STABILITY OF EVAPORATING SESSILE DROPS COMPRISING BINARY MIXTURES

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1.   BACKGROUND AND MOTIVATION

In nature, as well as in a broad range of everyday and industrial applications, droplets occur and often consist of more than one component. The fluid dynamics, heat and mass transfer phenomena of such mixtures are still not fully understood. The evaporation and spreading dynamics of a binary mixture sessile droplet are complex due to the rich interplay of thermal and solutal Marangoni stresses alongside the hydrodynamic transport, evaporation, mass diffusion, and capillary stress of the droplet.

Droplet evaporation is an important area of research for applications such as phase change cooling of microelectronics [1]. Most coolants are not pure fluids but are often made up of mixtures. Therefore, it is important to understand more about the fundamentals and phenomena that govern such mixtures. We aim to understand more about these key heat and mass transfer interactions through investigating the stability of a volatile bi-component sessile droplet with high wettability (where droplet contact angles < 30°) comprising ethanol-water deposited onto a heated substrate. Previous experimental results on evaporating volatile mixtures of ethanol-water show fingering contact line instabilities in an "octopi" type arrangement (Figure 1) [2]. Large surface tension gradients occur between the apex and the contact line of the droplet, and rapid spreading occurs due to high ethanol concentration within the drop. We identify and investigate these instabilities of a single volatile sessile droplet comprising ethanol-water through a detailed theoretical model.
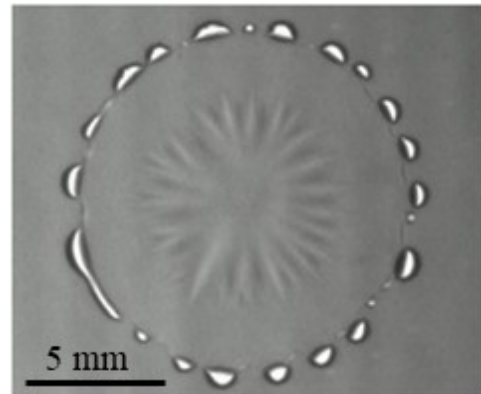

Figure 1: Experimental results for an evaporating droplet comprising a 50% ethanol and water [2]. Instabilities at the contact line are shown.

2.   PROBLEM STATEMENT AND METHOD

We obtain the transient base state, a_0, using a one-sided model (Figure 2) under the lubrication approximation [2] before 'freezing' the base state at a small time of $t = 0.1$ and introducing small disturbances, a_1, in the azimuthal direction, to perform a quasi-steady-state linear stability analysis,

$$a(r,\ \theta,\ z,\ t) = a_o(r,z) + \epsilon a_1(r,z)e^{ik\theta+\omega t} \tag{1}$$

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where ω corresponds to the complex eigenvalue and k is the real part of the wavenumber in the azimuthal direction, θ, t represents time, and ϵ is the perturbation amplitude assumed to be infinitesimally small. Subscript 0 denotes the instantaneous base state variables and subscript 1 denotes the perturbations of these variables.
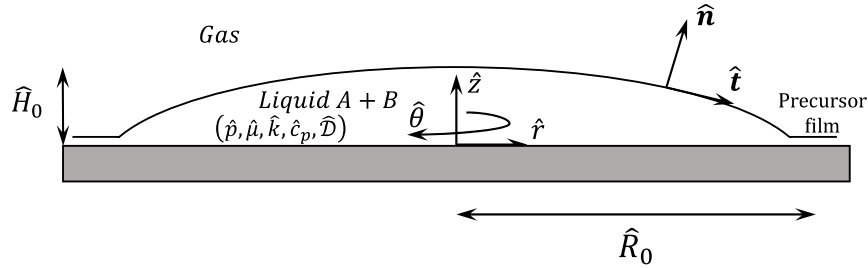

Figure 1: Schematic of droplet flow geometry in cylindrical coordinates where $\hat{H}_0$ and $\hat{R}_0$ are the initial height and radius of the drop, respectively. The drop is sufficiently thin such that $\hat{H}_0/\hat{R}_0 \ll 1$ and it sits on a heated substrate. $\hat{n}$ and $\hat{t}$ represent the outward unit vectors in the normal and tangential directions from the interface, respectively. A thin precursor film is assumed to exist on the solid surface.

The base state equations are derived assuming an ideal miscible mixture comprising of two volatile, miscible liquids A and B. Liquid A is the more volatile component in the bi-component mixture and liquid B is the less volatile component. The droplet is considered Newtonian and we assume the liquid mixture to be incompressible. The surface tension linearly depends on temperature and concentration. The gas phase in our system is considered to be negligible, giving a one-sided model assumption. We also make an assumption that the time-scale of evaporation is longer than the time-scale of instabilities which enables us to perform quasi-steady instability analysis. The stress singularity at the contact line is avoided by including a thin precursor film.

