boldsymbol{F}_{\text{Euler}} = -\rho\frac{d\boldsymbol{\Omega}}{dt} \times \boldsymbol{R} \tag{3}$$

$$\boldsymbol{F}_{\text{gravity}} = -\rho g \boldsymbol{T}_{\mathbf{r}}\widehat{\boldsymbol{g}} \tag{4}$$

When considering a liquid coating on a curved substrate such as a sphere, it can be helpful to define governing laws and tensor quantities in curvilinear co-ordinate systems. Figure 2 illustrates the use of Cartesian and spherical coordinate systems to define the dynamics of a fluid layer on the surface of a rotating spherical body.

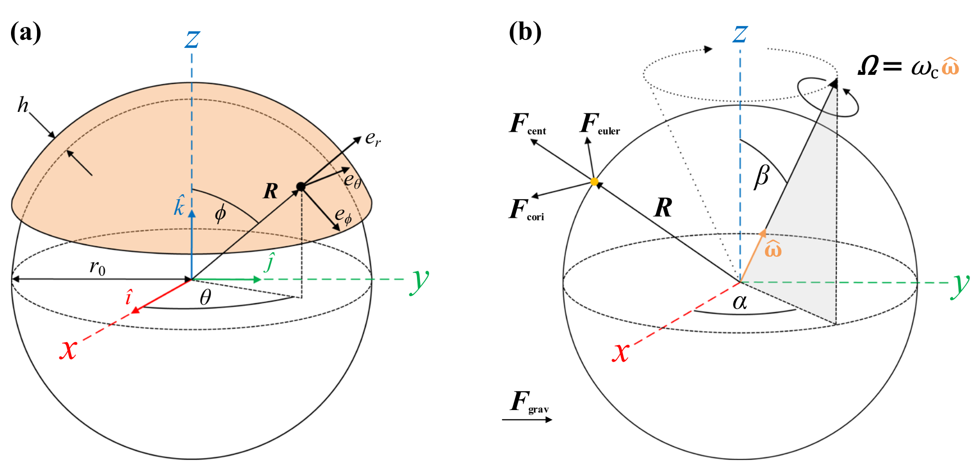

Fig. 2 **a** Geometry of a liquid film on the exterior of a sphere and **b** system dynamics resulting from rotation about a central axis $\widehat{\omega}$ with angular velocity ω_c

Table 1 Dimensionless terms relating forces acting on a rotating fluid body

Dimensionless number	Definition	Force relationship
Taylor number	$Ta = \frac{\rho^2 L_c h_c^3 \omega_c^2}{\mu^2}$	$= \frac{\text{angular inertia}}{\text{viscosity}}$
Weber number	$We = \frac{\rho L_c^2 \omega_c^2 h_c}{\sigma}$	$= \frac{\text{angular inertia}}{\text{surface tension}}$
Froude number	$Fr = \frac{L_c \omega_c^2}{g}$	$= \frac{\text{angular inertia}}{\text{gravity}}$

Substrate curvature also influences the film thickness because of surface tension on the free surface. Without any other body forces present, the pressure on the liquid interface works to minimize the surface's mean curvature, spreading the fluid film over the substrate. Capillary forces disperse fluid over areas with negative mean curvature (convex) towards regions of highest mean curvature (concave). Models have been used to depict capillary flows on single and double curved substrates [6, 7], as well as moving surfaces [8].

Coatings on substrates with constant mean curvature, like cylinders and spheres, can exhibit even thickness distributions due to the balanced pressure at the free surface. However, gravity disrupts this and can create instabilities in the fluid flow. This phenomenon has been investigated both experimentally [9] and analytically [10–12], by studying the evolution of a thin viscous film over cylindrical and spherical surfaces. It was observed that the fluid would drain down the curved surface towards the bottom of the substrate where the thickening film could exhibit a Rayleigh–Taylor instability. Balestra et al. [13] also showed instabilities can occur at an advancing contact line if the substrate is not initially coated. This is because the uniform expansion of the gravity-driven thin film layer can break up into fingers at a critical surface inclination. When experimentally investigating advancing thin film flows over spherical and cylindrical substrates, Takagi and Huppert [14] observed that these fingers would flow to the underside of the curved surface and detach before reaching the lowermost point.

The flow dynamics of a thin, viscous liquid layer over a substrate are often characterized with reference to one or more dimensionless groups that describe the relationship between different forces acting on the fluid film. In the case of gravity-driven flow over a curved surface, the Bond number is used to relate the capillary and gravitational forces acting on the fluid. It was shown by Qin et al. [12] that the Bond number correlates with the shape and stability of the film's free surface draining over a spherical substrate. Whereas Balestra et al. linked the bond number to the formation of different instability modes [10, 11]. When considering a non-inertial frame of reference due to substrate kinematic motion, however, groups such as the Taylor, Weber, and Froude numbers must be introduced to describe the various forcing conditions. Table 1 shows the definition of the dimensionless numbers which can be used along with the aspect ratio, $\delta = h_c/L_c$, to identify the dominant forces within the system [15]. In these expressions, L_c denotes the characteristic length of the surface or substrate radius for the case of a sphere, and h_c describes the average film thickness over the substrate surface [4]. ω_c is the characteristic angular velocity which is commonly expressed as the magnitude of rotational speed achieved by the substrate during the coating process. The properties ρ, μ, and σ denote the fluid density, viscosity, and surface tension, respectively.

The fluid dynamics of spin coating on a flat surface was first considered by Emslie et al. [16], where it has continued to be the subject of further investigations including the effects of varied dynamics, surface tension, and evaporation [17, 18]. Similar methods utilizing the lubrication approximation have been employed to model the thin film flow over a spherical substrate rotating about a vertical axis, considering both gravitational and surface tension effects [19–22]. These models have been extended to other substrate geometries such as spheroids [23], arbitrary axisymmetric curved surfaces [24, 25], and even non-axisymmetric surfaces [4, 26]. Recently, the effect of varied substrate dynamics was considered when investigating the evolution of a thin film coating on rectangular [27], and spherical substrates [28] rotating about multiple axes. Numerous attempts have also been made to extend the possibilities of spin coating through experimental investigations. The ability to coat a convex lens for optical applications was explored by Reichle et al. [29]. This concept was expanded upon by Jose [30], where the conventional single-axis technique was used to apply coatings to hemispherical substrates. However, both studies found that the resulting thickness distribution increased radially, making the films unsuitable for functions requiring uniform layers. The effects of an additional degree of freedom has also been investigated, where dual-axis spin coating has resulted in improved coating performance on both planar [31] and spherical substrates [32].

