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Marangoni flows induced by atmospheric-pressure plasma jets

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Abstract

We studied the interaction of atmospheric-pressure plasma jets of Ar or air with liquid films of an aliphatic hydrocarbon on moving solid substrates. The hydrodynamic jet-liquid interaction induces a track of lower film thickness. The chemical plasma-surface interaction oxidizes the liquid, leading to a local increase of the surface tension and a self-organized redistribution of the liquid film. We developed a numerical model that qualitatively reproduces the formation, instability and coarsening of the flow patterns observed in the experiments. Monitoring the liquid flow has potential as an *in-situ*, spatially and temporally resolved, diagnostic tool for the plasma-liquid surface interaction.

Keywords: atmospheric-pressure plasma jet, thin liquid films, solutocapillary flow, Marangoni flow

(Some figures may appear in colour only in the online journal)

1. Introduction

Atmospheric-pressure plasma jets [1, 2] have generated significant interest for their versatile applications in material processing [1–4], surface modification [5–8], medicine [9–21] and chemical reaction engineering [22–25]. Fricke *et al* studied the etching of polymers using atmospheric-pressure Ar plasma jets with different oxygen admixtures and found etch rates in the order of 20 nm s^{-1} for polyethylene [4]. Using similar plasma jets, Vogelsang *et al* locally reduced the water contact angle of polymer surfaces from above 90° to about 30° [6], mediated by surface functional groups containing oxygen and nitrogen. Dorai and Kushner presented a model for the plasma modification of polypropylene using atmospheric pressure discharges [26].

The interaction of plasmas with liquids has been studied in a variety of contexts [25, 27–29]. Mechanisms that can induce flow or surface deformations are stagnation pressure and shear of the gas flow, local temperature increase [30], chemical reactions or electric fields [31–34]. In this manuscript, we report on the interaction of cold, atmospheric-pressure Ar- and air plasma jets with liquid hydrocarbon films on moving substrates. Due to the jet impact, a film thickness depression forms underneath the plasma jet. Due to the plasma-liquid interaction, the chemical composition of the liquid is altered, most likely via partial oxidation or the

addition of nitrogen-containing functional groups. The liquid surface tension changes with composition and becomes spatially non-uniform, which induces solutocapillary Marangoni flows [35–41] and redistributes the liquid film. We developed a model that qualitatively reproduces many of the morphological and dynamical features observed in the experiments.

2. Experimental methods

2.1. Thin liquid film deposition

We deposited a liquid film of the essentially non-volatile liquid squalane (purity 99%, Aldrich, product number 234311) onto polymeric substrates using spin-coating (Brewer Scientific, model CEE200). The initial film thickness was kept constant at $h_0 = 4.5 \text{ }\mu\text{m}$. The substrates consisted of optical-quality polycarbonate plates (Bayer, Makrofol DE1-1) of thickness $d_{\text{sub}} = 750 \text{ }\mu\text{m}$ and dimensions of $6 \times 6 \text{ cm}^2$. Before spin-coating, we removed static surface charges [42] from the substrate using an antistatic bar (Simco-Ion MEB).

2.2. Material properties of squalane

The viscosity of squalane at 23°C is $\mu_{\text{liq}} = 31.9 \text{ mPa s}$, the surface tension [43] $\gamma = 28.15 \text{ mN m}^{-1}$, the density [44] $\rho = 805 \text{ kg m}^{-3}$ and the refractive index is

Figure 1. (a) Sketch of experimental setup for exposure of liquid films to atmospheric plasma jets. (b, c) *In-situ* dual-wavelength interference micrographs of liquid films exposed to (b) Ar and (c) air plasma-jets on a substrate moving with a speed of $U_{\text{sub}} = 6 \text{ mm s}^{-1}$.

$n_D = 1.452$. The self-diffusion coefficient of squalane [45] is $D_s \approx 3 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Kowert and Watson studied the diffusion of organic solutes in squalane [46].

