Thermal effects of substrate on Marangoni flow in droplet evaporation: Response surface and sensitivity analysis

Xue Chen\textsuperscript{a,b}, Xun Wang\textsuperscript{b,1}, Paul G. Chen\textsuperscript{b}, Qiusheng Liu\textsuperscript{a,c,*}

\textsuperscript{a}Key Laboratory of Microgravity, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{b}Aix Marseille Univ, CNRS, Centrale Marseille, M2P2, Marseille, France
\textsuperscript{c}University of Chinese Academy of Sciences, Beijing 100049, China

**A R T I C L E  I N F O**

Article history:
Received 14 December 2016
Received in revised form 17 May 2017
Accepted 20 May 2017

Keywords:
Droplet evaporation
Marangoni flow
Thermal property
Response surface
Sensitivity analysis

**A B S T R A C T**

In this paper, the evaporation of sessile droplets resting on a substrate with different thermal properties is numerically investigated. Computations are based on a transient axisymmetric numerical model. Special attention is paid to evaluate thermal effects of substrate on the structure of bulk fluid flow in the course of evaporation. Numerical results reveal that Marangoni convection induced by non-uniform distribution of temperature along the interface exhibits three distinctly different behaviours: inward flow, multicellular flow and outward flow, consequently resulting in different particle deposits. It is highlighted that three factors (i.e. relative thermal conductivity, relative substrate thickness and relative substrate temperature) strongly affect the flow pattern. In order to further investigate the coupling effects of different influential factors, a Kriging-based response surface method is introduced. We model the flow behaviour as a function of continuous influential factors using a limited number of computations corresponding to discrete values of the inputs. The sensitivities of the Marangoni flow are also analysed using Sobol’ index to study the coupling mechanisms of influential factors. The proposed method can be used to forecast the flow patterns for any input parameter without additional sophisticated computer simulation, and allows to confidently estimate an unknown environmental parameter.

\copyright 2017 Elsevier Ltd. All rights reserved.

**1. Introduction**

The evaporation of a liquid drop resting on a solid substrate is not only of fundamental scientific interest but also of great importance in a wide variety of industrial and scientific applications, such as evaporative self-assembly technique (DNA mapping, MEMS cooling)\textsuperscript{[1,2]}, evaporation-induced particle deposition (thin film coating, ink-jet printing)\textsuperscript{[3,4]} and the design of more efficient heat transfer devices\textsuperscript{[5]}. Among the mechanisms involved, the behaviour of Marangoni flow induced by temperature gradient along the liquid-gas interface can significantly influence deposition patterns upon drying. For this reason, understanding the flow characteristics inside the drop plays a vital role in controlling the distribution of the particle deposition in evaporating droplet.

Extensive theoretical and experimental researches have been motivated in recent years\textsuperscript{[6–8]}. Most of the previous works were based on diffusion-limited process, normally focusing on predicting the evaporation rate. Hu & Larson\textsuperscript{[9]} suggested a simple approximation to summarise the total mass flux across the droplet surface and then in turn to solve the free-surface problem. Other investigations like Ruiz & Black\textsuperscript{[10]} provided insight into revealing the mechanisms within the liquid drop. Similarly, the experimental work by Girard et al.\textsuperscript{[11]} explained that the flow inside the drop was induced by the non-uniform temperature distribution along the interface. Although surface-tension-driven flow (i.e. Marangoni flow) and resultant bulk flow have been extensively studied, the influence of thermal effects of the substrate on Marangoni flow patterns is less well-understood. Further theoretical analysis has pointed out that the direction of Marangoni flow is determined by both the relative thermal conductivity\textsuperscript{[12]} and the relative substrate thickness\textsuperscript{[13]}, ultimately alters the deposition patterns. However, these investigations were limited to the case of non-heated substrate; the impact of substrate temperature was not taken into account. Furthermore, the above-mentioned studies were based on a pseudo-transient process which implies that the
solution is a steady-state solution rather than a pure transient one. In this paper, we present numerical computations on the evaporation of sessile droplets resting on a heated substrate; we are particularly interested in evaluating thermal effects of the substrate on Marangoni flow in the course of evaporation, and determining typical bulk flow structures as a function of influential parameters related to the substrate. Indeed, based a transient, fully coupled three-phase (liquid-solid-gas) model, we clearly determined three distinct behaviours of Marangoni flow inside an evaporating droplet.

The efficient numerical technique is a more reliable tool for simulating the droplet evaporation process owing to its capability to consider the fully coupled mechanisms, like heat and mass transfer, thermal effects of substrate, evaporative cooling and thermocapillary convection [14,15]. In the present work, the effects of the substrate on Marangoni flow with respect to the influential parameters (thermal conductivity, thickness and substrate temperature) in a wide range are investigated. For this purpose, we need to simulate the evaporation process for all the possibilities of influential parameters. An alternative approach is to utilise response surface method (RSM). This approach aims to construct a continuous parameters. An alternative approach is to utilise response surface method (RSM). This approach aims to construct a continuous parameters. An alternative approach is to utilise response surface method (RSM). This approach aims to construct a continuous response surface for different contact angles 

\[ \theta \]

Greek symbols

?? \( \vartheta \) \text{ contact angle [°]}
maintains a spherical-cap shape due to the effect of liquid-gas surface tension \( \sigma = \sigma_0 - \sigma_\Gamma (T - T_0) \), in which \( \sigma_0 \) and \( \sigma_\Gamma \) are the surface tension at the reference temperature \( T_0 \) and its (negative) gradient with temperature, respectively. Moreover, the buoyancy effect may be neglected in microgravity, i.e. Marangoni effect dominates the whole process. The bottom of the substrate is maintained at a temperature \( T_w \) while the gas far from drop is at temperature \( T_\infty \).