We assume that the precursor layer comprises of the least volatile component only and that there is no phase-change flux in the precursor layer. These assumptions are similar to those used in Williams et al (2021) [2]. In order to avoid any artificial diffusion and condensation behaviour occurring in the precursor film due to the addition of the second component, a forcing-type penalty function is applied to the concentration equation to control the composition of the precursor film. This forces the concentration of the more volatile component, x_A, to zero. This assumes that the more volatile component evaporates from the precursor film immediately, leaving the film to consist solely of the lower volatile component, B.

Once we obtain a transient base state for an axisymmetric flat droplet deposited over a precursor layer under lubrication approximation, the quasi-steady state stability analysis is performed. The perturbations are applied to the governing equations and boundary conditions as per equation 1, and then this constructs an eigenvalue problem where the stability of the flow is determined from the real part of the eigenvalues ω,

$$\mathbf{J}\mathbf{v} = \omega\mathbf{M}\mathbf{v} \qquad (2)$$

where J is the Jacobian matrix, M is the mass matrix, ω is the complex eigenvalues ($\omega = \omega_R + i\omega_I$) and v are the corresponding eigenvectors.

The real part of the eigenvalue, ω_R, represents the temporal growth rate of the perturbation which gives information about the stability of the flow in our linear system. If all the ω_R eigenvalues are negative, the corresponding eigen modes will decay, making the binary system linearly stable. However if a growth rate ω_R is positive, this corresponds with growing eigen modes which in turn makes the system linearly unstable.

The perturbed linear stability equations for the binary system are solved for the unknown system variables and their perturbations using the Newton-Raphson method in the same Fortran90 program used for the transient base state. The wavenumbers in the azimuthal direction are then evaluated to reveal the most dangerous unstable modes, shown in the results section below.

3.   RESULTS

3.1   Pseudo-single component evaporating sessile droplet

We first consider a pseudo-single component case where all property ratios are set to 1 and the initial concentrations of each component are equal. The dispersion curve and eigenvector in the perturbed height associated with the most unstable eigenmode are shown in Figure 3. These results agree with those predicted by the Williams *et al.* [2] model for a pure single component droplet. The results indicate that the system is linearly unstable, and the disturbances are localised at the droplet contact line.
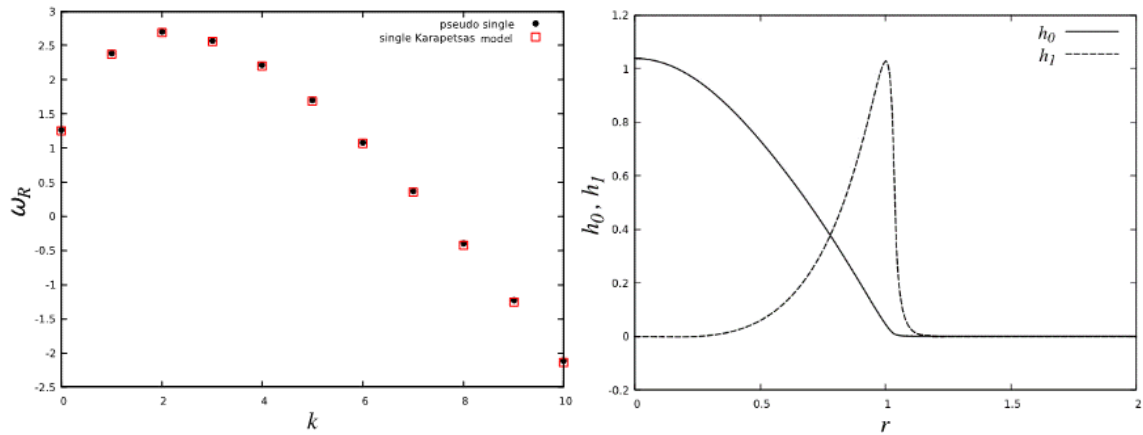

Figure 3: Plots (a) and (b) depict the dispersion curve showing the real part of the eigenvalues, ω_R, for each wave number, k and the resulting eigenvector in the height, h_1, at the most unstable mode $k_d = 2$ alongside the corresponding base state, h_0, at the frozen time $t = 0.1$ s for pseudo-single component case. The dispersion plot (a) is compared to Karapetsas model [2] for pure single component droplet. h_1 is multiplied by an arbitrary scaling factor.