2.3. Atmospheric-pressure plasma treatment

We used a commercial atmospheric-pressure plasma jet (KinPen 09, NeoPlas Tools) [47], operated at a flowrate of approximately 1 l min^{-1} at normal incidence onto the substrate, see figure 1. In this fashion, the deformation of the liquid film can be visualized *in-situ* in transmission through the optically transparent substrate during the plasma jet impingement from the top side (figures 1(b) and (c)). The plasma was generated via capacitive radiofrequency (rf) excitation at 1.1 MHz and a voltage amplitude of 2–6 kV. We used either Ar gas or purified air. We adjusted the electrical power input such that the visible length of the plasma jets was maintained at about 3 mm. The exit nozzle diameter is $D \approx 1 \text{ mm}$ resulting in a jet-Reynolds number $\text{Re}_D \equiv \rho U D / \mu \approx 1360$, which is in the laminar regime. The stand-off distance between the nozzle-exit and the liquid film was kept constant at $H = (2.5 \pm 0.1) \text{ mm}$. The samples were maintained in a horizontal orientation and the plasma jets were impinging from the top, perpendicular to the substrate surface. The substrates were rotated at a constant angular velocity Ω_{sub} . The radial distance of the plasma jet from the (vertical) axis of rotation was approximately 1 cm, which

implies that a value of $\Omega_{\text{sub}} = 1 \text{ rpm}$ corresponds to a translation speed of $U_{\text{sub}} \approx 1 \text{ mm s}^{-1}$. The dashed yellow lines in figure 1 indicate the jet trajectory. The diffuse regions in the right hand sides of figures 1(b) and (c) correspond to camera pixels that were saturated by the light emission from the plasma jets.

Figure 2 shows photographs of the plasma jets and corresponding emission spectra acquired using a portable spectrometer (Ocean Optics, model USB4000). Figure 2(c) shows, besides Ar-lines, a part of the N_2 second positive system (SPS) [48–50] (350–410 nm) and the 777 nm line of the O-atom. This is an indication of air entrainment into the plasma. Figure 2(d) shows the N_2 -SPS and N_2 first negative system (FNS) [51, 52] in the wavelength range 500–900 nm and two O-lines at 777 and 845 nm. The band structure between 420 and 500 nm is unidentified. Comparison shows that it is not CH, CO, CN or C_2 . The rather large distance between the peaks indicates a heavier molecule, possibly an oxidation product of squalane.

We determined whether an electrical surface charge was induced by the interaction of the plasma with the thin liquid film, which could cause flow of electrically insulating liquids via dielectrophoresis [42]. For this purpose, we scanned the plasma-treated sample using an electrostatic voltmeter (Monroe Electronics, Isoprobe 244) with a high-resolution probe (Isoprobe 1017AEH) [42]. The probe-sample distance was approximately 0.5 mm. There was no signature of any charge deposition along the trajectory of the plasma jet along

Figure 2. (a, b) Photographs of the atmospheric pressure plasma-jets: (a) Ar and (b) air plasma jet. (c, d) Emission spectra of (c) Ar and (d) air plasma jets.

the substrate. The measured rms background charge density was below $1.5 \mu\text{C m}^{-2}$.

2.4. Flow visualization

After subjecting the slowly rotating liquid film to the plasma jet, we placed the sample under an upright optical microscope (Olympus BX-51), fitted with a CCD camera (AVT Pike) and a $1.25\times$ objective. For illumination, we used an LED light source (Thorlabs, model M660L3-C1) with a center wavelength of 660 nm. The first frame is recorded approximately one minute after termination of the plasma treatment. The evolution of the liquid height profile $h(x, y, t \gtrsim 1 \text{ min})$ along the jet trajectories is visualized using optical interferometry.