It is further assumed that the drop forms a constant contact line, i.e. the base radius of the drop remains pinned at \( R = R_0 \). The assumption of constant-radius model is consistent with the evaporation process observed in our experiments. In our ground and space experiments, we used a solid substrate and injected sufficient liquid volume to make sure that the contact line is well anchored to the substrate with radii being at the edge of the substrate. Under such conditions, the evaporation process observed follows essentially the constant-radius mode during most of the drop’s lifetime (90%). Therefore, it can reasonably be assumed that the contact radius \( R \) remains unchanged in our numerical simulations.

The physical problem is mathematically described by the continuity equation and incompressible Navier-Stokes equations in the liquid phase, the energy equations in all the domain regions (liquid-solid-gas), complemented by the diffusion equation for vapour in the gas phase:

In the liquid phase:

\[
\nabla \cdot \mathbf{u}_l = 0, \tag{1}
\]

\[
\rho_l (\partial_t \mathbf{u}_l + \mathbf{u}_l \cdot \nabla \mathbf{u}_l) = \nabla \cdot \left[ -p_l \mathbf{I} + \mu_l \left( \nabla \mathbf{u}_l + (\nabla \mathbf{u}_l)^T \right) \right], \tag{2}
\]

\[
\partial_t T_l + \mathbf{u}_l \cdot \nabla T_l = \kappa_l \nabla^2 T_l, \tag{3}
\]

where \( \mathbf{u}_l, p_l, I, \mu_l, T_l \) are the liquid velocity vector, hydrodynamic pressure, identity tensor, dynamical viscosity and temperature, respectively. Here, \( \omega_l = k_l / \rho_l c_l \) is the thermal diffusivity, whereas \( \rho_l, c_l \) and \( k_l \) refer to density, specific heat capacity and thermal conductivity for the liquid.

In the gas phase, vapour and heat transport in the atmosphere are solely by diffusion:

\[
\partial_t c = D_v \nabla^2 c, \tag{4}
\]

\[
\partial_t T_g = \alpha_c \nabla^2 T_g, \tag{5}
\]

where \( c \) stands for the mol concentration of the liquid vapour and \( D_v \) is the diffusion coefficient of vapour in air. For simplicity, we only consider the fluid flow in the liquid phase, hence the advection in the gas phase is neglected.

In the solid phase (substrate), the heat transfer is due to heat conduction:

\[
\partial_t T_s = \alpha_s \nabla^2 T_s, \tag{6}
\]

The boundary conditions are described hereafter. The bottom of the substrate is maintained at a temperature \( T_w \), in the range of 20–50 °C. Temperature continuity is applied at all the interfaces. The no-slip boundary condition is used at the solid-liquid interface and the non-permeable wall at the solid-gas interface. The continuity of heat flux is applied at both solid-liquid and solid-gas interfaces. On the outer boundary of the computational domain, chosen typically several dozens of times larger than the radius of drop, the values of an ambient temperature \( T_\infty \) and vapour concentration \( c_\infty \) are prescribed. More specifically, the ambient concentration \( c_\infty = H p/(RT_\infty) \), here, \( p(T_\infty) \) is the pressure at ambient temperature \( T_\infty \) and \( R = 8.31451 \) J/(mol K) is the universal gas constant.

At the liquid-gas interface, the condition of stress balance gives

\[
(n \cdot \mathbf{T}) \cdot n = -2(\sigma K + p_n), \tag{7}
\]

\[
(n \cdot \mathbf{T}) \cdot \mathbf{n} = \sigma \nabla T, \tag{8}
\]

in which \( n \) and \( \mathbf{n} \) are the unit normal and tangential vector to the liquid-gas interface (denoted by \( \Gamma \)), \( \mathbf{T}_l = -p_l \mathbf{I} + \mu_l \left( \nabla \mathbf{u}_l + (\nabla \mathbf{u}_l)^T \right) \) stands for the full stress tensor of fluid, \( K \) is the mean curvature of the liquid-gas interface, and \( \nabla T \) denotes the gradient tangent to the interface. It is worth noting that the right-hand side of Eq. (7) represents the pressure inside a droplet at equilibrium while that of Eq. (8) describes the driving force of bulk flow, i.e. the thermocapillarity. A characteristic velocity can also be inferred from the balance between viscous force \( \mu_l \nabla^2 U \) and thermocapillarity \( \sigma \nabla T \), which results in a characteristic velocity scale \( U \sim \sigma \Delta T / \mu_l \).

For the concentration of vapour \( c_\infty \) at drop surface, it assumes to be ideal gas and saturated according to the Clausius-Clapeyron equation, defined by

\[
c_\infty(T) = \frac{p_\text{sat}(T)}{R T}, \tag{9}
\]

\[
\ln \left( \frac{p_\text{sat}(T)}{p_{\text{ref}}(T)} \right) = -\frac{H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right), \tag{10}
\]

where \( p_\text{sat}(T) \) and \( p_{\text{ref}}(T) \) are the pressure of saturated vapour at temperature \( T \) and \( T_{\text{ref}} \), respectively.