Accurately measuring the thickness of thin films is essential for controlling their quality and function. Different characterization techniques have been developed to measure film thickness, each with its advantages and limitations. One common way to categorize these techniques is by the type of interaction they rely on, such as mechanical, thermal, electromagnetic, acoustic, or optical interactions [33]. Optical characterization techniques offer several advantages over other methods, especially for applications involving liquid coatings. These optical systems leverage interactions at the interfaces of thin films when exposed to incident electromagnetic radiation. Some prevalent optical methods for thin film thickness measurement include fluorescence [34, 35], absorbance [36], and reflection, which produce detectable spectral changes that can be used to deduce the film's thickness.

2 Methods

2.1 System development

Conventional single-axis spin coating on curved substrates results in non-uniform film layers because of the unbalanced gravitational and centrifugal forces over the surface [29, 30]. To successfully spin coat on curved surfaces, it becomes necessary to introduce three-dimensional (3D) inertial forces by incorporating a non-vertical rotation axis. The kinematic freedom provided by additional rotation axes can be utilized to manipulate the body forces, enabling the production of thin film coatings with improved uniformity. Many multi-axis machines, ranging from basic rotors to complex robotic arms, have been designed to generate this type of motion with different configurations being used for a variety of applications [37]. Several options were explored for the context of multi-axis spin coating, as outlined in recent research [32].

The resulting prototype system utilized two independently controlled axes oriented perpendicular to each other, as illustrated in Fig. 3. A gimbal assembly spins about a fixed vertical axis with an angular velocity of ω_1, from which a horizontal motor rotates the spherical substrate about a dynamic axis with a speed of ω_2. Dual-axis rotation imparts the substrate with complex kinematic motion described by Eq. (5). Where axis orientation, as expressed in Eq. (6) is represented by θ_i and denotes the angular displacement of the respective axis at time t. The characteristic speed ω_c describes the maximum instantaneous magnitude of angular velocity experienced by the substrate, and in the case of constant rotation speeds, can be expressed as in Eq. 7.

$$\boldsymbol{\Omega} = \begin{bmatrix} \omega_1 \sin(\theta_2) \\ \omega_1 \cos(\theta_2) \\ \omega_2 \end{bmatrix} \tag{5}$$

$$\theta_\mathrm{i} = \int_0^t \omega_\mathrm{i}(\tau) d\tau \tag{6}$$

$$\omega_c = \|\boldsymbol{\Omega}\| = \sqrt{\omega_1^2 + \omega_2^2} \tag{7}$$

A lack of viable measurement techniques for accurately characterizing curved surfaces has previously hindered the analysis of film layers produced through spin coating [30]. Optical methods lend themselves to this application as they are non-destructive and fast responding, making them ideal for capturing the dynamics of thin fluid flows. White Light Reflectance Spectroscopy (WLRS) is a specific optical film characterization technology developed by ThetaMetrisis© that provides simultaneous thickness and refractive index measurements of thin film layers. Utilizing a broad-band (white) light source operating in a configurable range on the UV–Vis-NIR spectrum (350–1000 nm), WLRS can be used to characterize single or multiple thin film layers in the order of nanometres to millimetres [38]. The robust WLRS method utilizes a portable probe that combines a directed broad-spectrum light source and corresponding spectrometer to provide point-of-interest measurements on arbitrary surfaces. A series of these thickness measurements can then be combined to construct a two-dimensional map of the coating

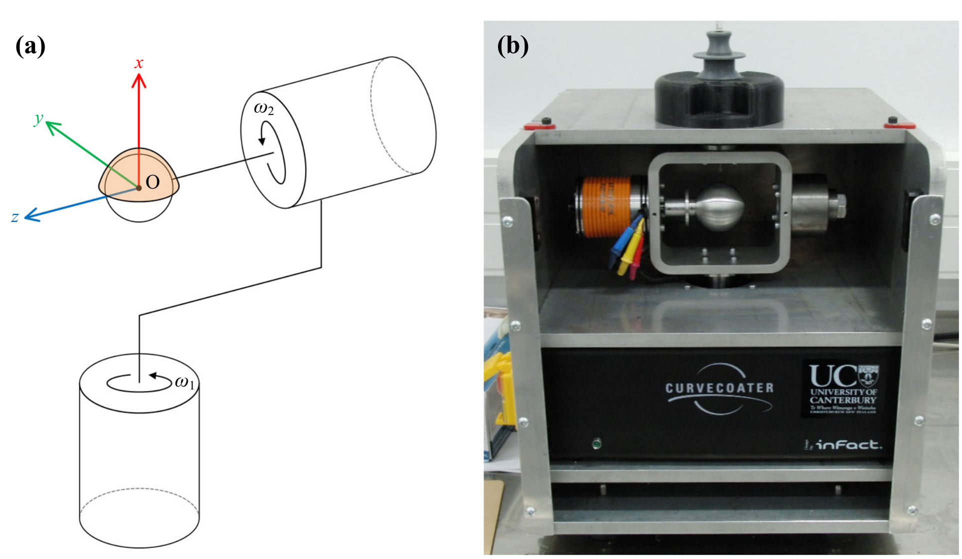

Fig. 3 Dual-axis spin coating system used to control the distribution of a thin film coating on a spherical substrate. **a** Manipulator schematic and, **b** experimental prototype machine [32]

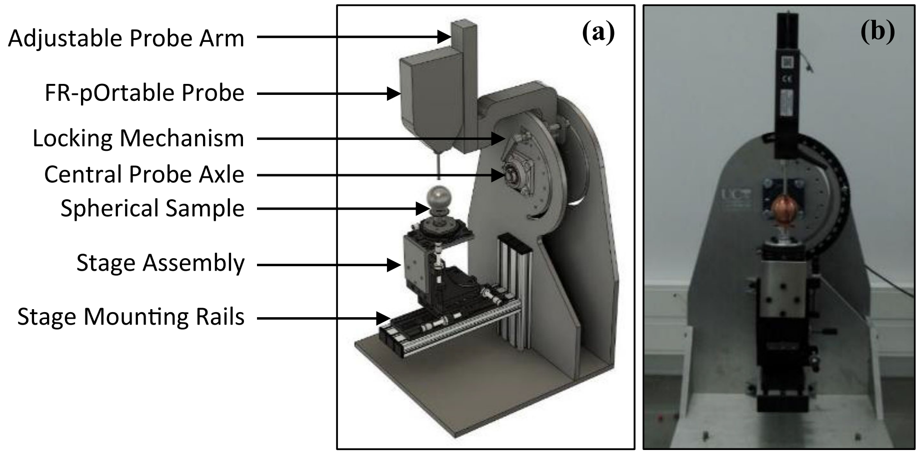

Fig. 4 Curved surface characterization system utilizing the ThetaMetrisis © FR-pOrtable WLRS probe. **a** Model showing key design features, **b** prototype machine [32]

distribution over any 3D surface. For the analysis of thin film layers produced on a spherical substrate, the characterization system consisted of a unique mounting unit for the reflection probe and sample as shown in Fig. 4. This enabled the careful manipulation and indexing of the probe head, ensuring consistent spacing and a normal orientation to the substrate surface. The emitted light reflects off both the solid and fluid interfaces, generating an interference pattern in the reflected signal, allowing the film thickness to be calculated based on the phase of the observed fringes.

