SOLUTAL MARANGONI EFFECT IN AN EVAPORATIVE MENISCUS

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When a solution or dispersion dries in the vicinity of a contact line, self-organization of the deposit in periodic regular structures might be observed. Recent approaches have been developed to try to capture the dynamics of the contact line in the framework of a hydrodynamics model. This approach has been used for instance for evaporation of dewetting liquid layers (Warner et al [1], Frastia et al [2,3]), evaporation of droplets (Craster et al [4]), or transfer of a surfactant monolayer over a moving substrate (Köpf et al [5]). In the present study, a model simulating the drying of a solution in a meniscus in contact with a moving substrate is developed. The model takes into account hydrodynamics in the solution in the framework of lubrication approximation. The free surface is in contact with air and drying is limited by solvent vapor diffusion in the gas phase. Thus the free surface profile and spatial evaporation flux are not imposed a priori but result from the mass transfer in the liquid/gas system (1.5-sided model, cf. [6,7] for details). The model is used to simulate the drying of a polymer solution (Polyisobutylene (PIB) /toluene). Physical properties of the solution depend on solute concentration:

- viscosity exhibits a strong increase with the solute volume fraction (12 orders of magnitude from pure toluene to pure PIB, for PIB molar mass M_W = 500 $kg.mol^{-1}$),
- solvent activity is given by the Flory-Huggins law, with a strong decrease of the saturated vapor pressure for solute volume fraction larger than about 0.6,
- surface tension is assumed to increase linearly with the solute volume fraction, from $\sigma = 28 \times 10^{-3}$ $N.m^{-1}$ (pure toluene) to $\sigma = 34\times10^{-3}$ $N.m^{-1}$ (pure PIB). Thus the non volatile solute increases the surface tension, unlike for a solution containing surfactants.

At the inlet of the computational domain (x=0, see Fig. 1), the solute volume fraction in the meniscus is equal to the bulk solute volume fraction, and we impose the liquid height and the curvature of the meniscus. A no-slip condition is imposed at the substrate. For the gas phase, the vertical walls are assumed impermeable. Dirichlet condition with zero solvent vapor concentration is imposed at the top of the gas domain. The last boundary condition corresponds to the coupling between the liquid and the gas phases and is achieved by writing the mass flux conservation and the local thermodynamic equilibrium at the interface.

A two-dimensional Cartesian coordinates system is used for simulations. They are performed in the evaporative regime, i.e. for low substrate velocities (10 *µm/s* <V_{sub}<100 *µm/s*), when evaporation at the meniscus significantly impacts the flow [6]. In this regime, previous studies have shown that the evaporation flux is maximal at the edge of the meniscus (Fig.2, bottom) and that the dry deposit thickness may be obtained by simple mass balances [8-10] and scales as $1/V_{sub}$ (unlike in the classical Landau-Levich regime where the film thickness scales as $V_{sub}^{2/3}$).