The heat flux across the interface experiences discontinuity due to the latent heat of vaporisation \( H_{\text{vap}} \):

\[
k_g \nabla T_g \cdot \mathbf{n} = -k_l \nabla T_l \cdot \mathbf{n} = j_m H_{\text{vap}}. \tag{11}
\]

where \( j_m \) is the local evaporation flux, which can be calculated by Fick’s law:

\[
j_m = -D_v \nabla c \cdot \mathbf{n}. \tag{12}
\]

The condition of mass conservation across the interface leads to:

\[
\rho_l (\mathbf{u}_l \cdot \mathbf{n} - u_t) = j_m. \tag{13}
\]

where \( u_t \) is the normal velocity of the interface. We assume that the droplet remains a spherical-cap shape during the evaporation and that the contact line is pinned at \( R = R_0 \) (but the instantaneous contact angle \( \theta \) decreases with time). Given the total mass evaporation flux \( j_m = \int f \right d \Gamma. \) the normal velocity can be geometrically determined:

\[
u_t = \frac{j_m}{\pi \rho_l R_0^2} \left( \sqrt{1 - \left( \frac{\sin \theta}{R_0} \right)^2} \frac{1 + \cos \theta}{1 - \cos \theta} \right). \tag{14}
\]

Since we are seeking a transient solution, the initial conditions also need to be prescribed. At \( t = 0 \), the drop is a spherical cap with height \( h_0 \) and base radius \( R_0 \) (initial contact angle \( \theta_0 \) can be deduced by \( \theta_0 = 2 \tan^{-1}(h_0/R_0) \)); the bulk flow inside the drop is at rest (i.e. \( u = 0 \)). The initial pressure within the drop is set to the ambient pressure augmented by the Laplace pressure \( \Delta p = 2\sigma_0 / R_0 \). The initial temperature in the whole domain is set to an ambient temperature \( T_\infty = 20 \) °C. The drop evaporates into a non-saturated surrounding air with relative humidity \( H = 50 \% \) and the initial concentration in the vapour equals to \( c_\infty = H_{\text{vap}}(T_\infty) \).

3. Response surface, sensitivity analysis and inverse problem

The purpose of the present work is to investigate how the thermal properties of a heated substrate affect the direction of Marangoni flow inside an evaporating drop. For a given input parameter, the droplet evaporation process can be numerically simulated, but the results cannot be realised for all the possible situations due to
the restricted computational resources. Therefore, the response surface is constructed using the Kriging method, as a function of concerned input parameters, via a limited number of simulations. With the Kriging-based response surface, the proposed results of the Marangoni flow pattern can be easily predicted. The reliability of the constructed response surface is evaluated via a LOO cross validation criterion. After that, in order to investigate the correlation of multiple parameter, the Sobol’ sensitivity analysis method is introduced. Finally, an inverse problem is considered: in the case that one of the input parameters is ill-observed, it can be estimated via the Kriging-based response surfaces.

### 3.1. Response surface method

RSM is a useful tool to model the behaviour of a physical phenomenon with respect to the influential parameters variation, starting from a certain number of numerical experiments. Let Ω denote the considered input parameter space and \( X(\omega) \) denote the quantity of interest (QoI), given \( n \) measurements \( X(\omega_i) \) \( (s = 1, \ldots, n) \) at measured locations \( \omega_i \), the estimate of the QoI at an unmeasured location \( \omega \) is a weighted linear combination:

\[
\bar{X}(\omega) = \sum_{i=1}^{n} \lambda_i(\omega)X(\omega_i),
\]

in which \( \lambda_i(\omega) \) is the Kriging weight depending on the concerned unmeasured location, more exactly the distance between the unmeasured sample location \( \omega \) and the \( s \)-th sample location \( \omega_s \). The QoI \( X(\omega) \) is decomposed into

\[
X(\omega) = \beta(\omega) + \zeta(\omega).
\]

Here, the residual component \( \zeta(\omega) \) can be treated as a stationary random process with 0-mean and covariance \( \text{Cov}(\zeta(\omega), \zeta(\omega + \gamma)) = C(\gamma) \), where \( C(\gamma) \) is called the covariance function, and \( \beta(\omega) \) is a trend component. In this work, the spline covariance function is used to build the response surface, i.e.,

\[
C(\gamma) = \begin{cases} 
1 - 6(\gamma/\varepsilon)^2 + 6(\gamma/\varepsilon)^3, & \gamma < 1/\varepsilon \\
2(1 - \varepsilon)^3, & 1/2\varepsilon \leq \gamma < 1/\varepsilon \\
0, & \gamma \geq 1/\varepsilon
\end{cases}
\]

in which \( \varepsilon \) can be obtained via maximum likelihood estimation or empirical tuning.

The Kriging method minimises the variance of the estimator \( \text{Var}(\bar{X}(\omega) - X(\omega)) \) under the unbiasedness constraint \( \mathbb{E}[\bar{X}(\omega) - X(\omega)] = 0 \), from which Kriging weights \( \lambda_i(\omega) \) are obtained. It is remarkable that the Kriging estimate is a best linear unbiased predictor (BLUP). Actually, variant Kriging methods exist in the literature, among which Ordinary Kriging is used in this paper. This approach assumes that the trend component is constant but unknown, denoted as \( \beta(\omega) = \delta_0 \). The unbiasedness constraint implies that the sum of Kriging weights is equal to 1. Finally, minimising the error variance and adding a Lagrange parameter to fulfil the unbiasedness condition result in the Ordinary Kriging system:

\[
\begin{align*}
\sum_{i=1}^{n} \lambda_i(\omega_i)C(\omega_i - \omega_j) + \delta_0 = C(\omega_i - \omega) & \quad i = 1, \ldots, n \\
\sum_{j=1}^{n} \lambda_j(\omega) = 1
\end{align*}
\]

A response surface can be built with any number of samples, however, its reliability has to be assessed. Then, a LOO cross-validation strategy [23] is considered, which quantifies the relative variation of the constructed surface after removing one sample. The cross-validation value is expressed here as a global relative \( L_2 \) error:

\[
CV_s = \frac{\sqrt{\int_\Omega (\bar{X} - X^s)^2 \, d\omega}}{\sqrt{\int_\Omega \bar{X}^2 \, d\omega}},
\]

where \( \bar{X}^s \) is the Kriging response surface built without the \( s \)-th sample. A threshold \( \varepsilon \) on the maximum cross-validation value is imposed to assess the convergence, i.e., \( \max_s CV_s < \varepsilon \).

