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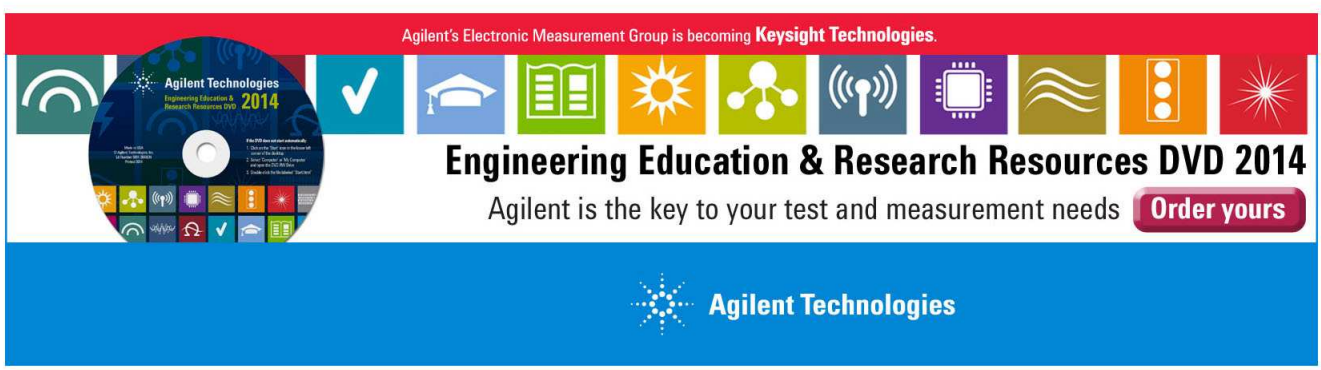

Time-resolved interference unveils nanoscale surface dynamics in evaporating sessile droplet

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We report a simple optical technique to measure time-resolved nanoscale surface profile of an evaporating sessile fluid droplet. By analyzing the high contrast Newton-ring like dynamical fringes formed by interfering Fresnel reflections, we demonstrated $\lambda/100 \approx 5$ nm sensitivity in surface height (at 0.01–160 nm/s rate) of an evaporating water drop. The remarkably high sensitivity allowed us to precisely measure its transient surface dynamics during contact-line slips, weak perturbations on the evaporation due to external magnetic field and partial confinement of the drop. Further, we measured evaporation dynamics of a sessile water drop on soft deformable surface to demonstrate wide applicability of this technique. © *2014 AIP Publishing LLC*.
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The evaporation of fluid drops is a well-known phenomenon. It finds technological applications in printing,[1,2] cooling of electronic devices,[3] and in micro-lithography on biomaterials.[4] The evaporation is very sensitive to small impurities in fluids, external electric and magnetic fields, as well as substrate properties.[5] Its nanoscale measurement is essential to better understand the behavior of evaporating drop in various circumstances.

Previous measurements on evaporation of fluid drops employed diverse techniques such as gravimetric measurements of mass-loss using quartz crystal micro balance,[6] Raman thermometry,[7] and atomic force microscopy cantilevers.[8] Various optical techniques have also been used such as microscopic imaging of the drop,[9,10] fiber-optic sensing,[11] light scattering from fiber suspended drop,[12] reflectometry,[13] and two-beam Mach Zehnder interferometry.[14] However, few techniques offer nm resolution for *in situ* measurement of surface height change due to evaporation.

During evaporation of a sessile drop from a solid substrate, its contact-line could slip due to imbalance of interfacial stresses. This leads to fast nanoscale surface instabilities.[15,16] Many theoretical studies exist,[17,18] however, time-resolved measurements of slipping events with few nm precision has not been demonstrated yet. Moreover, measurement of surface dynamics of an evaporating drop resting on soft deformable substrate (water drop on oil) is also of great recent interest.[19,20] Therefore, a simple optical technique offering time-resolution, precision, and flexibility to probe such diverse situations is desired.

In this Letter, we show that by analyzing high-contrast Newton ring like fringes one can dynamically resolve nanometric surface changes in an evaporating water drop. A resolution of $\lambda/100 \approx 5$ nm in its height at 0.01–160 nm/s rate was demonstrated until the drop was nearly dried. This high sensitivity allowed us to measure nanoscale surface dynamics when the contact line of the shrinking water drop slipped on a glass substrate. Applications of the technique to measure perturbations on the evaporation rate by static magnetic field, by partial confinement of the drop, and evaporation dynamics of a water drop resting on a soft deformable substrate are demonstrated.