3. Experimental results

For both Ar and air plasma jets we systematically varied the substrate rotation speed Ω_{sub} . The corresponding morphology of the thin liquid films at certain times after termination of the plasma jet treatment is presented in figures 3 and 4. The stagnation pressure and wall shear stress of the gas flow induce a depression in the liquid film along the jet trajectory [53]. Depending on the rotation rate, the remaining film thickness along the track centerline is in the range of approximately $0.1\text{--}1 \mu\text{m}$. The grayscale fringes in figures 3 and 4 represent curves of constant film thickness. The dashed yellow line in figure 3(a) corresponds to the centerline of the jet trajectory as indicated in the same fashion in figure 1.

The most striking feature as a consequence of Ar plasma jet treatment is the formation of a pair of rims extending parallel to the centerline of the jet trajectory with initial separation $d_{\text{rim}} \approx 2 \text{ mm}$, as indicated by the red arrows in figure 3(b). The rims move towards each other and merge within 5–9 min for figures 3(b) and (e). Moreover, the rims tend to become unstable and break up into a series of droplets that grow and coarsen in time, as visualized e.g. in figures 3(b) and (c). For air plasma jets, we observed pairs of rims for $\Omega_{\text{sub}} = 0.5$ and 1 rpm in figures 4(a) and (b), but only a single rim for $\Omega_{\text{sub}} \geq 2 \text{ rpm}$.

4. Modeling

4.1. A simplified model for the plasma-liquid interaction

We hypothesize that the primary interaction between the plasma jet and the hydrocarbon is partial oxidation at the liquid-air interface as a consequence of exposure to UV/VUV radiation [54] and activated oxygen species such as O_3 and O-radicals [30, 55–61]. The surface tension of e.g. alkanols and alkanolic acids is typically higher than that of the corresponding alkanes [62–64], due to the higher polarity of oxygenated molecular groups. Consequently, oxygenated liquid species tend to increase the surface tension when present as a mixture with an alkane. Thereby the surface tension of the liquid increases. Moreover, the oxygenated species desorb from the liquid-air interface, where they are formed, thus continually exposing fresh alkane molecules to the plasma environment [22].

The distribution of plasma-activated species at the liquid-air interface depends on the feed gas. We assume that the lifetime of the reactive species in the gasphase outside the plasma jet is short, such that a reaction only occurs close to the direct impingement zone. In the case of Ar, activated oxygen species are produced only in the boundary layer of the jet, where oxygen is entrained from the ambient atmosphere. Therefore, reactive species can only reach the liquid film in a circular ring at the periphery of the jet as sketched in figure 5(a). In an air plasma jet, chemical reactions can occur across the entire jet impingement zone (figure 5(b)).

It is likely that a large number of different chemical species with a distribution of molecular weights (MWs) result from the plasma interaction. In the following, however, we account for the oxidized species by means of a single concentration variable c and assume that surface tension has a linear dependence

$$\gamma(c) = \gamma_0 + \frac{\partial\gamma}{\partial c}c, \quad (1)$$

with a *constant* coefficient $\partial\gamma/\partial c > 0$. For binary mixtures of alkanes and alkanols this is a realistic assumption [63].

The oxidation reaction is a highly complex process that may involve many individual steps and transitory species [26], many of which may not have been identified, yet. Therefore, the starting point for our model of the liquid redistribution is the assumption that the reaction occurs at the liquid-air interface and leads to an increase in $c_s \equiv c(z = h)$ at a certain rate,

Figure 3. Optical interference micrographs of a squalane film at different times t after termination of the argon plasma jet treatment at rotation speeds of (a) $\Omega_{\text{sub}} = 0.5$ rpm, (b) 1 rpm, (c) 2 rpm, (d) 3 rpm, (e) 6 rpm, (f) 10 rpm.

Figure 4. Optical interference micrographs of a squalane film at different times t after termination of the air plasma jet treatment at rotation rates of (a) $\Omega_{\text{sub}} = 0.5$ rpm, (b) 1 rpm, (c) 2 rpm, (d) 3 rpm, (e) 6 rpm, (f) 10 rpm.

which depends on the local concentration of the activated species, the local jet velocity and boundary layer thickness.