2.2 Experimental procedure

The coating material was selected based on factors including the fluid properties, solvent, refractive index, commercial application, and cost. Photo-sensitive polymer resins, or photoresists, were an ideal choice due to the range of viscosities among commonly available coating fluids used in the microfabrication industry. Positive tone photoresist (AZ-1518, MicroChemicals) [39] was selected for the experimental analysis as it had appropriate material properties for the motion capabilities of the prototype system. The fluid density was measured before a rheometer (Anton Paar MCR 302) was used to determine the viscosity of the fluid across a range of shear rates (1–1000 s^{-1}). The AZ-1518 fluid exhibited Newtonian behaviour with a constant viscosity of 0.049 ± 0.001 Pa.s at a temperature of 20 $^\circ$C. A goniometer (KSV Instruments CAM200) was then used to conduct a pendant drop test, from which the surface tension coefficient of the liquid–air interface was found to be 0.030 ± 0.004 N/m.

Preliminary testing by McIntyre [32] showed that a fully wetted substrate was required before initiating rotation to avoid the formation of contact line instabilities. Therefore, the spherical substrates were pre-coated to ensure a stable initial condition for the experiments as recommended by Takagi and Huppert [14]. A four-stage process like that of conventional spin-coating was used, whereby the liquid was initially deposited over the entire surface before the sample was mounted and spun up to the desired rotational velocity using a set acceleration ramp rate. This motion was then held for a set duration, during which time the volatile solvent in the liquid film starts evaporating. Once the spinning had ceased, the evaporation of the solvent was accelerated through a baking process, leaving behind a thin solid layer. Table 2 outlines the standard testing parameters that were used consistently throughout the subsequent experimental study.

Table 2 Experimental fluid properties of photoresist AZ-1518 (MicroChemicals), and test conditions used for spin coating on spherical substrates [39]

Parameter	Value	Unit
Substrate radius	25	mm
Fluid density	1.1	g/cm^3
Surface tension	30	mN/m
Initial viscosity	49	mPa • s
Acceleration rate	2000	rpm/s
Spin duration	150	S
Bake temperature	110	°C
Bake duration	90	S

3 Results

3.1 Gravity driven coating—no rotation

A common deposition technique used to quickly cover complex surfaces is dip coating, where a substrate is immersed in the coating fluid, allowing the excess material to drain off due to gravitational forces. Thus, leaving behind a liquid layer that can solidify into a thin film where the coating distribution is dominated by gravity due to the lack of other body forces. Fluid flows towards the lowest point where it drains off the substrate as the gravitational force overcomes the surface tension. This can lead to the formation of a Rayleigh–Taylor instability at the free surface, as observed by Balestra et al. [11]. Viscous liquids can form large bulges as shown in Fig. 5a, where the coating on the upper portion of the spherical surface is reasonably uniform [9]. Figure 5b displays the experimental result produced from no substrate rotation, where the film thickness profile is depicted in Fig. 6. The AZ-1518 resist film had an even distribution over the upper hemisphere with an average thickness of 8.82 μm and a standard deviation of 1.0 μm, however this increased to a peak thickness of 49.8 μm on the underside of the sphere. This gravity driven case provided a control result to compare against, whilst also serving as a consistent pre-coated initial condition that eliminated the potential for contact line instabilities forming.

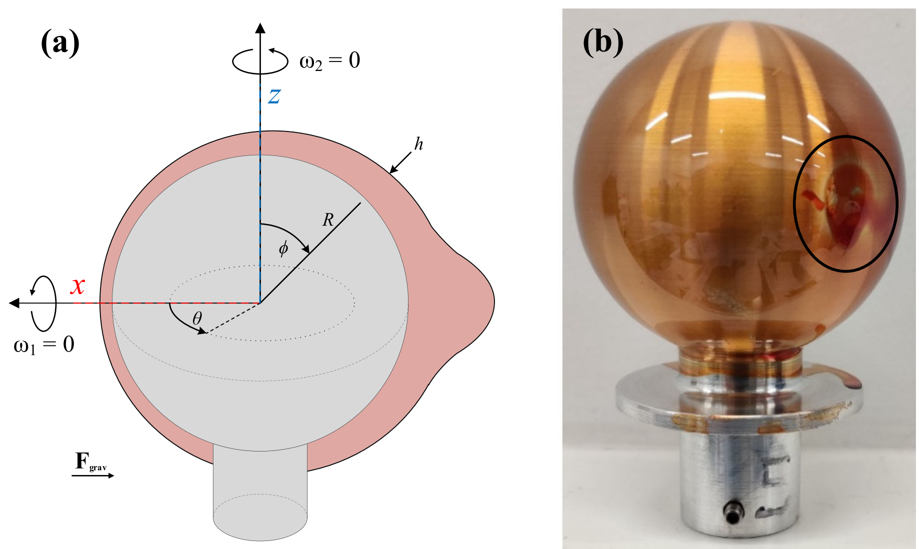

Fig. 5 Liquid film distribution produced on a spherical surface with no substrate rotation. **a** Qualitative representation of an expected thickness profile, & **b** experimental AZ-1518 photoresist film showing drainage location

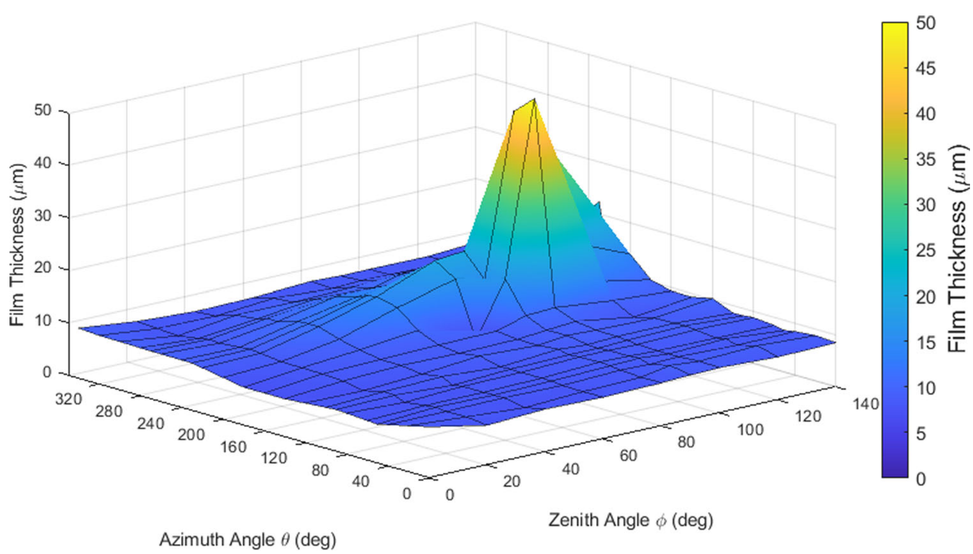

Fig. 6 Film thickness profile resulting from an AZ-1518 coating on a spherical surface with no substrate rotation and gravity acting through (θ, ϕ) = (180, 90). Distribution produced from 184 point measurements taken using the WLRS characterization method