3.2   Bi-component volatile sessile droplet

We now consider droplets comprising volatile ethanol-water mixture in order to compare with previous experiments which focused on these mixtures [2]. Preliminary results in a binary droplet of initial ethanol concentration $x_{A0} = 0.5$ and substrate heated at a constant dimensionless temperature are shown in Figure 4. These results show that the addition of another component significantly promotes the instabilities represented by a substantial increase in the growth rates, given by the real part of the eigenvalues, ω_R, and the most unstable eigenmode increases from $k_d = 2$ to $k_d = 6$.
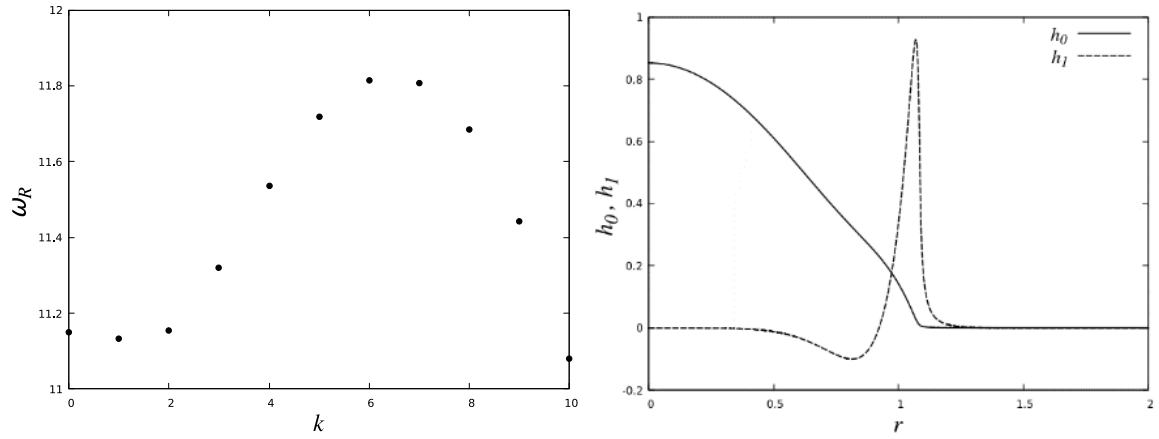
Figure 4: Plots (a) and (b) show the dispersion curve showing real part of eigenvalues, ω_R, for each wave number, k and the eigenvector in the height, h_1, at the most unstable mode $k_d = 6$ alongside the corresponding base state, h_0, at the frozen time $t = 0.1$ s for a bicomponent case with initial concentration $x_{A0} = 0.5$. h_1 is multiplied by an arbitrary scaling factor.

The number of active instability modes is much higher for the bi-component case, with all perturbation growth rates giving strongly positive values for all wavenumbers, including $k = 0$. This shows the addition of another component increases instabilities significantly in comparison to the pseudo single component case, and it also suggests our initial quasi steady state assumption may not be fully representative of our system here. To validate these results, as well as uncover more information on the characteristics of the instability modes, a transient growth linear stability analysis is currently being carried out for the volatile binary droplet system. Performing a transient growth stability analysis on our bi-component droplet theoretical model will help further understand the development of these instability modes. The method for this is outlined in the following section.

3.3 Parameter Analysis

After conducting an elaborate analysis to understand the effect of physical parameters on the stability of evaporating bi-component sessile droplets using our quasi-steady state stability analysis, it was found that the surface tension ratio, σ_R, and ethanol concentration, x_{A0}, play a key role in the evaporation dynamics and instabilities. For the bi-component case, initial concentrations and surface tension ratios were varied between $0.1 \leq x_{A0} \leq 1$ and $1 \leq \sigma_R \leq 4$, respectively. The most unstable wave number and growth rate were mapped onto a 2D plot against concentration and surface tension ratio (Figure 5) to show how the instabilities are affected with these parameters. These show that by increasing concentration of the more volatile component and/or increasing surface tension ratio, the flow in the droplet becomes significantly more unstable linearly with a wider range of unstable modes characterised by larger growth rates.
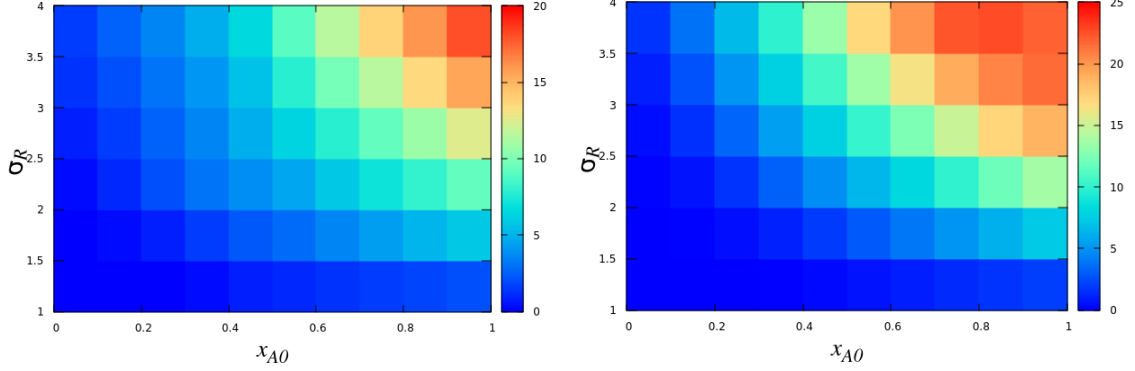
Figure 5: 2D contour plots showing the most unstable (a) wave numbers, k_d and (b) eigenvalues, ω_d, respectively, for each corresponding concentration x_{A0} and surface tension ratio σ_R for bi-component ethanol-water mixture.