The schematics of our experimental setup are shown in Fig. 1. Two complementary arrangements are possible to probe a sessile fluid-drop. One can use a laser beam incident at an angle θ_i from above the drop as in Fig. 1. The beam can also be couple into the drop from below using a prism (see inset, Fig. 3(a)). In the first case, a standard microscope glass slide was mounted on a *xyz* micro-positioner. A range of base radii $w = 1$–10 mm of water drops (10–100 μl) were placed on the horizontal glass-surface using a syringe. The ambient temperature was 300 K and 50% relative humidity. A collimated low power linearly polarized diode pumped solid-state laser (10 mW, $\lambda = 532$ nm, and $1/e^2$ full-waist $\simeq 0.70$ mm) entered into the drop from above. While most of the power (≈95%) was transmitted through the fluid-glass system, we made the two Fresnel reflections from the

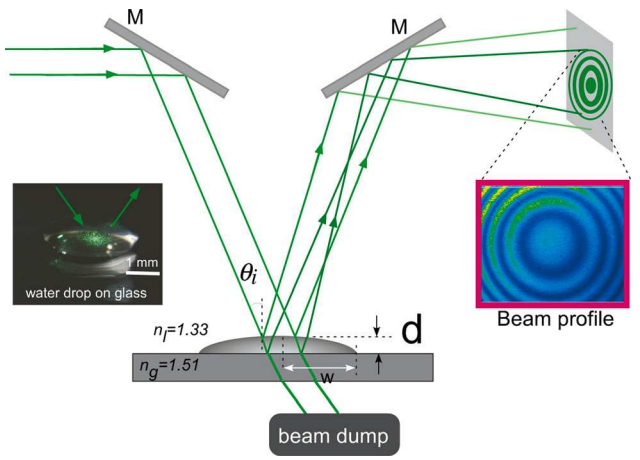

FIG. 1. Schematics of the experimental setup. A cw green laser ($\lambda = 532$ nm, 10 mW) is incident at an angle θ_i from above a water drop resting on a glass slide. *M* flat mirror. The fringes due to interference between Fresnel reflections are observed on a CCD beam-profiler. An actual picture of the water drop is also shown.

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air-water (AW) interface and from the water-glass (WG) interface to spatially overlap as depicted in Fig. 1. This resulted in a Newton-ring like interference pattern that was dynamic due to change in central thickness $d(t)$ of the drop. The interference was video recorded using a CCD beam-profiler at 25 fps and was computer analyzed.

For a range of incident angles of the collimated beam $(0^\circ < \theta_i < 30^\circ)$, we observed remarkably high-contrast circular fringes for a sessile fluid drop (Figs. 2(a)–2(c)). The two Fresnel reflections from AW and WG interfaces exhibited 0.4%–2% intensity reflection coefficients for $\theta_i \approx 0$. The good contrast of these fringes can be experimentally optimized by matching the relative intensities of these two Fresnel beams by varying the angle of incidence θ_i. The phase difference between the two reflections for a fluid drop of thickness d and refractive index n_l is given by, $\Delta\phi(t) = (2\pi n_l/\lambda)(2d(t)/\cos\theta_r)$, where θ_r is determined by the Snell's law, $n_l = \sin\theta_i/\sin\theta_r$. When $d(t)$ changes, e.g., due to evaporation, the intensity at the central fringe is modulated in time, $I(t) \propto \cos^2(\alpha\, d(t))$, where $\alpha = 4\pi n_l/\lambda\cos\theta_r$ is a constant for the experimental arrangement. This dynamical interference pattern was used to extract time-resolved height variation. Note that this technique is self-referencing for nanoscale measurements. One fringe collapse, i.e., central maximum to the next minimum of $I(t)$, as shown in Figs. 2(a)–2(c), corresponded to thickness change of $\lambda\cos\theta_r/4n_l \approx 96$ nm in our experimental conditions! Interestingly, by fitting experimental intensity variation to the theoretical one, we obtained <5 nm precision as shown in the inset in Fig. 2(d).