3.2 Single-axis spin coating

The multi-axis spin coating system was then used to manipulate the evolution of the liquid film on the surface of the spherical substrate by inducing rotation during the coating process. Results indicated that the thickness profile was directly dependent on fluid viscosity and substrate motion, enabling test categorization using the Taylor, Weber, and Froude numbers shown in Table 3. Spinning about a single axis consistently produced axisymmetric coating distributions, where the film's thickness profile was smallest at the axis poles and increased towards the equator. The maximum thickness depends on spin speed whereby exceeding a threshold velocity ω_t would enable the centrifugal force to overcome gravity. Thus, the threshold velocity could be determined based on the ratio of these forces, represented by the Froude number, as shown in Eq. 8.

$$\omega_\mathrm{t} = \sqrt{\frac{g}{L_\mathrm{c}}} = 19.8\,\frac{\mathrm{rad}}{\mathrm{s}} = 189.2\,\mathrm{rpm} \tag{8}$$

Surface tension effects are linked to the Weber number which relates the capillary and centrifugal pressures. By using the tangential velocity of the substrate surface as the velocity scale (see Table 1), its magnitude refers to the force balance at the point furthest from the spin axis. Here, centrifugal force competes against surface tension forces, driving fluid away from the substrate. In regions with constant curvature and tangential fluid velocity, surface tension effects are negligible. Higher Weber numbers indicate that surface instabilities will form, shedding liquid on breakup which decreases the overall fluid volume.

The effect of spinning about a vertical axis (as depicted in Fig. 3) was tested initially as this has been modelled extensively [19–22], and investigated experimentally by Jose [30]. Figure 7a illustrates the expected coating distribution whereby aligning the rotation axis with gravity resulted in a constant gravitational body force. This caused the free surface to protrude outward below the equatorial belt in correlation with the Froude number, driving the bulge upwards with increasing angular velocity. Aligning the rotation axis with gravity created challenges as the flow was impeded by the sample shaft and the thickest region often slumped due to gravity as the solvent evaporated. This introduced uncertainty in the results whilst the misalignment of the thickness profile with the sample axis made the characterization process inefficient.

Table 3 Dimensionless numbers resulting from the experimental test parameters used for the single-axis trials investigating spin coating on a spherical substrate

Dimensionless number	Angular velocity (rpm)				
	200	400	600	800	1000
Taylor number	9300	21,400	24,400	29,600	43,000
Weber number	120	398	713	1120	1700
Froude number	1.12	4.47	10.1	17.9	27.9

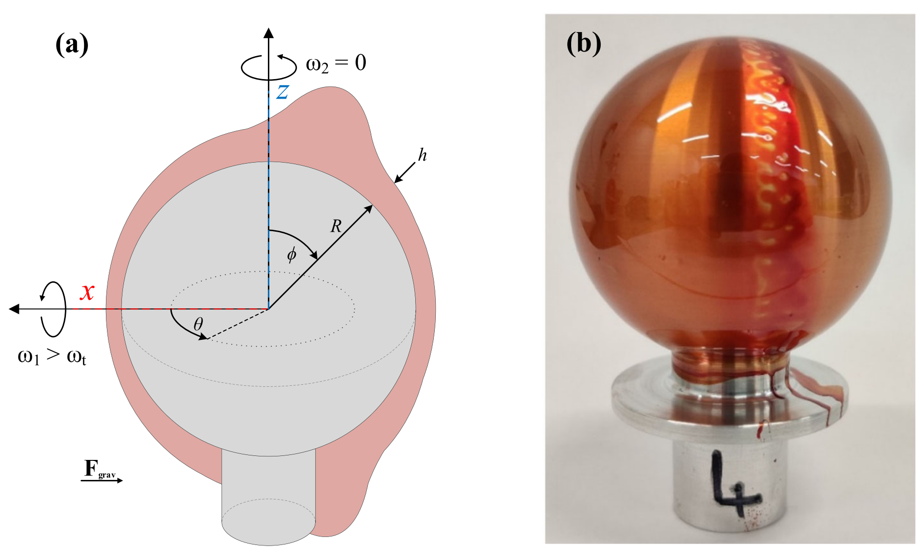

Fig. 7 Liquid film distribution on the surface of a pre-coated sphere rotating about an axis aligned with gravity ($\widehat{\omega} \bullet \widehat{g} = 1$) at a velocity exceeding the threshold ω_t. **a** Qualitative representation of an expected film thickness profile, & **b** experimental result produced from 1000 rpm rotation about the vertical axis

Alternatively, rotation about the horizontal axis produced similar axisymmetric coating distributions. However, gravitational effects were less apparent as the sample spun about an axis perpendicular to gravity, producing a negligible time-averaged force in the rotating reference frame. This isolated the inertial body forces acting on the fluid layer to generate film thickness profiles that were both symmetric about the sample axis, and the $x-y$ plane, as shown in Fig. 8a. Hence, the location of maximum and minimum thickness was consistent across all rotation speeds, with the angular velocity only influencing the height of these regions.

Areas of the surface closest to the axis of rotation presented even film distributions with thicknesses in a comparable range (4–20 μm) to the expected values for a conventional flat surface spin coating process [18, 40]. This has also been observed in previous studies of spin coating on spherical surfaces, where the polar regions of the film show good uniformity [21, 41]. This is because of the negligible impact of the surface curvature in these areas, where the spin axis is essentially normal to the substrate surface. Therefore, the thin film evolution around the spin axis can be accurately predicted using reduced order lubrication models, enabling the effective optimization of motion kinematics for desired film characteristics over a portion of the spherical sample.