4. TRANSIENT GROWTH ANALYSIS

From the results, the quasi-steady state linear stability analysis performed on the volatile binary droplet system demonstrates that the addition of a second more volatile component strongly destabilises the system. For a bi-component case, there are clearly a much larger number of multiple competing active instability modes. The growth rates are significantly higher than the single component case, with the base state showing similar growth rates to the instability modes. The larger number of competing active modes means our quasi-steady state assumption may not be fully representative of our system. In order to uncover more information regarding the characteristics of these modes and achieve a better understanding, a transient growth linear stability analysis is currently being developed.

A transient growth stability analysis will assess the instabilities of the droplet as a time dependent problem which will give us more information about the development of these instability modes as well as validate the results already obtained from the quasi-steady state analysis. This will let us further analyse what truly governs these instabilities.

Similarly to the quasi-steady state analysis, small disturbances are applied to the base state governing equations and boundary conditions in the azimuthal direction θ,

$$a(r,\ \theta,\ z,\ t) = a_o(r,z,t) + \epsilon a_1(r,z,t)e^{ik\theta} \qquad (3)$$

Where a is a general system variable and subscript 0 denotes the base state terms and subscript 1 denotes the perturbed terms. Similar to the quasi-steady state stability analysis, ϵ is assumed to be an infinitesimally small perturbation amplitude, and k is the wavenumber where only the real part is considered here. Here, i is the $\sqrt{-1}$.

These perturbed stability equations are then solved alongside the base state equations as a time dependent problem in a Fortran90 program to find the growth rates for a range of wavenumbers in order to produce similar stability dispersion curves to compare to our original quasi-steady state analysis study.

The following definition from Edmonstone et al [3] is used to evaluate the growth rate, ω_i, of a perturbation,

$$\omega_i = \lim_{t \to \infty} \frac{\ln \mathcal{G}_i(t)}{2t} \qquad (4)$$

Where i represents the eight unknown variables in the bi-component droplet system; the dimensionless height of the droplet interface h, dimensionless total pressure p, dimensionless flow velocities f and g in the radial and azimuthal directions, respectively, dimensionless temperature θ, dimensionless evaporative fluxes of the more and less volatile components J_A and J_B, respectively and the concentration of the more volatile component, x_A. $\mathcal{G}_i$ is the amplification ratio which is defined by the energies, $E_q(t)$, relating to each unknown variable, i, and it's perturbation.

$$E_q(t) = \frac{\dfrac{E_{i1}}{E_{i0}(t)}}{\left(\dfrac{E_{i1}}{E_{i0}}\right)(t=0)} \tag{5}$$

This is further detailed and outlined in Edmonstone et al (2006) [3].

This alternative method of assessing the instabilities through transient growth linear stability analysis is currently underway, with results expected soon to compare to our dispersion curves perturbation eigenvectors results from the original quasi-steady state linear stability analysis.

5.   CONCLUSIONS

We developed a quasi-steady state linear stability analysis for a binary droplet system and the instabilities have been investigated. Preliminary results from the stability analysis qualitatively agree with the contact line instabilities seen in experiments for evaporating volatile binary droplets comprising ethanol-water mixtures. An increased initial concentration of the more volatile component (ethanol) is shown to destabilise the droplet system and to increase the solutocapillary forces which enhance spreading. This shows that the solutal Marangoni stress is a strong destabiliser in bi-component droplet evaporation. Our analysis further shows several competing modes for bi-component drops, therefore we are currently developing a transient growth stability analysis to achieve a better understanding of these instability modes and characteristics. Once these results are obtained, we can analyse more specifically what governs these instabilities.

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