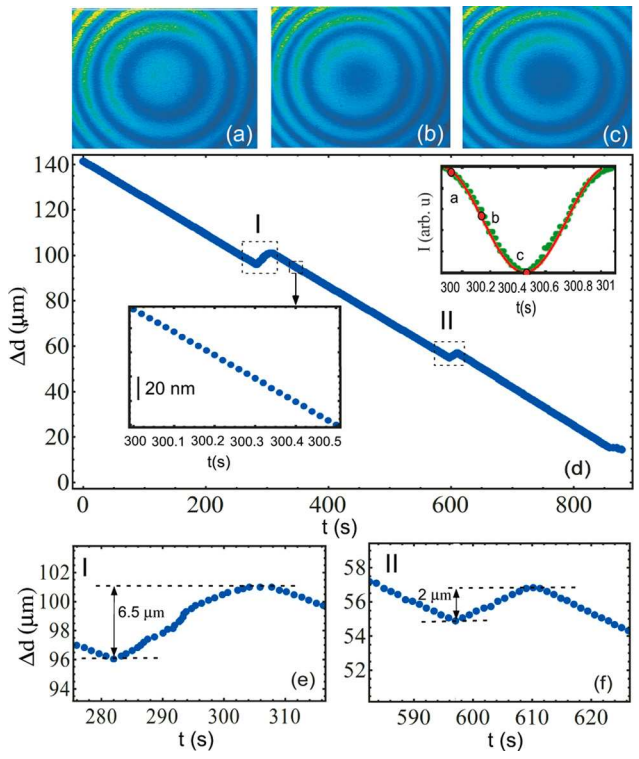

FIG. 2. (a)–(c) Three snapshots of interference pattern corresponding to one fringe collapse. (d) Variation of Δd of the water drop versus time. Top inset: $I(t)$ for the central fringe with corresponding fit. Points a–c correspond to the three snapshots shown above. Bottom Insets: a zoom into the linear regime. Note that the scale bar is 20 nm and (e) and (f) Zoom into contact lines slipping events labeled *I* and *II*. Average slope of the linear fit: 160 nm/s

Our measurements of change in thickness $\Delta\, d(t) = d(t) - d(t=0)$ for an evaporating water drop $(w = 2.0\,\text{mm})$ resting on a glass slide is shown in Fig. 2. We observed a linear reduction in Δd during steady state evaporation. It was interrupted by brief nonlinear events (marked as I and II in Fig. 2(d)) due to contact line slipping on the glass. The average slope of the linear regime was 160 nm/s, which agreed with the constant contact line evaporation mode.[21,22] Zooming into the linear regime (inset, Fig. 2(d)), we measured Δd with 5 nm precision. The mass-loss corresponding to 5 nm height change for our spherical-cap drop $(d = 500\,\mu\text{m})$ was around 19 pg under constant contact-area mode.[23]

Figs. 2(e) and 2(f) show a zoom of the two contact line slipping events I and II. During these events, the collapsing fringes start emerging due to increase in the height of the AW interface. Event-I lasted around 24 s and produced maximum amplitude around 6.5 μm, while the next one lasted only 12 s with 2 μm amplitude. We computed approximate slipping duration following,[24,25] $\delta t = \pi w^3 \delta\theta/(1+\cos\theta_0)^2 \cdot \text{dV/dt}$. Using the contact angle $\theta_0 = 40^\circ$, $\delta\theta = 0.37^\circ$, and dV/dt $= 2\ \text{pm}^3/\text{s}$, we obtained for the first slipping $\delta t \approx 25$ s that is consistent with our observation. These data unveil first nanoscale measurements on competition between slipping and evaporation. When the drop becomes very thin, $d(t) \ll \lambda/2n_l$, the fringe pattern eventually disappears analogous to the Newton's dark soap films.[26]

We exploited remarkably high sensitivity of this technique to measure response of evaporation rate of water drop subjected to various external perturbations. For example, we demonstrated how a static magnetic field affects the evaporation of the water drop. Although, it was proposed that the magnetic field enhances the evaporation rate by reducing its surface energy.[27] However, a precise measurement of this effect, for weak magnetic fields is still interesting. For this measurement, a sessile water drop $(w = 2\,\text{mm})$ was placed under a homogeneous magnetic field created by a 10 mm diameter disk-magnet producing $B \approx 0.1$ T on the slide (see schematics in inset, Fig. 3(a)). Notably, naked-eye observation showed that fringes collapsed at a faster rate compared to without the magnetic field. Measured value of the slope was 171 nm/s, which was higher than the zero field value of 134 nm/s. In another application, we measured evaporation suppression when a sessile drop was partially covered by a dry glass-slide kept at $z = 3$ mm above its surface. In this case, the laser beam was coupled into the drop from below using an equilateral prism as shown in the inset of Fig. 3(a). Now the Fresnel reflections from GW and AW interfaces overlapped around $\theta_i \approx 60^\circ$, which was aligned by overlapping corresponding spots on the exit face of the prism. As soon as we kept the slide, we observed that the rate of fringe collapse was reduced by 47 nm/s to 87 nm/s.