The interaction time t_{int} of the plasma with a point along the jet trajectory is given by the ratio of D and the substrate speed U_{sub} . A faster U_{sub} will reduce t_{int} and thus reduce the average concentration, while preserving the shape of the distribution. However, a small value of U_{sub} gives rise to an additional dispersion effect induced by the jet shear stress τ_{gas} . A typical value [65] at the liquid–air interface is $\tau_{\text{gas}} = 50$ Pa, which gives rise to a shear flow of the liquid with speed $h\tau_{\text{gas}}/\mu_{\text{liq}}$, which equals 1.5 mm s^{-1} for $h = 1 \text{ μm}$. For a sufficiently long t_{int} , the widening of the distribution due to this gas induced shear flow becomes comparable to D , which is consistent with the increased value of $d_{\text{rim}}(t = 60 \text{ s}) \approx 4 \text{ mm}$ observed in figure 3(a).

The oxygenated species desorbs from the surface and equilibrates with the bulk liquid across the film thickness within a time

on order of $h^2 / \mathcal{D}_s \approx 30 - 675 \text{ ms}$ for h in the range of $1 - 4.5 \text{ μm}$. We neglect material loss due to volatilization of the liquid, e.g. via the formation of CO, CO₂, H₂O and other low MW species.

The experimental data depicted in figures 3 and 4 correspond to times $t \geq 60 \text{ s}$, which by far exceed $h_0^2 / \mathcal{D}_s \lesssim 0.7 \text{ s}$. Consequently, the concentration distribution can be assumed to be vertically equilibrated. Thus, we only need to consider the height-averaged concentration defined as

$$C \equiv \frac{1}{h} \int_0^h c dz, \quad (2)$$

which only depends on the lateral coordinates x and y . We consider a Cartesian model for the flow of the liquid and the convection and diffusion of the oxidized species, where the track extends along the y -axis. This is permissible as the track

Figure 5. (a, b) Sketches of the distributions of plasma-activated species. (c) Hypothetical initial species concentrations for Ar- (green solid line) and air plasma jets (red dashed line).

width is much smaller than the track radius. As an initial condition we assume empirical concentration distributions of the oxidized species $C(x, t = 0)$ as sketched in figure 5(c). Here, x is the coordinate perpendicular to the jet trajectory and $x = 0$ corresponds to its centerline (see figure 1).

We have detailed the interaction of gas jets and heat sources with liquid films in the absence of plasma previously [53, 65–67]. Therefore, we do not focus on the hydrodynamic or thermal interaction between the jet and the liquid here, but rather on the dynamics and morphology of the plasma-induced redistribution of the liquid *after the jet has passed*. For this reason, we consider an initial film thickness profile in the form of a parabolic depression

$$h(x, y, t = 0) = \min \{h_0, h_c(1 + x^2/w^2)\}. \quad (3)$$

The film thickness h_c remaining at the track centerline after the jet has passed depends on the rotation rate [53] and is in the range of 0.1–1 μm . The initial concentration distributions are assumed of the form $C(x, y, t = 0) =$

$$C_c\Theta(1 - x/d_p) + C_{\max} \exp[-(x - d_p)^2/w_p^2] \quad (4)$$

for Ar plasma jets and a smoothed step-function

$$C(x, y, t = 0) = C_{\max} \Theta(1 - x/d_p) \quad (5)$$

for air plasma jets and are sketched in figure 5(c). The smoothed step function in equations (4) and (5) is implemented via the Comsol function fl2chs as

$$\Theta(x) = \text{fl2chs}(1 - x/d_p, w_p), \quad (6)$$

where the parameter w_p quantifies the distance over which the step function changes smoothly from 0 to 1.