### 3.2. Sobol’ sensitivity analysis

Sensitivity analysis is adopted to quantify the contribution of each input parameter to the response variability, as well as to assess the coupling effects related to the multiple parameters of the response surface. The sensitivity of the model with respect to the input parameters is quantified via Sobol’ variance-based sensitivity indices [24], which are obtained from quasi Monte Carlo samples (Sobol sequences) [25]. The mean and variance estimates are obtained by

\[
\bar{X} = \frac{1}{n_{\text{qMC}}} \sum_{i=1}^{n_{\text{qMC}}} \bar{X}_i
\]

and

\[
\sigma^2(X) = \frac{1}{n_{\text{qMC}}} \sum_{i=1}^{n_{\text{qMC}}} (\bar{X}_i - \bar{X})^2,
\]

where \( n_{\text{qMC}} \) is the number of quasi Monte Carlo samples obtained from the Kriging meta-model of \( X(\Omega) \).

In order to compute the first-order sensitivity indices, two independent quasi Monte Carlo sample sets of \( \Omega \) are generated, denoted as \( \Omega_1 \) and \( \Omega_2 \). Each of the sample set is a \( q_{\text{qMC}} \times D \) matrix and \( D \) is the number of input variables. The Sobol indices \( S_j = \sigma_j^2/\sigma^2 \) for \( j \)-th variable is derived from the estimate of the variance and the partial variance \( \sigma_j^2 \):

\[
\sigma_j^2 = \frac{1}{q_{\text{qMC}}} \sum_{i=1}^{q_{\text{qMC}}} \sum_{\Omega_j} (\bar{X}_i(\Omega_2) - \bar{X}_i(\Omega_1))^2,
\]

where \( \Omega_j \) is the first samples set \( \Omega_j \), where the \( j \)-th column has been replaced by the corresponding column of the second sample set \( \Omega_2 \).

### 3.3. Inverse problem

In this article, not only simulation and prediction referring to a forward problem is considered, but also the inverse problem, which consists in finding the optimal values for the input model parameters, is investigated. In the real experiments, some of the input parameters cannot be accurately measured, we can use the Kriging-based response surface to estimate the unknown input. Let \( \phi \) be an unknown parameter and \( \Phi \) be the set of other input parameters. The former can be estimated via the observed results \( \theta \) and other input parameters:

\[
\hat{\phi} = \arg\min_{\phi} |f_i(\phi, \Phi)|, \quad i = 1, 2.
\]

It is remarkable that both response surfaces can be used to estimate an unknown parameter. However, the one with higher reliability, which is quantified by the LOO criterion, is preferable, since the corresponding response surface has less local fluctuations which lead to a more robust estimation. Furthermore, the estimation accuracy of each parameter also depends on the sensitivity of the proposed response surface with respect to the corresponding
parameter, which is reflected by Sobol’ index. In general, a parameter with higher sensitivity can be more accurately estimated, and vice versa.

4. Results and discussion

Numerical simulations of transient Marangoni flow together with heat and mass transfer have been performed using COMSOL Multiphysics. Numerical procedure and model validation can be found in [26]. In short, a grid sensitivity analysis has been first undertaken and grids consisting of 18,160 elements were selected to control the relative error within 1%. The computational domain is selected up to 50\(\text{R}_0\) of the surrounding air in order to eliminate the boundary effects and minimise the computational cost. As a further validation of the implemented numerical model, we first compare our numerical results with a previous work and explain three typical patterns of Marangoni flow inside an evaporating droplet. Then, thermal effects of substrate on the direction of Marangoni flow are investigated. In particular, their coupling mechanisms are taken into consideration, using response surface method and Sobol’ sensitivity analysis. Finally, the inverse problem is discussed for the ill-known influential parameter.

4.1. Marangoni flow pattern

We compare our numerical results with an asymptotic analysis reported in the literature [13], where a quantitative criterion to determine the direction of the induced Marangoni flow is described. The curve of the critical function \(R_N = \alpha(\theta)\) is plotted in Fig. 2 together with the symbols obtained from our computations. Here, \(R_N = h_R k_L / R_0 k_s\) is a non-dimensional parameter: the product of relative substrate thickness \(h_R/ R_0\) and relative thermal conductivity of liquid and substrate \(k_L/k_s\). The analysis of Xu et al. [13] for a non-heated substrate indicates that for the values of \(R_N\) above the curve, i.e. \(R_N \geq \alpha(\theta)\), the resultant Marangoni flow is directed radially outward along the liquid-gas interface. On the contrary, if \(R_N < \alpha(\theta)\), the temperature decreases with distance from the contact line to the apex, the direction of the flow is reversed. The presented numerical model for a sessile droplet evaporating on a heated substrate reproduces these features with respect to the direction of bulk flow. It is found that droplets evaporating on a heated substrate with poor thermal conductivity undergo a three-stage lifetime: inward flow (open symbol), multicellular flow (semi-filled symbol) and outward flow (filled symbol). It is worth noting that our numerical model is valid in a wider range of \(R_N\) whereas the analytical prediction is limited to small values of \(R_N\), i.e. \(R_N < 0.3\).