Changing the orientation of the rotation axis also meant the flow was less disturbed by the sample shaft, enabling an improved characterization of the region of max thickness. Figure 9 compares the two thickness profiles of a

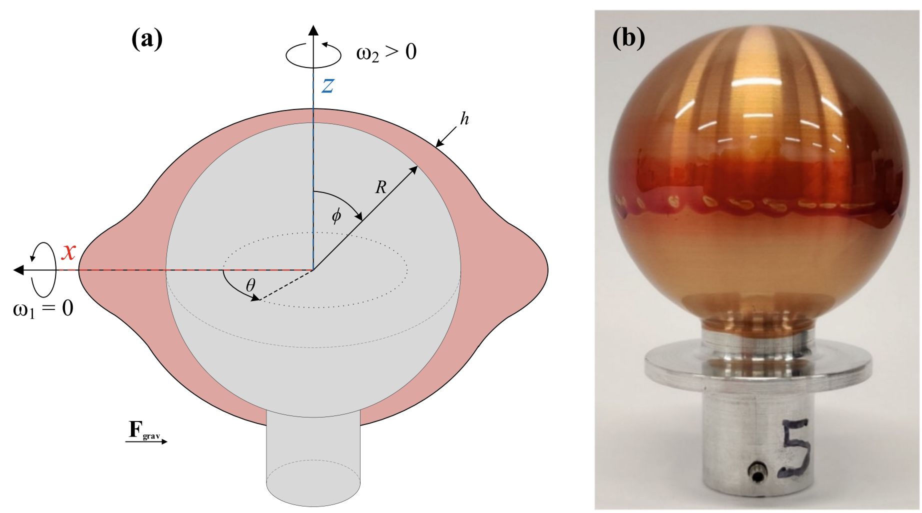

Fig. 8 Liquid film distribution on the surface of a pre-coated sphere rotating about an axis orthogonal to gravity ($\widehat{\omega} \bullet \widehat{g} = 0$). **a** Qualitative representation of an expected film thickness profile, & **b** experimental result produced from 1000 rpm rotation about the horizontal axis

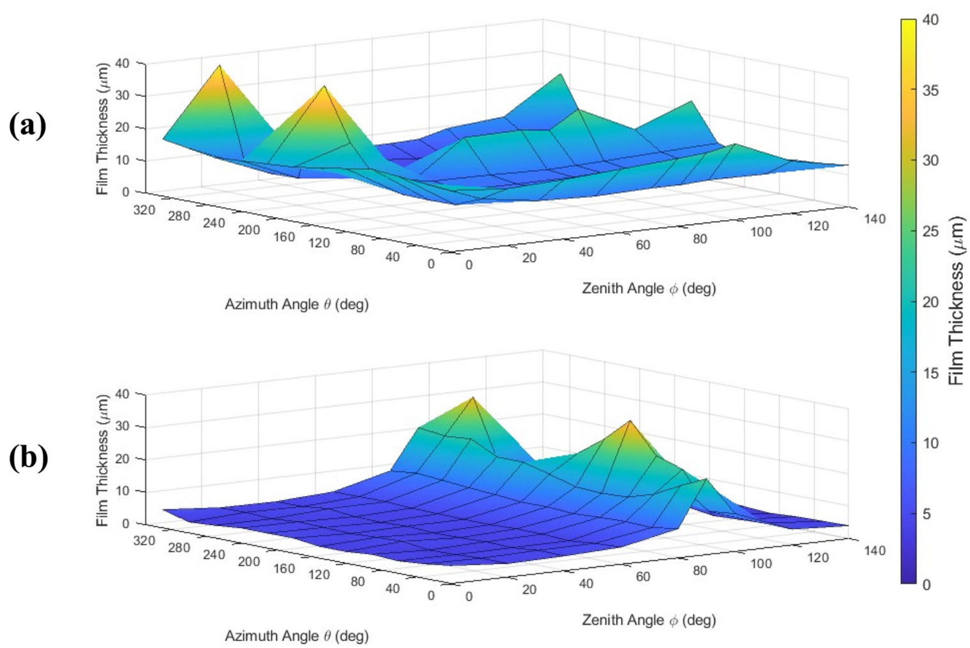

Fig. 9 AZ-1518 coating distributions resulting from spinning a pre-coated spherical substrate at 1000 rpm about a: **a** vertical axis & **b** horizontal axis. Profiles represented in spherical co-ordinates consist of 108 points characterized using WLRS

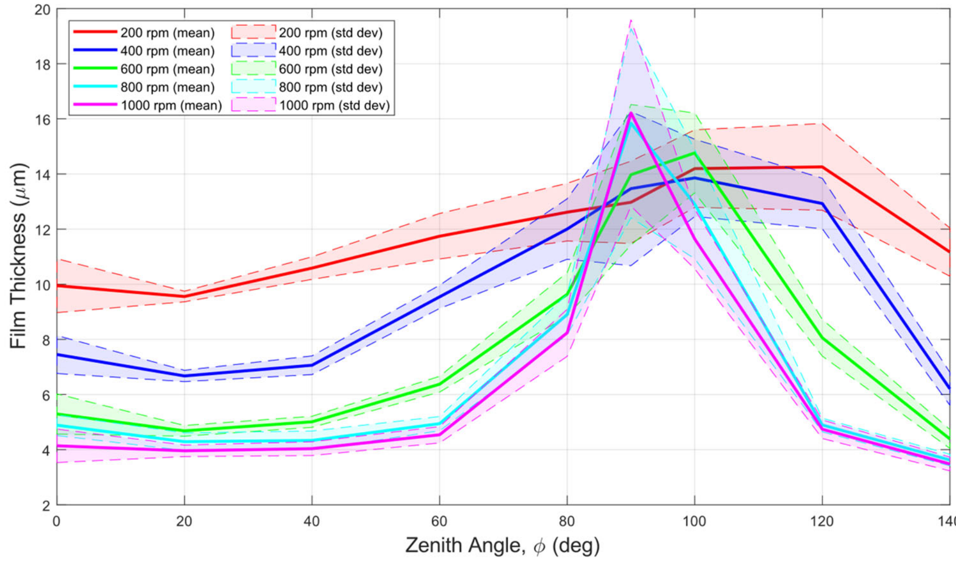

Fig. 10 Axisymmetric film thickness profiles produced on the surface of a pre-coated sphere rotating about an axis perpendicular to gravity ($\widehat{\omega} \bullet \widehat{g} = 0$) for range of angular velocities. Profile curves show the mean result and standard deviation of 12 measurements in the azimuthal direction θ, averaged for 2 tests (216 total data points). The Zenith angle ϕ represents the angle from the spin axis, where the sample stem interferes above 140°

thin film coating on the surface of a sphere, produced by spinning about a vertical and horizontal rotation axis (with reference to Fig. 3) at 1000 rpm respectively. Both profiles show similar general features in relation to the spin axis with an area of minimum thickness in the range of 3–4 μm occurring at the rotation axis poles. This gradually increases to an equatorial belt with a thickness ranging between 15–25 μm. However, the maximum film thickness is observed at discrete locations along this belt where the fluid was dispelled from the sample because of perturbations in the free surface, resulting in regions of the film that are up to 40 μm thick.

Although both coating distributions reveal a clear symmetry about the spin axis, a key difference is observed in the total volume of the thin film layer, which can be approximated by the average thickness across the substrate surface. Vertical axis rotation resulted in an average thickness of 11.5 μm, notably larger than the 8.0 μm average film thickness of the horizontal equivalent. Possible reasons for this could be due to interference from the sample shaft or time-dependent alignment of the gravitational and centrifugal forces. Additionally, the larger gimbal's mass moment of inertia resulted in a slower acceleration rate and hence less fluid is dispelled during the critical spin-up stage. Therefore, horizontal axis rotation provided the best option for analysing the motion sensitivities due to the isolation of the dynamic force effects.