4.2. Model for thin film redistribution

The flow of thin liquid films is governed by the so-called lubrication equation [68]

$$\frac{\partial h}{\partial t} + \frac{\partial Q_x}{\partial x} + \frac{\partial Q_y}{\partial y} = 0, \quad (7)$$

where

$$Q_x \equiv \frac{h^2\tau_x}{2\mu_{\text{liq}}} - \frac{h^3}{3\mu_{\text{liq}}} \frac{\partial p}{\partial x} \quad \text{and} \quad Q_y \equiv \frac{h^2\tau_y}{2\mu_{\text{liq}}} - \frac{h^3}{3\mu_{\text{liq}}} \frac{\partial p}{\partial y} \quad (8)$$

are the volumetric flowrates,

$$\tau_x \equiv \frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial C} \frac{\partial C}{\partial x} \quad \text{and} \quad \tau_y \equiv \frac{\partial \gamma}{\partial y} = \frac{\partial \gamma}{\partial C} \frac{\partial C}{\partial y} \quad (9)$$

are the Marangoni stresses [36] along the x - and y -directions and

$$p = -\gamma \left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) + \rho gh \quad (10)$$

is the augmented pressure, representing capillary and hydrostatic pressure contributions. Here, $g = 9.81 \text{ m s}^{-2}$ is the gravitational acceleration. The terms containing τ_x and τ_y represent Marangoni fluxes in response to surface tension gradients, which are caused by gradients in concentration of the oxidized species C owing to equation (1). Generally, the direction of Marangoni flow in thin liquid films is from regions of lower towards regions of higher surface tension. The non-uniform species distribution that sets up the surface tension gradients, however, changes continuously due to diffusion and convection with the flow. Therefore, equation (7) is coupled to a convection-diffusion equation [69] that governs the dynamics of $C(x, y, t)$

$$\begin{aligned} h \frac{\partial C}{\partial t} + Q_x \frac{\partial C}{\partial x} + Q_y \frac{\partial C}{\partial y} \\ = \frac{\partial}{\partial x} \left(h D_s \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(h D_s \frac{\partial C}{\partial y} \right). \end{aligned} \quad (11)$$

We solved the set of equations (7)–(11) numerically using the finite element software Comsol 3.5a. The computational domain extends typically a distance $L_x = 10 \text{ mm}$ normal to the jet centerline and—in the case of 2D simulations—a distance of $L_y = 2\text{--}8 \text{ mm}$ along the jet centerline. The boundary conditions were chosen as

$$\frac{\partial h}{\partial x} = 0, \quad \frac{\partial p}{\partial x} = 0 \quad \text{and} \quad \frac{\partial C}{\partial x} = 0. \quad (12)$$

at $x = 0$ and $x = L_x$ and

$$\frac{\partial h}{\partial y} = 0, \quad \frac{\partial p}{\partial y} = 0 \quad \text{and} \quad \frac{\partial C}{\partial y} = 0 \quad (13)$$

at $y = 0$ and $y = L_y$, all of which represent mirror symmetries. The boundary at $x = L_x$ is sufficiently remote from the centerline, such that the surface deformation does not reach it within the typical duration of an experiment.

4.3. One-dimensional model calculations

We first performed one-dimensional model calculations. Figure 6(a) shows a typical time evolution of the film thickness $h(x, t)$ and the concentration profile $C(x, t)/C_{\max}$ after interaction with an Ar plasma jet. The individual curves are offset along the ordinate for clarity.

The general morphology observed in figure 3 is well reproduced. Two rims form within seconds, move towards each other and coalesce after about 1000 s. The rim profiles do not transition smoothly into their surrounding, but rather strong thinning with a minimum film thickness on order of 20 nm occurs at the rim edges (indicated by the red and blue triangles in figure 6(a)). The concentration profile exhibits self-steepening as indicated in figure 6(b) and has the appearance of a shock-wave. The origin is the strong film thinning at the