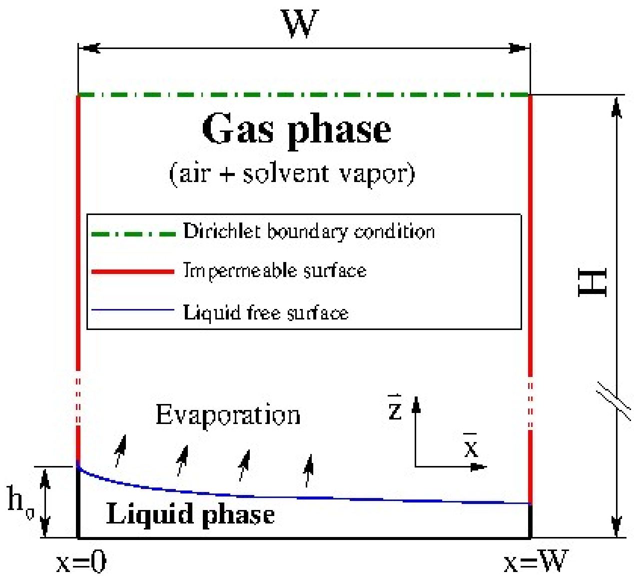

Fig. 1: Computational domain

For some configurations, the simulations show the apparition of a bump on the meniscus profile (Fig. 2, top) that can be qualitatively understood from the following argument. To ensure local mass conservation, the Marangoni flux driven by surface tension gradients must be balanced by a modification of the capillary flux, which may induce the bump formation. Here the shape of the meniscus results from a complex interplay between the different components of the volume flux, as well as the variable viscosity. In some cases, a stationary solution does not exist, or is unstable, and simulations converge towards a periodic regime where the bump grows as the same time as it moves, dries with a dramatic increase of viscosity and then is advected by the substrate. This results in periodic deposits, as shown in Fig.3. We analyze this mechanism (onset of the periodic regime, amplitude and wavelength) as a function of the process parameters.

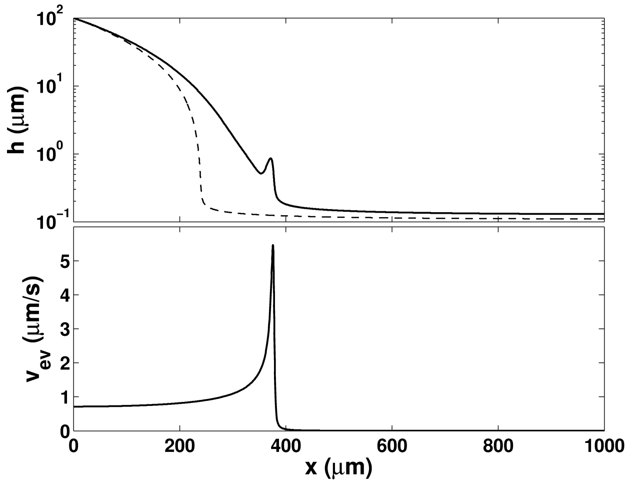

Fig. 2: Steady regime obtained for V_{sub} = 40 µm/s (receding meniscus), bulk PIB volume fraction = 1%.
Top: meniscus profile (semi-logarithmic scale), dashed line: no Marangoni effect (constant surface tension), continuous line: with Marangoni effect (variable surface tension).
Bottom: evaporation rate.

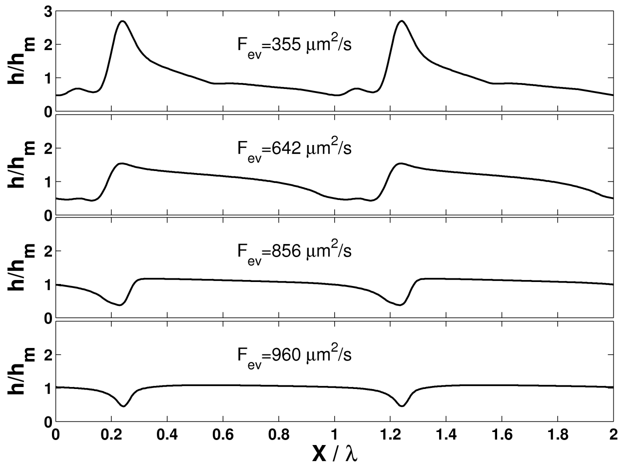

Fig. 3: Periodic regime: morphology of the deposit for different evaporation fluxes F_{ev}. V_{sub} = 30 µm/s (receding meniscus), bulk PIB volume fraction = 1%. The deposit thickness h and abscissa X (arbitrary origin) are scaled by the mean thickness h_m and wavelength λ, respectively.
From top to bottom: h_m = 0.12 µm, 0.21 µm, 0.29 µm, 0.32 µm ; and λ =270 µm, 300 µm, 500 µm, 820 µm.

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