To better understand the physical phenomenon related to a poor thermal conductivity of the substrate, it is useful to first identify the structure of flow field within the drop; the velocity and temperature field are illustrated in Fig. 3. It can be seen that bulk flow exhibits different behaviours in the course of evaporation, which can be distinguished as: (a) Inward flow pattern: at the beginning the induced Marangoni flow is directed radially inward along the liquid-gas interface. Recall that the apex of the droplet is expected to be coolest due to a longer conduction distance from the substrate. As such, a positive tangential temperature gradient is generated from the droplet apex to the triple line, then Marangoni stress drives the hot water (near the triple line) to the cold region (at the top) resulting in an anticlockwise circulation; (b) Multicellular flow pattern: when the contact angle diminishes continuously during droplet evaporation and reaches a critical value \(\theta_1\), the surface temperature is no longer monotonic, consequently multiple clockwise and anticlockwise convective cells appear. The appearance of multicellular flow pattern refers to the breakup of the flow inside the droplet and corresponds to a nonmonotonic surface temperature function of \(r\) with maximal or minimal extremum along the interface due to convective instability; and (c) Out-

![Fig. 2](image-url) The direction of Marangoni flow in evaporating droplets on non-heated substrates. The solid line is the asymptotic solution \(R_N = \alpha(\theta)\) [13], where \(\alpha(\theta) = |\sin(2\theta) - 4(1/2 - \theta/\pi)\tan(\theta/2))/(4(1/2 - \theta/\pi) + 2\sin^2(\theta))\) is a function of the contact angle. Computations are conducted for an initial contact angle \(\theta_0 = 50^\circ\) and instantaneous contact angle \(\theta\) decreased with time. Regions above and below the line correspond to flow directions sketched in the figure; open symbol represents the inward flow; filled symbol stands for the outward flow and semi-filled symbol means the multicellular flow.
ward flow pattern: the temperature distribution is inverted with respect to outward flow. If the contact angle decreases below a threshold of \( \theta_2 \), the energy is not readily supplied to the contact line region where the local heat flux is the largest. In this situation the heat conduction through the drop is dominant and the drop is warmest at the centre, thereby leading to an outward flow behaviour.

4.2. Thermal effects of substrate on Marangoni flow: single influential factor

In this section, the influence of thermal effects of substrate on the direction of Marangoni flow is numerically investigated. We highlight that during evaporation three influential factors determine the flow patterns inside the drop: relative thermal conductivity, relative thickness and relative substrate temperature. Each factor contributes to forming different structures of flow field and in turn controlling the particle deposition patterns.

4.2.1. Effect of relative thermal conductivity

The water drop evaporation with same initial conditions and various substrates is numerically studied. We choose six kinds of substrates, namely PTFE, glass, POM, PDMS, Macor and Al, for their widely differing thermal conductivities. Relevant physical properties of the liquids and substrates are listed in Table 1. It has been found that the thermal conductivities of the liquid and substrate strongly affect the structure of flow field [27]. In order to better characterise the influence due to thermal conductivities, we introduce a dimensionless number \( k' = k_i/k_t \) in the following discussion.

In Fig. 4, two characteristic contact angles as a function of the relative thermal conductivity \( k' \) for a water droplet in the course of its evaporation are plotted. These two contact angles mark a transition of bulk flow pattern as a result of matching the heat transfer from the substrate and heat flux losing through the liquid-gas surface, associated with evaporative cooling effect. For a relative higher \( k' \), say \( k' > 0.5 \), the bulk fluid flow clearly undergoes three different radial patterns as illustrated in Fig. 3: the transition from an inward flow to an outward pattern corresponds to the change of sign of the tangential component of the temperature gradient at the interface, passing through a multicellular flow pattern. In a manner similar to that observed in the coffee-ring problem [28], the particles ultimately assemble to the region near triple-line. In contrast, if \( k' \) is extremely small \( (k' \sim 0) \), for instance, a water drop deposited on an Al substrate, then the energy provided from the substrate is enough for evaporation process, which results in an inward flow until the end of the evaporation. This can be explained by the fact that the area close to the triple-line is the warmest due to adjacent perfectly conducting substrate and the apex of the drop is colder, partially due to the long distance conduction. A similar behaviour was reported previously in [12] that Marangoni flow ultimately forces the particles toward to the centre and there will be no possibility for a multicellular flow arises.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \rho ) (kg/m(^3))</th>
<th>( \mu ) (Pa s)</th>
<th>( k ) (W/m K)</th>
<th>( c_p ) (J/kg K)</th>
<th>( H_{vap} ) (kJ/kg)</th>
<th>( \sigma ) (N/m)</th>
<th>( k'_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>997</td>
<td>0.89 \times 10^-3</td>
<td>0.6</td>
<td>4070</td>
<td>2440</td>
<td>71.97 \times 10^-3</td>
<td>2.4</td>
</tr>
<tr>
<td>Air</td>
<td>1.178</td>
<td>1.79 \times 10^-3</td>
<td>0.025</td>
<td>1006</td>
<td></td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>2200</td>
<td>0.25</td>
<td>1010</td>
<td></td>
<td></td>
<td>1.935</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>2200</td>
<td>0.625</td>
<td>730</td>
<td></td>
<td></td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>POM</td>
<td>1420</td>
<td>0.31</td>
<td>1500</td>
<td></td>
<td></td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>PDMS</td>
<td>970</td>
<td>0.16</td>
<td>1460</td>
<td></td>
<td></td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Macor</td>
<td>2520</td>
<td>1.46</td>
<td>750</td>
<td></td>
<td></td>
<td>1.935</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>2700</td>
<td>240</td>
<td>900</td>
<td></td>
<td></td>
<td>0.0025</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Temperature field (left side) and bulk flow pattern (right side) within a water droplet evaporating on a PTFE substrate. Initial conditions: \( \theta_0 = 50^\circ \), \( R_0 = 1 \) mm, \( h_0 = 0.1 \) mm, \( T_\infty = T_w = 20^\circ \) C, \( H = 50\% \), and \( p_\infty = 1 \) atm. The streamlines are shown at different behaviours of Marangoni flow (denoted by three characteristic contact angles: \( \theta_0, \theta_1 \) and \( \theta_2 \)).
4.2.2. Effect of relative thickness