Figure 6. Time evolution of (a) the height profile $h(x, t)$ and (b) the concentration profile $C(x, t)/C_{\max}$ for an Ar plasma jet treatment and parameters $C_c/C_{\max} = 0.2$, $D_s = 3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $h_c = 250 \text{ nm}$, $w = 1.2 \text{ mm}$, $d_p = 1.1 \text{ mm}$, $w_p = 250 \mu\text{m}$, $C_c/C_{\max} = 0.2$ and $\Delta\gamma = 2 \text{ mN m}^{-1}$. The individual curves are progressively shifted along the ordinate for clarity by increments of (a) $0.5 \mu\text{m}$ and (b) -0.2 .

rim edges, which constitutes a high resistance to mass transfer and causes the very steep concentration gradients. Inside the ridge, Marangoni convection efficiently equilibrates the concentration distribution, giving rise to the flat-top-like profile. The concentration distribution thus induces both inwards- and outwards-oriented Marangoni stresses. However, due to the larger overall concentration difference at the exterior rim edge, the inwards-oriented forces prevail and eventually induce coalescence.

Figure 7 shows a typical evolution of the height- and concentration profiles for the case of an air plasma jet. The most striking difference is that the coalescence time is more than a factor of 10 shorter. Moreover, the maximum concentration remains at a value of approximately one until coalescence and the self-steepening observed with Ar plasma jets is much less pronounced. Consistent with the shallower concentration gradients, also the film thinning is less pronounced and is observed only at the exterior edges of the rims, but not at the interior edges. The substantially faster coalescence for air is thus due to the absence of film thinning inbetween the two rims as well as the absence of outwards-oriented solutocapillary driving forces as compared to the Ar case.

Figure 7. Time evolution of (a) the height profile $h(x, t)$ and (b) the concentration profile $C(x, t)/C_{\max}$ for an air plasma jet treatment and parameters $D_s = 3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $h_c = 250 \text{ nm}$, $w = 1.2 \text{ mm}$, $d_p = 1.1 \text{ mm}$, $w_p = 250 \mu\text{m}$, $C_c/C_{\max} = 0.2$ and $\Delta\gamma = 2 \text{ mN m}^{-1}$.

Figure 8(a) presents numerical simulations of the rim coalescence time t_c as a function of the total surface tension modulation amplitude $\Delta\gamma \equiv \frac{\partial\gamma}{\partial c} C_{\max}$. For $\Delta\gamma$ increasing, t_c decreases, because the convection rate is proportional to the surface tension gradient $\partial\gamma/\partial x$. For an air plasma jet ($C_c/C_{\max} = 1$), t_c is more than a factor of 10 shorter than for Ar. Specifically for $\Delta\gamma \gtrsim 2.5 \text{ mN m}^{-1}$, t_c is shorter than 1 min as indicated by the blue rectangle, which is consistent with the observation of a single rim in figures 4(c)–(e). For an air plasma jet ($C_c/C_{\max} = 1$), t_c to good approximation scales as $t_c \sim (\Delta\gamma)^{-1}$, because the maximum concentration, occurring at $x = 0$, remains at the initial level (see figure 7(b)). Due to the self-steepening effect observed with Ar plasma jets and the dilution-induced decrease of the maximum concentration level (figure 5(e)), the dependence of t_c on $\Delta\gamma$ is weaker: to good approximation $t_c \sim (\Delta\gamma)^{-0.6}$ for $C_c = 0.2$.

Figure 8(b) illustrates the influence of the species diffusion coefficient D_s on the coalescence time t_c . For an air plasma jet ($C_c/C_{\max} = 1$), t_c is independent of D_s for $D_s \lesssim 6 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$. For Ar plasma jets ($C_c/C_{\max} < 1$), t_c increases with decreasing D_s for $D_s \lesssim 1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The dashed line in figure 8(b) represents the diffusional equilibration time $t_{\text{eq}} = (\Delta x)^2 / D_s$ for a distance $\Delta x \approx 2 \text{ mm}$ approximately equal to the track width. When the curves in figure 8(b) get close to this limit, t_c increases, because diffusion becomes so strong that it quenches the driving force of the flow.