The angular velocity was gradually increased from 200 rpm (20.9 rad/s) to 1000 rpm (104.7 rad/s) where the resulting films were characterized to produce thickness distribution profiles. Figure 10 illustrates the axisymmetric mean average of these coatings, where a distinct correlation can be made between spin speed and eventual film shape. Low angular velocities produced a coating with a slight bulge around the equator, and an average thickness of 10 μm. Although initially presenting reasonable uniformity, the excess thickness of the fluid layer caused gravity to have greater effect during the evaporation stage. This induced a downward flow (increasing Zenith angle), which showed the belt to form below the equator with increased variance around the regions of maximum thickness. As the speed increases, the growing centrifugal force drives the fluid away from the axis of rotation, which thins the film layer at the pole as liquid collects into ligaments that extend away from the substrate around the equator. At high enough spin speeds the film becomes very thin and uniform across the upper and lower hemispheres, with minimum thicknesses ranging from 4–8 μm.

The experimental results produced in the single axis study provided an ideal comparison case for many of the fluid mechanics models published in the literature [28, 41]. A basic 2D fluid mechanics model was developed in COMSOL Multiphysics® as described by McIntyre et al. [28] to simulate the evolution of a thin liquid layer on the surface of a rotating sphere. The model utilized a finite element analysis solver with Lagrangian shape functions to compute the Navier–Stokes equations using a laminar two-phase flow regime. A mapped mesh that moves with the interfaces used a Yeoh smoothing method to calculate the deformation of the free surface. The predicted film thickness profiles were compared with the experimental results, where it was found that the characteristics of the observed coating distributions agreed well with the numerical model. Figure 11 shows the free surface profiles generated from simulations of the various single-axis trials, considering both with and without gravitational forces acting along the axis of rotation. The numerical model accurately predicted the minimum thickness and the rate of thickening toward the equatorial belt. However, several inconsistencies were also noted, revealing limitations with the fluid dynamical models.

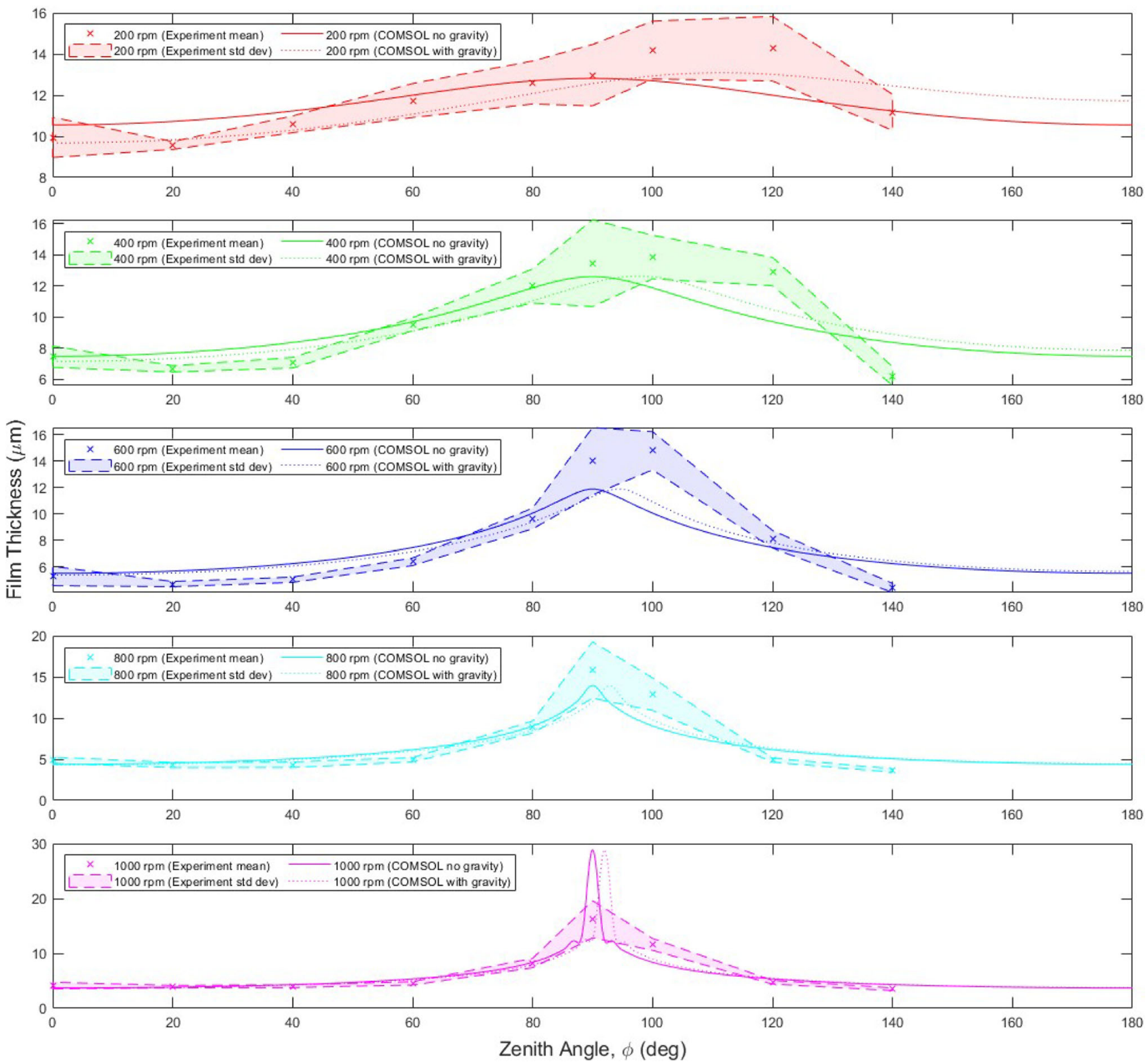

Fig. 11 Comparison of the experimental thickness profiles produced on the surface of a pre-coated sphere rotating about a horizontal axis for 150 s with a range of speeds. Compared with distributions generated from corresponding finite element fluid mechanics models

Model outcomes were found to be highly dependent on the initial conditions, particularly the initial average thickness as the fluid volume had to be maintained throughout the simulations. This clearly differs to the experimental process, where excess liquid is expelled from the substrate surface until an equilibrium is reached between the surface tension and centrifugal forces. Therefore, better correlations between the simulated and experimental results were observed for tests using higher spin speeds ($\geq$ 600 rpm), where fluid volume stabilizes quickly because of the stronger body forces. A key source of uncertainty results from the drainage that occurs before and after the rotational motion. The setup and baking process allow for gravitational forces to disrupt the initial and final coating distributions respectively, causing the peak thickness to shift towards the bottom of the sphere. This is most prevalent when using slower rotational speeds as the larger coating volume has greater mass and therefore, increased gravitational effects. Another reason for differences between the simulated and experimental thickness distributions can be attributed to the resolution of the characterization method shown in Fig. 15. As the thickness is measured at discrete locations over the surface, many details of specific features within the coating are not captured in the experimental characterization.