We also study the dependence of Marangoni flow on the substrate thickness since it has similar role as the thermal conductivity [29]. Here, we define \( \frac{h_s}{C_s} = \frac{h_s}{R_0} \) as relative thickness, representing the ratio of the substrate thickness to the contact radius of the droplet. Fig. 5 shows that the different regimes of convective Marangoni flow shift when the contact angle diminishes with respect to relative thickness. It displays that for a very thin substrate \( (h_t - 0) \), the flow circulation is always radially inward due to a positive temperature gradient from apex to the triple-line. In this case heat transfer from the substrate dominates the whole process, hence surface temperature distribution remains monotonic corresponding to the inward flow of region I. Otherwise, the total amount of energy from the substrate is not enough to support evaporation and associated evaporative cooling effect, then convective multicellular flow occurs in region II and ultimately reverses the flow direction in region III.

4.2.3. Effect of relative substrate temperature

In terms of heated substrate, the evaporation rate is expected to be accelerated by higher temperature of substrate and consequently leads to enhance thermocapillary flow together with the appearance of multicellular flow pattern. The objective here is to depict Marangoni flow transition with multiple relative substrate temperature \( T_{w*} = \frac{(T_s - T_{w*})}{T_{w*}} \), that is, the relative difference between the substrate and ambient environment, ranging from 0 to 2. It can be concluded from the \( T_{w*} - \theta \) plane in Fig. 6 that at varied substrate temperature the convective multicellular flow occurs at the same contact angle \( \theta_1 \), different from the other influential factors of \( k_r \) or \( h_t \). The plotted curves also make it clear that the convective Marangoni flow lasts longer as the temperature becomes higher. This result is helpful for the prediction of particle deposition: multicellular flow pattern always appear at a certain height of droplet with respect to a wide range of substrate temperature during evaporation. If the deposition needs to be performed in a more regular pattern, then the substrate temperature must be decreased.

4.3. Coupling mechanisms of the substrate on Marangoni flow: multiple factors

In what follows, we attempt to emphasis the coupling mechanisms of multiple influential factors \( (k'_r, h'_t \text{ and } T_{w*}) \) by using
response surface method and Sobol’ sensitivity analysis. It is the first study of its kind in solving the coupling effects on Marangoni flow by using the novel method RSM and SSA. In this section, we pay attention to three highlighted issues. The first one is to predict the multicellular flow pattern at any possible model input in a given range using RSM. Secondly, we analyse the coupling mechanisms via SSA. Finally, the inverse problem in terms of estimating unknown input parameter is discussed.

4.3.1. Predict the multicellular flow pattern using RSM
Since the internal flow pattern subjected to a wide range of influential parameters, it is impossible to compute all the possibilities due to the high computational cost. To globally evaluate the correlation between different influential factors, Kriging-based response surfaces are built with a limited number of various \((k', h')\) and \((R_0, T_w)\), consequently the Marangoni flow patterns for any input value in a given range could be rapidly forecast.

At first, the correlation of relative thermal conductivity and relative thickness is studied. A regular grid with 20 samples in \((k', h')\) is used, which is shown by the crosses in Fig. 7. Generally speaking, the required number of samples of the grid depends on the dimension of the input parameters, the physical range of each input parameter and the complexity of the response. In this case, the 20-sample grid is proven to be reasonable such that the Kriging response surface converges; further tests with additional samples do not significantly increase the response surface reliability. Then, the response surfaces for the flow patterns reflected by the characteristic angles \(\theta_1\) and \(\theta_2\) are constructed using the Kriging method, as is shown in Fig. 8. The two surfaces represent the three behaviours of Marangoni flow: inward flow (I), multicellular flow (II) and outward flow (III), which are separated by the response surfaces \(f_{\theta_1}\) and \(f_{\theta_2}\). The color maps (b) and (c) are the projections of \(f_{\theta_1}\) and \(f_{\theta_2}\) in the \((k', h')\) plane, respectively. To further assess the validity of the Kriging-based response surface, the LOO cross-validation is computed: the maximum cross-validation are respectively \(max CV_f(\theta_1) = 1.44\%\) and \(max CV_f(\theta_2) = 3.98\%\), which means that the second response surface is less robust due to more irregular observations from the sample points.