Figure 8. Rim coalescence time t_c as a function of (a) the total surface tension modulation amplitude $\Delta\gamma$ and (b) the species diffusion coefficient D_s . The parameters that were not varied in (a, b) were set to $D_s = 3 \cdot 10^{-10}$ m² s⁻¹, $h_c = 180$ nm, $w = 1.2$ mm, $d_p = 1.1$ mm, $w_p = 330$ μ m and $\Delta\gamma = 2$ mN m⁻¹. The solid lines in (a) represent power law relations $t_c \sim \Delta\gamma^\beta$.

Figure 9(a) illustrates the influence of the center film thickness h_c on t_c . A larger value of h_c increases the coalescence time for an air plasma jet treatment ($C_c/C_{\max} = 1$), which is intuitively consistent with the notion that thicker films provide for a higher mobility of the rim. However, for an Ar plasma jet and $C_c/C_{\max} \leq 0.2$, a smaller value of h_c slightly speeds up coalescence, which is perhaps counterintuitive, but agrees with the trend observed in figures 3(b)–(d).

Figure 9(b) illustrates the influence of the initial width of the species distribution w_p on t_c . Since according to equation (4) the total mass of species increases with increasing w_p (for $C_c/C_{\max} < 1$), which foregoes the dilution-induced reduction in driving force, the coalescence time eventually decreases for large w_p . For an air plasma treatment ($C_c/C_{\max} = 1$), the coalescence time is well approximated by a power law $t_c \sim w_p^{-0.53}$ as represented by the dashed line in figure 9(b).

Figure 10 shows experimental and numerical results for the rim separation d_{rim} as a function of time. The influence of the substrate rotation rate Ω_{sub} , which determines the interaction time with the passing plasma jet, is presented in figure 10(a). Presumably, a smaller value of Ω_{sub} induces a larger $\Delta\gamma$, which

Figure 9. Rim coalescence time t_c as a function of (a) the minimum film thickness in the track h_c and (b) the initial width of the species distribution w_p . The parameters that were not varied in (a, b) were set to $D_s = 3 \cdot 10^{-10}$ m² s⁻¹, $h_c = 180$ nm, $w = 1.2$ mm, $d_p = 1.1$ mm, $w_p = 330$ μ m and $\Delta\gamma = 2$ mN m⁻¹. The solid lines in (a) and the dashed line in (b) represent power law relations $t_c \sim h_c^\alpha$ and $t_c \sim w_p^\beta$, respectively.

leads to a smaller value of t_c , which is consistent with the simulation results in figures 10(b) and 8. The initial species distribution, as parametrized by $C_c/C_{\max}$ has a strong influence on the shape of $d_{\text{rim}}(t)$ as detailed in figure 10(c). For $C_c/C_{\max} = 0.5$ and 1, the rim migration speed is monotonically decreasing from the onset essentially until coalescence. In contrast, for $C_c/C_{\max} = 0$ and 0.2 the curves have an inflection point, i.e. the rim migration speed accelerates as t approaches t_c , which is consistent with the experimental data in figure 10(a).

4.4. Two-dimensional simulations

The one-dimensional simulations presented in the previous section are computationally efficient and reproduce many features of the experiments. However, they inherently preclude any study of the rim instability and the growth- and coarsening dynamics of the droplet arrays. For this reason we also performed two-dimensional simulations, of which figure 11 presents a typical example. Pseudocolor plots of the 2D height profile $h(x, y, t)$ are shown at different times after passing of the plasma jet. The computational domain had dimensions of

Figure 10. Rim separation d_{rim} as a function of time. (a) Experimental data for an Ar plasma jet and different substrate rotation rates $\Omega_{\text{sub}} = 1, 2$ and 4 rpm. The solid lines are guides to the eye. (b) Numerical simulations of $d_{\text{rim}}(t)$ for different surface tension modulation amplitudes $\Delta\gamma = 2, 4$ and 8 mN m^{-1} and parameters $C_c/C_{\text{max}} = 0.2$, $\mathcal{D}_s = 3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $h_c = 180$ nm, $w = 1.2$ mm, $d_p = 1.1$ mm, $w_p = 330$ μm . (c) Numerical simulations of $d_{\text{rim}}(t)$ for different initial species distributions $C_c/C_{\text{max}} = 0, 0.2, 0.5$ and 1 and parameters $\mathcal{D}_s = 1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $h_c = 250$ nm, $w = 1.2$ mm, $d_p = 1.1$ mm, $w_p = 250$ μm and $\Delta\gamma = 2$ mN m^{-1} .