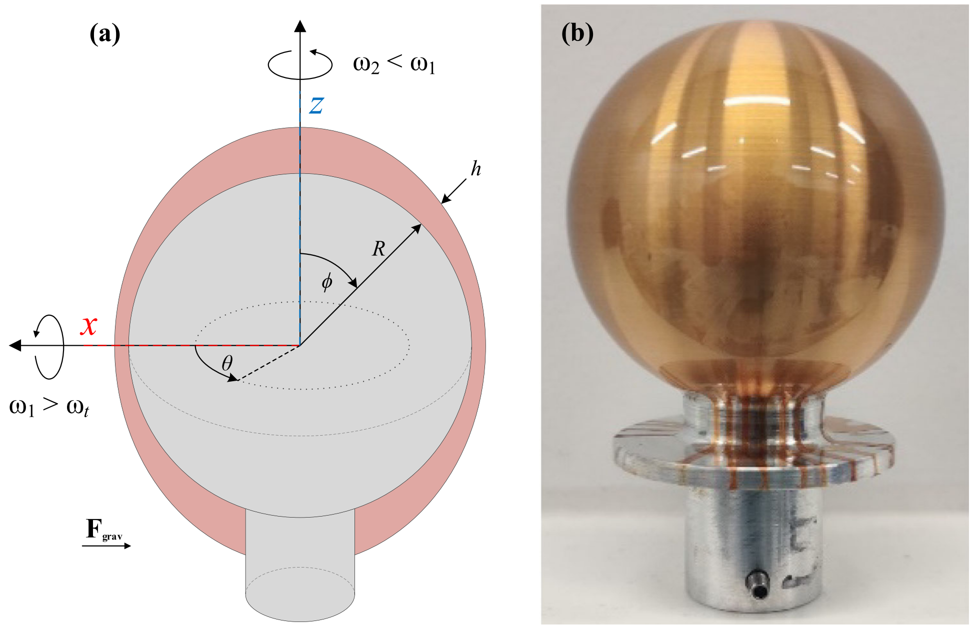

Fig. 12 Liquid film distribution produced on a pre-coated sphere rotating about dual axes with a greater vertical spin velocity than the threshold ω_t. **a** Illustration of a typical film thickness profile & **b** experimental result generated from vertical and horizontal axis rotation at 1000–200 rpm

3.3 Dual-axis spin coating

Simultaneous rotation about two intersecting axes results in complex substrate dynamics that produce 3-dimensional inertial forces. This time-dependent body force can therefore be manipulated to control the thickness distribution. At lower rotation rates the process exhibited similarities to the rotational moulding processes, where the viscous liquid adhered to the substrate allowing gravity to direct the flow by adjusting the sample's orientation. Increasing the spin speed generated a dominating centrifugal force, driving the fluid flow away from the instantaneous axis of rotation. As the timescales for the flow dynamics is slower than the substrate motion, the resulting coating profile was dependent on the time-averaged body forces. The force vector field, and therefore resulting thickness distribution mimicked the symmetry of the motion dynamics around the body-fixed (horizontal) axis. However, the additional inertial force from the global (vertical) axis pulled the fluid away from the sample's equator toward the Z-axis poles as illustrated in Fig. 12a.

The thin film evolution was strongly influenced by the rotation around the (horizontal) sample axis as the orientation is fixed within the rotating reference frame. Therefore, when the ratio of angular velocities $\lambda = \frac{\omega_1}{\omega_2} \ll 1$, the film exhibits a profile very similar to that observed from single-axis rotation. Therefore, to utilize dual-axis motion to control the flow, the vertical axis rotation ω_1 had to be dominant. This provided a consistent time-averaged inertial force, where the horizontal axis was used to manipulate the sample's orientation whilst the vertical rotation produced the driving centrifugal force. The effect of various dual-axis velocity ratios was investigated by decreasing λ, holding the vertical rotation rate (ω_1) constant at 1000 rpm whilst changing the horizontal spin speed (ω_2) from 200 to 1000 rpm. The resulting thin film layers revealed a symmetry around the body-fixed (horizontal) axis, where the fluid collected in a bulge at the sample pole. The smooth axisymmetric distributions suggest that the centrifugal force remains dominant compared to the Coriolis and Euler forces due to a low surface flow velocity and short dynamic timescale. However, excessive characteristic angular velocities or unstable accelerations can induce instabilities at the free surface. These perturbate over the substrate surface, creating defective regions of coating as shown by the significant increase in thickness variance observed in Fig. 13.

3.4 Coating implications

Spin-coating on curved surfaces introduces significant challenges, particularly concerning interfacial dynamics where instabilities form, producing defective films as observed in Fig. 14. The interplay of highly dynamic body forces and drag forces at the air-fluid interface can influence the coating dynamics, resulting in non-uniform film distributions. Additionally, the introduction of Coriolis force at elevated angular velocities further complicates the flow dynamics. This force can introduce biases in the coating process, potentially leading to non-homogeneous film deposition. Balancing these intricacies becomes crucial when aiming for precise and uniform coatings on curved substrates. Therefore, careful control of spin parameters is needed to mitigate these instabilities and achieve the desired coating quality.

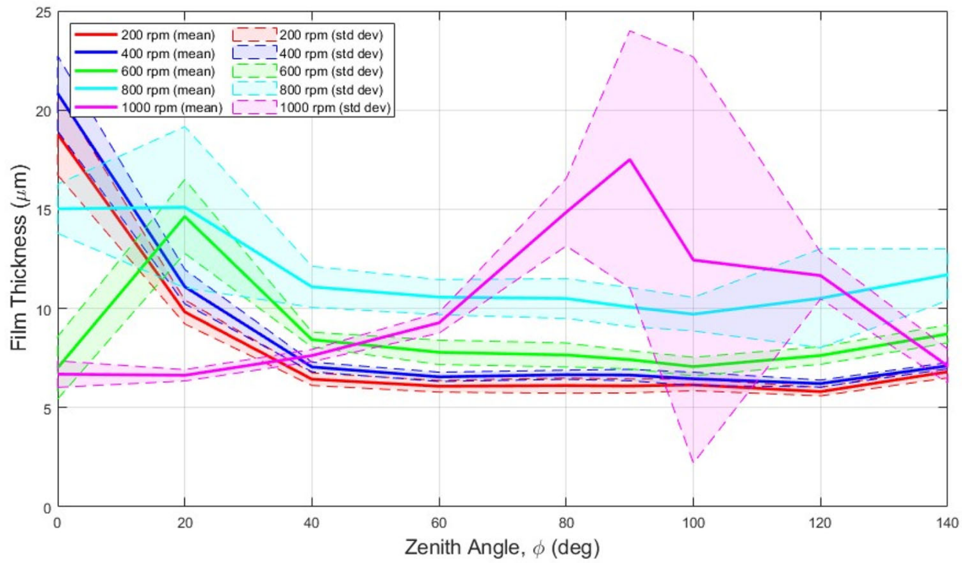

Fig. 13 Average axisymmetric film thickness profiles produced from varied dual-axis rotation of a pre-coated sphere spinning with a constant vertical velocity of 1000 rpm. Profile curves show the mean result and standard deviation of 12 measurements in the azimuthal direction θ, averaged for 2 tests (216 total data points). The Zenith angle ϕ represents the angle from the spin axis, where the sample stem interferes above 140°