Then, the Marangoni flow pattern could be simply forecast via the constructed response surface without further numerical simulation, within the range of \(k' \in [0.375], h' \in [0.1, 0.4]\). Here, we consider six samples, which are labelled by the circles in Fig. 7. For each case, the corresponding critical angles \(\theta_1\) and \(\theta_2\) are computed via the numerical simulations and compared with the output of the response surfaces. The forecast value and the corresponding relative error (RE) for the six points obtained from the surfaces \(f_{\theta_1}\) and \(f_{\theta_2}\) are shown in Table 2. By given the used liquid and substrate \((k'_0 = 3.16)\) and geometrical parameters like initial contact radius and substrate thickness \((h'_0 = 0.2)\), we can easily forecast the convective multicellular flow occurs at \(\theta_1 = 0.4529\) and disappears at \(\theta_2 = 0.3788\) from the response surfaces. The observed value of numerical simulation shows that the multicellular flow is at 0.454 and 0.384 for different contact angle \(\theta_0\), which demonstrates a good agreement. It is clear that \(\theta_1\) is accurately forecast by the Kriging-based response surface at all the six points with a mean RE being 1.56%. By contrast, the forecast of \(\theta_2\) is less accurate whose mean RE is around 4%, but in general the error is acceptable. Actually, the higher error of \(\theta_2\) forecast can be explained by the lower reliability of the response surface \(f_{\theta_2}\), which can be observed from Fig. 8 and justified by the LOO cross-validation values.

We now study the correlation between relative thermal resistance and relative substrate temperature \((R_0, T_w)\). Since \(k'_c\) and \(h'_c\) are involved together in the thermal resistance of the substrate [30], let \(R_0 = k'_c h'_c\) denote its variation. The function relationship of different characteristic angles with respect to \(R_0\) and \(T_w\) are investigated. Numerical computations of \(\theta_1\) and \(\theta_2\) are performed for 20 discrete points at \((\langle R_0, T_w \rangle) : R_0 = 0.125, 0.25, 0.387, 0.63, 0.75; T_w = 0.0.5, 1, 1.5)\), as shown in Fig. 9 (crosses). As previously, the response surfaces of \(\theta_1\) and \(\theta_2\) are constructed using the Kriging method; the results are displayed in Fig. 10. Then, the LOO cross validation is computed to assess the reliability of the constructed response surface. Here the maximum value of \(CV_f\) is 2.66% for \(f_{\theta_1}(R_0, T_w)\) and 5.61% for \(f_{\theta_2}(R_0, T_w)\), which implies that both surfaces are reliable enough, given that only 20 samples are used.

Furthermore, the forecast is also proceeded for six sample points, which are indicated by the circles in Fig. 9. The forecast results of \(\theta_1\) and \(\theta_2\) and the corresponding REs are shown in Table 3. Results reveal that for a water droplet evaporating on PTFE substrate with \(T_w = 35\) °C, i.e., \((R_0, T_w) = (0.48, 1.25)\), \(\theta_1\) and \(\theta_2\) are equal to 0.44 and 0.2172 in numerical work, while in the forecast approach, its value deviates from the RSM keeping 0.4272 and 0.2218 and the relative error is less than 3%. It is obvious that the forecast of \(\theta_1\) is as accurate as the previous \((k'_c, h'_c)\) case. In addition, the forecast of \(\theta_2\) is less accurate (mean RE is 3.49%) than \(\theta_1\) due to a lower reliability of the response surface \(f_{\theta_2}\).

4.3.2. Coupling mechanisms on Marangoni flow
The Sobol sensitivity analysis is introduced to investigate the coupling mechanisms of Marangoni flow in two aspects: with or without heated substrate. The imposed temperature of a non-heated substrate equals to the ambient value \(T_w = T_a\). While for a heated substrate \(T_w\) ranges from 20 °C to 50 °C. There is no doubt that the relationship between input and output variables shown in Figs. 8 and 10 is non-linear, which cannot be easily represented by a certain function. Therefore, we can use Sobol’ index to analyse the sensitivity: higher Sobol’ index implies higher sensitivity of the corresponding input parameter, and vice versa.

For droplet evaporating on a non-heated substrate, the Sobol index for \(k'_c\) and \(h'_c\) for the response surfaces plotted in Fig. 8 is computed: \(S_{f_1}(k'_c) = 81.31\%, S_{f_2}(h'_c) = 15.95\%\), \(S_{f_1}(k'_c) = 68.39\%\), and \(S_{f_2}(h'_c) = 25.51\%\). It is obvious that the convective Marangoni flow reflected by \(\theta_1\) and \(\theta_2\) are much more sensitive with respect to \(k'_c\) than \(h'_c\): this conclusion can also be observed in Fig. 8. The result also indicates that convective Marangoni flow strongly depends on the relative thermal conductivities: when the relative...
thermal conductivity changes a little, the convective multicellular flow changes a lot. On the other hand, the relative thickness has little impact on the resulting flow patterns due to its weak sensitivity.

In terms of heated substrates, Sobol’ indices are also calculated:

\[
S_{h_1}(\theta) = 0.06; \quad S_{h_1}(T) = 1.15; \quad S_{h_2}(T) = 42.9; \quad S_{h_2}(\kappa) = 48.25.
\]

It is remarkable that \( h_1 \) is almost independent of \( T \), so the substrate temperature has little influence on the appearance of the convective Marangoni flow. However, \( h_2 \) is sensitive with respect to both influential parameters, indicating that thermal resistance of the substrate and substrate temperature have the same impact on the duration of the convective Marangoni flow.