$L_y = 2$ mm and typically $L_x = 5$ mm. For clarity the results are mirrored across $x = 0$ in figure 11(a–g) and additionally across $y = 0$ in figure 11(h).

The formation and instability of the rims and the subsequent coarsening of the resulting droplets observed in figure 3 is qualitatively well reproduced. The instability wavelength at the onset is $\lambda_o \approx 0.45$ mm in figure 11(b). Only very weak dependencies of λ_o on h_c and C_c/C_{max} were observed. Large values of $\mathcal{D}_s$ or small values of $\Delta\gamma$ tend to delay the onset, increase λ_o or even suppress the occurrence of the instability, which is consistent with the trend observed in figures 3(d)–(f) and 4(d)–(f).

Figure 11. Pseudocolor plot of film thickness evolution $h(x, y, t)$ for $\Delta\gamma = 2$ mN m^{-1} and parameters $C_c = 0$, $\mathcal{D}_s = 5 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $h_c = 250$ nm. The white line in panel (a) labeled $x = 0$ represents the jet trajectory. The parameter $L_y = 2$ mm in (d) is the width of the computational domain.

The driving forces of the coalescence and coarsening of the droplets are on the one hand a reduction of interfacial area and on the other hand differences in the overall species concentration in neighboring droplets. This concentration difference corresponds to a surface tension difference that causes the droplet with lower surface tension to flow towards the droplet with higher surface tension [70–78]. Since the concentration differences in neighboring droplets are very likely small, a coalescence delay [73–78] does not occur.

5. Discussion

According to figure 8(b), a value of $\mathcal{D}_s$ close to the self-diffusion coefficient of squalane $3 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ does not give a coalescence time t_c in the experimentally observed range of 400–600 s for Ar plasma jets. Rather, a much larger value of $\mathcal{D}_s$ is required for a good match with the experiments in figure 3, which may indicate molecular fragmentation as a consequence of plasma-induced oxidation.

There is an inherent ambiguity in the model as all results are only sensitive to the product $(\partial\gamma/\partial C)(\partial C/\partial x)$, which scales as $(\partial\gamma/\partial C)(C_{\text{max}}/w_p)$, but not separately to $(\partial\gamma/\partial C)$ and C_{max} . However, if the reaction products are known, the Marangoni coefficient $(\partial\gamma/\partial C)$ can be measured independently in principle. In this fashion, the experiments allow for an indirect, but otherwise fast and simple visualization of the species concentration distribution. Although we monitored the deformation of thin liquid films after the jet has passed, the technique also has the potential to serve as an *in-situ* diagnostic tool for elucidating the dynamics and spatial dependence of the interaction between cold atmospheric plasma jets and condensed matter.

6. Summary

In summary, we studied the interaction of cold, atmospheric-pressure plasma jets of Ar or air with liquid hydrocarbon films on moving substrates. Due to the chemical plasma-surface interaction, the liquid most likely becomes oxidized, leading to a local surface tension increase and subsequent solutocapillary redistribution. In the case of an Ar plasma jet, two rivulets are formed that move towards the center of the jet trajectory. In the case of an air plasma jet, a single rivulet is observed in the center of the track. These rims tend to be unstable and break-up into regular arrays of droplets that grow and coarsen over time. We systematically studied the influence of the substrate speed, which determines the plasma-liquid interaction time and thus the degree of oxidation. We developed a numerical model that qualitatively reproduces the experimental observations, i.e. the formation of rims, their coalescence, instability and coarsening.

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