Fig. 14 Qualitative examples of common instabilities observed in the experimental analysis of thin film flows over spherical substrates

4 Conclusion

For decades spin coating has produced thin film layers for many applications, yet the technology has never been capable of uniformly distributing a liquid over a highly curved substrate. The additional inertial forces made possible through a second degree of rotational freedom have enabled the manipulation of the thickness distribution over a spherical surface. A prototype multi-axis spin coating system was developed alongside a curved surface characterization tool. This novel laboratory setup has been used to investigate the fabrication of polymer films on curved surfaces, aiming to improve the uniformity of these micro-thin layers.

A parametric study was conducted to understand the effect of angular velocity in single and dual-axis rotations. Both coating regimes produced axisymmetric thickness profiles around the spherical sample's central axis. Increasing the substrate's rotational velocity above a threshold speed generated significant inertial body forces, which could be used to control the flow of the liquid layer. The varying centrifugal acceleration created a dynamic three-dimensional force that could be used to counter the effects of gravity, producing a consistent thickness distribution.

Implementing the additional axis of rotation expands the capabilities for spin coating curved surfaces, providing opportunities in microfabrication and coating applications. Future optimization studies will use a computational model of the fluid dynamic process to ascertain the optimal substrate motion schemes for uniform film deposition on highly curved objects. Furthermore, the research endeavours to refine the current experimental setup by addressing various limitations for a broader commercial viability.

Author's Contributions

The presented work is part of a multidisciplinary group project led by Mathieu Sellier, where author contributions are as follows: Finn McIntyre—Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing; Mathieu Sellier—Conceptualization, Visualization, Funding acquisition, Supervision; Shayne Gooch—Conceptualization, Supervision; Volker Nock—Conceptualization, Methodology, Resources, Writing review, Supervision. The authors would like to acknowledge the many colleagues, technicians, and other collaborators whose efforts have made this research possible.

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Data Availability Statement Data sets generated throughout the current study are withheld to protect the IP rights of the authors as mentioned above. However, data supporting the findings of this study will be made available under the conditions of a Data Use Agreement (DUA) upon reasonable request of the corresponding author.

Declarations

Conflict of interest The research group is currently undertaking a preliminary investigation to commercialize the technology. Accordingly, the authors assert all their rights in compliance with the law, arising out of and in connection with the intellectual property referred to in this paper (the **IP rights**) and all future sensitive disclosures made in connection with the IP rights in any way. Notwithstanding the authors' future sensitive disclosures protections referred to herein and without prejudice to the authors exercising any of the authors' IP Rights, the authors are interested in applications or potential opportunities for collaboration in respect of the discussed technology, in which case contact should be made with the corresponding author.

Appendix A: Experimental characterization

The WLRS characterization technique provides an effective way of determining the thickness of an inclined thin film layer by orienting the angle of incidence normal to the substrate surface. However, the limitation to single point measurements restricted the ability to generate high resolution maps of the coating distribution. This results in a time-consuming process for characterizing entire substrate surfaces, where many details of the thin film coating may not be captured, such as free surface curvature or the location of instabilities. Figure 15 depicts the map of measurement nodes over the spherical substrates, where no measurements could be made at the base of the sphere due to the sample shafts. Axisymmetric thickness profiles as seen in Figs. 11 and 13 were then generated by averaging all measurements for a given Zenith angle.

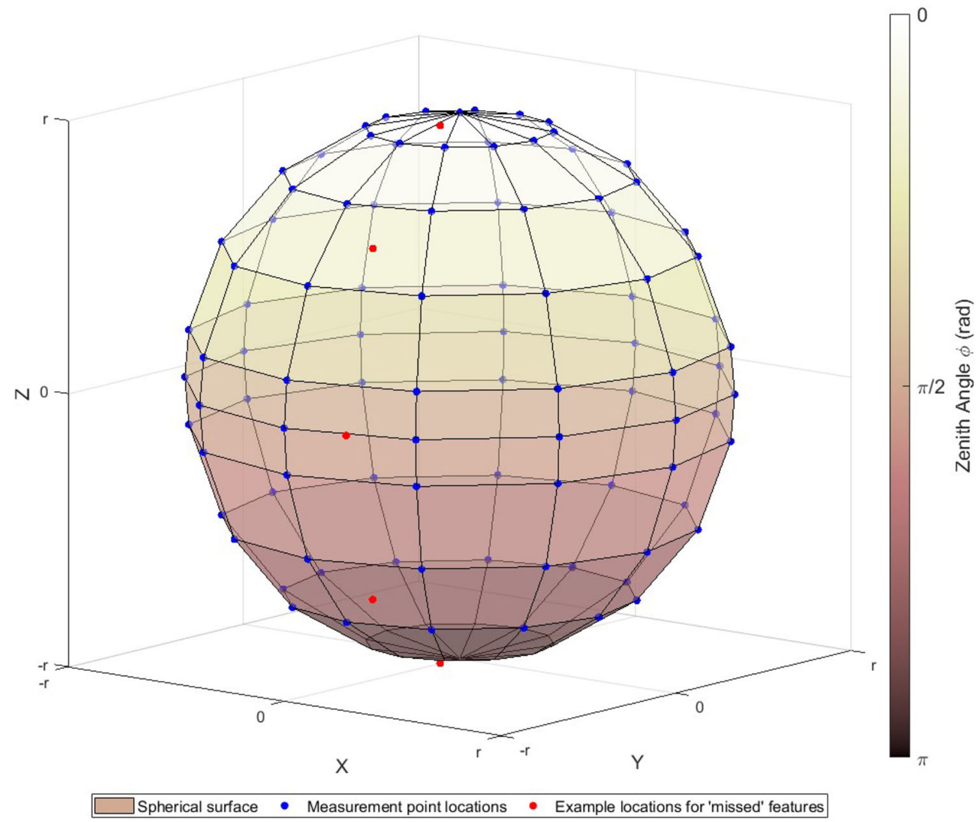

Fig. 15 Measurement points (108) used to characterize the film thickness distribution on the surface of a spherical substrate showing 'missed' features due to discrete resolution

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