Furthermore, our technique can also be applied to measure surface dynamics of a sessile drop on another soft deformable surface. To prove this, we carefully placed a water drop on a large mobile oil $(n = 1.45)$ drop (see insets, Fig. 3(b)). The entire system was made stable on a floating optical table. By tuning $\theta_i \approx 30^\circ$ of the incident laser, we obtained good contrast fringes, in this case, which were evolving due to evaporation of water. A rate of 80 nm/s was measured in Fig. 3(b), which is lower when compared to

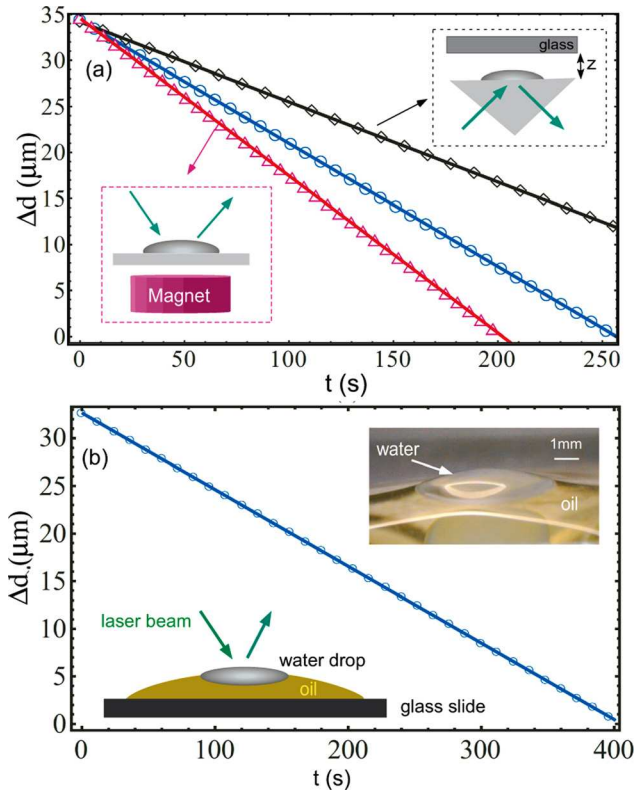

FIG. 3. (a) $\Delta d(t)$ versus time for a sessile water drop on a glass slide with magnetic field $B = 0.1$ T (triangles) and without magnetic field (circles). Corresponding slopes from linear fits are 171 nm/s and 134 nm/s, respectively. Squares: date when the drop was covered by a glass slide $z = 3$ mm and its fit with slope 87 nm/s. Insets show schematic of the setup. (b) $\Delta d(t)$ for a sessile water drop ($w = 4.0$ mm) on a mobile oil drop with fits at 80 nm/s slope. Insets: setup schematic and actual picture of the drops.

Fig. 3(a). We did not observe any abrupt slipping events during our measurement because the contact line was not pinned as the substrate was deformable.[20,28]

Three remarks regarding the technique are worth mentioning. (i) We have verified that $I(t)$ can also be measured using a fast photo-diode (1 ns rise time). It can thus offer ns time-resolution to probe ultrafast interface phenomena. (ii) Similar fringes were also observed when the drop rested on a patterned substrate, such as a grating (600 lines/mm) or rough *Al* sheets/foil. (iii) The fluid drop could also be semi-transparent such as the colloidal coffee-drop suspensions.[28] These suggest wide applicability of our optical technique.

In conclusion, we demonstrated a simple optical technique for non-contact nanoscale measurement of surface deformation of evaporating sessile drop from hard or soft substrates. The high-contrast fringes allowed us to measure resulting surface height variation with 5 nm precision and rates (0.01–160 nm/s) until it nearly dried. A variety of applications of the technique were demonstrated such as surface dynamics during slipping contact line on the glass, enhancement of evaporation due to static magnetic field, and its suppression due to partial confinement of the droplet. The flexibility of the technique also allowed us to measure evaporation of a sessile water drop on oil. It should be possible to improve the resolution in sub-nm regime employing lock-in detection for modulated intensity. Due to high sensitivity, simplicity, and time-resolution, this optical technique could find diverse applications in precision measurements on evaporation of fluid mixtures,[29] fast shape-oscillations induced by external fields (electromagnetic, acoustic),[30] and in opto-fluidics.[31,32]

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