### 4.3.3. Inverse problem

Typically, inverse problem relates to the situation that the input parameters cannot be accurately measured in some experiments. For example, the thickness of a very thin substrate is difficult to measure, since the contact measurement technique may destroy its surface structure. Thus, the thickness can be estimated by an indirectly method with the known numerical results containing the possible range and the Kriging-based response surface \( f_{h_1} \) and \( f_{h_2} \). In what follows, we give an example to explain how to use the method to estimate the unknown parameters of \( \kappa \) or \( h_s \).

The inverse problem is considered for the six sample circles in Fig. 7. First, \( \kappa \) is assumed to be an unknown parameter and is

<table>
<thead>
<tr>
<th>( (\kappa, h_s) )</th>
<th>Forecasting ( h_1 )</th>
<th>Forecasting ( h_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (1.765, 0.15) )</td>
<td>0.415</td>
<td>0.4145</td>
</tr>
<tr>
<td>( (1.765, 0.25) )</td>
<td>0.383</td>
<td>0.3925</td>
</tr>
<tr>
<td>( (1.765, 0.35) )</td>
<td>0.361</td>
<td>0.3818</td>
</tr>
<tr>
<td>( (3.16, 0.1) )</td>
<td>0.502</td>
<td>0.5014</td>
</tr>
<tr>
<td>( (3.16, 0.2) )</td>
<td>0.454</td>
<td>0.4529</td>
</tr>
<tr>
<td>( (3.16, 0.3) )</td>
<td>0.416</td>
<td>0.4133</td>
</tr>
<tr>
<td>Average</td>
<td>1.56</td>
<td>3.96</td>
</tr>
</tbody>
</table>
estimated by the measurements of $h_i/C_3$ and $h_i/C_3$ ($i = 1, 2$) via Eq. (23).

The estimation results are shown in Table 4. Here, $k^*_r$ represents the estimation value of relative thermal conductivities, the relative error (RE) is also shown. It is observed that $k^*_r$ is precisely estimated, except the two points (1.765, 0.25) and (1.765, 0.35), which are in a region less sensitive to $k^*_r$ (see Fig. 8 (b)). Similarly to the forecast problem, the parameter estimation via the surface $f_{h_i}$ results in a higher error, as expected. Again, due to the lower reliability of the response surface and more local fluctuation, the estimation is less robust than using $f_{h_i}$.

Similarly, in the case of unknown $h^*_r$, the parameter can also be estimated by the observed $k^*_r$ and $\theta_i$ ($i = 1, 2$), as in the previous case. However, due to the low sensitivity of $h^*_r$ with respect to $\theta_1$ and $\theta_2$, which is reflected by Sobol’ indices (less than 11% for the both response surfaces), the estimation errors are relatively high, especially for the sample (1.765, 0.25) and (1.765, 0.35). The computation results are shown in Table 5. Furthermore, the estimates obtained from $f_{h_i}$ is more precise than $f_{h_i}$ due to the higher reliability of the constructed response surface.

We briefly conclude the use of the Kriging-based response surface and the strategy in the problem of forecasting the behaviour of Marangoni flow and the inverse problem. The observation of $\theta_2$ is more irregular distributed than $\theta_1$, such that the response surface is relatively less reliable. Therefore, in the forecast problem $\theta_1$ can be more accurately given. For the same reason, it is well-advised to use the response surface $f_{h_i}$ in the parameter estimation problem. Besides, the estimation accuracy of input parameter in the inverse problem largely depends on the parameter sensitivity.
In this case, since both response surfaces are more sensitive to $k_r/C_3$ than to $h_s/C_3$, the former can be well-estimated while the latter generally has a more imprecise estimate.

5. Conclusions

We have presented numerical computations on the evaporation of sessile droplets resting on a heated substrate. Special emphasis has been put on evaluating thermal effects of substrate on Marangoni flow in the course of evaporation. Three influential factors within thermal properties of substrate (e.g. relative thermal conductivity, relative substrate thickness and relative substrate temperature) have been investigated. We found a strong impact on the behaviours of Marangoni flow and clearly identified three characteristic bulk flow structures as a function of influential parameters when the contact angle diminishes with time during evaporation. These Marangoni flow patterns generated by the non-uniform temperature distribution along the interface allow to predict and control the evaporative deposition patterns. The underlying mechanism of the transition is primarily a result of matching the heat transfer from the substrate and heat flux losing through the liquid-gas interface, associated with evaporative cooling effect.

In order to better understand the Marangoni flow pattern with respect to the influential parameters in a wide range, a Kriging-based response surface method is proposed to forecast the flow patterns for any influential parameter in a given range. This approach, which only needs a limited number of simulations corresponding to a few discrete input parameters, has been applied successfully in the understanding of the hydrodynamics within evaporating droplets. The Sobol sensitivity analysis is recommended to quantify the relative importance of each influential parameter in determining the coupling mechanisms of Marangoni flow. The proposed method is also able to estimate the environmental parameters which may be ill-observed in the real situations. It is remarkable that the computational cost of Kriging-based response surface method and Sobol’ sensitivity analysis is very low, particularly compared with the numerical simulation of Marangoni flow. Therefore, the combination of computer simulation and response surface method provides a useful guide to interpreting experimental results, especially in an uncertain environment.

Conflict of interest

None declared.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grants Nos. 11532015, 11302236), by the Strategic Priority Research Program on Space Science, Chinese Academy of Sciences (Grants Nos. XDA04073000, XDA04020202-02), and by the CNES (Centre National d’Etudes Espa-
The work was conducted within the framework of a joint Doctoral Training Program (DPP) between Chinese Academy of Sciences (CAS) and Centre National de la Recherche Scientifique (CNRS). Funding from the CAS and support from the CNRS/CNES are gratefully acknowledged.

References